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*., 2008 a, 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 km^2: 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 Norweigian 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:

$$HL_{e,corr} = \frac{HL_e}{f_{diss}} \quad (1)$$

where $HL_{e,corr}$ is the corrected half life, HL_e is the temperature- and pH- adjusted half-life and f_{diss} is the fraction of total mass predicted to be in the dissolved phase:

$$f_{diss} = \frac{1}{(1 + C_{SS} . f_{OC} . K_{OC})} \quad (2)$$

where C_{SS} is the steady state concentration of suspended solids in the water column (kg L^{-1}), f_{OC} is the fraction of organic carbon in the water column (g C g^{-1} solid) and K_{OC} (L kg^{-1}) is the organic carbon:water partition coefficient (derived from the temperature-adjusted value of K_{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_{SS} and f_{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 adjusments from the model described originally by Czub and McLachlan (2004a, b), as detailed in Breivik e*t 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):

$$\frac{d(V_F.Z_F.f_F)}{dt} = D_V.f_W + E_{OF}.\sum(D_{UF}.f_{prey}) - \left(D_V + D_M + \frac{E_{OF}}{Q_F}.\sum(D_{UF})\right).f_F \qquad (3)$$

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

169 *D*-values for ingestion and egestion: dimensionless). Note that E_{OF} for fish is described by
170 the following empirical equation (Niimi and Oliver, 1983; Clark *et al*., 1990) derived for
171 Rainbow Trout (*Oncorhynchus mykiss*) since no experimental data on absorption was
172 available for cod and herring:
173
174 $$E_{OF} = \left(1.33 + 9.7 \times 10^{-11}.K_{OW}\right)^{-1} \quad (4)$$
175
176
177 A distinguishing feature of ACC-HUMAN is the fact that it considers several different age
178 classes of fish simultaneously. There are ten age classes for herring and ten for cod, with
179 fish moving between age classes on the first of March each year. New fish develop from
180 eggs with the same initial fugacity as the mother fish. At the very start of the simulation,
181 there are no mother fish and the eggs are assumed to have the same fugacity as the water.
182 The rate of food ingestion is assumed to be a function of fish species and fish age.
183 However, no account is taken of potential changes in metabolism rates with age or body
184 size (e.g. Nichols *et al*., 2007; Arnot *et al*., 2008). Cod are assumed to eat a varied diet
185 consisting of zooplankton and a distribution of different age classes of herring, as well as
186 some small cod. Fish growth is described using an empirically-fitted modified
187 Bertalanffy growth equation (see Czub and McLachlan, 2004a).
188
189 In the application to Oslofjord described here, the time series of predicted dissolved-phase
190 concentration of cVMS in water was exported from the OPM and imported into ACC-
191 HUMAN. All food chain parameters were left unchanged from the Baltic scenario, except
192 for the metabolism rate constants for herring and cod which were set to 4×10^{-4} h^{-1} for
193 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 4.5×10^{-5} h^{-1} for D5 to 5.2×10^{-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 1.14×10^{-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, 5.32×10^{-4} h^{-1}, 1.07×10^{-4} h^{-1} and 2.59×10^{-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,

244 respectively have been derived for D4 and D5 for sediment collected from Lake Pepin
245 (Minnesota, USA) for 25 °C at pH 7.9 (Xu *et al*., 2010). These values are, respectively,
246 higher and lower than those assumed here. However, in any case, all multi-media fate and
247 transport models will be insensitive to sediment half lives for slowly degrading substances
248 because residence time becomes limited by physical processes such as sediment
249 resuspension and burial.
250
251 TABLE 1 HERE

252 **Emission scenario**

253

254 Emission rates of D4, D5 and D6 were based on *per capita* usage estimates in "cosmetic"
255 products (i.e. those products which are most likely to result in domestic emissions to waste
256 water) reported by Brooke *et al.* (2008a, b, c) for the UK, combined with an assumption
257 that 10% is lost to the waste water stream. The remainder is assumed to volatilise before
258 wash-off to drains. The *per capita* emission estimates were multiplied by the population
259 of the contributing catchment (approximately 1.6 million in total: City of Oslo, 2003) and
260 the fraction not removed in waste water treatment to determine total emissions to the fjord
261 and its contributing catchment (Table 2). Predicted removal of the cVMS compounds
262 during secondary sewage treatment is based on predictions generated using the STP
263 Model (v 2.11: Clark *et al.*, 1995) which simulates the chemical behaviour in an activated
264 sludge type WWTP. Default treatment plant parameters were assumed with three tanks in
265 series (primary settling, aeration basin and final clarifier). The prediction of 97% for D5
266 agrees approximately with estimates of removal based on measured influent and effluent
267 concentrations which ranged from 91-99% (Boehmer and Gerhards, 2003 reported in
268 Brooke *et al.*, 2008b). However, it should be noted that the removal efficiency of different
269 waste water treatment plants is likely to vary. Overall, emission estimates are highly
270 uncertain but will be very important in determining the absolute concentrations predicted
271 for each compound in each compartment of the receiving environment.

