Modelling the diagenetic fate of persistent organic pollutants in organically enriched sediments

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Abstract

The fate of persistent organic pollutants (POPs) in aquatic ecosystems is intimately linked to the cycling of organic matter. In this paper, we present a model of the effect of organic matter decomposition on the distribution of persistent organic pollutants in sediments. The model predicts a diagenetic (sediment-ageing) magnification of chemical concentrations in sediments enriched with labile organic matter. We predict two- to four-fold diagenetic magnification across a wide range of realistic parameter values, and higher levels (up to 20-fold) for labile organic matter in systems with low burial rates (i.e., residence times on the order of years). As an illustration, we apply our model to understand the fate of waste organic matter and associated PCBs discharged by marine fish farms. The available data support both the spatial pattern (as a function of burial rate) and the range of sediment PCB concentrations predicted by our model. This model explains why equilibrium models fail to predict the very high sediment-water partitioning coefficients often observed in the field. Effectively, diagenetic processes impose an additional biomagnification step at the bottom of the detritus-based food web, increasing the exposure to POPs of organisms at higher trophic levels.
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1. Introduction

Inland and coastal waters worldwide are subject to long-term and increasing pollution with waste organic matter (OM) from human activities (e.g., sewage, agriculture, aquaculture). This OM frequently carries a wide variety of anthropogenic contaminants, including many persistent organic pollutants (POPs) (e.g., Spies, 1984; Levings, 1994). The fate of these "piggybacking" chemicals in receiving systems is intimately linked to the fate of the host OM (Koelmans et al., 2001). Most current models of chemical fate treat the distribution of POPs between organic matter and water as an equilibrium partitioning, viewing this OM as an inert matrix within which POPs achieve a chemical equilibrium according to their thermodynamic properties. However, it is widely recognized that OM in aquatic systems is a dynamic entity that cycles on time scales that can be much shorter than those required for many chemical distribution processes to approach equilibrium.

The generally high lability of anthropogenic waste OM to bacterial decomposition raises a particular concern about the risk of contamination to benthic biota in organically enriched systems. Experiments with fish have shown that digestion of dietary OM can result in

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an elevation of chemical fugacities in the gut, providing a mechanism for biomagnification between trophic levels (Gobas et al., 1999). OM decomposition during early sediment diagenesis is an analogous process that likely has similar effects on chemical concentrations in sediment. This hypothesis is supported by experiments with decomposing phytoplankton (Koelmans et al., 1993), observations of enrichment of PCBs and PAHs on settling particles (Baker et al., 1991; Axelman et al., 2000), and evidence that sediment-water distribution coefficients can be orders of magnitude greater than those expected from chemical partitioning (Koelmans et al., 1997; Gobas and MacLean, 2003). We hypothesize that decomposition of OM effectively adds an additional biomagnification step at the bottom of the detritus-based food web.

Enrichment with waste OM is typically accompanied by an increase in abundances of deposit feeders (Pearson and Rosenberg, 1978), and a corresponding increase in the incidence of these organisms in the diets of demersal fish (Steimle et al., 1994). Previous work has demonstrated strong coupling between organically enriched benthic habitats and populations of epibenthic and pelagic organisms around major sewage outfalls and sewage-sludge dumpsites (Spies, 1984; Van Dover et al., 1992), and consequently elevated concentrations of contaminants in bottom-feeding fish in these areas (Spies, 1984). Similarly, many indigenous fish species are known to be attracted to fish farms and to be actively feeding on the enriched benthic communities there (Carss, 1990; Dempster et al., 2002). Given the large amounts of organic contaminants being released with waste OM worldwide and the ease with which these contaminants can enter benthic food webs, the potential for rapid OM decomposition to magnify chemical concentrations in sediment is ecologically and toxicologically important. In this paper, we present a set of models designed to assess the magnitude of this process in enriched sediments, and to delineate the range of conditions under which diagenetic magnification of chemical concentrations may be large.

