Dynamic modelling of aquatic exposure and pelagic food chain transfer of cyclic volatile methyl siloxanes in the Inner Oslofjord

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Abstract

The marine fate and pelagic food chain transfer of three cyclic volatile methyl siloxanes (cVMS: D4, D5 and D6) was explored in the Inner Oslofjord, Norway, using two dynamic models (the Oslofjord POP Model and the aquatic component of ACC-HUMAN). Predicted concentrations of D4, D5, and D6 in the water column were all less than current analytical detection limits, as was the predicted concentration of D4 in sediment (in agreement with measured data). The concentrations predicted for D5 and D6 in sediment were also in broad agreement with measured concentrations from the Inner Oslofjord. Volatilisation was predicted to be the most important loss mechanism for D5 and D6, whereas hydrolysis was predicted to dominate for D4. Concentrations of all three compounds in sediment are controlled by burial below the active mixed sediment layer. The marine food web model in ACC-HUMAN predicted “trophic dilution” of lipid-normalised cVMS concentrations between zooplankton and herring (Culpea harengus) and between herring and cod (Gadus morhua), principally due to a combination of in-fish metabolism and reduced gut absorption efficiency (as a consequence of high $K_{ow}$).

Predicted D5 concentrations in herring and cod agree well with measured data from the inner fjord, particularly when measured concentrations in zooplankton were used to set the initial dissolved-phase aqueous concentrations. Predicted concentrations of D4 and D6 in fish were over- and under-estimated by the model – possibly due to extrapolation of the metabolism rate constant from D5.

Key Words: cyclic volatile methyl siloxanes, trophic transfer, model
Introduction

Cyclic volatile methyl siloxanes (cVMS) are used in a wide range of personal care products (e.g. Horii and Kannan, 2008). Recently, concerns have been raised about their environmental profile (e.g. Brooke et al., 2008a, b, c), particularly their potential for environmental persistence and bioaccumulation. They are relatively long lived in water because they are not biodegradable, although they do undergo acid- and base- catalysed hydrolysis with estimated half lives ranging from a few hours to a few hundred days, depending on the compound, pH and temperature (e.g. Brooke et al., 2008a, b, c). cVMS compounds have very high air : water partition coefficients and they tend to partition to the atmosphere (Whelan et al., 2004; Price et al., 2010) where they can potentially be transported over long distances (McLachlan et al., 2010). Once airborne, they are unlikely to repartition appreciably to surface media (Wania, 2006) and are broken down primarily by reaction with OH radicals to silanols, which are more water-soluble (Whelan et al., 2004) and are eventually mineralised to SiO$_2$, CO$_2$ and water. A fraction of the chemicals used in personal care products will be transferred to waste water. In waste water treatment plants (WWTPs), cVMS compounds are likely to sorb significantly to sludge solids and to partition to the atmosphere, owing to their unusual combination of hydrophobicity and volatility. However, a small fraction of the influent load will be emitted to surface waters in treated effluent (Sparham et al., 2008; Price et al., 2010). The fate of cVMS compounds in freshwater environments has been discussed by Whelan et al. (2009; 2010) and by Price et al. (2010). However, to date, there has been little consideration of the fate of these chemicals in marine systems.
Whilst they are very hydrophobic, with reasonably high aquatic bioconcentration factors, cVMS compounds have been shown to metabolise in fish (Domoradzki et al., 2006) and are excreted by air-breathing organisms via the lungs, owing to their high volatility. Their behaviour in aquatic food webs is, therefore, potentially complex. Of particular interest is the debate about the propensity of cVMS materials to biomagnify. Powell et al. (2009) have reported that lipid-normalised cVMS concentrations in aquatic organisms sampled from Lake Pepin (Minnesota, USA), a freshwater lake on the Mississippi River, decreased with increasing trophic level (assigned using stable isotope analysis).

There is a need to improve our understanding of how these materials behave in order to evaluate any environmental risks posed by their use. The objective of this work was to explore the environmental behaviour of three cVMS compounds: [octamethylcyclotetrasiloxane(D4), decamethylcyclopentasiloxane (D5) and dodecamethylcyclohexasiloxane (D6)] in the Inner Oslofjord (Norway) using a bespoke dynamic (time explicit) non-equilibrium multimedia fate and transport model. We also investigate the fate of these compounds in the pelagic food web using a dynamic food web model, in order to evaluate their potential for trophic transfer.

**Exposure Model**

We employed the dynamic fugacity-based Oslofjord POP Model (OPM: Breivik et al., 2003; 2004) which was developed from the steady-state QWASI model (Mackay et al., 1983a,b) specifically for representing processes in the Inner Oslofjord (surface area approximately 191 km²: Ruud, 1968). It considers a number of different interconnected aquatic compartments representing the two main basins of the inner fjord (Vestfjorden and
Bunnefjorden: Figure 1). Each basin is represented by three compartments (each of which, in turn, is composed of water and sediment) which are shown schematically in Figure 1 with the following mean depth ranges: W1 and W4 (0 – 20 m); W2 and W5 (20 - 50 m); W3 and W6 (≥ 50 m). However, it is recognised that there are parts of the deepest compartments which greatly exceed 50 m. The Bunnefjorden has a maximum depth of ca 164 m and the Vestfjorden has a maximum depth of ca 160 m. Water fluxes between freshwater and the coast and between the marine compartments (Figure 1b) were derived by NIVA, the Norwegian Institute for Water Research (Bjerkeng, 1994). Sediment transfer and organic carbon dynamics were constructed for the inner fjord by Breivik et al. (2003). Salient model parameters are reproduced in the Supplementary Information (Table S1). It should be noted that in the model runs presented in this report no ice cover was assumed. Whilst sea ice does form in the coastal areas of the Inner Oslofjord, most of the sea area usually remains ice free.

