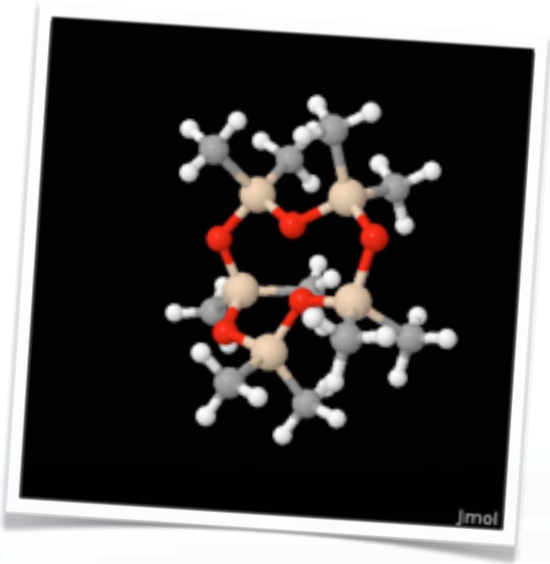
Biomagnification of cyclic volatile methyl siloxanes, cVMS, in Lake Mjøsa



Presentation for Nordic workshop
"Today´s chemical solutions – problems of tomorrow?"

by

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cefic

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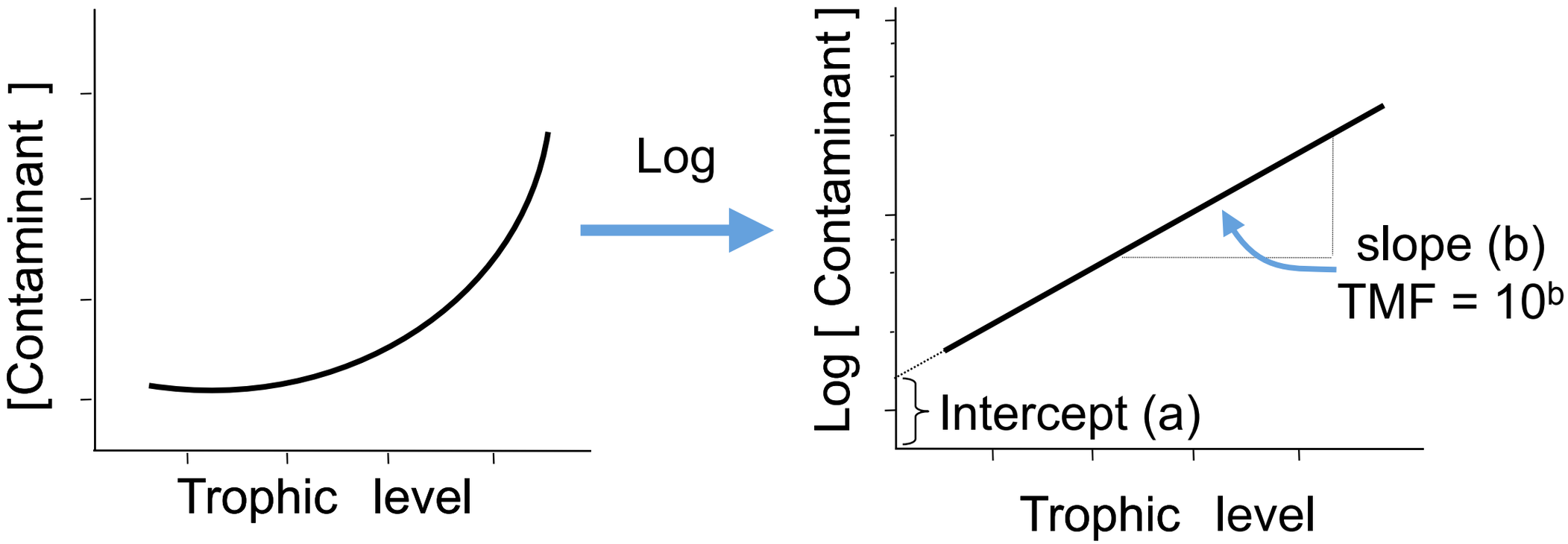
KLIMA- OG FORURENSNINGS-DIREKTORATET

Outline

- Background for project
  - Trophic magnification factors (TMF)
  - Siloxanes
  - Lake Mjøsa food web
- Results
  - cVMS levels
  - Food web magnification
- Lessons learned

Trophic Magnification Factor – TMF



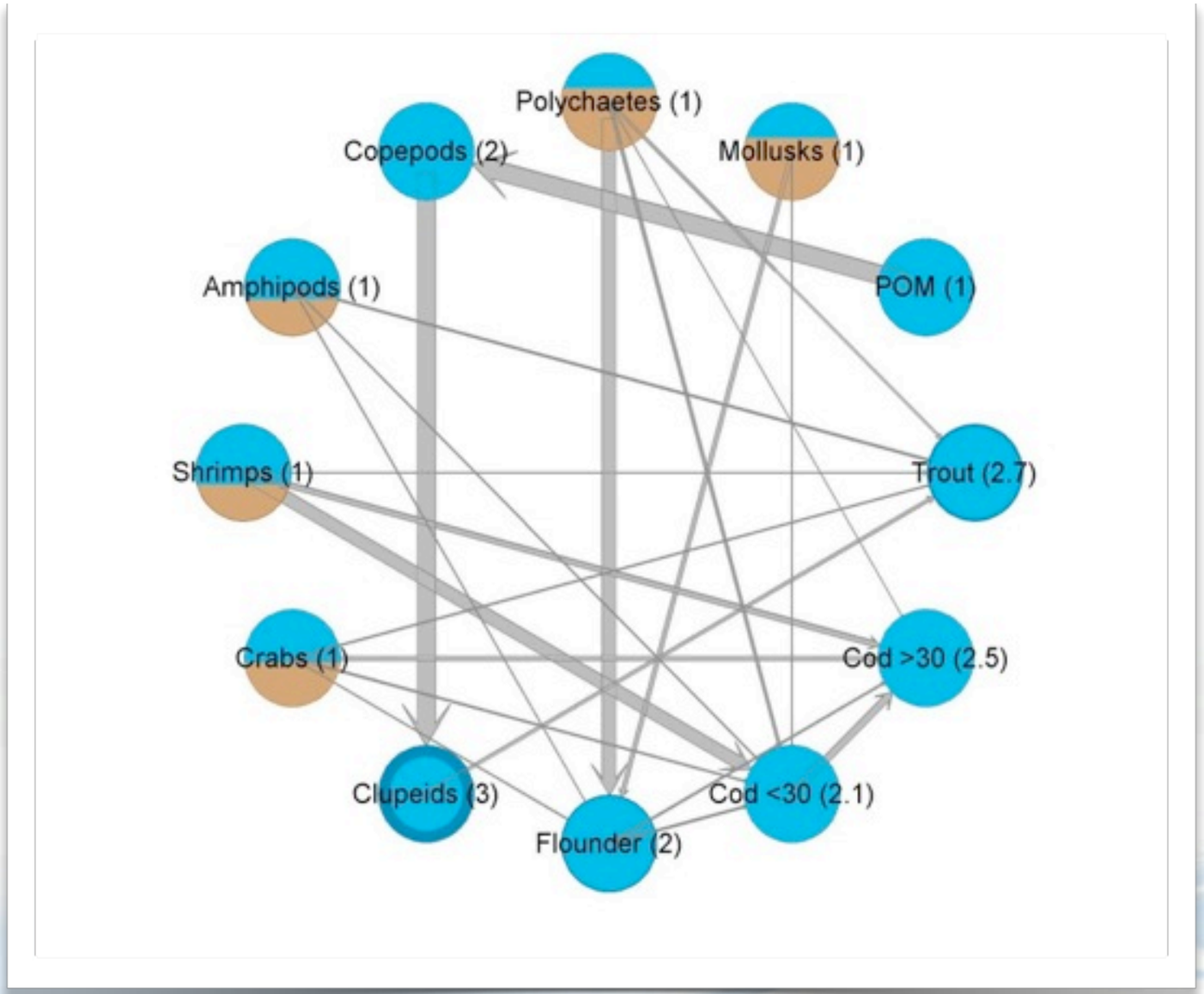
$$\text{Log[Contaminant]} = a + bTL + \varepsilon$$