We focus on the waste OM and chemicals released by salmon aquaculture as an example of a situation in which diagenetic magnification may be important. Organic contaminants from aquaculture enter the marine ecosystem in association with OM that is easily digested and incorporated in the food web (Mazzola and Sara, 2001; Ye et al., 2001). With the rapid expansion of the salmon aquaculture industry in many parts of the world, there has been increasing public concern about the potential for transfer of farm-associated chemicals to indigenous marine biota. Organic chemicals associated with aquaculture include both intentionally used substances (e.g., pesticides, antimicrobials) and chemicals that are unintentionally introduced as contaminants of feed. This latter group includes a number of persistent organic pollutants of global concern such as polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), polybrominated diphenyl ethers (PBDEs), DDT and toxaphene (Easton et al., 2002; Jacobs et al., 2000, 2002). The highly chlorinated compounds are of particular concern because they are hydrophobic, strongly sorptive, degrade very slowly, and may biomagnify in food webs.

2. Theory

2.1. Dynamic model

Waste OM is released from fish farms primarily as uneaten feed pellets and particulate salmon feces (Tlusty et al., 2000). After release from the farm, particulate OM begins to degrade. Settling particulate OM is rapidly colonized by bacteria, and feces emerges from the fish with bacteria already present. At the same time, associated chemicals begin to exchange with the water, seeking to achieve thermodynamic equilibrium with the dissolved phase. We can illustrate the outcome of these competing kinetic processes by considering the progressive decomposition of the mass of OM (M) and the desorption of the mass of PCBs (X) from a single particle through time, according to the following equations:

$$\frac{\mathrm{d}M}{\mathrm{d}t} = M\sum_{i}[-k_{\mathrm{R}i}F_i] \tag{1}$$

and

$$\frac{\mathrm{d}X}{\mathrm{d}t} = -k_{\mathrm{D}2}X \tag{2}$$

where the subscript i refers to the fractions of fast- and slow-decomposing OM, $k_{\mathrm{R}i}$ the OM decomposition rate, $k_{\mathrm{D}2}$ the desorption rate, and F the proportion of each OM fraction initially. For simplicity, Eq. (2) assumes that further uptake of chemical from water is

negligible. The relative PCB concentration at time t (versus $t = 0$) is then given by

$$\frac{C_t}{C_0} = \frac{e^{-k_{D2}t}}{\sum_i F_i e^{-k_{Ri}t}} \tag{3}$$

The change in PCB concentration of this particle ($C_t = X_t/M_t$) is expressed by the ratio C_t/C_0, which we will refer to here as the diagenetic magnification factor (DMF).

2.2. Steady-state model

Next, we consider the outcome of competing decomposition and desorption kinetics for a water column-sediment system at steady state. This treatment implicitly incorporates the residence time of a particle in each compartment, and thus the scope for diagenetic magnification to proceed. For a farm discharging a flux Q_F of farm waste with a PCB concentration C_F, the suspended (M_S) and active (surface, well-mixed) sediment (M_A) OM pools are described by

$$\frac{dM_S}{dt} = \sum_i [Q_F F_i - k_{Ri}M_{Si} - k_{SS}M_{Si}] \tag{4}$$

and

$$\frac{dM_A}{dt} = \sum_i [k_{SS}M_{Si} - k_{Ri}M_{Ai} - k_B M_{Ai}] \tag{5}$$

where the subscripts S and A refer to the (well-mixed) suspended and active sediment pools, respectively, the subscript i refers to fast- and slow-decomposing fractions of OM, F the proportion of each OM fraction in Q_F, k_{SS} the settling rate of suspended sediment, and k_B the burial rate of active sediment. Buried sediment is assumed to have no free oxygen or sulfate (no appreciable OM decomposition) and saturated porewater (no appreciable desorption). The masses of PCB (X) associated with these OM pools are described by

$$\frac{dX_S}{dt} = \sum_i [Q_F F_i C_F - k_{D2}M_{Si}C_{Si} - k_{SS}M_{Si}C_{Si}] \tag{6}$$

and

$$\frac{dX_A}{dt} = \sum_i [k_{SS}M_{Si}C_{Si} - k_{D2}M_{Ai}C_{Ai} - k_B M_{Ai}C_{Ai}] \tag{7}$$

In the case where there is only a single fraction of OM (i.e., $F_1 = 1$, $F_2 = F_3 = 0$), the steady-state concentrations in suspended (C_S) and active sediment (C_A) pools can be derived from equations (4) (with $dM_S/dt = 0$) and (6) (with $dX_S/dt = 0$):

$$\frac{C_S}{C_F} = \frac{k_{R1} + k_{SS}}{k_{D2} + k_{SS}} \tag{8}$$

and

$$\frac{C_A}{C_F} = \frac{(k_{R1} + k_{SS})(k_{R1} + k_B)}{(k_{D2} + k_{SS})(k_{D2} + k_B)} \tag{9}$$

That is, the ratios C_S/C_F and C_A/C_F are independent of Q_F, and depend only on the relative rates of decomposition, desorption, settling, and burial.