Degradation rates in water are expressed in the OPM as bulk half lives. However, hydrolysis (the only aquatic degradation process considered here for cVMS compounds) will only affect the dissolved fraction of chemical in the water column. Half lives were, therefore, adjusted by:

\[ HL_{e,corr} = \frac{HLe}{fdiss} \]  

(1)

where \( HL_{e,corr} \) is the corrected half life, \( HLe \) is the temperature- and pH- adjusted half-life and \( fdiss \) is the fraction of total mass predicted to be in the dissolved phase:
\[ f_{\text{diss}} = \frac{1}{(1 + C_{\text{SS}} \cdot f_{\text{OC}} \cdot K_{\text{OC}})} \]  

(2)

where \( C_{\text{SS}} \) is the steady state concentration of suspended solids in the water column (kg L\(^{-1}\)), \( f_{\text{OC}} \) is the fraction of organic carbon in the water column (g C g\(^{-1}\) solid) and \( K_{\text{OC}} \) (L kg\(^{-1}\)) is the organic carbon:water partition coefficient (derived from the temperature-adjusted value of \( K_{\text{OW}} \)). This ignores sorption to dissolved organic carbon (DOC) which can limit volatilisation in freshwaters (Whelan et al., 2009; 2010). However, there is considerable uncertainty in both \( C_{\text{SS}} \) and \( f_{\text{OC}} \), which may be at least as important for predicted chemical fate as neglecting interactions with DOC. Sea water is assumed to have a constant pH of 8.

**Figure 1 here**

**Food web model**

Chemical transfer in the marine food chain is represented in the dynamic fugacity-based ACC-HUMAN model (Czub and McLachlan, 2004a, b). This model has been applied successfully to predict PCB concentrations in fish, beef, milk and human tissue in Sweden (Czub and McLachlan, 2004a). The model used here has minor adjustments from the model described originally by Czub and McLachlan (2004a, b), as detailed in Breivik et al (2010). The default marine food chain in ACC-HUMAN contains zooplankton (assumed to be in chemical equilibrium with sea water), herring (*Culpea harengus*, a planktivorous fish) and cod (*Gadus morhua*, a piscivorous fish, feeding on herring and small cod) and has been parameterised for the Baltic Sea. It should be noted that there is some evidence that the food web in the Inner Oslofjord may differ significantly from that in the Baltic,
particularly with respect to the diet of cod. NIVA has indicated (based on a food web study by Heggelund (2001, unpublished, and a food web model being developed for Oslofjord) that >90% of the diet of cod in the Inner Oslofjord is shrimp, with the deep water shrimp (*Pandalus borealis*) dominating cod stomach contents in terms of both biomass (80%) and number (51%). In contrast, herring accounted for less than 2% of the diet of cod in the Inner Oslofjord. The chemical uptake mechanisms prevalent in deep water shrimp may be quite different from the exposure routes assumed for zooplankton (i.e. in equilibrium with the water column) and herring in ACC-HUMAN, especially if the shrimp live in or ingest bottom sediments, which could have high concentrations of cVMS. However, full evaluation of these factors is beyond the scope of this paper. In any case it is, perhaps, more helpful to think about the organisms represented in ACC-HUMAN as generic trophic levels rather than, necessarily, as individual taxa.

Bioaccumulation in fish is described using the following dynamic equation (from Gobas et al., 1988):

\[
\frac{d(V_F Z_F f_F)}{dt} = D_V f_w + E_{OF} \sum (D_{UF} f_{prey}) - \left( D_V + D_M + \frac{E_{OF}}{Q_F} \sum (D_{UF}) \right) f_F \tag{3}
\]

where \(V_F\) is the volume of fish (m\(^3\)), \(Z\) is the fugacity capacity (mol m\(^-3\) Pa\(^{-1}\)), \(f\) is the fugacity (Pa), \(D\) refers to chemical transport or degradation per unit fugacity (mol Pa\(^{-1}\) h\(^{-1}\)), subscripts \(F\), \(W\), \(V\), \(M\), \(UF\) and \(prey\) refer to fish, water, ventilation, metabolism in fish, uptake via food and prey (zooplankton in the case of herring; zooplankton, herring and small cod in the case of cod) respectively, \(E_{OF}\) is the gut absorption efficiency (fraction of ingested chemical which is absorbed: dimensionless) and \(Q_F\) is the egestion factor (ratio of
D-values for ingestion and egestion: dimensionless). Note that $E_{OF}$ for fish is described by the following empirical equation (Niimi and Oliver, 1983; Clark et al., 1990) derived for Rainbow Trout (*Oncorhyncus mykiss*) since no experimental data on absorption was available for cod and herring:

$$E_{OF} = \left(1.33 + 9.7 \times 10^{-11} K_{ow}\right)^{1}$$  \hspace{1cm} (4)

A distinguishing feature of ACC-HUMAN is the fact that it considers several different age classes of fish simultaneously. There are ten age classes for herring and ten for cod, with fish moving between age classes on the first of March each year. New fish develop from eggs with the same initial fugacity as the mother fish. At the very start of the simulation, there are no mother fish and the eggs are assumed to have the same fugacity as the water.

The rate of food ingestion is assumed to be a function of fish species and fish age. However, no account is taken of potential changes in metabolism rates with age or body size (e.g. Nichols *et al.*, 2007; Arnot *et al.*, 2008). Cod are assumed to eat a varied diet consisting of zooplankton and a distribution of different age classes of herring, as well as some small cod. Fish growth is described using an empirically-fitted modified Bertalanffy growth equation (see Czub and McLachlan, 2004a).

In the application to Oslofjord described here, the time series of predicted dissolved-phase concentration of cVMS in water was exported from the OPM and imported into ACC-HUMAN. All food chain parameters were left unchanged from the Baltic scenario, except for the metabolism rate constants for herring and cod which were set to $4 \times 10^{-4}$ h$^{-1}$ for both species. These values were derived from a laboratory-derived fish feeding study for
D5 (Dow Corning: Domoradzki et al., 2006). There is some unpublished empirical
evidence to suggest that the metabolism rate constant for D4 in fish is similar to that for
D5 and that D6 may metabolise more slowly, if at all (e.g. Woodburn et al., 2008). Note
that metabolism rate constants for D4, D5 and D6 have been reported for Fathead Minnow
(Pimephales promelas) in a database of fish biotransformation rates (Arnot et al., 2008).
After adjusting for fish mass and temperature, they range from $4.5 \times 10^{-5}$ h$^{-1}$ for D5 to $5.2$
$\times 10^{-4}$ h$^{-1}$ for D4, which are not dissimilar to the measured value derived directly for D5.
Unexpectedly, the value derived for D6 was higher than that derived for D5 at $1.14 \times 10^{-4}$
h$^{-1}$. However, all these values were estimated using a combination of unpublished
laboratory data (e.g. BCF studies) and mass balance modelling which employed much
lower estimates for $K_{OW}$ than those reported in Table 1. We have, therefore, not included
them in our analysis. Estimates of metabolism rate constant are also calculated by the
BCFBAF estimation model (v3.01) in EPI Suite v4.1 (US EPA, 2011) which employs the
Arnot at al. (2008) database to derive empirical relationships between $K_{OW}$ and
metabolism rate constant. Using values for $K_{OW}$ which are consistent with those reported
in Table 1, the calculated values for D4, D5 and D6 are, respectively, $5.32 \times 10^{-4}$ h$^{-1}$, 1.07
$\times 10^{-4}$ h$^{-1}$ and $2.59 \times 10^{-5}$ h$^{-1}$, which are in reasonable agreement with the assumptions
made here.