272

TABLE 2 HERE

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

298 of up to approximately 8, 2 and 5 times for D4, D5 and D6, respectively). This suggests
299 that the emissions assumed in Table 2 are erroneous – either because the *per capita* usage
300 is lower in Norway compared to the UK or because the assumption of 10% wash off for
301 cosmetic products is too high. The latter explanation has been suggested by Price *et al*.
302 (2010) to explain the fact that measured D5 concentrations in WWTP influents in the UK
303 were lower than estimates based on Brooke *et al*. (2008b). The difference between
304 measured and predicted concentrations in WWTP effluent is better for D5 and D6,
305 suggesting that the STP model may overestimate cVMS removal. The extent of this
306 overestimation is even more pronounced for D4, for which the predicted effluent
307 concentration is several times lower than that measured at the VEAS plant. More data are
308 needed on effluent concentrations in order to confirm the validity of these initial
309 interpretations.
310
311 TABLE 3 HERE
312
313 Predicted concentrations in water and sediment
314 OPM-predicted concentrations of D4, D5 and D6 in the various marine compartments of
315 Inner Oslofjord are shown in Figures 2 and 3 for water and sediment, respectively; note
316 the different y-axis scales in these figures. Although the time step used for model
317 integration was one hour, results have only been written every 1752 hours (73 days), i.e.
318 five times per year. The lines, therefore, appear to be more discontinuous than the actual
319 time series of predicted concentrations calculated by the model.
320
321 Predicted concentrations are highest for D5 (Figure 2b), followed by D6 (Figure 2c) and
322 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 degrade slowly relative 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_{AW} at reduced temperatures which will increase the fugacity capacity of water and, to a lesser extent a reduction in K_{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

421 measured data (Table 3), the source of the error could be over-estimating f_{diss} (Equation 2)
422 – for example, as a consequence of neglecting to account for interactions with DOC, from
423 errors in K_{OC} estimation or from underestimating the rate of hydrolysis. These
424 explanations are, of course, speculative at this stage. Note that the mean measured lipid-
425 normalised cVMS concentrations result in Trophic Magnification Factors (TMFs) of 0.514
426 (p = 0.27), 0.202 (p = 0.147) and 0.587 (p = 0.023) for D4, D5 and D6, respectively, using
427 average data and following the method described by Borgå *et al*. (2012), where *p*-values
428 are given for the slope of the regression. Values of TMF < 1 are assumed to be indicative
429 of trophic dilution although, in this case, the slope of the regression between trophic level
430 and log concentration is statistically significant ($p < 0.05$) only for D6. The reader is
431 referred to Powell *et al*. (2010) for a more complete analysis of cVMS trophic transfers in
432 Oslofjord.
433
434 FIGURE 4 HERE
435
436 The prediction of trophic dilution for the cVMS compounds in marine biota generated by
437 ACC-HUMAN can be explained by two main factors: (1) in-fish metabolism and (2)
438 reduced gut uptake efficiency due to the high hydrophobicity of the cVMS compounds
439 (see Equation 4). Predicted concentrations in fish are quite sensitive to the metabolism
440 rate constants (k_{cod} and k_{herr}), provided that values are greater than about 4 x 10^{-6} h^{-1}.
441 Since there is some uncertainty about the values of these parameters, particularly for D4
442 and D6, there will necessarily be uncertainty about the model predictions. Some
443 metabolism is required in order to generate a dilution effect for the mean concentrations in
444 fish. When metabolism is switched off completely ($k_{cod} = k_{herr} = 0$ h^{-1}), average
445 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 soley 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:

$$C_W(free) = \frac{C_Z \cdot \rho}{K_{OW}} \quad (5)$$

where C_Z is the concentration in zooplankton (ng g^{-1} lipid) and ρ 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. 1.24×10^{-1}, 0.72 and 1.34×10^{-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 4×10^{-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.

519

520 FIGURE 5 HERE

521

522 *Model predictions for PCB congeners*

523 In order to benchmark the predicted behaviour of cVMS compounds against the predicted
524 behaviour of known POPs, the ACC-HUMAN model was run for seven PCB congeners
525 (PCBs 28, 52, 101, 118, 138, 153 and 180). The physicochemical properties of these
526 compounds were taken from Breivik *et al*. (2004) but were originally derived from a range
527 of sources including Li *et al*. (2003) and Wania and Daly (2002). In all cases, the same
528 arbitrary constant concentration in sea water was assumed at 0.1 ng L^{-1}, which allows the
529 relative pattern of PCB behaviour in the model to be compared to the predictions for D4,
530 D5 and D6. Predictions of PCB behaviour reported here should only be considered in
531 relative terms.