3. Model scenarios and parameterization

3.1. Dynamic model

Using the dynamic model, we first explore the schedule of diagenetic magnification (i.e., the time course of C_t/C_0 using Eq. (3)) for different chemicals and different kinds of OM, considering a realistic range of parameter values. We consider fresh farm-waste OM to consist of two components ($F_1 = 0.2$ or 0.8, $F_2 = (1 - F_1)$) with first-order decomposition rates $k_{R1} = 0.04$ per day and $k_{R2} = 0.002$ per day (Westrich and Berner, 1984; Wijsman et al., 2002). We assume that PCBs associated with this OM reside entirely in the slow-desorbing pool, with k_{D2} on the order of 10^{-4} to 10^{-2} per day (Cornelissen et al., 1997; Ten Hulscher et al., 1999). The rationale for these parameter values is as follows.

3.1.1. Organic matter composition and decomposition rate, F and k_{Ri}

Organic detritus contains many different constituents with different degradabilities. More labile fractions are consumed by bacteria at higher rates (by definition), so the overall rate of decomposition of a given particle decreases with age (Middleburg, 1989; Henrichs, 1992). We use here a common modelling approach that represents the bulk OM as two or three pools (e.g., fast-decomposing, slow-decomposing, and refractory), each with a first-order decomposition rate (e.g., Westrich and Berner, 1984; Soetaert et al.,

1996; Wijsman et al., 2002; Jamu and Piedrahita, 2002; cf. Middleburg, 1989 for a treatment that considers an infinite number of pools). More complex models of diagenesis link decomposition processes explicitly to the geochemical cycling of electron acceptors (e.g., Soetaert et al., 1996). This level of detail is unnecessary to illustrate the general phenomena that are the focus of this paper, however, and we have consequently adopted the simpler treatment described above.

Rapid aerobic decomposition (k_{R1}) in marine sediments proceeds on the order of several % per day, slow aerobic decomposition (k_{R2}) on the order of tenths of a % per day, and recalcitrant fractions do not degrade appreciably on the time scales of early diagenesis (Westrich and Berner, 1984; Wijsman et al., 2002). Bulk marine sediment contains mainly slow-degrading and recalcitrant materials, so overall aerobic decomposition rates are typically on the order of 0.78 per year for the first year after deposition, declining to 0.1 per year thereafter (Middleburg, 1989). In anoxic sediments, decomposition proceeds primarily by sulfate reduction and rate constants are about one-half to one-tenth those for aerobic processes (Westrich and Berner, 1984; Kristensen et al., 1995; Harvey et al., 1995). Very high OM loading rates can thus inhibit decomposition by exceeding and ultimately inhibiting the supply of oxygen to the sediment (Findlay and Watling, 1997; Duplisea, 1998; Heilskov and Holmer, 2001).

As long as the sediment column is not completely anoxic, decomposition rates under fish farms appear to be comparable to those reported for normal marine sediments. Hall et al. (1990) report 3–20% remineralization of sedimented farm waste over the 8-month growing season of a salmon farm in Sweden, during which period the sediment was completely anoxic (evidenced by surface mats of the sulfate-reducing bacterium *Beggiatoa*). The long-term average decomposition rate was much higher (0.75 per year), however, despite persistent and recurring sediment anoxia. Data reported by McGhie et al. (2000) indicate similarly high rates of OM degradation (0.73–0.89 per year) in sediment under a fallowing salmon farm in Tasmania, representing a combination of aerobic decomposition in the 1–2 cm of surface sediment and sulfate reduction in deeper, anoxic sediment. These are rather high decomposition rates for largely anoxic sed-

iments, suggesting that the waste OM in these systems is predominantly labile (fast-decomposing) materials.