$$TMF = 10^b \quad (\text{or } e^b)$$

Broman et al. ET&C 1992;
Fisk et al. ES&T 2001
Borgå et al., IEAM, in press

Calculation of trophic level

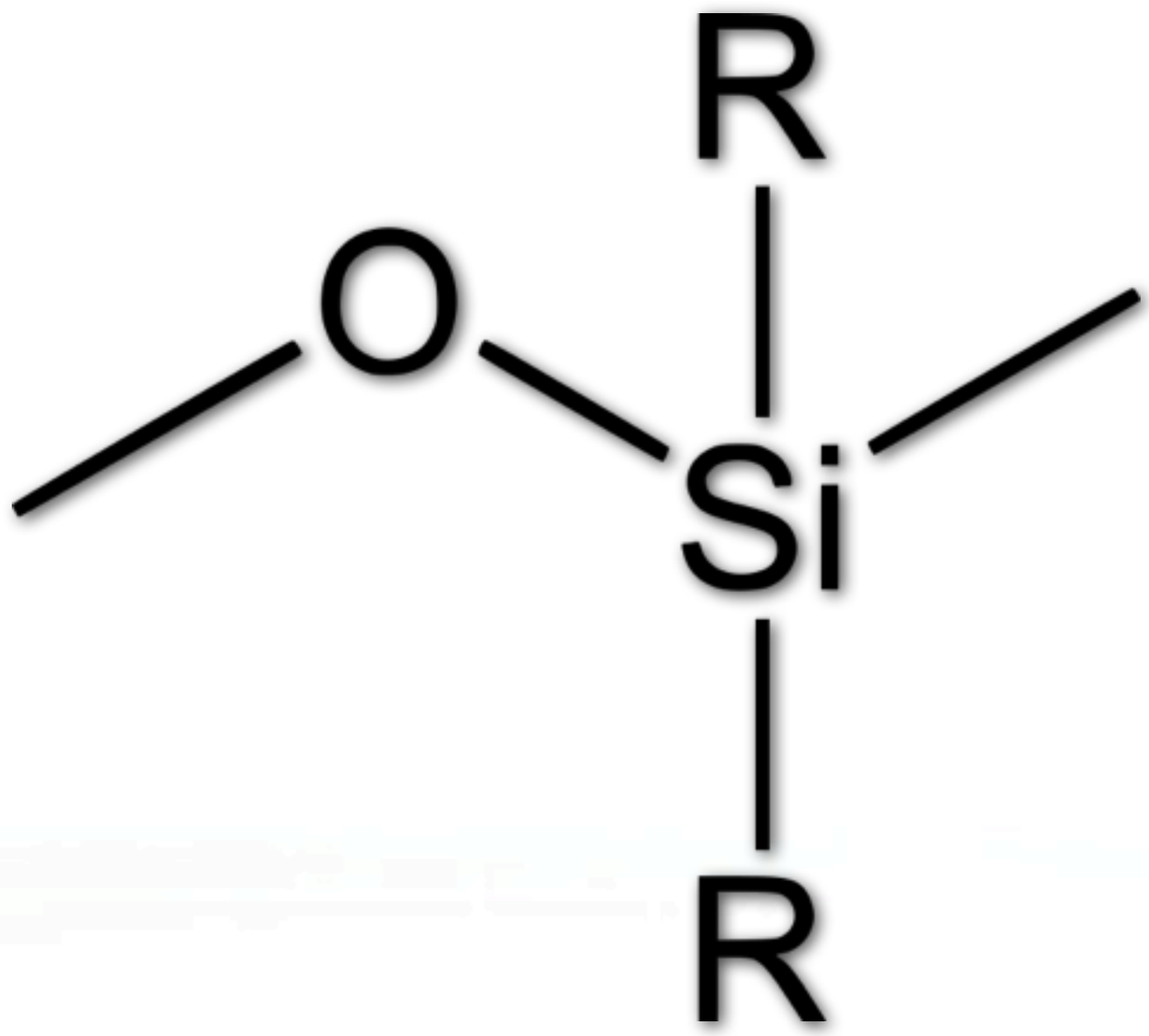
$$TL = 1 + (\delta^{15}N_{consumer} - \delta^{15}N_{prim.\ prod.})/3.4$$



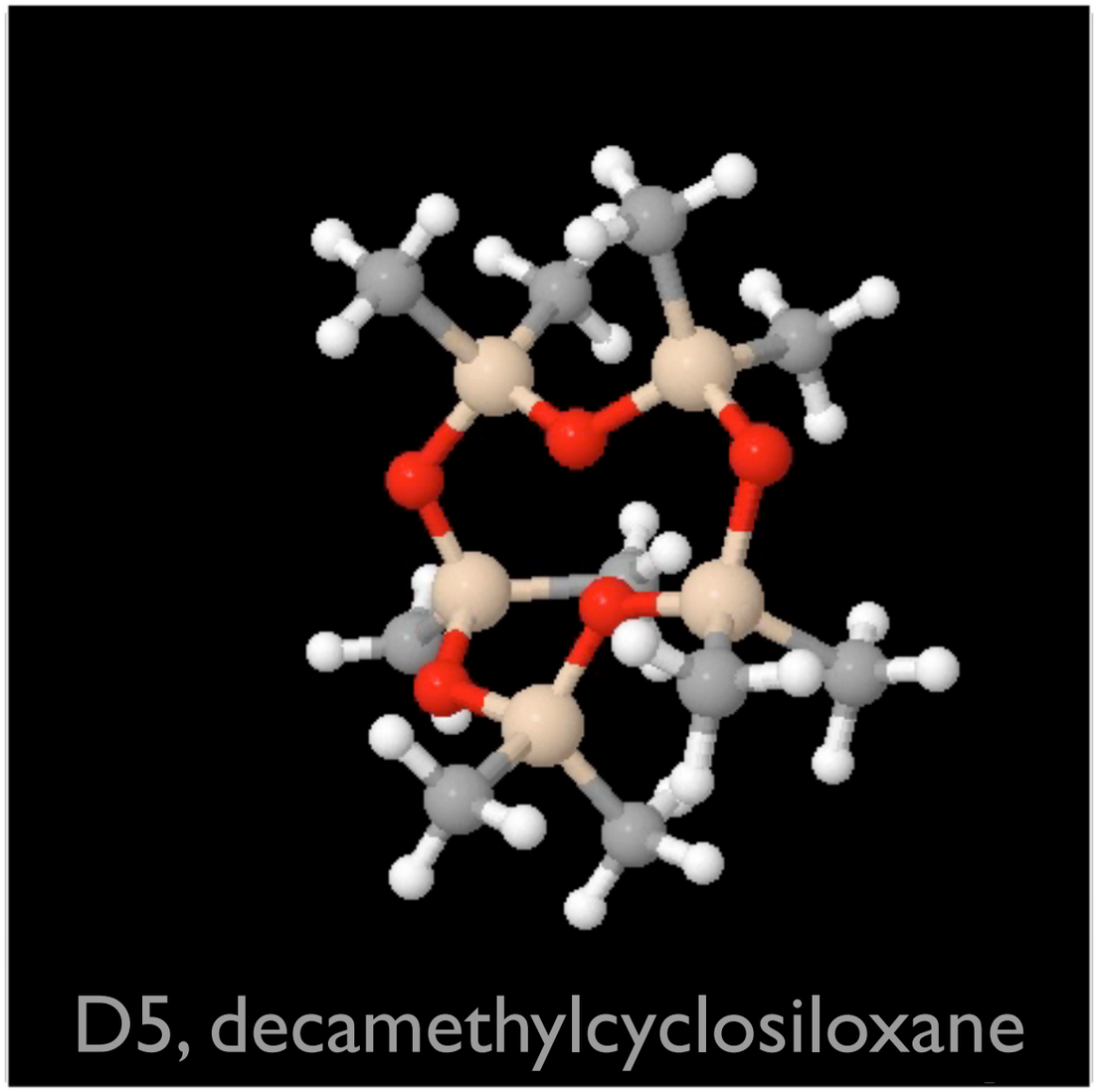
What is cVMS?