532

533 Two sets of predictions for PCBs were generated: (1) Assuming zero metabolism in fish
534 and (2) Assuming that the metabolism rate constant for all PCBs in fish was equal to that
535 assumed for cVMS compounds in the scenarios reported above (i.e. 4×10^{-4} h^{-1}). It should
536 be noted that this second assumption was made with the sole purpose of highlighting the
537 influence of metabolism on the predicted behaviour of chemicals in this model and does
538 not relate to assumptions about the possible behaviour of PCB in real environments.
539 Predicted concentrations for PCBs 52, 101, 118, 138, 153 and 180 under the zero
540 metabolism assumption are shown in Figure 6. As expected, in all cases, the predicted
541 concentrations in both fish species were higher than the concentration predicted for
542 zooplankton. Similarly, in all cases (including PCB 28: data not shown), the chemical
543 concentration in cod is predicted to be higher than the concentration in herring. This is in

544 broad agreement with observed trophic magnification for many hydrophobic persistent
545 organic pollutants (e.g. Fisk *et al*., 2001; Mackintosh *et al*., 2004; Sobek *et al*., 2010). As
546 expected, the concentration predicted in all organisms for the different congeners increases
547 with increasing K_{OW} value.
548
549 FIGURE 6 HERE
550
551 It should be noted that in the case of zero metabolism, the mix of herring and cod age
552 classes assumed in the diet of the cod plays a very important role in determining the size
553 and direction of trophic magnification. When a simple diet for cod is assumed (50%
554 zooplankton, 50% 1st age class herring) trophic dilution is predicted between herring and
555 cod for PCBs 118, 138, 152 and 180 (data not shown). This is because both zooplankton
556 and young herring are predicted to have much lower lipid-normalised chemical
557 concentrations than older fish, which, in turn means that the total chemical intake via food
558 in the cod is reduced compared with an assumed complex diet. Low chemical ingestion
559 and lower gut absorption efficiency with increasing K_{OW} (e.g. Gobas *et al*., 1993) combine
560 to generate a predicted trophic dilution, which is inconsistent with most empirical
561 observations for PCBs reported elsewhere.
562
563 When a metabolism rate constant of 4×10^{-4} h^{-1} was assumed for both herring and cod, the
564 predicted concentration patterns for PCBs (data not shown) demonstrate trophic dilution,
565 with lipid normalised concentrations in cod lower than those in herring, which are lower
566 than those in zooplankton. The relative extent of trophic dilution is enhanced in the
567 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.

571

572 **Conclusions**

573

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

580

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

589

590 When dissolved-phase cVMS concentrations in water were imported into ACC-HUMAN,
591 "trophic dilution" was predicted, for all three compounds, between zooplankton and
592 herring and between herring and cod. This was largely due to fish metabolism,
593 exacerbated by high K_{OW} values, which reduce gut uptake efficiency. Some organisms at
594 higher trophic levels (e.g. mammals, birds) may not exhibit reduced gut absorption
595 efficiency for hydrophobic chemicals (e.g. Kelly *et al*., 2004). However, the high K_{AW} and

596 relatively low K_{OA} values for cVMS compounds suggest that they will be eliminated
597 effectively via the lungs in air breathing organisms (see also Andersen *et al*., 2008),
598 thereby further reducing the potential for biomagnification, in contrast to the behaviour of
599 other hydrophobic compounds in these organisms (Kelly *et al*., 2007). Measured lipid-
600 normalised concentrations of D4 in biota were notably underestimated by the model and
601 those of D5 and D6 were notably over-predicted. This suggests that dissolved phase
602 concentrations might have been over estimated by the OPM. When measured cVMS
603 concentrations in zooplankton were used to drive the food chain model, the predictions for
604 D5 in herring and cod matched the measured data very well. However, predictions for D4
605 and D6 systematically over- and under- estimated equivalent measured concentrations in
606 fish caught in Inner Oslofjord. This could be due to the assumption that the metabolism
607 rate constants for D4 and D6 in fish were the same as that derived experimentally for D5,
608 which may be incorrect – particularly in the case of D6, which is believed to metabolise
609 very slowly, if at all, in fish according to unpublished data from industry (Woodburn *et*
610 *al*., 2008).
611
612 In general, the lipid-normalised concentrations of cVMS compounds measured in biota
613 sampled from the Inner Oslofjord are higher than those recently reported for other marine
614 systems which are more distant from pollution sources or less enclosed. Kierkegaard *et*
615 *al*. (2010), for example, report concentrations of D5 in herring samples from the Baltic
616 Sea in the 100 -500 ng g^{-1} lipid range. They found highest levels in the Baltic Proper and
617 lowest values along the Swedish west coast, suggesting that the source of D5 in the Baltic
618 is wastewater emission. They also measured D4 and D6 concentrations in herring which
619 were generally in the range 5-30 ng g^{-1} lipid for D4 and 10-90 ng g^{-1} lipid for D6. In
620 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.

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839 **Table 1** Properties of D4, D5 and D6. K_{OW}, K_{AW} and K_{OC} are partition coefficients for
840 octanol: water, is the air : water and organic carbon: water based on Xu and Kozerski
841 (2007). [2] Derived using the STP model (Clark *et al*., 1995). [3]Consensus value from G.E.
842 Kozerski (Dow Corning, *Personal Communicatio*n).
843

Property	**D4**	**D5**	**D6**
Molar Mass (g mol^{-1})	297	371	445
Aqueous Solubility (g m^{-3})	0.056	0.017	0.0053
Vapour Pressure (Pa)	122	30.4	2.2
Melting Point (°C)	17.5	-38	-3
Log (K_{OW})	6.5	8.05	9.06
Log (K_{AW})	2.69	3.13	3.3
Log (K_{OA})	3.81	4.92	5.76
Log (K_{OC})	4.22	5.2	6.03[3]
Half Life in Water (h) at pH 8, 25 °C	9.4	206	962
Half Life in Sediment (h) at pH 8, 25 °C	2640	554389	554389
Activation Energy (kJ mol^{-1})	87.6	87.2	93.5
ΔU_{OW} (kJ mol^{-1})	7.9	29	33.6
ΔU_{OA} (kJ mol^{-1})	-44	-51.4	-58.5
ΔU_{AW} (kJ mol^{-1})	51.9	80.4	92.1
Removal in STP (%)[2]	99	97	94