Salmon farm waste OM has fairly low C:N ratios relative to other forms of marine detritus, and is generally considered to be a particularly labile form of detritus (Holmer and Kristensen, 1992; McGhie et al., 2000; Sutherland et al., 2001). Salmon feed is formulated for high digestibility, and even salmon feces has 30–40% organic carbon and 3–5% nitrogen (Chen et al., 1999; McGhie et al., 2000). Decomposition rates for nitrogen-rich material can be very high (0.1–0.2 per day; Enriquez et al., 1993; Ianson and Allen, 2002). We therefore consider the daily rates reported for aerobic decomposition in normal marine sediments (k_{R1} = 0.04 per day, k_{R2} = 0.002 per day; Westrich and Berner, 1984; Wijsman et al., 2002) to be minimum values for the decomposition of fresh farm waste. Greater values may overestimate true rates in heavily polluted areas with completely anoxic sediment, but should be good approximations in more peripheral areas, or after some decomposition has occurred. Furthermore, the low C:N ratio of farm waste suggests that this OM is largely fast-decomposing material (lipids, proteins) and slow-decomposing material (carbohydrates), and that the recalcitrant fraction is small.

3.1.2. Chemical desorption rate k_{Di}

There is accumulating evidence that partitioning of hydrophobic chemicals in natural OM requires substantial time to equilibrate. A series of recent experiments has revealed that desorption of hydrophobic chemicals from natural soils and sediments is best described as a two- (or three-) phase process consisting of an initial fast release, followed by a prolonged period of much slower release (Gong and Depinto, 1998; Gong et al., 1998; Ten Hulscher et al., 1999). This behaviour is believed to result from resistance to diffusion by physical forces within the sorbent (Pignatello and Xing, 1996). The overall kinetics of desorption depend, then, on the distribution of chemical between fast- and slow-desorbing pools and the first-order rate constants for desorption from each pool (k_{D1} and k_{D2}).

The fast-desorbing pool of chemical typically reaches equilibrium in minutes to hours, but the slow-desorbing pool may take weeks to years. Reported values of k_{D1} are typically 0.1–1 h^{-1}, whereas k_{D2} can be as low as 10^{-7} h^{-1} (Cornelissen et al., 1997 and references therein; Ten Hulscher et al.,

1999). k_{D2} depends on the properties of the sorbent (molar volume, hydrophobicity) and age of the sorbent-sediment association (Cornelissen et al., 1997; Gong and Depinto, 1998; Gong et al., 1998; van Noort et al., 2002). For PCBs in sediment, k_{D2} is typically on the order of 10^{-3}–$10^{-4}\,\mathrm{h^{-1}}$ (Cornelissen et al., 1997; Ten Hulscher et al., 1999), or 10^{-2}–10^{-3} per day, and tends toward lower values with increasing octanol–water partition coefficient (K_{OW}).

The fraction of chemical in the slow-desorbing pool increases with increasing planarity (van Noort et al., 2002) and hydrophobicity (Karickhoff and Morris, 1985; Cornelissen et al., 1997) of the sorbent, and with increasing age (equilibration time, for spiked sediments) of the sorbent-sediment association (Gong and Depinto, 1998; Gong et al., 1998). This fraction is typically around 0.5 in natural sediments, but may exceed 0.9 for hydrophobic chemicals (e.g., hexachlorobenzene, log $K_{OW} \sim 6$) at high solids concentrations (Karickhoff and Morris, 1985; Cornelissen et al., 1997).

Contaminants in fish feed presumably have experienced long equilibration times, so the slow-desorbing fraction will likely be large for hydrophobic chemicals like PCBs. Digestive processes within the fish's gut will preferentially deplete the fast-desorbing pool of chemical, so the slow-desorbing fraction will likely be even greater for fish feces than for feed. If fish tissues and intestinal contents are near chemical equilibrium, a significant amount of chemical will partition back into the gut contents and may re-enter the fast-desorbing pool. Fast-growing farmed salmon are likely far from such a chemical equilibrium. Hence, the net flux of chemical is predominantly from the gut contents into fish tissue. We therefore assume that all of the POPs on farm-waste OM are in the slow-desorbing pool. This does not affect the qualitative predictions of the models that follow.