- Acronyme: **c**yclic **V**olatile **M**ethyl **S**iloxanes
- Siloxanes: composed of units of the form R2SiO, where R is a hydrogen atom or a hydrocarbon group
- Siloxane is derived from the words silicon, oxygen, and alkane
- Octa-, deca- and dodomethylcyclosiloxane (D4, D5 and D6) are collectively called cVMS
- -Si(CH3)2-O- repeating unit

What is cVMS?



What is cVMS?



cVMS, physiochemical properties

Property	D4	D5	D6
Melting Point, °C	17.7	-38	-3
Boiling Point, °C	175	211	245
Density, g/cm^3 at 25°C	0.95	0.954	0.963
Vapour Pressure, Pa at 25°C	132	33.2	4.6
Water Solubility, mg/L at 23°C	0.056	0.017	0.053
Henry's Law Constant, Pa m^3/mol at 25°C	1,214,000	3,342,000	14,667
Heat of Evaporation, kJ/mol	44	51.4	-
Octanol/water partition coefficient (log K_{OW}):	6.49	8.03	9.06

Why do we care?

- Suspected to biomagnify
- Persistent in the environment
- Volatile and potentional for long range transport
- Suspected to have adverse effects
- cVMS are currently under review for priority pollutant classification in North America and Europe
- High volume production – wide applications, building blocks for many silicones and used in personal care products, dry cleaning
- Total sales of silicones (siloxanes included) in Europe are estimated at 2.5 billion euro a year, and generate an income of 9 billion euro per year for the European society

SEHSC SILICONES ENVIRONMENTAL, HEALTH AND SAFETY COUNCIL of NORTH AMERICA

[SCIENCE, HEALTH AND SAFETY]

Silicones are among the most extensively studied materials used in consumer and industrial applications today. More than 1,000 studies have been conducted by silicone manufacturers to assess the safety of silicones relative to workers, consumers, the environment and manufacturing processes. The results of this continued research and testing demonstrate the safety of silicones in their diverse and important applications.

Committed to the responsible use of silicones, the industry continues to evaluate the science behind the material through several rigorous research programs. Research methodologies include modeling, testing, monitoring and other approaches to these assessments.

SEHSC research is concentrated primarily on the most commonly used siloxanes:

- Decamethylcyclopentasiloxane (D_5)
- Dodecamethylcyclohexasiloxane (D_6)
- Hexamethyldisiloxane (HMDS)
- Octamethylcyclotetrasiloxane (D_4)
- Polydimethylsiloxanes (PDMS)

Silicone manufacturers regularly communicate research findings to SEHSC members, customers, government officials and the scientific community.

For more information on Environment and Health Canada's draft assessment of D_4, D_5 and D_6 under the Chemicals Management Program, click here.

For more information regarding D5 and the California Air Resources Board determination under AB 998, click here.

European Silicones Centre
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Environmental Data

The environmental properties and fate of cyclic siloxanes have been subject to extensive research for many years – including recent monitoring programmes.

In February 2012, the Canadian Environment Minister endorsed the findings of an independent scientific panel, known as a Board of Review, which concluded that siloxane D5 is safe for the environment.

The Board of Review was composed of a panel of three renowned experts appointed by the Canadian Environmental Minister. The panel conducted a comprehensive scientific evaluation to assess all available environmental data on D5, including 2-weeks of testimony from a dozen additional experts. The Board's final report, which was released in October 2011, concluded that "Siloxane D5 does not pose a danger to the environment or its biological diversity." Furthermore, the Board found that *"based on the information presented, Siloxane D5 will not pose a danger to the environment or its biological diversity in the future."*

The review followed and overruled an assessment done by Environment Canada in 2008 which at that time identified the substance as possibly warranting environmental measures.

The Minister did not grant a similar Board of Review process for siloxane D4. Consequently, the Canadian authorities, in collaboration with the silicone industry and downstream user, are currently discussing risk management measures for D4. Environment Canada's proposals focus on limiting D4-emissions in industrial effluent (waste water) and product regulations. The emission regulation is due to be published in July 2012 while the product regulation proposal has been put on hold by Environment Canada.

A complete review of D4's environmental properties was published by C. Stevens (1998) (Environmental fate and effects of dimethicone and cyclotetrasiloxane from personal care applications) in International Journal of Cosmetic Science 20 (5), 296-304. (Download the full paper.)

Program, click here.

Environment and Health Canada's draft assessment of D_4, D_5 and D_6 under the Chemicals Management

For more information regarding D5 and the California Air Resources Board determination under AB 998, click here.

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The unexpected earlier findings (e.g. L.B. Knudsen et al., SFT Report 977/2007) by Scandinavian researchers of detectable levels of D5 in biota tissues taken from the arctic environment triggered detailed studies involving Norwegian Institutes and the Silicone Industry. Resulting from this it could be established that:

- Possible sample contamination during sample collection and storage as well as during the analytical process itself is a severe challenge when analyzing trace concentrations of D4 and D5. Possible contamination can only be identified by applying a detailed quality control program involving blank standards in the field as well as in the laboratory. Data without these quality control measures can hardly be interpreted.
- Quantifiable concentrations of D5 even in the arctic environment were only found close to urban emission sources (e.g. WWTPs)
- Even the concentrations found in highly populated and industrialized areas all remain within safe limits

Detailed food chain studies in different areas of the world showed that D4and D5 concentrations do not increase (bio magnify) in the food chain, although screening criteria predicted biomagnification. The reason for this non-predicted behavior of the siloxanes results from their specific solvation properties in different media, being different to standard carbon-based substances

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Program, click here.

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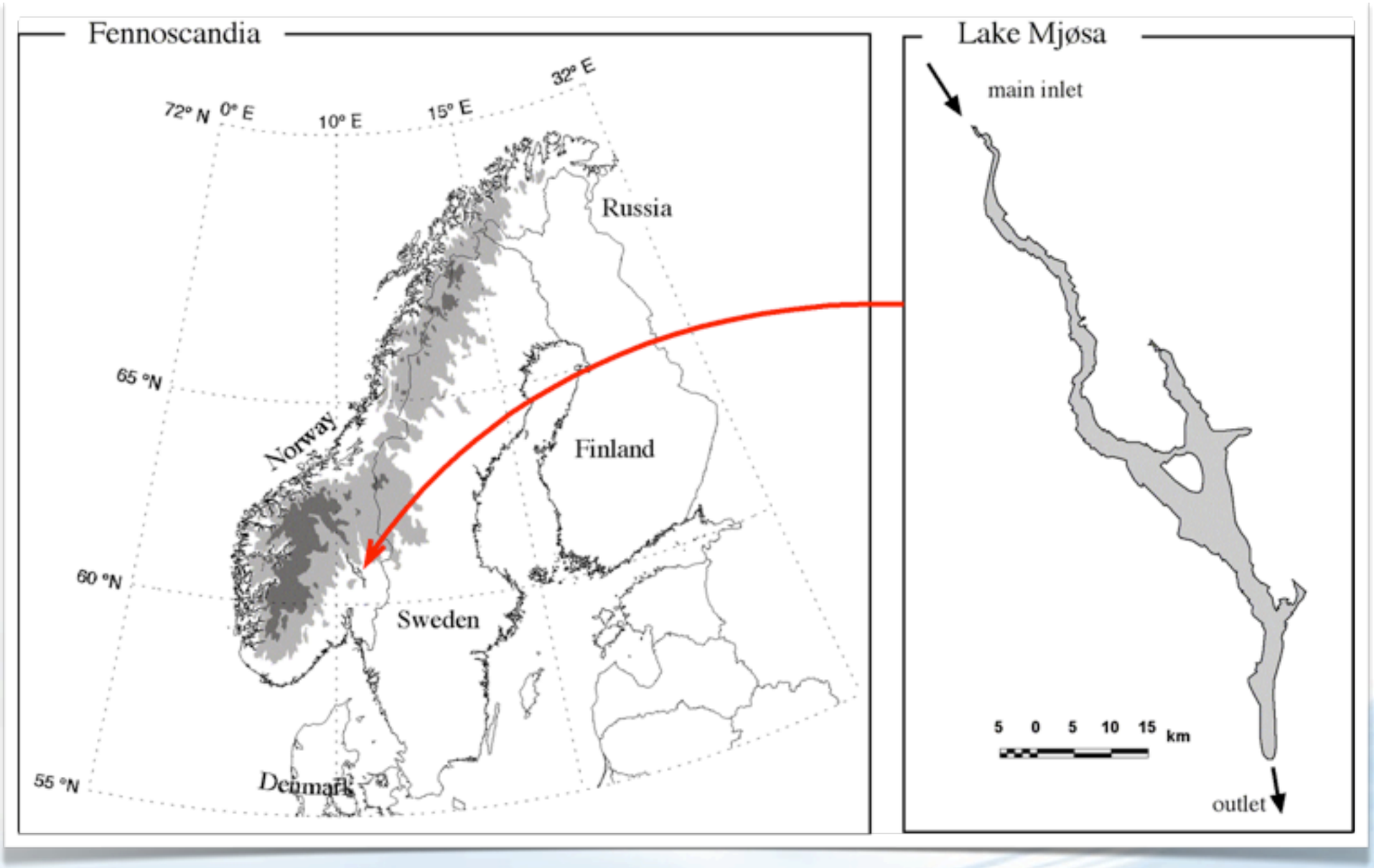
Recent Canadian Review