The seasonal distribution of temperature in the deep compartments of the Inner Oslofjord
was used to adjust temperature-dependent partition coefficients in ACC-HUMAN. The
use of deep water temperatures resulted in a reduced seasonal variation in predicted
concentrations in fish compared with using surface water temperatures, due to the
reduction of seasonal temperature amplitude with depth.
**Chemical properties**

Key properties of D4, D5 and D6 are shown in Table 1. It should be noted that the value for $K_{OC}$ is derived in the OPM from $K_{ow}$ via a linear Karickhoff (1981)-type relationship, with slope $m_{OC}$ which is fixed at 0.35 L kg$^{-1}$, after Mackay (2001). However, this assumption results in a significant over-estimation of $K_{OC}$ compared with measured values (e.g. Durham, 2007; Miller and Kozerski, 2007; Whelan et al., 2009; 2010). Input values of log($K_{OW}$) were, therefore, adjusted to 4.68, 5.66 and 6.49 for D4, D5 and D6 respectively, in order to force the model to derive values of $K_{OC}$ which were consistent with the measured values. In order to maintain consistency with the other primary partition coefficients, i.e. to conserve the relation log($K_{OW}$) = log($K_{AW}$) + log($K_{OA}$), values of $K_{AW}$ were adjusted downwards in proportion with the adjustment in the $K_{OW}$ values. This is unlikely to affect water to air transfer, which will be limited by the water-side partial mass transfer coefficient, rather than by the Henry’s law constant, at such high $K_{AW}$ values. However, it will influence the relationship between fugacity and concentrations because $Z$ values (fugacity capacity) all depend on the Henry’s law constant (Mackay, 2001). It should be noted that in ACC-HUMAN no adjustment was made to the value of log ($K_{OW}$). Degradation half life values in sediment were derived from experimentally-derived and temperature adjusted hydrolysis half lives in water at pH 8 (see Brooke et al., 2008a, b, c), assuming that degradation occurs only by hydrolysis in the freely dissolved form in pore water (described using first order kinetics). The effective hydrolysis half lives for D5 and D6 in sediment are very long because of the very low fraction of chemical which is predicted to be in the dissolved phase (i.e. available for hydrolysis). Further details can be found in the Supplementary Information. It should be noted that unpublished experimental half life values of approximately 365 and 3100 days,
respectively have been derived for D4 and D5 for sediment collected from Lake Pepin (Minnesota, USA) for 25 °C at pH 7.9 (Xu et al., 2010). These values are, respectively, higher and lower than those assumed here. However, in any case, all multi-media fate and transport models will be insensitive to sediment half lives for slowly degrading substances because residence time becomes limited by physical processes such as sediment resuspension and burial.

TABLE 1 HERE
Emission scenario

Emission rates of D4, D5 and D6 were based on per capita usage estimates in “cosmetic” products (i.e. those products which are most likely to result in domestic emissions to waste water) reported by Brooke et al. (2008a, b, c) for the UK, combined with an assumption that 10% is lost to the waste water stream. The remainder is assumed to volatilise before wash-off to drains. The per capita emission estimates were multiplied by the population of the contributing catchment (approximately 1.6 million in total: City of Oslo, 2003) and the fraction not removed in waste water treatment to determine total emissions to the fjord and its contributing catchment (Table 2). Predicted removal of the cVMS compounds during secondary sewage treatment is based on predictions generated using the STP Model (v 2.11: Clark et al., 1995) which simulates the chemical behaviour in an activated sludge type WWTP. Default treatment plant parameters were assumed with three tanks in series (primary settling, aeration basin and final clarifier). The prediction of 97% for D5 agrees approximately with estimates of removal based on measured influent and effluent concentrations which ranged from 91-99% (Boehmer and Gerhards, 2003 reported in Brooke et al., 2008b). However, it should be noted that the removal efficiency of different waste water treatment plants is likely to vary. Overall, emission estimates are highly uncertain but will be very important in determining the absolute concentrations predicted for each compound in each compartment of the receiving environment.
Two large WWTPs serve Oslo city (Bekkelaget and VEAS). Bekkelaget treats approximately 37% of the effluent stream from Oslo and VEAS about 63%. Both these WWTPs have deep water effluent outfalls at a depth of approximately 50 m, to which treated waste water is pumped. Emission was, therefore, assumed to occur in the mid-depth compartments, W2 and W5, in proportion to the respective fractions emitted to the Bekkelaget and VEAS WWTPs.

In all cases, simulations are assumed to start in the year 1998 and to run (arbitrarily) for 40 years. Emission is assumed to be constant for any single year. Emissions for each chemical are assumed to be at the rate shown in Table 2 for the first twenty years (to the end of 2017), after which emission is assumed to cease completely (2018-2037), in order to evaluate the rate at which each chemical is expected to clear from the system.