3.2. Steady-state model

In the second scenario, we use the steady-state model to assess diagenetic magnification factors as a function of characteristics of the local ecosystem. In this case, we consider fresh farm-waste OM to consist of three components ($F_1 = F_2 = 0.495$, $F_3 = 0.01$) with first-order decomposition rates $k_{R1} = 10^{-1}$ per

day, $k_{R2} = 10^{-2}$ per day, and $k_{R3} = 0$. We assume that PCBs associated with this OM reside entirely in the slow-desorbing pool, with k_{D2} on the order of 10^{-4}–10^{-2} per day.

3.2.1. Settling rate k_{SS}

Residence time in the suspended pool is determined by settling rate k_{SS}. The sinking velocity of fish fecal pellets is about 2–$5\,\mathrm{cm\,s^{-1}}$ in a nonturbulent water column (Findlay and Watling, 1994; Chen et al., 1999), so maximum settling rate can be very high (20–40 per day for a 100 m water column). Fecal pellets break up quickly in the water column, however, and smaller particles sink more slowly (Findlay and Watling, 1994). Moreover, turbulence in natural systems will further reduce sinking velocities. We consider here a range of lower values for k_{SS} to represent water-column residence times on the order of days to months.

3.2.2. Sediment burial rate k_B

Residence time of a particle in the active sediment is determined by burial rate k_B. If k_B is fixed at a constant value in the steady-state model, the size of the active sediment pool (M_A) and the absolute rate of sediment decomposition ($k_{R1}M_{A1} + k_{R2}M_{A2}$) will increase with Q_F. In reality, the maximum absolute rate of sediment decomposition is limited by the supply of electron acceptors (mainly oxygen and sulfate). As Q_F increases beyond this limit, electron acceptors are depleted, the active sediment pool shrinks and k_B increases. We can illustrate the effect of this limit to absolute decomposition rate by considering variation in k_B to be proportional to Q_F. This simulates the rapid burial of active sediment by fresh material when Q_F is large and decomposition kinetics are saturated. The effect of increasing k_B is to reduce the residence time of a given particle in the active sediment layer, which reduces the extent to which decomposition and desorption may proceed.

Q_F is a function of fish-stocking density, feed application rate, feed wastage, and the degree to which particulates leaving the cages are diluted by local hydrodynamics. These parameters all vary substantially among farms and over time (e.g., through the grow-harvest cycle) and Q_F is rarely measured directly. A simple way to estimate Q_F is to assume that all dilution of waste OM occurs immediately after release and that the fraction of OM lost during

settling (to dissolution and bacterial decomposition) is small. At steady state, when there is no accumulation of waste OM in the water column, Q_F is then approximately equal to the rate at which waste OM is delivered to the sediment. Measured sedimentation rates under salmon farms vary widely, but the range of values is usually on the order of 5 to 80 g m^{-2} per day (dry weight) near the farm perimeter, with values up to 300 g m^{-2} per day directly under cages (Winsby et al., 1996; Hall et al., 1990; Nash, 2001; Sutherland et al., 2001).

We can derive a conservative minimum value to k_B under salmon farms by considering a mildly impacted sediment underlying a farm with a low waste OM output ($Q_F = 10$ g m^{-2} per day). Assuming an active sediment layer thickness of 5 cm, an organic matter content of 5%, and a sediment density of 1.15 g ml^{-1}, the mass of organic matter in the active sediment pool (M_A) is 2875 g m^{-2}. Rearranging Eq. (5) gives

$$k_B = \frac{Q_F}{M_A} - \sum_i [k_{Ri} F_i M_A] \tag{10}$$

where the OM decomposition term is summed over all the i fractions of OM (i.e., labile, recalcitrant). Assuming that the majority of the OM remaining in the sediment is highly recalcitrant ($k_R \sim 0$), the burial rate k_B is 0.0035 per day. Greater values of M_A (i.e., thicker active sediment layer, greater OM content) or overall k_R (more labile OM) will produce lower burial rate constants.

We have not considered here the effect of OM consumption by metazoan consumers on sediment residence time. Specific consumption rates can be expected to decline with increasing Q_F as the volume of habitat for aerobic organisms shrinks. This will further enhance burial rate and increase the rate of sediment accumulation. This could be modelled as an accelerating (more than linear) increase in burial rate as Q_F increases.

3.3. Application to PCBs in farm waste

In a final scenario, we use the diagenetic magnification factors derived in the steady-state model to predict a likely range of concentrations for PCBs in the organically enriched sediments underlying salmon farms.