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845

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847

848 **Table 2** Usage (Brooke *et al.*, 2008a, b, c) and emission estimates for D4, D5 and D6 in

849 Inner Oslofjord.

850

Compound	Usage in cosmetics (mg cap^{-1} yr^{-1})	Total Flux (tonnes yr^{-1})	Flux to waste water (mg cap^{-1} yr^{-1})	Removal in STP (%)	Flux to water (kg yr^{-1})
D4	1400	2.24	140	99	2.24
D5	42500	68	4250	97	204.0
D6	4900	7.84	490	94	47.04

851

852 **Table 3** Predicted and measured concentrations (μg L^{-1}) of D4, D5 and D6 in WWTP influent and effluent samples from the Oslofjord area

853 (measured data from Schlabach *et al.*, 2007).

854

WWTP	D4		D5		D6	
	INFLUENT	EFFLUENT	INFLUENT	EFFLUENT	INFLUENT	EFFLUENT
Bekkelaget	0.10	<0.03	9.8	0.20	0.50	<0.02
VEAS	0.20	0.10	12.0	1.00	1.00	0.10
Model	0.96	0.01	29.1	0.87	3.36	0.20

855

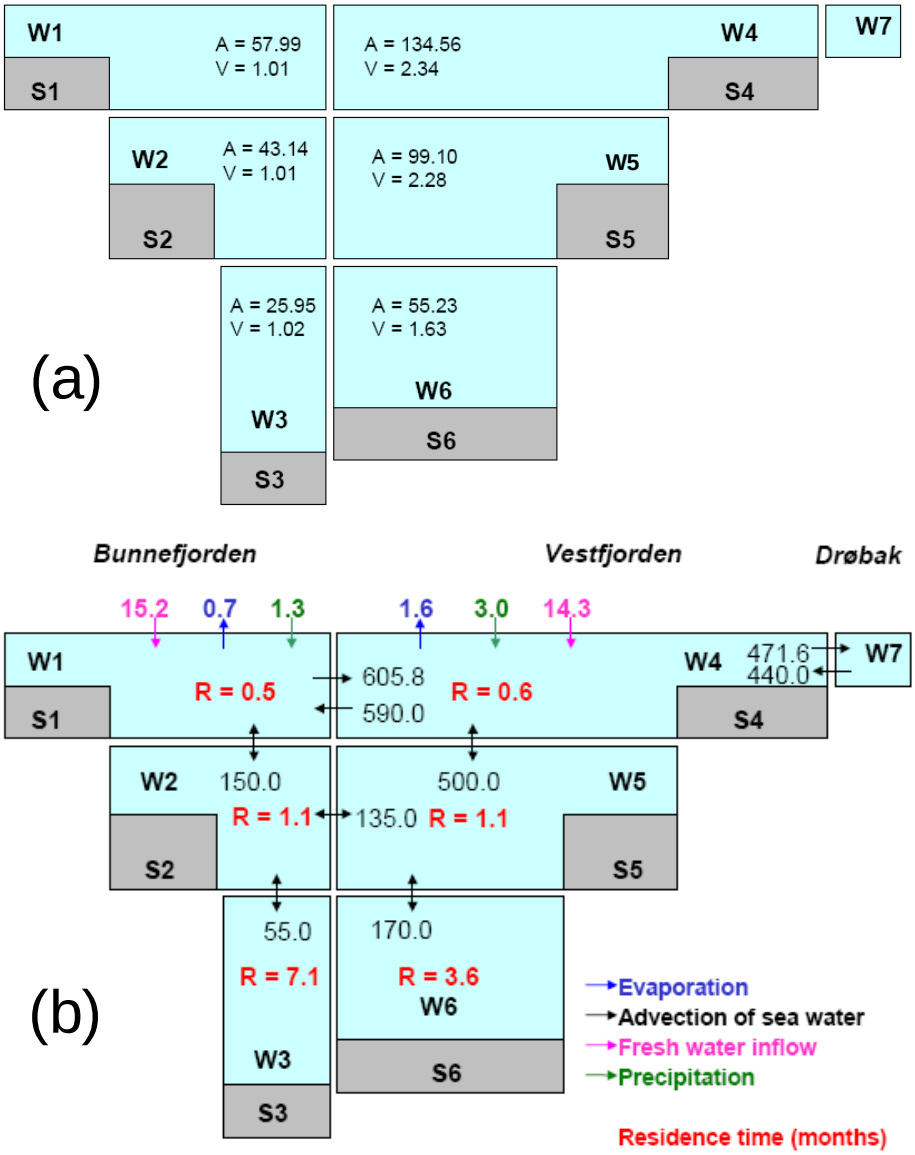


Figure 1. Schematic representation of the inner Oslofjord in the OPM (from Breivik *et al.*, 2003) showing (a) the area and volume of each compartment and (b) the long term average water balance. *A* is the surface area of each water compartment in km^2. *V* is volume in km^3. W1, W2 and W3 are in the 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}.