Results and Discussion

Predicted concentrations in WWTPs

Effluent concentrations of D4, D5 and D6 were calculated from the emission estimates to water shown in Table 2 and a per capita water flow rate of 400 L cap\(^{-1}\) d\(^{-1}\) (representing domestic water use, trade effluent and surface runoff directed to combined sewers: see data given by Keller et al., 2007 and Sparham et al., 2008 for the UK). These are shown in Table 3 along with measured concentrations in the influent and effluent streams of both Bekkelaget and VEAS WWTPs (Schlabach et al., 2007). The model estimates of influent concentration are much higher than the measured data for all three compounds (by factors...
of up to approximately 8, 2 and 5 times for D4, D5 and D6, respectively). This suggests that the emissions assumed in Table 2 are erroneous – either because the per capita usage is lower in Norway compared to the UK or because the assumption of 10% wash off for cosmetic products is too high. The latter explanation has been suggested by Price et al. (2010) to explain the fact that measured D5 concentrations in WWTP influents in the UK were lower than estimates based on Brooke et al. (2008b). The difference between measured and predicted concentrations in WWTP effluent is better for D5 and D6, suggesting that the STP model may overestimate cVMS removal. The extent of this overestimation is even more pronounced for D4, for which the predicted effluent concentration is several times lower than that measured at the VEAS plant. More data are needed on effluent concentrations in order to confirm the validity of these initial interpretations.

TABLE 3 HERE

Predicted concentrations in water and sediment

OPM-predicted concentrations of D4, D5 and D6 in the various marine compartments of Inner Oslofjord are shown in Figures 2 and 3 for water and sediment, respectively; note the different y-axis scales in these figures. Although the time step used for model integration was one hour, results have only been written every 1752 hours (73 days), i.e. five times per year. The lines, therefore, appear to be more discontinuous than the actual time series of predicted concentrations calculated by the model.

Predicted concentrations are highest for D5 (Figure 2b), followed by D6 (Figure 2c) and then D4 (Figure 2a). Concentrations for all three compounds vary seasonally with water
temperature, reflecting the temperature dependence of hydrolysis and volatilisation –
particularly for the near-surface compartments (W1 and W4). For all three compounds,
concentrations in the water column are predicted to be below current typical analytical
limits of detection (e.g. 10 ng L\(^{-1}\): Sparham et al., 2008) which agrees with the findings of
recent monitoring (e.g. Schlabach et al., 2007: LOD 20-30 ng L\(^{-1}\)). Concentrations in the
water column are predicted to achieve pseudo (annual) steady-state relatively quickly after
the start of the simulation and to decrease rapidly after cessation of emissions, particularly
for D4.

Predicted concentrations in sediment (Figure 3) were, again, highest for D5, followed by
D6 and D4. This is in broad agreement with the results of recent monitoring at six
locations in Oslofjord (Schlabach et al., 2007) which detected D5 at concentrations
between 93 and 920 ng g\(^{-1}\) dw and D6 at concentrations between <17 and 100 ng g\(^{-1}\) dw,
and which failed to detect D4 (LOD 4-38 ng g\(^{-1}\) dw). Two of these sediment samples
were collected from the Bunnefjorden at a water depth of about 50 m, close to the
Bekkelaget WWTP, two were in the main basin of the Vestfjorden and two were in the
north of the Vestfjorden (Lysaker at a water depth of about 60 m). CVMS concentrations
in Oslofjord sediment have also been measured by Powell et al. (2010), who report
average concentrations of 1.7 ± 0.15, 347 ± 26 and 70 ± 4.5 ng g\(^{-1}\) dw for D4, D5 and D6,
respectively (37.4 ± 9.6, 7609 ± 1899 and 1663 ± 323 ng g\(^{-1}\) OC). These values are
approximately consistent with the Schlabach et al. (2007) data and, so, serve to underpin
the validity of the model predictions presented here. It should be noted that concentrations
in sediment are predicted to reach steady state relatively rapidly for all three compounds
investigated here, in part due to the relatively high rates of net sedimentation assumed
relative to the assumed depth (5mm: Mackay, 2001) of the active mixed sediment layer. It
is important to note that the depth assumed for the active mixed sediment layer is critical
for the chemical response time in sediment predicted – particularly for chemicals which
degrad slow relatively to the rate of sediment burial, as is assumed for the cVMS
compounds considered here. It should also be noted that such a shallow sediment layer
may not be consistent with mixing depths in sediments which are subject to bioturbation –
where mixing can typically occur in the top 5-10 cm. A deeper mixed sediment layer
would result in slower time to steady state and clearance times after cessation of
emissions. The predicted sediment concentration of D4 is negligible compared to D5 and
D6 (four orders of magnitude lower than D6 and five orders of magnitude lower than D5).
The compartments for which the highest concentrations are predicted are, unsurprisingly,
the mid-depth compartments (W2 and W5) where emission is assumed.

FIGURE 2 HERE

FIGURE 3 HERE

Factors affecting fate and transport of cVMS

Concentration changes of cVMS in the water column are affected by a combination of
hydrolysis, volatilisation, advection out of the system and by exchange with sediment.
For D5 and D6, volatilisation is predicted to be the most important loss process in the
water column, accounting for >50% of emissions. Contrary to expectations, volatilisation
was predicted to peak in winter. Although \( K_{AW} \) will decrease in winter with reduced
temperatures, the rate of volatilisation is always limited by the water side partial mass
transfer coefficient, which means that it is relatively insensitive to \( K_{AW} \). Furthermore, a
decreased rate of hydrolysis in winter promotes higher total water column concentrations
which favour volatile losses, in the absence of an ice cover, by promoting a higher fugacity gradient across the air-water interface. This will be enhanced by a reduction in $K_{\text{AW}}$ at reduced temperatures which will increase the fugacity capacity of water and, to a lesser extent a reduction in $K_{\text{OW}}$ which will reduce the sorbed fraction in the water column. Both of these factors will also favour a slightly higher dissolved phase fraction. For D4, volatilisation is also important, although less so (in relative terms) compared with D5 and D6. Advection to other water compartments is a significant process for D5 and D6, but is less important for D4 on account of much lower total water column concentrations.

Degradation (by hydrolysis) in the water column is most important (as a fraction of emission) for D4 (which is predicted to exceed 60% of emission, even in winter), followed by D5 (where degradation losses exceed 10% of emission in summer). For D6 degradation is relatively unimportant. Net flux from the water column to the sediment compartments (followed by burial) is a significant pelagic loss mechanism for D6 but not for D5 and D4.