3.3.1. Farm waste PCB concentration C_F

The concentration of PCBs on waste OM leaving the farm (C_F, ng g^{-1}) is a function of PCB concentrations in waste feed and feces and the relative contributions of these two materials to the waste OM flux Q_F. High-energy salmon diets contain fish meal and up to 36% fish oils from marine forage fisheries, and are therefore subject to contamination by hydrophobic chemicals. PCB concentrations in feeds and farmed fish vary widely with the source and lipid content of the material, but geometric mean lipid-corrected concentrations are remarkably similar between the two published studies. Easton et al. (2002) reported a mean total PCB concentration of 244 ng g^{-1} lipid for five commercial salmon feeds used in British Columbia, and 319 ng g^{-1} lipid in farmed fish flesh. Jacobs et al. (2002) reported a mean total PCB concentration of 226 ng g^{-1} lipid in eight feeds used in Scotland and 252 ng g^{-1} lipid in farmed salmon. These values correspond to 60 ng g^{-1} wet weight in feed and 40 ng g^{-1} wet weight in farmed salmon. These values reflect unusually low lipid-based biomagnification factors (mean lipid-BMF = 1.2), which is consistent with the very high growth efficiency of farmed salmon.

Reports of feed wastage range from 1–2 to 30% (Nash, 2001). Typical recent values are on the order of 3–5% for hand-fed farms and slightly higher for machine-fed farms (Nash, 2001). Of the ingested fraction of the offered feed ($\sim$96%, conservatively), most is assimilated by the fish and the remainder is egested as feces. Reported apparent digestibility coefficients for salmon feeds are on the order of 65–85% of OM or gross energy (Winsby et al., 1996; Percival et al., 2001; Chen et al., 1999; Cho and Bureau, 2001). Assuming 25% egestion of 96%-ingested feed, feces constitutes 86% of bulk waste OM and uneaten feed constitutes the remaining 14%. This is consistent with the results of a fatty acid tracer study by McGhie et al. (2000), who reported that most of the waste OM delivered to the sediment under a farm in Tasmania was feces, although there was a measurable signal of waste feed. Overall, we estimate that about 29% of the added feed ends up on the seafloor. This is at the low end of the 29–71% range reported by Hall et al. (1990) for a farm in Sweden.

Manufactured feeds are designed to be highly digestible, and farmed salmon have less scope for energetically expensive activities than their wild counterparts,

so growth efficiency is very high. Farmers typically use 1.2 kg of feed (about 1 kg dry weight), to produce 1 kg of fresh salmon (about 0.3 kg dry weight), giving a gross dry weight conversion efficiency of 30%. Given a total PCB concentration in feed pellets of 60 ng g^{-1} wet weight (Easton et al., 2002; Jacobs et al., 2002), a farmer adds 72 μg of PCBs to the farm per kg wet weight of salmon produced. These are predominantly high-molecular weight, highly chlorinated (hexachloro and greater) congeners (Easton et al., 2002; Jacobs et al., 2002), so metabolic transformation and excretion rates are small (Kannan et al., 1995). Given a total PCB concentration in farmed salmon of 40 ng g^{-1} wet weight (Easton et al., 2002; Jacobs et al., 2002), 40 μg of PCBs (56% of inputs, consistent with reported assimilation efficiencies for PCBs from high-lipid diets; Gobas et al., 1993; Fisk et al., 1997) is leaving the farm in each kg of fresh salmon. The remaining 44% (32 μg/kg salmon produced) is egested with feces. If OM egestion is 25% of ingestion, this amounts to 250 g dry weight of feces per kg salmon produced, giving a PCB concentration of 128 ng g^{-1} dry weight in feces.

Given dry weight PCB concentrations of 128 ng g^{-1} dry weight in feces and 71 ng g^{-1} in feed (assuming 15% moisture content), and assuming that 86% of Q_F is feces and the remainder is waste feed, the PCB concentration in farm-waste OM, C_F, is then estimated to be 120 ng g^{-1} dry weight. This calculation assumes that all excreted OM is solid, and may therefore slightly underestimate C_F.