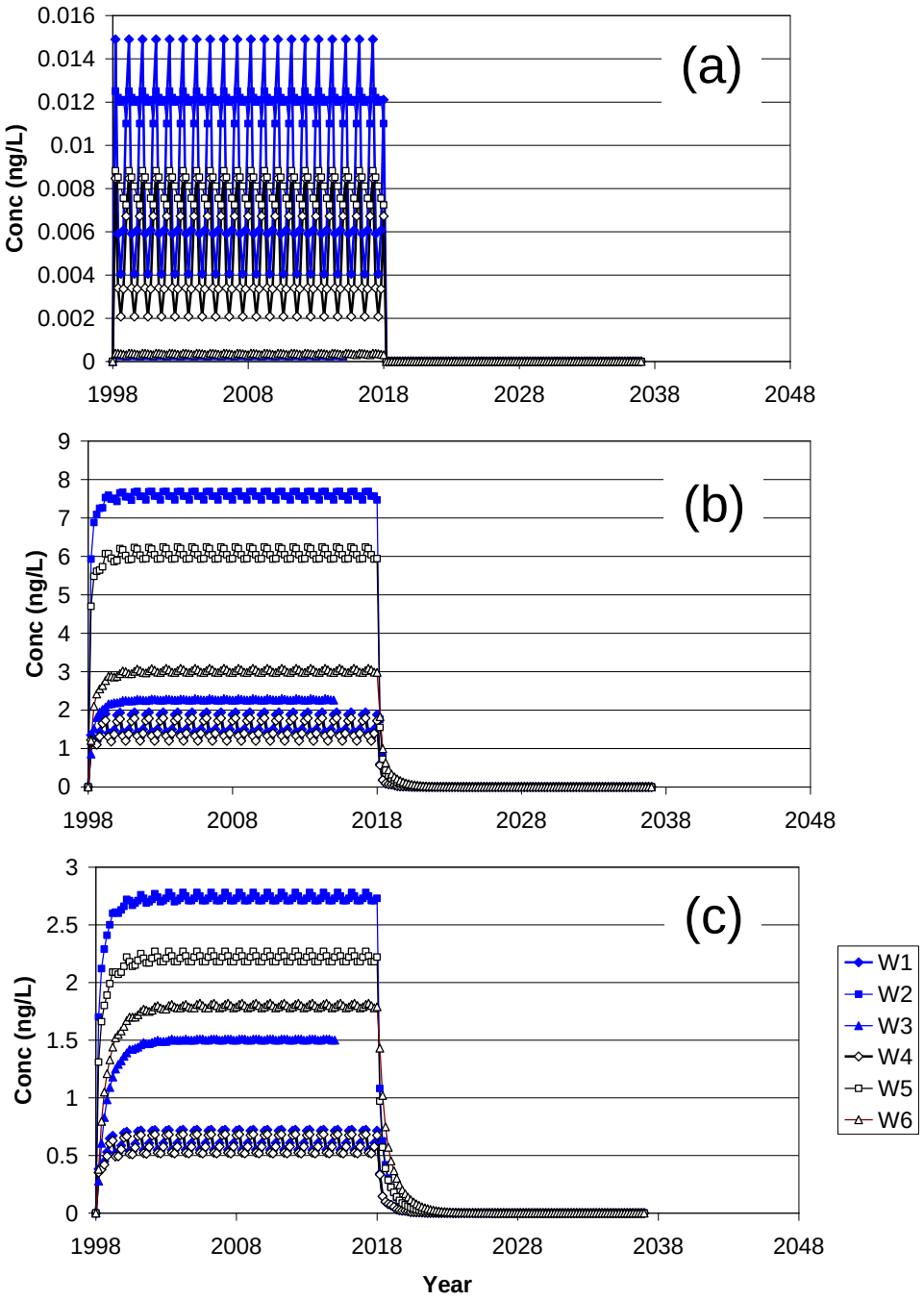


Figure 2 Predicted concentration of (a) D4, (b) D5 and (c) D6 in compartments 1-6 with release to compartments W2 and W5. Open symbols show the Vestfjorden compartments and closed symbols show the Bunnefjorden compartments.

