BENTHIC INVERTEBRATE EXPOSURE AND CHRONIC TOXICITY ANALYSIS FOR cVMS MATERIALS – A PROBABILISTIC RISK ASSESSMENT APPROACH

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ABSTRACT

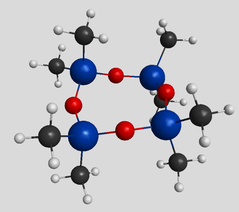
Lipophilic chemicals, such as the cyclic volatile methylsiloxane (cVMS) materials octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5), adsorb extensively to particles and surfaces in aqueous systems, making sediments a key sink when performing risk assessment evaluations. A widely accepted step for estimating the possible risk posed by such chemicals to sediment-dwelling species is to compare the observed sediment concentration with either published ecotoxicity guidelines or to chronic no-observed effect concentrations (NOECs) from standardized toxicity testing with benthic invertebrates. A comparison of field sediment concentrations with chronic NOEC levels from laboratory testing can be done with simple worst-case simulations or using a probabilistic distribution approach. In this work, a comparison was made using probabilistic methods of D4 and D5 residues from sediments and organisms collected in Canada, the United States, the UK, and European member states to chronic NOEC values determined using EPA/OECD test species such as *Chironomus tentans, Chironomus riparius, Hyalella azteca,* and *Lumbriculus variegates*. Comparisons were made using sediment levels on a dry weight (data not shown) and organic carbon basis. Probabilistic endpoints of ≥95% exposure and ≤5% chronic NOEC were extrapolated from the data, which were fit using log-normal assumed distributions. Using probabilistic techniques, field D4 and D5 sediment concentrations were far below chronic threshold NOEC values with benthic invertebrates, therefore very limited risk appears to exist with these materials. This probabilistic evaluation method is applicable to a wide range of lipophilic materials that preferentially bind to sediment and allows a quantitative assessment of the likelihood of risk to benthic species.

INTRODUCTION AND OBJECTIVES

- Cyclic volatile methylsiloxanes (cVMS) are primary compounds in personal care products and many other products
- cVMS compounds have high Henry's Law constants, low water solubility, and elevated lipophilicity (K_{ow} >10^6), so deposition in sediment is likely
- cVMS compounds exhibit low toxicity to pelagic and benthic species (chronic NOECs often >water & organic carbon solubility)
- Environment Canada conducted screening assessments on D5 and concluded a "*lack of evidence showing adverse effects in pelagic biota from short- and long-term exposure to D5, up to water solubility*".
- Further risk analysis has therefore concentrated on sediment-dwelling invertebrate species, where exposure is greater due to the lipophilicity of D4/D5 and the opportunity exists for concentrations to accumulate to levels of toxicological interest.
- Hazard quotient (HQ) assessments, while inherently protective in nature, are not predictive as to the level of potential risk. Higher tier, probabilistic risk assessment (PRA) methods allow the risk assessor to include stochastic properties of both exposure and response. The PRA technique was used with sediment exposure and chronic toxicity no-observed effect concentration (NOEC) data for both D4 and D5 to characterize the likelihood of an intersection or overlap of these events to occur.

OBJECTIVES

- Compare distributions of field exposure levels of D4 /D5 in sediment to toxicity trigger levels for these compounds determined in laboratory chronic toxicity tests with benthic organisms.
- Use data from chronic sediment toxicity assays conducted on both D4 and D5 in global regulatory standardized experiments, typically 28-day studies examining non-lethal endpoints such as fecundity, development, and biomass, to develop the distribution of toxicity threshold values.
- Develop probabilistic comparisons of measured D4 and D5 sediment residues to sediment chronic toxicity NOEC values for benthic species.



D4

Octamethylcyclotetrasiloxane

MW = 296 amu

Henry's Law =

1.22 x 10^6 Pa-m^3/mol

Water Solubility = 0.056 mg/L

Log K_{ow} = 6.49, log K_{oc} = 4.22

D5

Decamethylcyclopentasiloxane

MW = 370 amu

Henry's Law =

3.35 x 10^6 Pa-m^3/mol

Water Solubility = 0.017 mg/L

Log K_{ow} = 8.03, log K_{oc} = 5.17

EFFECTS ASSESSMENT

Chronic Toxicity of D4 and D5 :

- Chronic toxicity sediment bioassays have been conducted with D4 and D5 on *Hyalella azteca* (amphipod), *Chironomus* species (midge), and *Lumbriculus variegatus* (sludge worm).
- Observed chronic NOEC values (ng/g-OC) are generally in excess of the calculated solubility of D4 and D5 in organic carbon (OC), 9.3 x 10^5 and 2.5 x 10^6 ng/g-OC, respectively. (Table 1)

Hyalella azteca (amphipod)

Chironomus riparius (midge)

Lumbriculus varigatus (sludge worm)

Table 1. Laboratory chronic sediment no-observed effect concentration (NOEC) data on D4 and D5 with benthic organisms in standardized OECD bioassays.