With the exception of D4, degradation (via hydrolysis) in sediment is assumed to be very slow. Changes in the concentration of cVMS compounds in sediment are, therefore, controlled largely by exchanges of particulate organic carbon between the water column and the sediment and then by sediment burial. As a fraction of emission, the rate of burial is most significant for D6, where it can account for 10% of emission. For D5 and D4 it is less important in relative terms, accounting for only about 2.3% and 0.12% of emission respectively.
Bioaccumulation potential of cVMS

The predicted concentrations of D4, D5 and D6 in zooplankton, herring and cod in the Inner Oslofjord generated by ACC-HUMAN using predicted dissolved-phase concentrations generated by the OPM are shown in Figure 4. For herring and cod, the concentrations shown are the means predicted for all age classes of each species. There is considerable variation in the concentrations predicted for different age classes and concentrations overlap significantly between trophic levels. However, it is interesting to note that “trophic dilution” is predicted for all three compounds (i.e. concentrations in zooplankton were higher than for herring and concentrations in herring were higher than for cod).

For D4, the predicted concentration data significantly underestimate measured concentrations in zooplankton, herring and cod (379, 115 ± 22 and 100 ± 19 ng g\(^{-1}\) lipid, respectively) reported from a recent monitoring study conducted by Powell et al. (2010). In the case of D5, the predicted concentrations significantly overestimate measured concentrations in zooplankton, herring and cod (49594, 18379 ± 3113 and 2026 ± 265 ng g\(^{-1}\) lipid, respectively). The predictions also overestimate measured D5 concentrations in cod liver (5943-9607 ng g\(^{-1}\) lipid) in the Inner Oslofjord reported by Schlabach et al. (2007). For D6, the overestimation is even more exaggerated compared with measured concentration data reported by CES (397, 241 ± 30 and 137 ± 15 ng g\(^{-1}\) lipid, respectively, for zooplankton, herring and cod). This suggests that the aqueous concentrations of D5 and D6 may be overestimated by the OPM. Since the predicted concentrations of these compounds in sediment match the measured data from two independent campaigns quite well, and since emissions of these compounds appear to be approximately consistent with
measured data (Table 3), the source of the error could be over-estimating \( f_{diss} \) (Equation 2) – for example, as a consequence of neglecting to account for interactions with DOC, from errors in \( K_{OC} \) estimation or from underestimating the rate of hydrolysis. These explanations are, of course, speculative at this stage. Note that the mean measured lipid-normalised cVMS concentrations result in Trophic Magnification Factors (TMFs) of 0.514 \( (p = 0.27) \), 0.202 \( (p = 0.147) \) and 0.587 \( (p = 0.023) \) for D4, D5 and D6, respectively, using average data and following the method described by Borgå et al. (2012), where \( p \)-values are given for the slope of the regression. Values of TMF < 1 are assumed to be indicative of trophic dilution although, in this case, the slope of the regression between trophic level and log concentration is statistically significant \( (p < 0.05) \) only for D6. The reader is referred to Powell et al. (2010) for a more complete analysis of cVMS trophic transfers in Oslofjord.

The prediction of trophic dilution for the cVMS compounds in marine biota generated by ACC-HUMAN can be explained by two main factors: (1) in-fish metabolism and (2) reduced gut uptake efficiency due to the high hydrophobicity of the cVMS compounds (see Equation 4). Predicted concentrations in fish are quite sensitive to the metabolism rate constants \( (k_{cod} \text{ and } k_{herr}) \), provided that values are greater than about \( 4 \times 10^{-6} \text{ h}^{-1} \). Since there is some uncertainty about the values of these parameters, particularly for D4 and D6, there will necessarily be uncertainty about the model predictions. Some metabolism is required in order to generate a dilution effect for the mean concentrations in fish. When metabolism is switched off completely \( (k_{cod} = k_{herr} = 0 \text{ h}^{-1}) \), average concentrations in herring and cod exceed those in zooplankton, although the average
concentration in herring still exceeds that in cod. Although the complex diet assigned in
the default model scenario for cod is a key feature of ACC-HUMAN, the moderate
metabolism rate constant assumed for cVMS compounds in all fish means that predictions
are relatively insensitive to the age class distribution in the diet of the cod. At lower rates
of metabolism, diet becomes more important because older fish tend to have higher
concentrations due to the fact that they have higher net chemical accumulation than
younger fish due to their longevity. This is discussed further below with respect to the
relative behaviour of PCBs predicted by ACC-HUMAN.

It is important to note that chemical partitioning in the food chain in ACC-HUMAN is
assumed to be driven by $K_{OW}$, where octanol acts as a surrogate for lipids. However,
should the lipid-water partition coefficient differ significantly from $K_{OW}$ for cVMS
compounds, the predictions made, and the conclusions reached, could differ from those
presented here. The sensitivity of ACC-HUMAN-predicted food chain transfer to a range
of log ($K_{OW}$) values for D5 from 5.2 to 8.05 was investigated (data not shown). In all
cases, the value of log ($K_{OA}$) was kept constant at 5.04, but the value of log ($K_{AW}$) was
adjusted so as to maintain internal consistency between the values of the principal
partition coefficients. This means that any change in the value of $K_{OW}$ must also entail a
commensurate change in the value of $K_{AW}$. As the value of $K_{OW}$ increases, the chemical
concentration in both herring and cod is predicted to decrease. Although this is somewhat
counter intuitive, since we expect an increase in hydrophobicity to result in an increase in
lipid normalised concentration (as a consequence of an increased affinity for lipids), it can
be explained, in part, by a decrease in assumed gut absorption efficiency with decreasing
$K_{OW}$ (see Equation 3). Interestingly, predicted chemical concentrations in zooplankton are
not influenced by changes in $K_{OW}$, although we would expect the lipid-normalised
concentration to decrease with falling $K_{OW}$. This is a consequence of the commensurate adjustment in $K_{AW}$ as $K_{OW}$ changes. This highlights the need to take account of the complete partitioning and metabolic behaviour of the chemicals under consideration rather than relying solely on hydrophobicity as a predictor of biomagnification (cf Borgå et al., 2012; Mackintosh et al., 2004).