4. Results

4.1. Dynamic model

The trajectories of OM and PCB content for a single particle, and the resulting trajectory of PCB concentration are shown in Fig. 1. The values shown are for a particle of initial mass $M_0 = 1$ and initial PCB concentration $X_0 = 1$. The diagenetic magnification factor (DMF) is therefore expressed by the ratio C_t/C_0. This ratio varies greatly as the particle ages, increasing when the OM decomposition rate exceeds the desorption rate ($k_R > k_D$), and decreasing when the inverse is true. For relatively rapidly desorbing
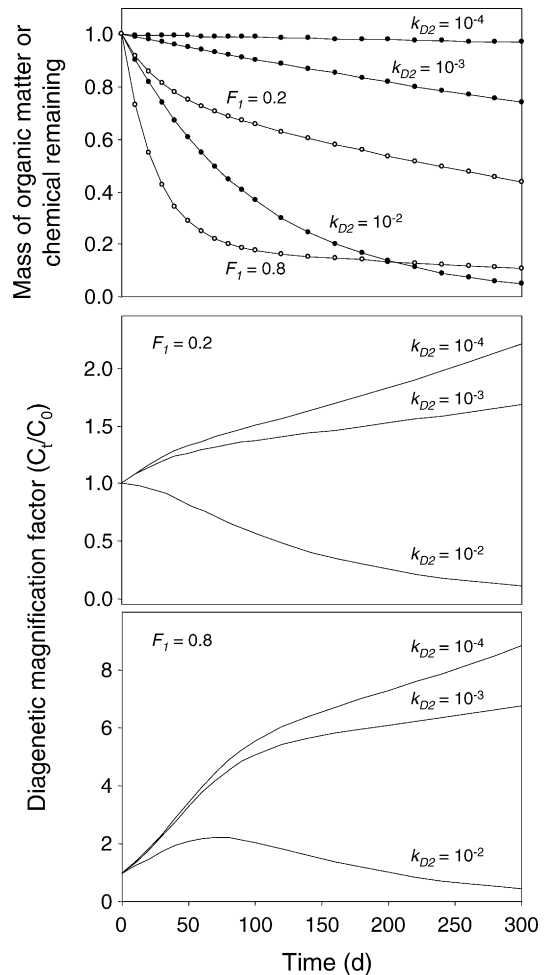

Fig. 1. Time courses of organic matter decomposition (open circles) and chemical desorption (closed circles) (top panel), and the resulting diagenetic magnification of chemical concentration (no symbols) for mostly recalcitrant organic matter ($F_1 = 0.2$, middle panel) and mostly labile organic matter ($F_1 = 0.8$, bottom panel). Trajectories are shown for three slow-pool chemical desorption rates (k_{D2}).

chemicals ($k_{D2} = 10^{-2}$ per day), the DMF increases with time only when the fraction of labile OM (F_1) is high. This is expected to be for less than a week when the initial F_1 is low, and for a few months when initial F_1 is high. When labile OM is depleted, desorption kinetics catch up with decomposition and the DMF returns to and below unity. For the more slowly desorbing chemicals, the DMF increases rapidly when F_1 is high, but then continues to increase because
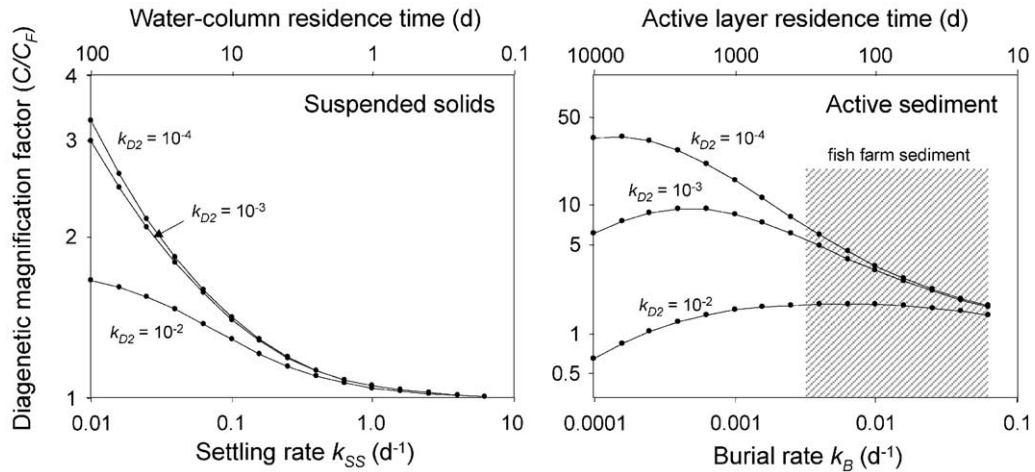
Fig. 2. Dependence of steady-state diagenetic magnification factors on particle residence time in the water column (left panel, determined by settling rate) and active sediment (right panel, determined by burial rate). Values are shown for three slow-pool chemical desorption rates (k_{D2}). Hatched region is likely range of burial rates under salmon farms (see text for details). Note that all axes are logarithmic.