Cmpd	Organism	Exp. Days	OC Solububility (ng/g-OC)*	Sed. %OC	NOEC (ng/g-dw)	NOEC (ng/ g-OC)
D4	*C. tetans*	14	9.3E05	2.5	1.2E5	8.0E6
	C. riparius	28		4.1	4.4E4	1.1E6
	L. variegatus	28		2.2	1.3E4	5.9E5
D5	*H. azteca*	28	2.5E06	4.8	1.3E5	2.7E6
	C. riparius	28		3.2	7.0E5	2.2E6
	L. variegatus	28		3.7	1.3E6	3.4E7

*Organic carbon solubility value = Water solubility * K_{oc}

EXPOSURE ASSESSMENT

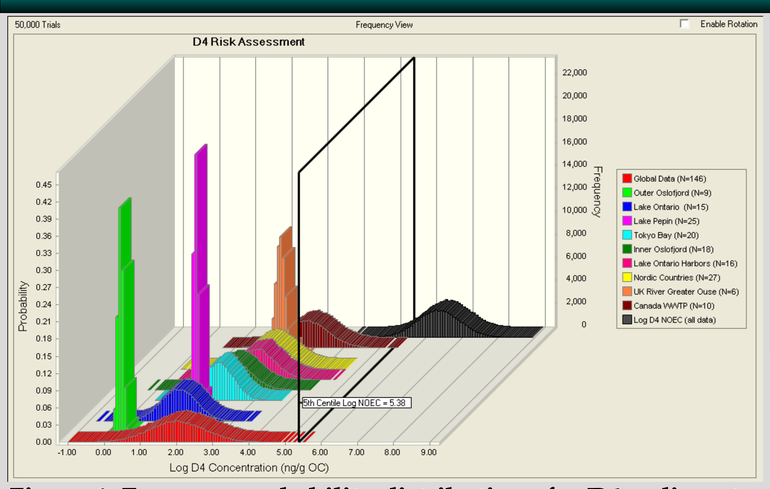


Figure 1. Exposure probability distributions for D4 sediment concentrations (ng/g-OC) compared to chronic toxicity NOEC values (ng/g-OC) for D4 with benthic invertebrate species.

Study Area (N)	Certainty (%) (C_{SED} ≥ 5% NOEC)	Overall Probability (%) (C_{SED} ≥ 5% NOEC)
Global Data (>150)	0.00000	0.00000
Outer Oslofjord (9)	0.00000	0.00000
Lake Ontario (25)	0.00000	0.00000
Lake Pepin (USA) (25)	0.00000	0.00000
Tokyo Bay (20)	0.00000	0.00000
Inner Oslofjord (18)	0.00000	0.00000
Lake Ontario Harbors (6)	0.00000	0.00000
Nordic Countries (25)	0.00000	0.00000
UK River Greater Ouse (6)	0.00000	0.00000
Canada WWTP Sediment (10)	0.00246	0.00012
Rhine River (Germany)		
UK Marine Sediment		
5th Centile D4 NOEC = 2.40E+05 ng/g OC		

Table 2. Exceedance % probability for D4 sediment concentrations of 5th centile chronic D4 NOEC and overall % probability of joint occurrence.

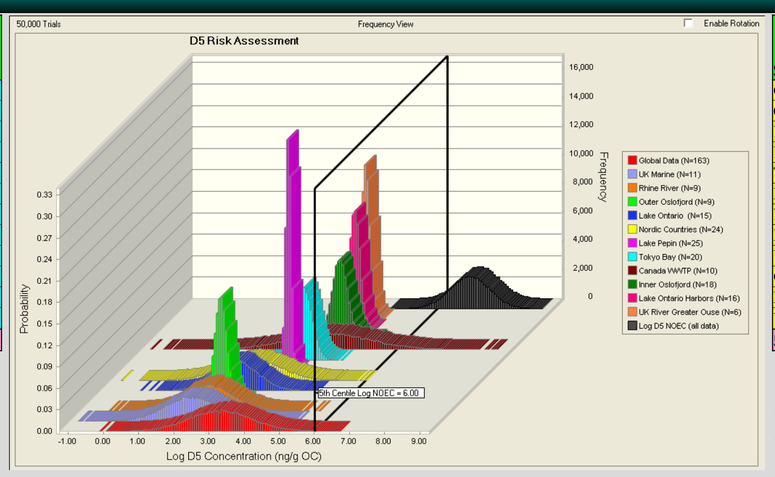


Figure 2. Exposure probability distributions for D5 sediment concentrations (ng/g-OC) compared to chronic toxicity NOEC values (ng/g-OC) for D5 with benthic invertebrate species.