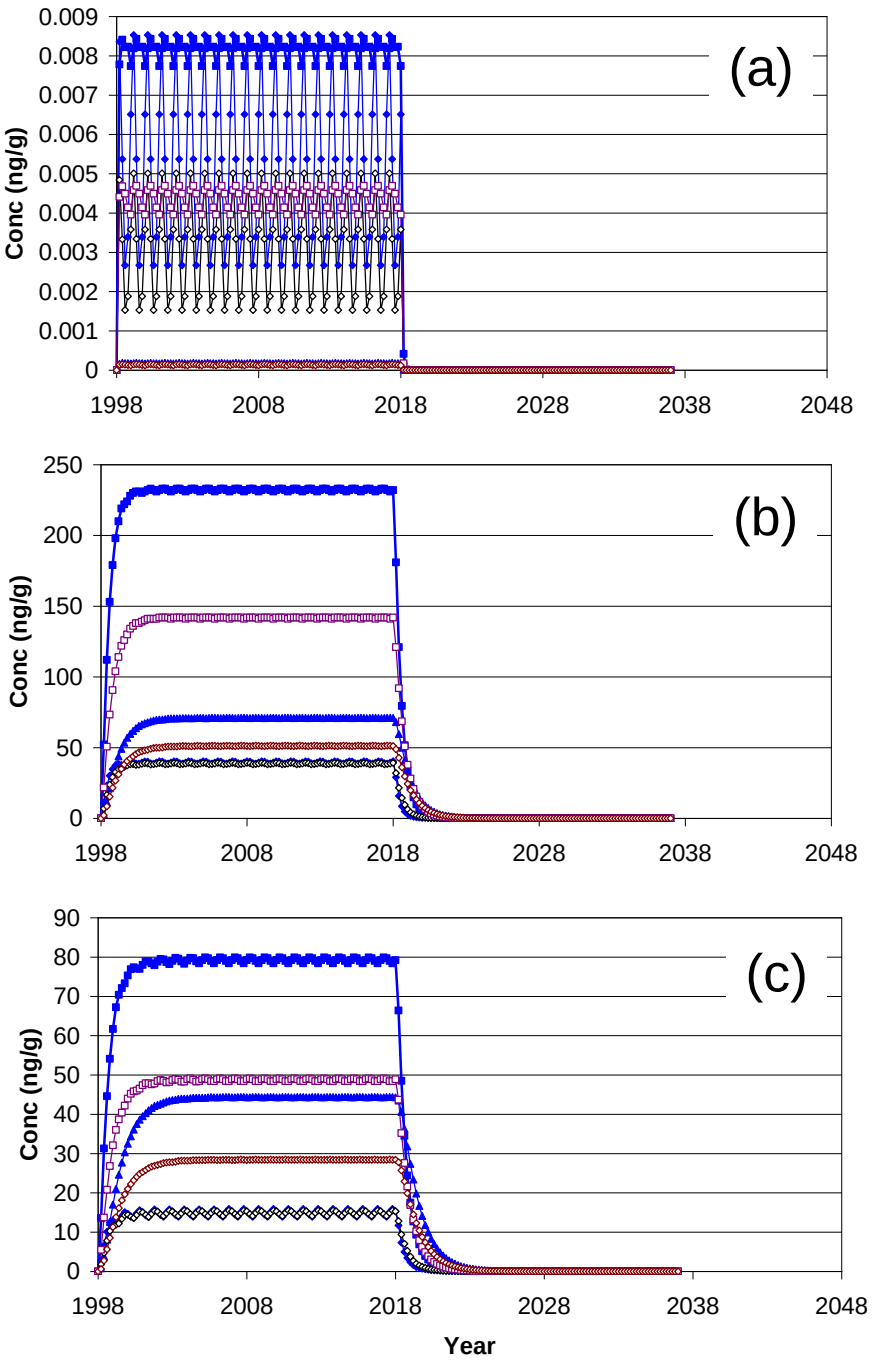


Figure 3 Predicted concentrations of (a) D4, (b) D5 and (c) D6 in the sediments of compartments 1-6 assuming release to compartments W2 and W5. Open symbols show the Vestfjorden compartments and closed symbols show the Bunnefjorden compartments.