In February 2012, the Canadian Environment Minister endorsed the findings of an independent scientific panel, known as a Board of Review, which concluded that siloxane D5 is safe for the environment.

23. There are three concepts related to the accumulation of chemicals into organisms. The first is bioaccumulation, which is the process of the chemical entering into an organism. The second is bioconcentration, where concentrations of the chemical are accumulated to values that are greater than, but proportional to, those in the surrounding medium. Finally, there is the concept of biomagnification or trophic magnification in which predators accumulate greater concentrations of the chemical than those in their prey. When expressed appropriately, concentrations of Siloxane D5 in organisms can be greater than those in the surrounding medium, i.e., it can bioconcentrate to some degree. **While Siloxane D5 can accumulate in organisms, it does not biomagnify through the food-chain.**

http://www.ec.gc.ca/lcpe-cepa/6E52AE02-5E01-48B0-86DE-0C366ACC863F/CdR-BoR-D5_eng.pdf

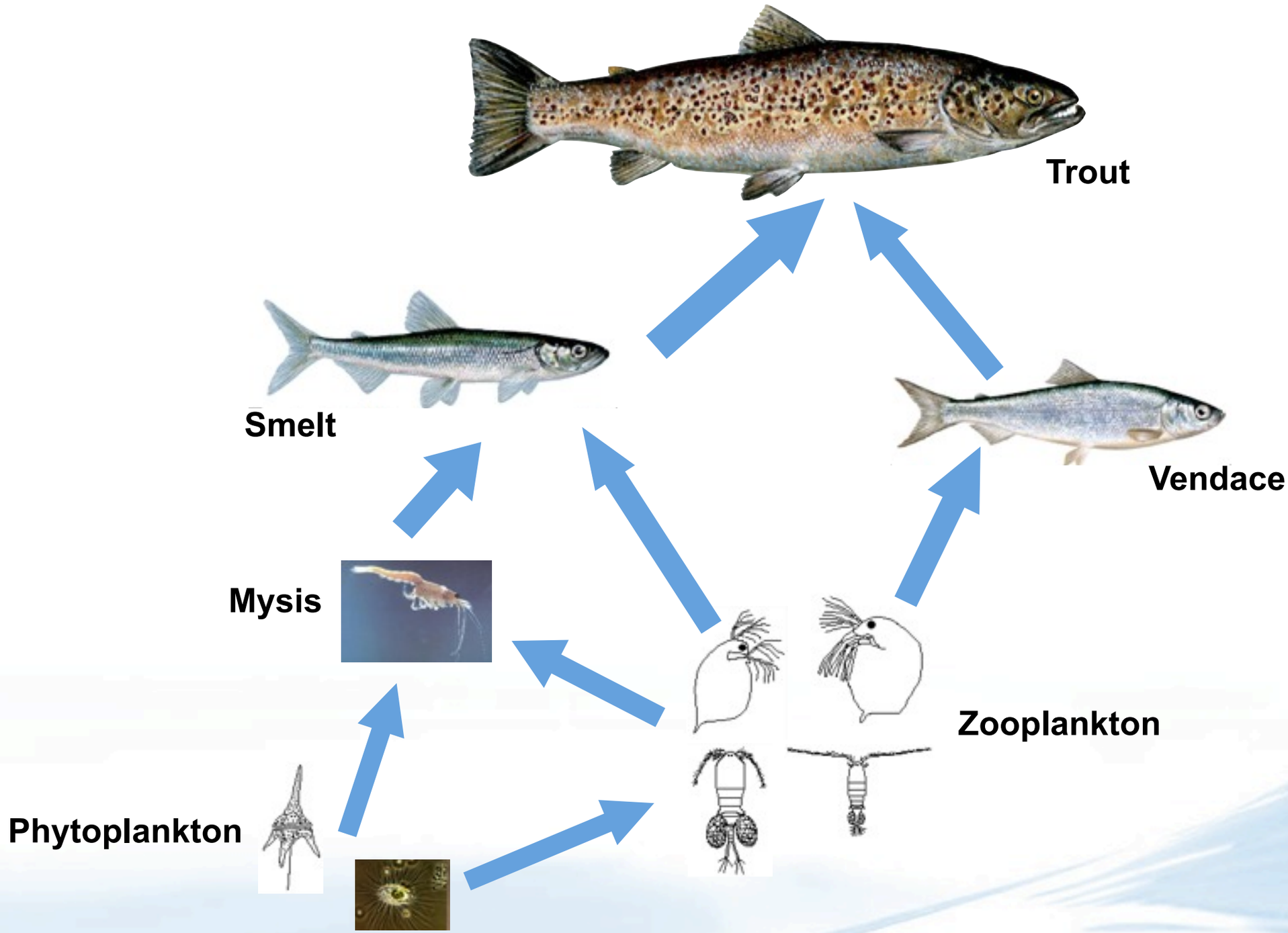
Lake Mjøsa


Fennoscandia
72° N
0° E
10° E
15° E
32° E
65 °N
60 °N
55 °N
Russia
Norway
Finland
Sweden
Denmark
Lake Mjøsa
main inlet
5 0 5 10 15 km
outlet

Lake Mjøsa

- Norway's largest lake
- Lake surface area: 363 km^2
- Maximum depth: 453 m
- Average depth: 150 m
- Mean residence time: 5.5 years
- Recipient for approx. 200 000 people

Lake Mjøsa pelagic food web



What did we do?

Collect samples of:

- Pelagic fish
  - Brown trout (*Salmo trutta*)
  - Vendace (*Coregonus albula*)
  - Smelt (*Osmerus eperlanus*)
- The omnivorous bentopelacic crustacean Opossum shrimp (*Mysis relicta*)
- Crustacean zooplankton
  - Epipelagic (dominated by cladocerans)
  - Hypopelagic (dominated by copepods)

Selected fish species

Selected fish species

Selected fish species

Zooplankton sampling

Zooplankton sampling

Zooplankton sampling

Sampling procedures

- Reduce (avoid) field contamination
  - clean equipment (acetone /methanol), cover in pre cleaned Al-foil, latex gloves
  - all sample treatment outdoors on land
  - no personal hygiene products 24 h prior to sampling
- Field blanks (passive samplers)
  - exposed to air in same manner as the samples to obtain a similar cumulative exposure to air.
  - in gill nets after retrieved, attached to zooplankton net

What more did we do?