**Zooplankton as passive samplers**

There is clearly considerable uncertainty about the concentration of cVMS in water because no aqueous concentration measurements have ever been reported in the Inner Oslofjord above an LOD. However, measurements of cVMS concentrations in zooplankton sampled from the fjord have been made recently by Powell et al., 2010). If we assume that lipid in zooplankton acts like octanol, and that the zooplankton act like a passive sampler in water, then we can calculate the free aqueous concentration of cVMS ($C_W$) from:

$$C_W (\text{free}) = \frac{C_Z \cdot \rho}{K_{OW}}$$

(5)

where $C_Z$ is the concentration in zooplankton (ng g$^{-1}$ lipid) and $\rho$ is the density of lipid (assumed to be 800 kg m$^{-3}$ in ACC-HUMAN). Note that here we make no correction for sorption to non-lipid biomass fractions, such as carbohydrates and proteins (Mackintosh et al., 2004) because such corrections are made neither in ACC-HUMAN nor in the reported concentration data. In any case, sorption to these fractions can be assumed to be independent of sorption to lipids at equilibrium since they are unlikely to significantly
reduce the aqueous concentrations, although they will affect the magnitude of
concentrations expressed in lipid equivalent terms.

The predicted concentrations of D4, D5 and D6 in zooplankton, herring and cod generated
by ACC-HUMAN using constant dissolved phase concentrations in water derived from
Equation 5 (i.e. $1.24 \times 10^{-1}$, 0.72 and $1.34 \times 10^{-4}$ ng L$^{-1}$ respectively for D4, D5 and D6
with $K_{ow}$ temperature-adjusted to 5 °C) are shown in Figure 5. In all cases, a value of 4 x
$10^{-4}$ h$^{-1}$ was assumed for the metabolism rate constant in both herring and cod,
respectively, in the absence of definitive substance-specific rate constants for D4 and D6.
Other unpublished industry data tend to confirm this assumption for D4, although it is
believed that the metabolism rate constant for D6 may be lower than for D5 (Woodburn et
al., 2008). Unsurprisingly, the predicted concentration in zooplankton matches the
measured data well for all three compounds since the starting concentrations in water were
derived from the measured data. However, the predicted concentrations for fish are also a
much better match compared with Figure 4. This is particularly the case for D5, where the
model captures the measured concentrations (indicated with symbols) well. For D4, the
model underestimates the extent of trophic dilution apparent in the measured data for
herring and cod and for D6 the extent of trophic dilution is over-predicted. This may be
due to the assumption of the same metabolism rate constant in fish as that derived from
the industry fish feeding study for D5 (Domoradzki et al., 2006). The comparisons of
predicted and measured concentrations in fish presented here suggest that the assumed
metabolism rate constant may be, respectively, too low and too high for D4 and D6. This
diagnosis is supported by BCFBAF estimations (US EPA, 2011) of the metabolism rate
constant for D4, D5 and D6 which suggest that the rate constant for D4 is expected to be
about five times higher than for D5 and that for D6 is about four times lower.
In order to benchmark the predicted behaviour of cVMS compounds against the predicted behaviour of known POPs, the ACC-HUMAN model was run for seven PCB congeners (PCBs 28, 52, 101, 118, 138, 153 and 180). The physicochemical properties of these compounds were taken from Breivik et al. (2004) but were originally derived from a range of sources including Li et al. (2003) and Wania and Daly (2002). In all cases, the same arbitrary constant concentration in sea water was assumed at 0.1 ng L\(^{-1}\), which allows the relative pattern of PCB behaviour in the model to be compared to the predictions for D4, D5 and D6. Predictions of PCB behaviour reported here should only be considered in relative terms.

Two sets of predictions for PCBs were generated: (1) Assuming zero metabolism in fish and (2) Assuming that the metabolism rate constant for all PCBs in fish was equal to that assumed for cVMS compounds in the scenarios reported above (i.e. \(4 \times 10^{-4}\) h\(^{-1}\)). It should be noted that this second assumption was made with the sole purpose of highlighting the influence of metabolism on the predicted behaviour of chemicals in this model and does not relate to assumptions about the possible behaviour of PCB in real environments.

Predicted concentrations for PCBs 52, 101, 118, 138, 153 and 180 under the zero metabolism assumption are shown in Figure 6. As expected, in all cases, the predicted concentrations in both fish species were higher than the concentration predicted for zooplankton. Similarly, in all cases (including PCB 28: data not shown), the chemical concentration in cod is predicted to be higher than the concentration in herring. This is in
broad agreement with observed trophic magnification for many hydrophobic persistent
organic pollutants (e.g. Fisk et al., 2001; Mackintosh et al., 2004; Sobek et al., 2010). As
expected, the concentration predicted in all organisms for the different congeners increases
with increasing $K_{OW}$ value.

FIGURE 6 HERE

It should be noted that in the case of zero metabolism, the mix of herring and cod age
classes assumed in the diet of the cod plays a very important role in determining the size
and direction of trophic magnification. When a simple diet for cod is assumed (50%
zooplankton, 50% 1st age class herring) trophic dilution is predicted between herring and
cod for PCBs 118, 138, 152 and 180 (data not shown). This is because both zooplankton
and young herring are predicted to have much lower lipid-normalised chemical
concentrations than older fish, which, in turn means that the total chemical intake via food
in the cod is reduced compared with an assumed complex diet. Low chemical ingestion
and lower gut absorption efficiency with increasing $K_{OW}$ (e.g. Gobas et al., 1993) combine
to generate a predicted trophic dilution, which is inconsistent with most empirical
observations for PCBs reported elsewhere.

When a metabolism rate constant of $4 \times 10^{-4}$ h$^{-1}$ was assumed for both herring and cod, the
predicted concentration patterns for PCBs (data not shown) demonstrate trophic dilution,
with lipid normalised concentrations in cod lower than those in herring, which are lower
than those in zooplankton. The relative extent of trophic dilution is enhanced in the
heavier congeners as a consequence of the combined influence of decreasing gut
absorption efficiency (Equation 4) and metabolism, as is the case for the cVMS compounds.
Conclusions

To our knowledge, this paper presents the first published attempt to explore the behaviour of cVMS compounds in marine systems. Although there were mismatches between measured and predicted values of WWTP influent concentrations and removal rates, which serve to highlight the uncertainties which remain about environmental emissions of cVMS materials, predictions of environmental and food web behaviour appeared to be reasonable.