Study Area (N)	Certainty (%) (C_{SED} ≥ 5% NOEC)	Overall Probability (%) (C_{SED} ≥ 5% NOEC)
Global Data (>150)	0.12440	0.00622
Outer Oslofjord (9)	0.00000	0.00000
Lake Ontario (25)	0.00000	0.00000
Lake Pepin (USA) (25)	0.00000	0.00000
Tokyo Bay (20)	0.00000	0.00000
Inner Oslofjord (18)	0.00000	0.00000
Lake Ontario Harbors (6)	0.00000	0.00000
Nordic Countries (25)	0.00029	0.00001
UK River Greater Ouse (6)	0.00000	0.00000
Canada WWTP Sediment (10)	5.10405	0.25520
Rhine River (Germany) (9)	0.00000	0.00000
UK Marine Sediment (10)	0.00000	0.00000
5th Centile D5 NOEC = 1.10E+06 ng/g OC		

Table 3. Exceedance % probability for D5 sediment concentrations of 5th centile chronic D5 NOEC and overall % probability of joint occurrence.

PROBABILISTIC RISK ASSESSMENT

- Probabilistic methods use the continuum of potential exposure and effect and the degree of overlap may be calculated, thereby providing a quantitative estimate of the probability of an adverse effect. The potential for impact by D4 and D5 on benthic invertebrates was assessed using a combination of field sediment concentrations and chronic, 28-day NOEC levels from laboratory studies on accepted sediment species (i.e., *Hyalella, Chironomus* , and *Lumbriculus* species).
- In probability theory, if two events, A and B, are independent, the probability (P) that they both occur is equal to the product of the probabilities of the two individual events: $P(A \cap B) = P(A) * P(B)$
- Hence, based on the data evaluated for D4 and D5, the probability of a 95th centile exposure event will occur simultaneously with a 5th centile benthic invertebrate organism chronic NOEC response is ≤0.25%. Alternatively, the probability that such a simultaneous event will **not** occur is ≥99.75%.
- **D4**: The individual site probability data in Figure 1 and Table 2 indicate there are no measured sediment concentrations, even in Canadian municipal and industrial WWTP sediments, where levels exceed the 5th centile chronic NOEC value more than 0.003% of the time. Even in this situation of a D4/D5 production site sediment, the overall collective % probability of 5th centile NOEC exceedence is only 0.00012%. When all site data are considered ('Global Data'), both the % certainty of exceedance and the overall % cumulative probability are essentially zero, less than 0.0002%.
- **D5**: The individual site probability data in Figure 2 and Table 3 indicate the only location to exceed the 5th centile chronic NOEC value more than 0.0003% of the time was the Canadian WWTP location 8, an industrial site producing D4/D5; the likelihood of exceeding the 5th centile chronic NOEC value was 5% for all sampled Canadian WWTP sediments and the overall cumulative probability of joint occurrence was 0.25% for these sites. When all site data are considered ('Global Data'), the % certainty of exceedance and the overall % cumulative probability are 0.12% and 0.006%, respectively. These data indicate that the overall likelihood of exceeding the 5th centile chronic NOEC for D5 is very small, less than 0.15%, and the joint probability of elevated sediment concentrations coinciding with a highly sensitive benthic invertebrate species is extremely low, less than 0.007%.

CONCLUSIONS

- There is an absence of overlap of individual sediment exposure concentrations with the interpolated, 5th centile benthic sediment NOEC trigger levels, except at locations where the compounds are manufactured. These results suggest the likelihood of chronic risk of D4 and D5 to benthic species is extremely low, less than 0.007%.
- For both D4 and D5, measured chronic benthic invertebrate NOEC values exist for three standard regulatory-approved species. The probability distributions allow for interpolation of 5th centile (HC5) benthic sediment NOEC values that are comparable to their respective OC solubility concentrations. This low level of toxicity with respect to benthic organisms is consistent with the recent work of Redman et al. (2012), who found the environmental toxicology data on D4/D5 compatible with a narcotic mode of action.
- With D4, the only exceedance of the 5th centile NOEC level was in Canadian municipal and industrial WWTP sediments where the levels exceed the value <0.003% of the time; the cumulative (i.e., 'global'), overall probability of exceeding the NOEC is ~0.0001%.
- For D5, the only location to exceed the 5th centile chronic NOEC value more than 0.0003% of the time was the Canadian WWTP location 8, an industrial site producing D4/D5. When all site data are considered ('Global Data'), the % certainty of exceedance and the overall % cumulative probability was 0.12% and 0.006%, respectively. These data indicate that the overall likelihood of exceeding the 5th centile chronic NOEC for D5 is very small, less than 0.15%, and the joint probability of elevated sediment concentrations coinciding with a highly sensitive benthic invertebrate species is extremely low, less than 0.007%.
- cVMS materials D4 and D5 are highly lipophilic (i.e., log K_{ow} >6) and are therefore will predominantly reside in sediment when exposed to natural aquatic systems, where these materials are predominately present in WWTP discharge streams. The analysis shown here demonstrates the advantage of probabilistic methods over more common hazard assessment techniques in that they allow the risk assessor to include stochastic properties of both exposure and toxicity. The probabilistic methods thereby provides a quantitative estimate of the likelihood of an adverse effect.

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