- Sent the samples to our Swedish partners at Department of Applied Environmental Science (ITM), Stockholm University for analyses of D4, D5 and D6

- Analyzed parallell samples (or pseudoreplicates of crustaceans) for legacy POPs (PCBs, DDT, PBDE) at NILU

- Determined the different organisms trophic posistions by using stabile istotopes ($\partial^{N}15$, analyzed at IFE)

Anal. Chem. **2010**, *82*, 9573–9578

Determination of Cyclic Volatile Methylsiloxanes in Biota with a Purge and Trap Method

Amelie Kierkegaard,* Margaretha Adolfsson-Erici, and Michael S. McLachlan

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The three cyclic volatile methylsiloxanes (cVMS), octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5), and dodecamethylcyclohexasiloxane (D6), are recently identified environmental contaminants. Methods for the trace analysis of these chemicals in environmental matrices are required. A purge and trap method to prepare highly purified sample extracts with a low risk of sample contamination is presented. Without prior homogenization, the sample is heated in water, and the cVMS are purged from the slurry and trapped on an Isolute ENV+ cartridge. They are subsequently eluted with *n*-hexane and analyzed with GC/MS. The method was tested for eight different matrices including ragworms, muscle tissue from lean and lipid-rich fish, cod liver, and seal blubber. Analyte recoveries were consistent within and between matrices, averaging 79%, 68%, and 56% for D4, D5, and D6, respectively. Good control of blank levels

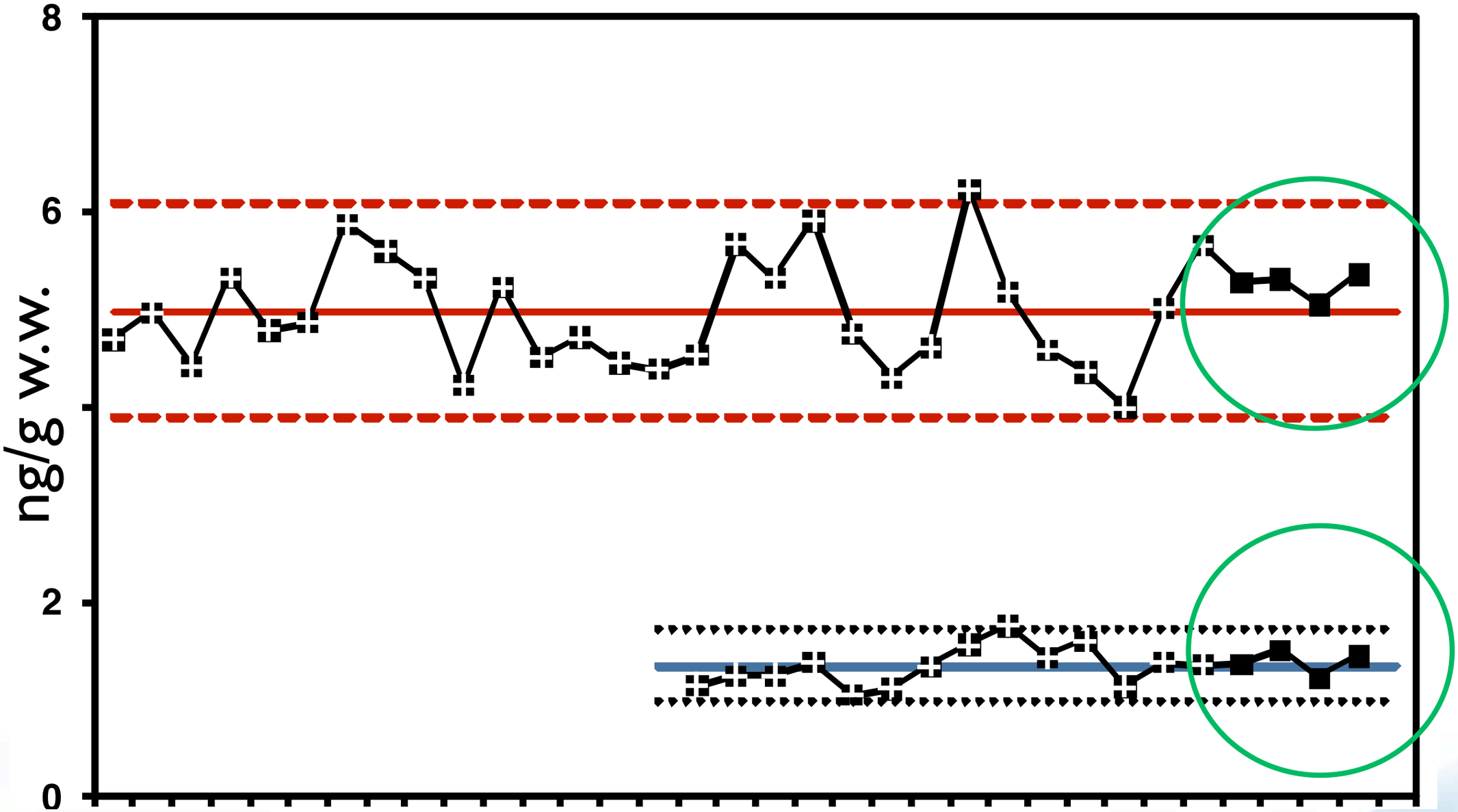
industrial chemicals, these substances were identified as priority chemicals for environmental risk assessment due to their large volume of usage, their persistence in the environment, and their bioaccumulative properties.[5] Risk assessments prepared by the United Kingdom indicate that, following their release to the environment in sewage treatment plant effluent, these chemicals will accumulate and persist in sediment, rendering fish particularly susceptible to exposure.[2−4] D4, D5, and D6 possess a high octanol−water partition coefficient (log K_{OW} of 6.49, 8.03, and 9.06, respectively[2−4]), which makes them prone to bioaccumulation in fish. Measuring bioaccumulation in aquatic organisms is thus one of the priorities in the risk assessment of these chemicals.

D4, D5, and D6 have been identified in a variety of freshwater and marine fish and benthic organisms, marine mammals, and seabirds from northern Europe and the North Atlantic. Concentrations of the order of 100 ng/g (D4, D6) and 1000 ng/g (D5) wet

QA/QC

- Field blanks:
  - Precleaned polyester pouches containing ~60 mg ENV were exposed and handled in a manner similar to the samples.
  - Unexposed pouches analysed for comparison (Field blanks – unexposed compared to biotic samples)
    - **D5 and D6:** the total content of the field blanks was in all cases insignificant compared to the total amount of these analytes extracted from the samples
    - **D4:** the difference between field blanks and samples was less, and in 19 of 32 samples the ratio (sample/field blank) was below 5 (thus < LOQ).
- The limit of quantification (LOQ):
  - either 5 x field blank or 5 x procedural blank of the extraction round.
  - Applying these criteria, **40% of D4, 100% of D5, and 78% of D6** results are above the LOQ.