Concentrations of D4, D5 and D6 in the water column and concentrations of D4 in the sediment of Inner Oslofjord were all predicted to be less than current analytical limits of detection, which is consistent with measured data. Predicted concentrations of D5 and D6 in sediment were also in broad agreement with data from two independent monitoring campaigns (Schlabach et al., 2007; Powell et al., 2010). Volatilisation was predicted to be the most important loss mechanism for D5 and D6. Hydrolysis was predicted to be the most important loss mechanism for D4. Concentrations of all three compounds in sediment are controlled by burial below the active mixed sediment layer.

When dissolved-phase cVMS concentrations in water were imported into ACC-HUMAN, “trophic dilution” was predicted, for all three compounds, between zooplankton and herring and between herring and cod. This was largely due to fish metabolism, exacerbated by high $K_{OW}$ values, which reduce gut uptake efficiency. Some organisms at higher trophic levels (e.g. mammals, birds) may not exhibit reduced gut absorption efficiency for hydrophobic chemicals (e.g. Kelly et al., 2004). However, the high $K_{AW}$ and
relatively low $K_{OA}$ values for cVMS compounds suggest that they will be eliminated effectively via the lungs in air breathing organisms (see also Andersen et al., 2008), thereby further reducing the potential for biomagnification, in contrast to the behaviour of other hydrophobic compounds in these organisms (Kelly et al., 2007). Measured lipid-normalised concentrations of D4 in biota were notably underestimated by the model and those of D5 and D6 were notably over-predicted. This suggests that dissolved phase concentrations might have been over estimated by the OPM. When measured cVMS concentrations in zooplankton were used to drive the food chain model, the predictions for D5 in herring and cod matched the measured data very well. However, predictions for D4 and D6 systematically over- and under-estimated equivalent measured concentrations in fish caught in Inner Oslofjord. This could be due to the assumption that the metabolism rate constants for D4 and D6 in fish were the same as that derived experimentally for D5, which may be incorrect – particularly in the case of D6, which is believed to metabolise very slowly, if at all, in fish according to unpublished data from industry (Woodburn et al., 2008).

In general, the lipid-normalised concentrations of cVMS compounds measured in biota sampled from the Inner Oslofjord are higher than those recently reported for other marine systems which are more distant from pollution sources or less enclosed. Kierkegaard et al. (2010), for example, report concentrations of D5 in herring samples from the Baltic Sea in the 100-500 ng g$^{-1}$ lipid range. They found highest levels in the Baltic Proper and lowest values along the Swedish west coast, suggesting that the source of D5 in the Baltic is wastewater emission. They also measured D4 and D6 concentrations in herring which were generally in the range 5-30 ng g$^{-1}$ lipid for D4 and 10-90 ng g$^{-1}$ lipid for D6. In contrast, to the apparent trophic dilution observed in the Inner Oslofjord, Kierkegaard et
al. (2010) did not observe any relationship between concentration and trophic level in a range of organisms including mussel, flounder, perch, smelt, white fish, herring, eelpout, turbot, cod and grey seal, except that concentrations in seal were always low, confirming our expectation that cVMS compounds are likely to be rapidly expelled by air breathing organisms. This is mainly due to their relatively low $K_{OA}$ values (see Table 1) which are several orders of magnitude lower than those reported for chemicals with potential to biomagnify in food chains containing air breaking organisms (Kelly et al., 2007). Given the importance of the sediment as a repository for cVMS materials in the Inner Oslofjord, the absence of benthic organisms in both ACC-HUMAN and in the measured data is unfortunate. Future studies should attempt to establish cVMS uptake from sediment, propagation through the benthic food web (see Kierkegaard et al., 2011) and interactions with pelagic organisms.

The application of dynamic models to explore the fate, transport and food-web transfer of cVMS materials in the Inner Oslofjord has generated a number of useful insights about the probable dominance of different loss processes and about the importance of metabolism in influencing trophic transfer. The uncertainty associated with the metabolism rate constants for cVMS compounds is high, particularly for D4 and D6. This may explain some of the discrepancies between model predictions and observed concentrations in different marine organisms. The other significant uncertainty which remains about the environmental behaviour of these widely used compounds is the emission rate. Good estimates of emission are essential in order to ensure that any agreement between predicted and measured concentrations is due to a reasonable representation of processes.
Acknowledgements

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References


Hori, Y. and Kannan, K., 2008. Survey of organosilicone compounds, including cyclic and linear siloxanes, in personal-care and household products. *Archives of Environmental Contamination and Toxicology* **55**(4), 701-710.


Corning Corporation. Available from the USEPA as a TSCA Section 8(e) Submission (www.epa.gov/oppt/tsca8a/pubs/8ehq/2010/feb10/).


4.10. United States Environmental Protection Agency, Washington, DC, USA.

• Wania, F., 2006. Potential of Degradable Organic Chemicals for Absolute and
Relative Enrichment in the Arctic. *Environmental Science and Technology* **40**(2),
569-577.

• Wania, F. and Daly, G., 2002. Estimating the contribution of degradation in air and
deposition to the deep sea to the global loss of PCBs. *Atmospheric Environment*
**36**, 5581–5593.

A fugacity-based dynamic multi-compartmental mass balance model of the fate of
884.

• Whelan, M.J., Estrada, E. and van Egmond, R., 2004. A Modelling Assessment of
the Atmospheric Fate of Volatile Methyl Siloxanes and their Reaction Products.
*Chemosphere* **57**, 1427-1437.

acid on water – atmosphere transfer of decamethylcyclopentasiloxane.
*Chemosphere* **74**(8), 1111-1116.

• Whelan, M.J., van Egmond, R., Gore D. and Sanders, D., 2010. Dynamic multi-
phase partitioning of decamethylcyclopentasiloxane (D5) in river water. *Water

Bioaccumulation food web models: Overview of input parameters, their
characteristics and distributions, and the resulting uncertainty of model
calculations using cyclic volatile methylsiloxanes as a test case. *Society of

Table 1 Properties of D4, D5 and D6. $K_{OW}$, $K_{AW}$ and $K_{OC}$ are partition coefficients for octanol: water, air: water and organic carbon: water based on Xu and Kozerski (2007). 2 Derived using the STP model (Clark et al., 1995). 3 Consensus value from G.E. Kozerski (Dow Corning, Personal Communication).