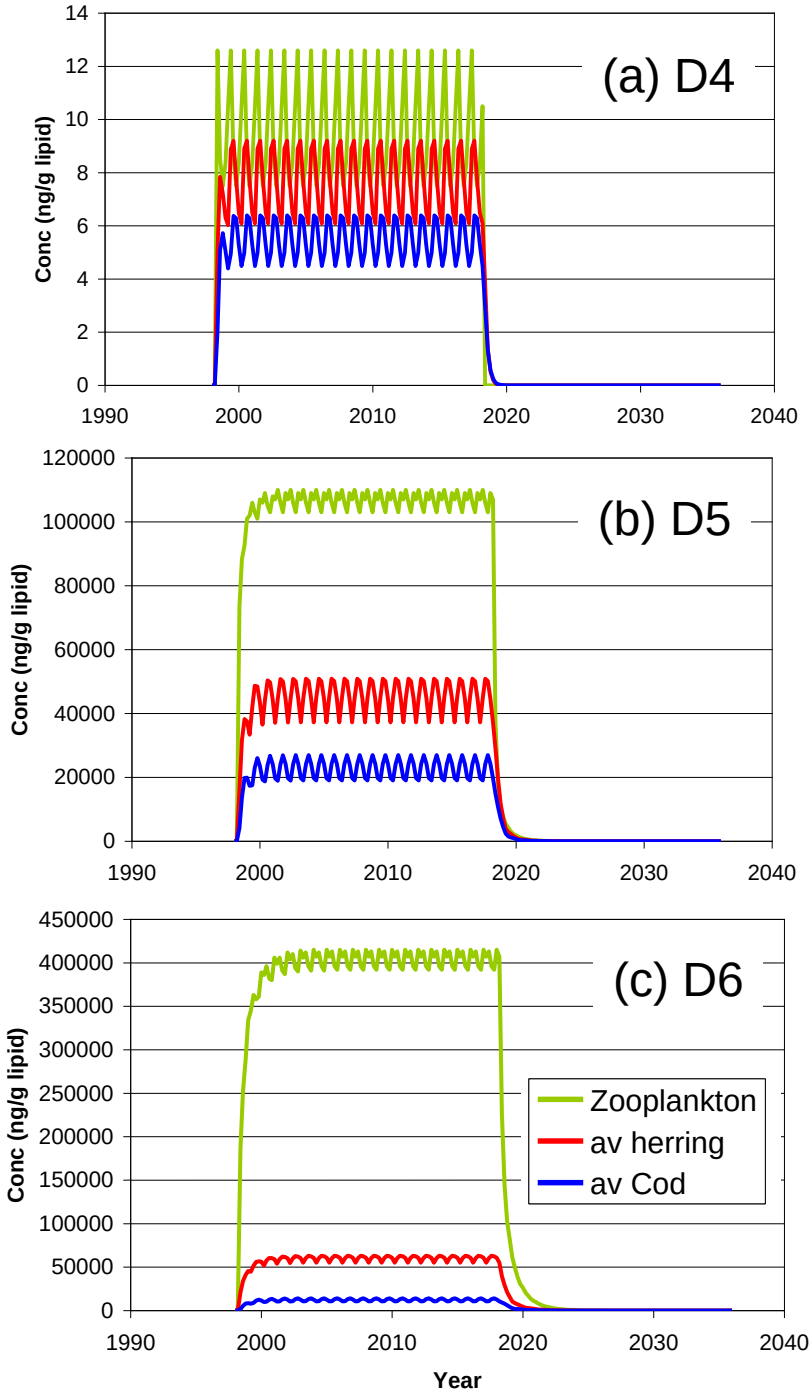
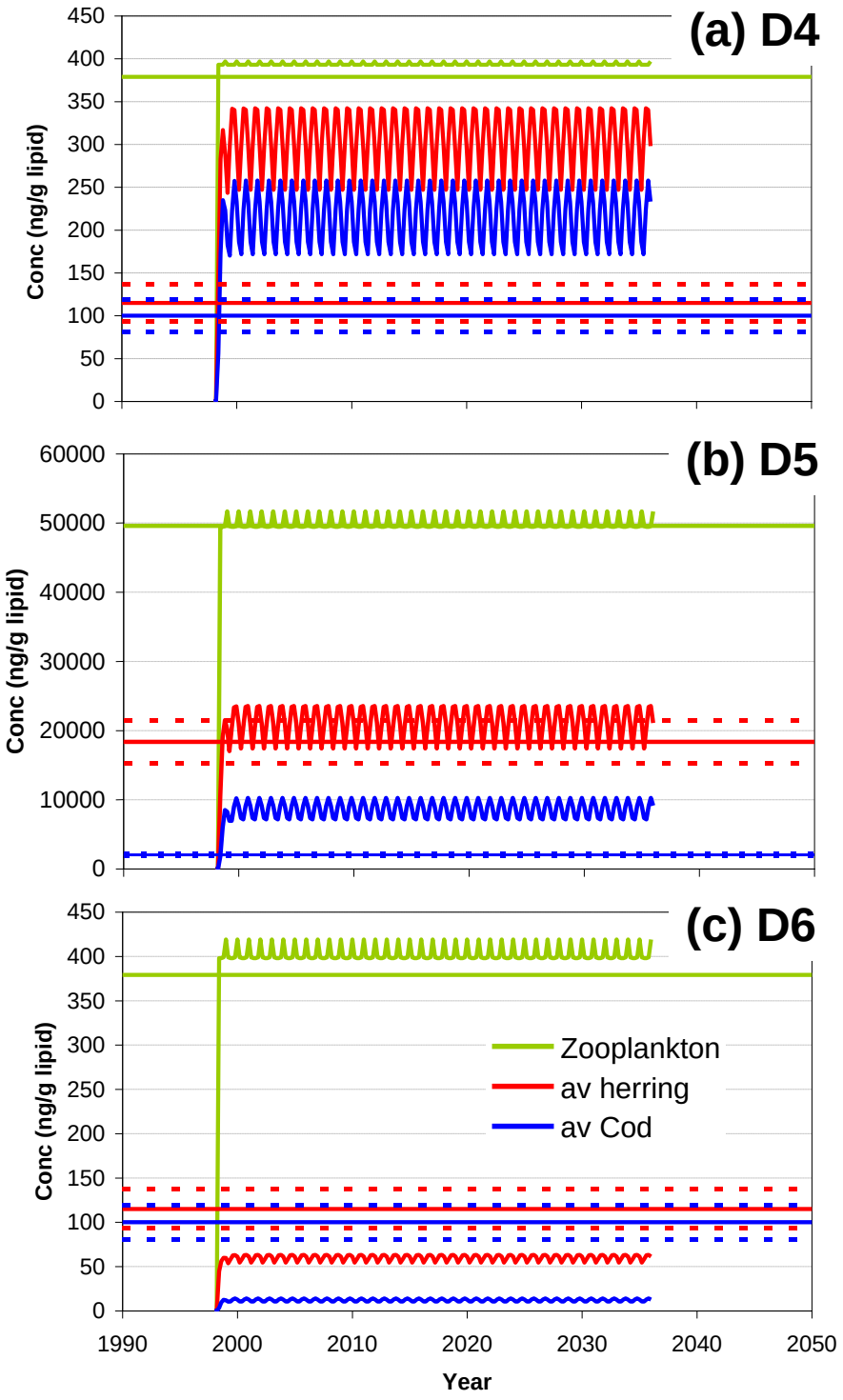


Figure 4. Predicted concentrations of (a) D4, (b) D5 and (c) D6 in zooplankton, herring and cod in the Inner Oslofjord generated by ACC-HUMAN using predicted average aqueous concentrations from the OPM.