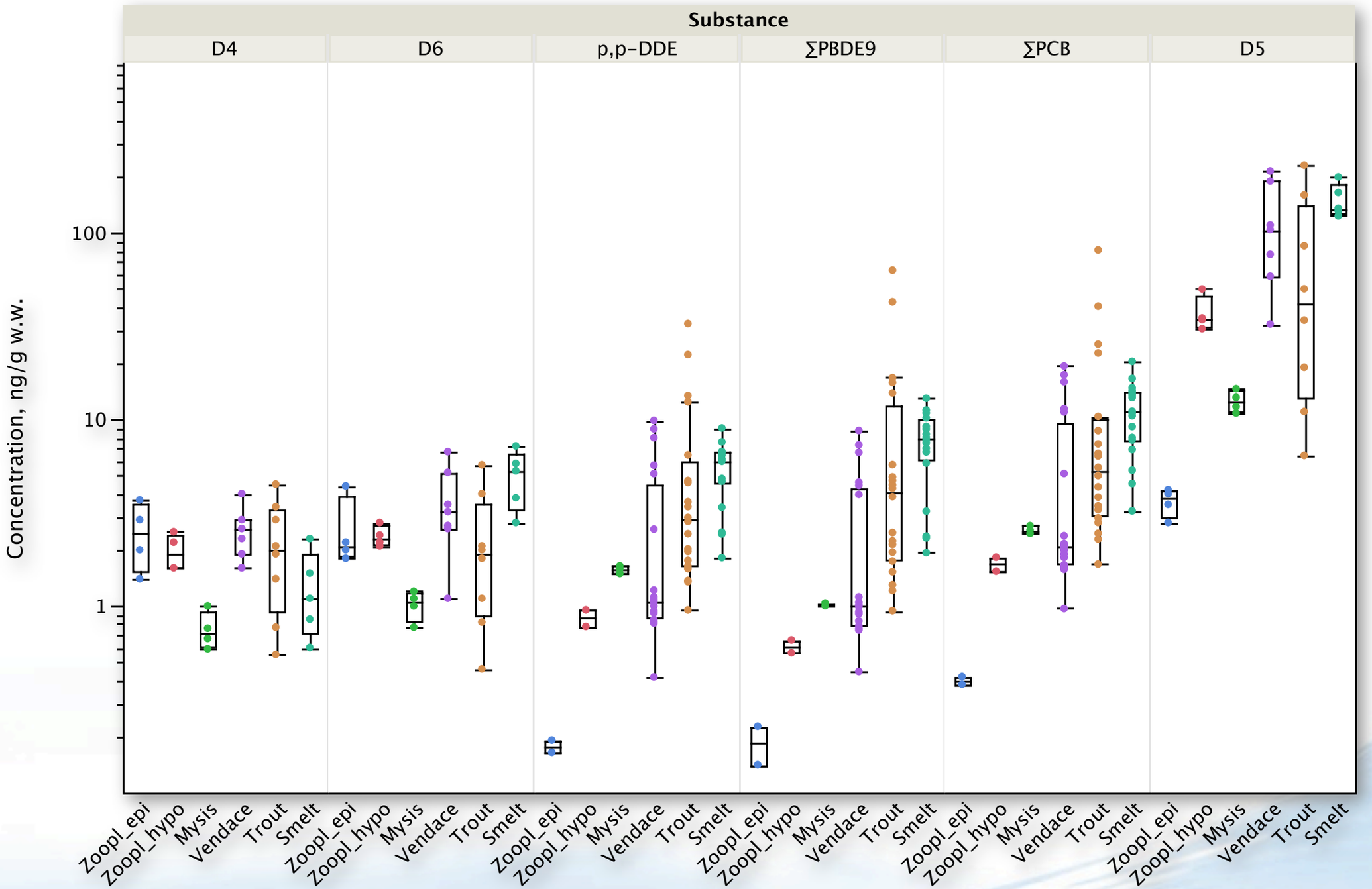
QA/QC: Control samples



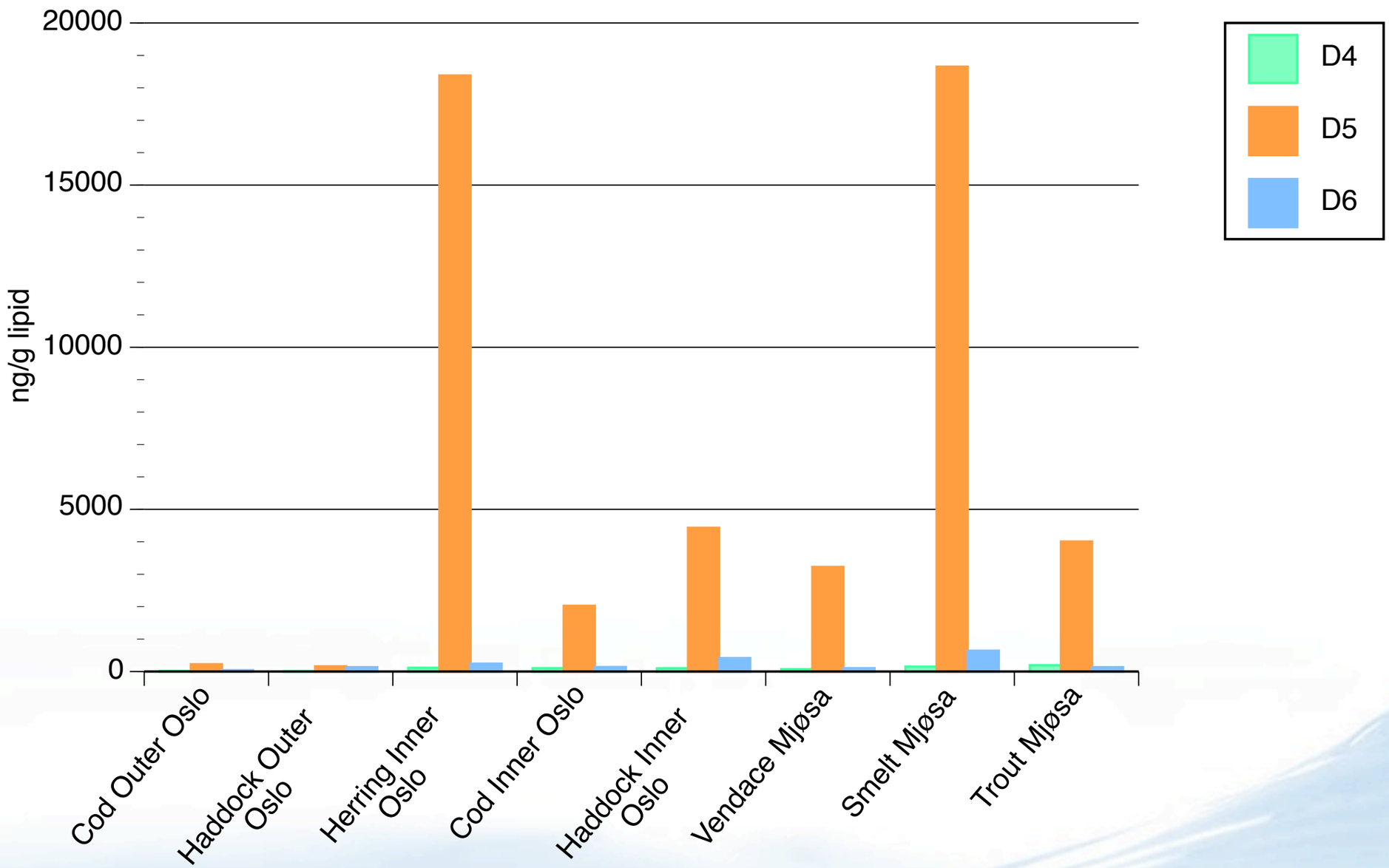
Repeated analysis of D5 and D6 in a herring muscle homogenate.

The solid lines mark the mean concentrations; the broken lines mark 2 times the standard deviation.