<table>
<thead>
<tr>
<th>Property</th>
<th>D4</th>
<th>D5</th>
<th>D6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar Mass (g mol$^{-1}$)</td>
<td>297</td>
<td>371</td>
<td>445</td>
</tr>
<tr>
<td>Aqueous Solubility (g m$^{-3}$)</td>
<td>0.056</td>
<td>0.017</td>
<td>0.0053</td>
</tr>
<tr>
<td>Vapour Pressure (Pa)</td>
<td>122</td>
<td>30.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Melting Point (°C)</td>
<td>17.5</td>
<td>-38</td>
<td>-3</td>
</tr>
<tr>
<td>Log ($K_{OW}$)</td>
<td>6.5</td>
<td>8.05</td>
<td>9.06</td>
</tr>
<tr>
<td>Log ($K_{AW}$)</td>
<td>2.69</td>
<td>3.13</td>
<td>3.3</td>
</tr>
<tr>
<td>Log ($K_{OA}$)</td>
<td>3.81</td>
<td>4.92</td>
<td>5.76</td>
</tr>
<tr>
<td>Log ($K_{OC}$)</td>
<td>4.22</td>
<td>5.2</td>
<td>6.03$^3$</td>
</tr>
<tr>
<td>Half Life in Water (h) at pH 8, 25 °C</td>
<td>9.4</td>
<td>206</td>
<td>962</td>
</tr>
<tr>
<td>Half Life in Sediment (h) at pH 8, 25 °C</td>
<td>2640</td>
<td>554389</td>
<td>554389</td>
</tr>
<tr>
<td>Activation Energy (kJ mol$^{-1}$)</td>
<td>87.6</td>
<td>87.2</td>
<td>93.5</td>
</tr>
<tr>
<td>$\Delta U_{OW}$ (kJ mol$^{-1}$)</td>
<td>7.9</td>
<td>29</td>
<td>33.6</td>
</tr>
<tr>
<td>$\Delta U_{OA}$ (kJ mol$^{-1}$)</td>
<td>-44</td>
<td>-51.4</td>
<td>-58.5</td>
</tr>
<tr>
<td>$\Delta U_{AW}$ (kJ mol$^{-1}$)</td>
<td>51.9</td>
<td>80.4</td>
<td>92.1</td>
</tr>
<tr>
<td>Removal in STP (%)$^2$</td>
<td>99</td>
<td>97</td>
<td>94</td>
</tr>
</tbody>
</table>
Table 2 Usage (Brooke *et al.*, 2008a, b, c) and emission estimates for D4, D5 and D6 in Inner Oslofjord.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Usage in cosmetics (mg cap⁻¹ yr⁻¹)</th>
<th>Total Flux (tonnes yr⁻¹)</th>
<th>Flux to waste water (mg cap⁻¹ yr⁻¹)</th>
<th>Removal in STP (%)</th>
<th>Flux to water (kg yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D4</td>
<td>1400</td>
<td>2.24</td>
<td>140</td>
<td>99</td>
<td>2.24</td>
</tr>
<tr>
<td>D5</td>
<td>42500</td>
<td>68</td>
<td>4250</td>
<td>97</td>
<td>204.0</td>
</tr>
<tr>
<td>D6</td>
<td>4900</td>
<td>7.84</td>
<td>490</td>
<td>94</td>
<td>47.04</td>
</tr>
</tbody>
</table>
**Table 3** Predicted and measured concentrations (µg L\(^{-1}\)) of D4, D5 and D6 in WWTP influent and effluent samples from the Oslofjord area (measured data from Schlabach *et al.*, 2007).

<table>
<thead>
<tr>
<th>WWTP</th>
<th>D4</th>
<th>D5</th>
<th>D6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>INFLUENT</td>
<td>EFFLUENT</td>
<td>INFLUENT</td>
</tr>
<tr>
<td>Bekkelagert</td>
<td>0.10</td>
<td>&lt;0.03</td>
<td>9.8</td>
</tr>
<tr>
<td>VEAS</td>
<td>0.20</td>
<td>0.10</td>
<td>12.0</td>
</tr>
<tr>
<td>Model</td>
<td>0.96</td>
<td>0.01</td>
<td>29.1</td>
</tr>
</tbody>
</table>
Figure 1. Schematic representation of the inner Oslofjord in the OPM (from Breivik et al., 2003) showing (a) the area and volume of each compartment and (b) the long term average water balance. A is the surface area of each water compartment in km$^2$. V is volume in km$^3$. W1, W2 and W3 are in the Bunnefjorden. W4, W5 and W6 are in the Vestfjorden. W7 represents the outer fjord. S represents the sediment associated with each water compartment. R is the mean residence time of each compartment (months). Water flux estimations are in m$^3$ s$^{-1}$.
Figure 2 Predicted concentration of (a) D4, (b) D5 and (c) D6 in compartments 1-6 with release to compartments W2 and W5. Open symbols show the Vestfjorden compartments and closed symbols show the Bunnefjorden compartments.
Figure 3 Predicted concentrations of (a) D4, (b) D5 and (c) D6 in the sediments of compartments 1-6 assuming release to compartments W2 and W5. Open symbols show the Vestfjorden compartments and closed symbols show the Bunnefjorden compartments.
Figure 4. Predicted concentrations of (a) D4, (b) D5 and (c) D6 in zooplankton, herring and cod in the Inner Oslofjord generated by ACC-HUMAN using predicted average aqueous concentrations from the OPM.
Figure 5. Predicted concentrations of (a) D4, (b) D5 and (c) D6 in zooplankton, herring and cod for the Inner Oslofjord generated by ACC-HUMAN using a constant dissolved-phase concentration derived from the respective measured zooplankton concentration using Equation 5. Straight solid horizontal lines show the mean measured concentrations in biota sampled from the Inner Oslofjord by Powell et al. (2010). Straight dashed horizontal lines denote standard errors.
Figure 6. Predicted concentrations (ng g\(^{-1}\) lipid) for PCBs 52, 101, 118, 138, 153 and 180 in zooplankton, herring and cod generated by ACC-HUMAN under the zero metabolism assumption.