887

888 **Figure 5.** Predicted concentrations of (a) D4, (b) D5 and (c) D6 in zooplankton, herring and cod
889 for the Inner Oslofjord generated by ACC-HUMAN using a constant dissolved-phase
890 concentration derived from the respective measured zooplankton concentration using Equation 5.
891 Straight solid horizontal lines show the mean measured concentrations in biota sampled from the
892 Inner Oslofjord by Powell et al. (2010). Straight dashed horizontal lines denote standard errors.

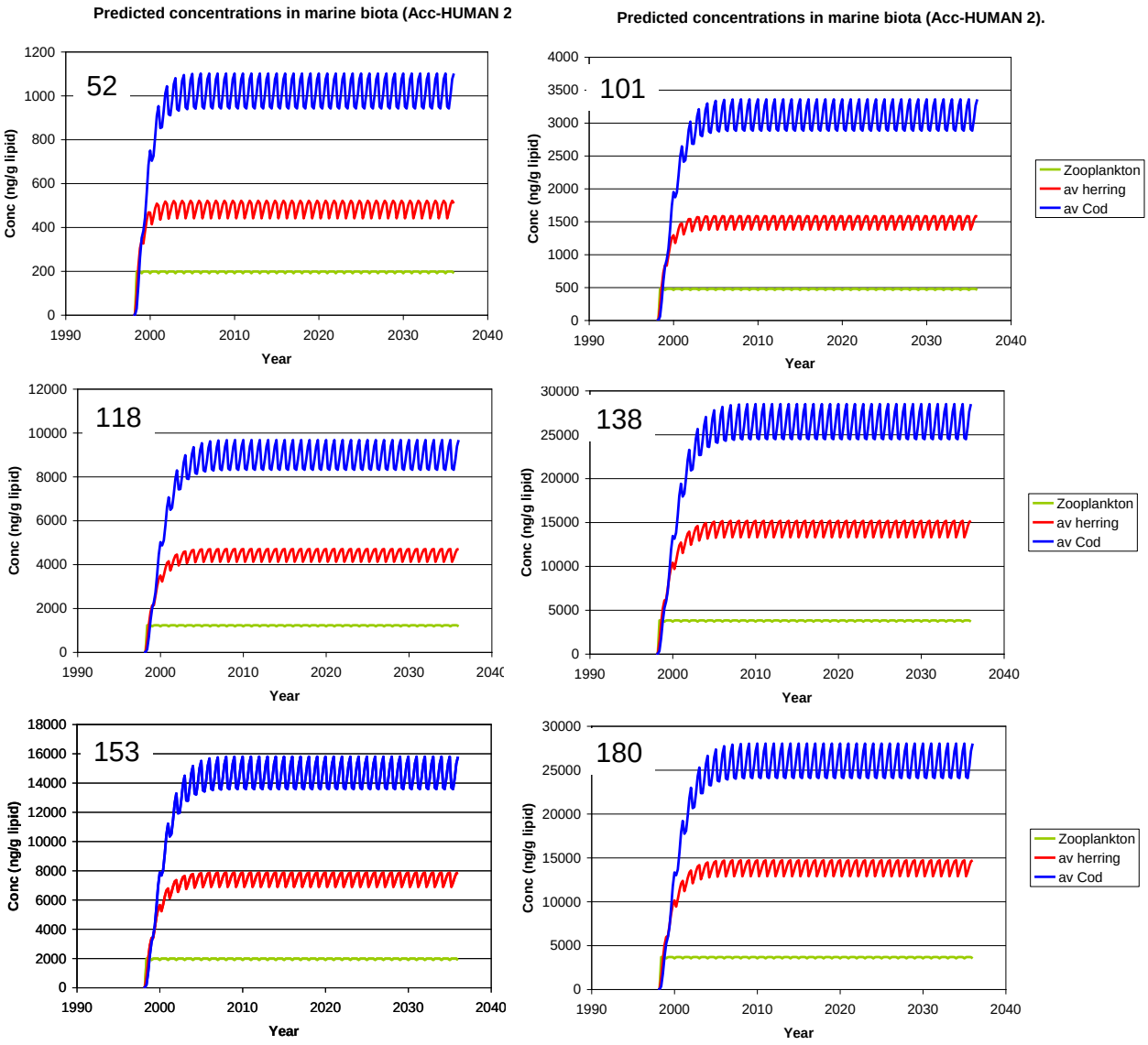


Figure 6. Predicted concentrations (ng g^{-1} lipid) for PCBs 52, 101, 118, 138, 153 and 180 in zooplankton, herring and cod generated by ACC-HUMAN under the zero metabolism assumption.