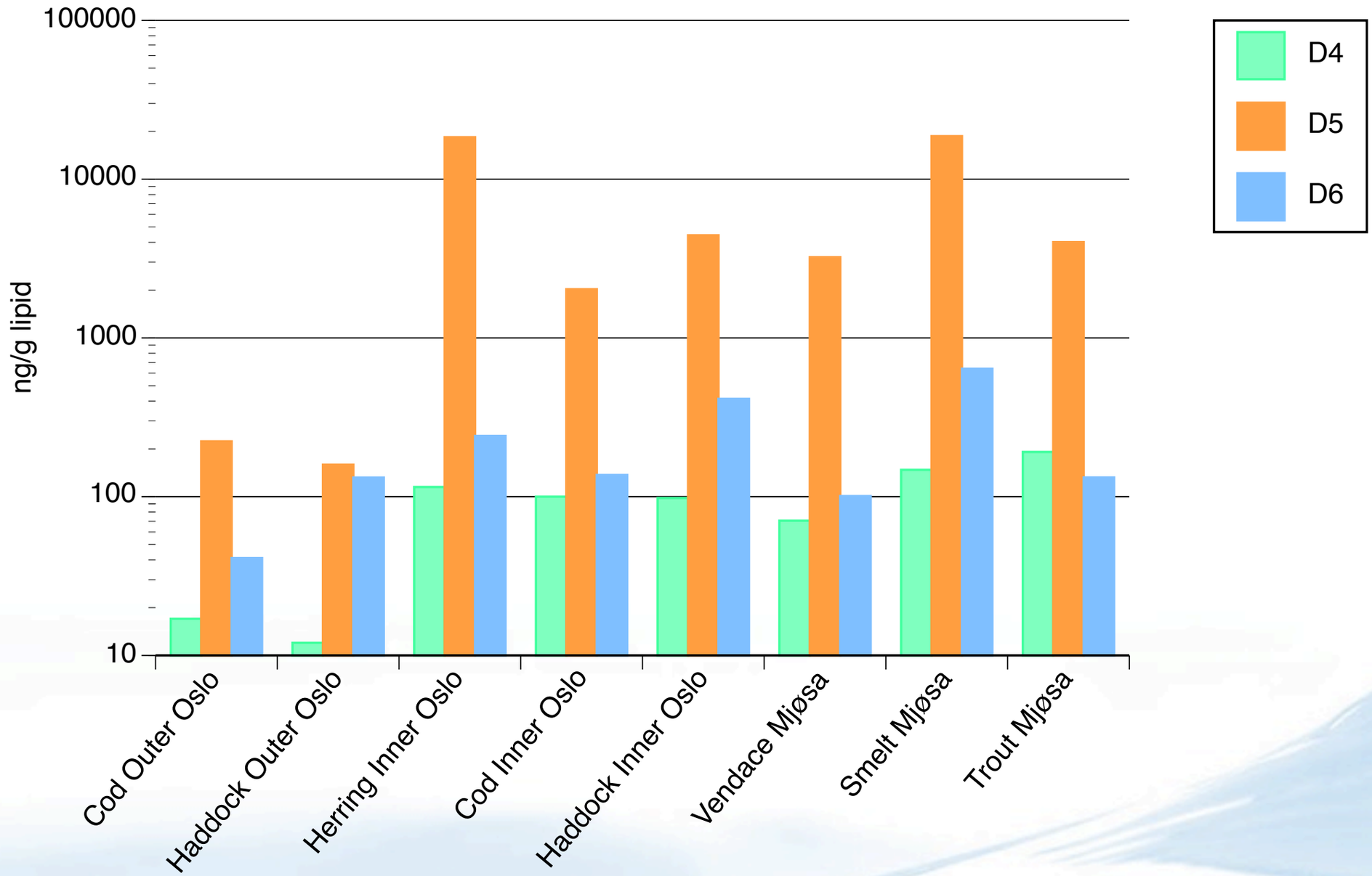
cVMS and POP levels



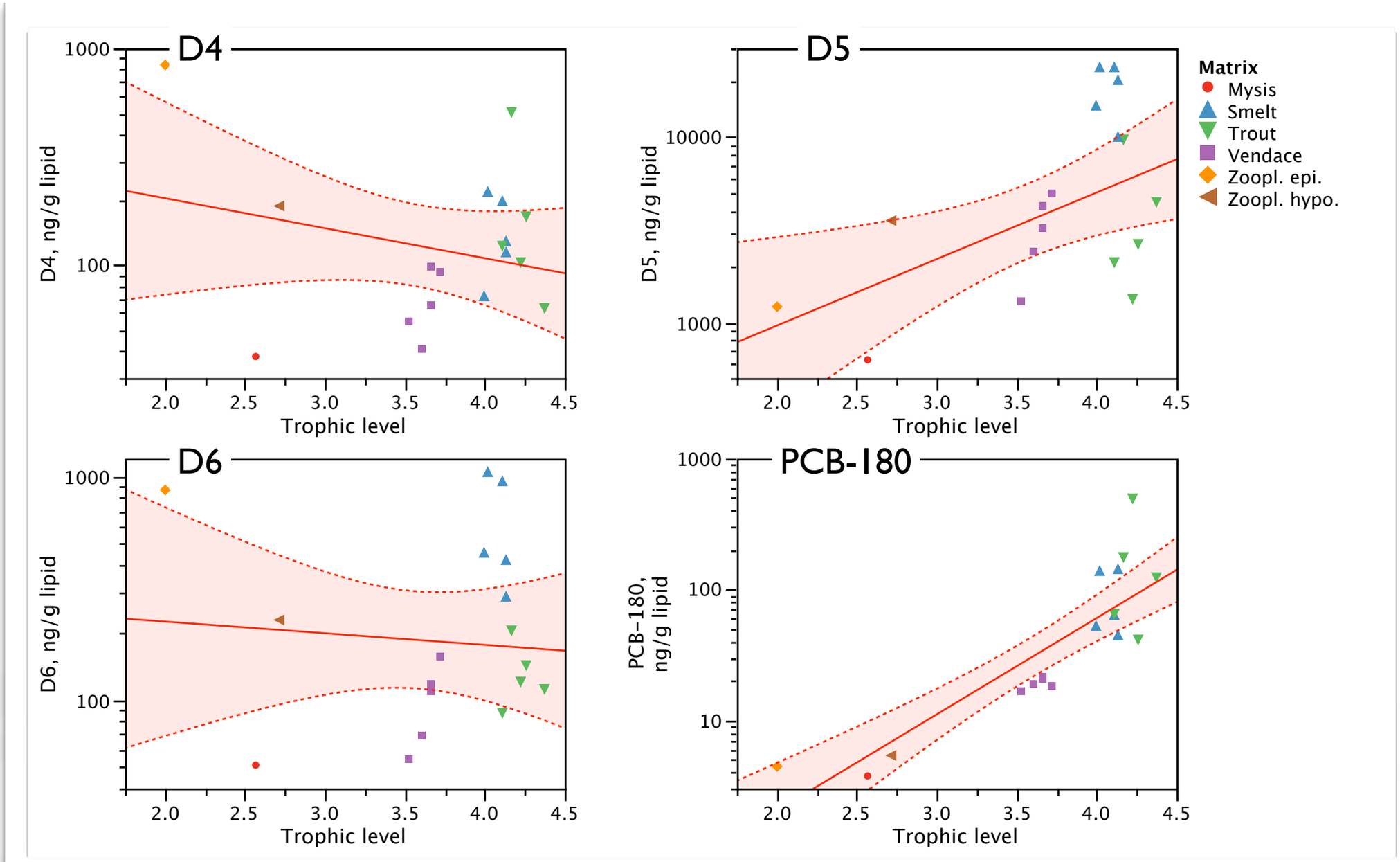
cVMS – Oslofjord and Lake Mjøsa



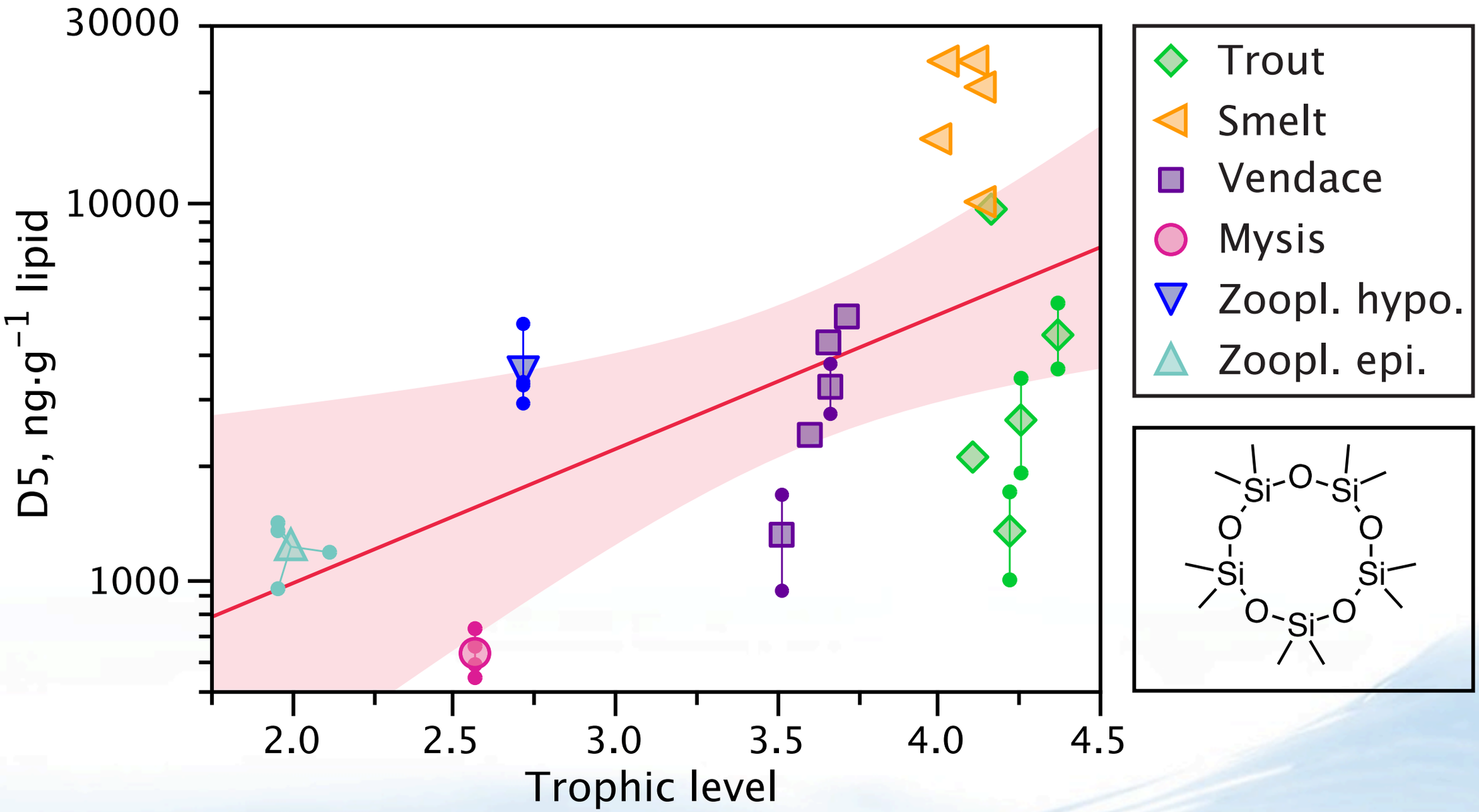
cVMS – Oslofjord and Lake Mjøsa



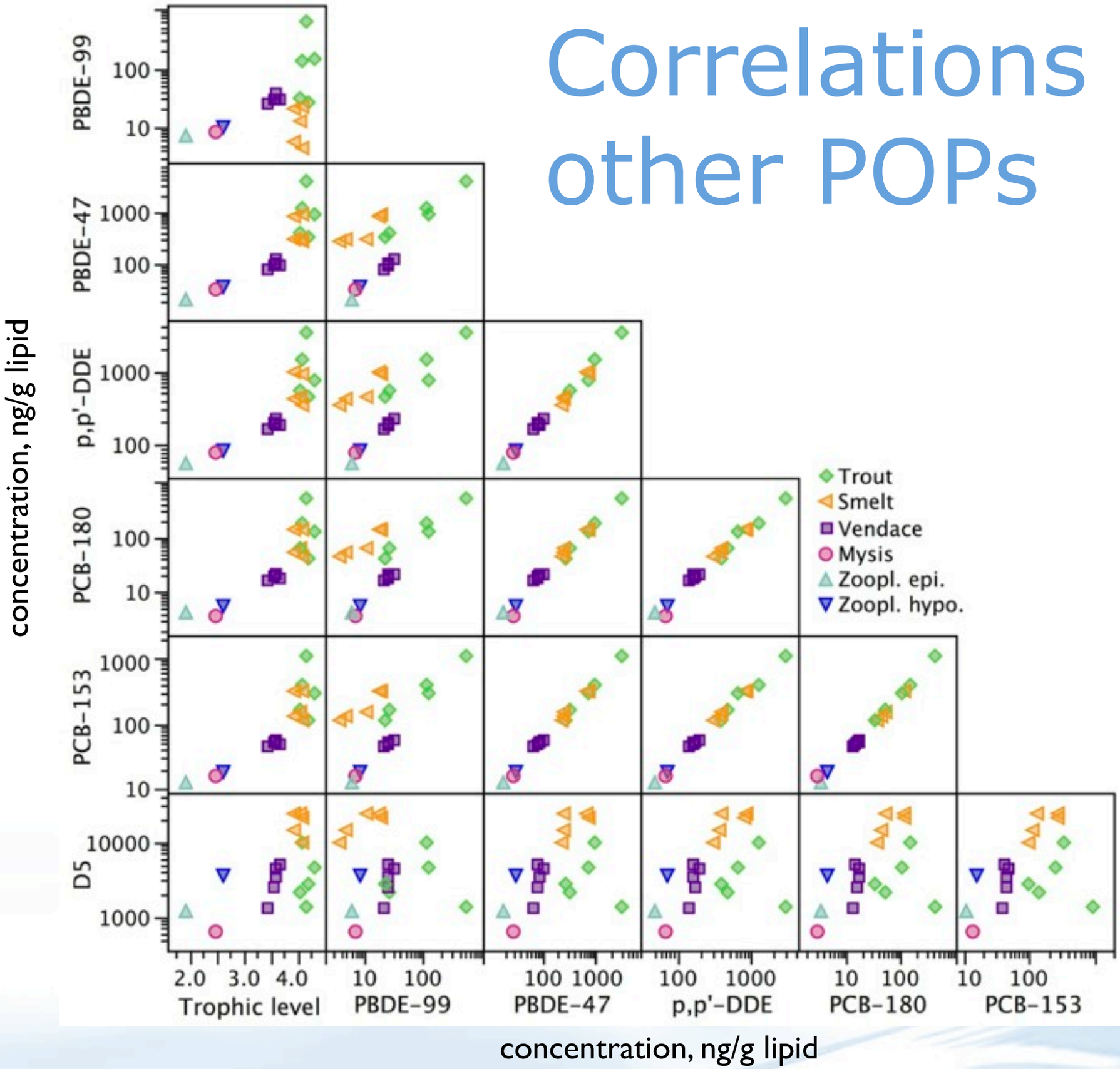
Concentration vs. Trophic Level



D5, concentration vs. Trophic Level



Correlations with other POPs



Trophic Magnification Factors – TMF

Data set	Contaminant	TMF	95% CL low	95% CL high	R^2	N (weights)	*p*
Whole food web	D5	2.28	1.22	4.29	0.33	23.07	0.013
Trout excluded	D5	3.58	1.82	7.03	0.61	16.83	0.0016
Smelt excluded	D5	1.62	0.96	2.72	0.28	18.07	0.065
Whole food web	PCB-153	4.9	3.06	7.85	0.76	19.15	< 0.0001
Trout excluded	PCB-153	4.05	2.64	6.2	0.83	14.15	< 0.0001
Smelt excluded	PCB-153	4.75	2.65	8.53	0.76	14.15	0.0001
Whole food web	PCB-180	6.01	3.62	9.98	0.78	19.15	< 0.0001
Trout excluded	PCB-180	5.06	3.13	8.19	0.83	14.15	< 0.0001
Smelt excluded	PCB-180	5.76	3.08	10.75	0.78	14.15	0.0001
Whole food web	BDE-99	2.43	1.08	5.43	0.32	19.15	0.033
Trout excluded	BDE-99	1.38	0.74	2.58	0.1	14.15	0.29
Smelt excluded	BDE-99	3.79	1.97	7.31	0.64	14.15	0.001

Lake Mjøsa - conclusions

- D5: biomagnifies, somewhat lower the classical POPs such as PCB-180 (with comparable K_{OW})
- D5: differences in species responses, species specific differences in uptake, metabolism or excretion?
- D4 and D6: no biomagnification could be demonstrated
- Wide confidence limits in estimated TMF
  - can be improved by studying expanded food webs and increased resolution of trophic levels?

Published paper

Borgå, K., Fjeld, E., Kierkegaard, A. and McLachlan, M. 2012. *Food web accumulation of cyclic siloxanes in Lake Mjøsa, Norway.* Environ. Sci. Technol. (in print)

Environmental Science & Technology http://pubs.acs.org/journal/esthag