even slow decomposition is faster than desorption. For initially labile OM, we estimate that early diagenesis could magnify concentrations of very slowly desorbing chemicals more than eight-fold within a year.

4.2. Steady-state model

The diagenetic magnification ratios C_S/C_F and C_A/C_F predicted by the steady-state model are shown in Fig. 2 for a range of chemical properties (k_{D2}) and residence times in each environment (k_{SS} and k_B). These predictions suggest that the DMF is unlikely to exceed unity in the suspended phase, except at very low values of k_{SS}. C_S/C_F increases rapidly as k_{SS} declines below about 0.3 per day, but only exceeds 2–3 even at the extremely low value of $k_{SS} = 0.01$. That is, diagenetic magnification does not proceed appreciably until a particle has spent several days in the water column, and is only substantial on the scale of several months.

Residence times in the active sediment layer are typically much longer than in the water column, and the scope for diagenetic magnification is consequently greater. Our model predicts DMF values on the order of 10–20 for slow-desorbing chemicals in sediments with low burial rates (e.g., deep ocean environments). Over the range of burial rates typical of salmon farm operations, however, predicted DMFs were on the order of 2–3 (Fig. 2).

The sensitivity of these predicted DMFs to variation in parameters is illustrated in Table 1. An order of magnitude change in k_{R1} and k_{R2}, k_{D2}, k_{SS}, or k_B produced only 1.3- to 3-fold changes in the predicted DMF, and all predicted DMFs were in the range 1.5–4.4 for the realistic ranges of rate parameter values considered here. Predicted DMF was much more sensitive to the assumed value of labile OM fraction (F_1), varying by nearly an order of magnitude when F_1 was varied from 0.09 to 0.9. For very labile OM ($F_1 = 0.9$), the predicted DMF of a slow-desorbing chemical was very high ($C_A/C_F = 12$ for $k_{D2} = 10^{-3}$).

4.3. Application to PCBs in farm waste

Given an initial PCB concentration on waste OM (C_F) of 120 ng g^{-1} dry weight OM (Section 3.3), the DMFs predicted by our model produce sediment PCB concentrations on the order of 200–500 ng g^{-1} dry weight OM over most of the parameter ranges considered here. The very high DMFs predicted for labile OM and slow burial produce sediment PCB concentrations on the order of 1500–2500 ng g^{-1} dry weight OM.

Unfortunately, there are no studies in the literature that report concentrations of PCBs in sediments under

Table 1
Sensitivity of the predicted diagenetic magnification factor (ratio of sediment concentration, C_A to farm-waste concentration, C_F) to an order of magnitude variation in each parameter (0.3× and 3× mean values)

Parameter	Mean value	Range of predicted C_A/C_F	Factor change in C_A/C_F
Decomposition rates	$k_{R1} = 10^{-1}$, $k_{R2} = 10^{-2}$	1.5–4.4	3.0
Desorption rate	$k_{D2} = 10^{-3}$	2.6–2.0	1.3
Settling rate	$k_{SS} = 10^0$	2.5–2.4	1.0
Burial rate	$k_B = 10^{-2}$	4.3–1.7	2.6
Labile OM fraction	$F_1 = 0.3$	1.3–12	9.5

fish farms. Preliminary results from a study currently underway in eastern Canada (Haya et al., 2001) are consistent with our predictions, however: PCB concentrations were found to be higher under farms than either background sediment or published fish feed concentrations, and higher at 25 m distance than directly under the cages, where k_B is highest (Hellou et al., 2003). Concentrations of PCB-153 were as high as $5 \, ng \, g^{-1}$ dry weight sediment (Hellou et al., 2003), or about $125 \, ng \, g^{-1}$ dry weight OM (given 2% organic carbon and 50% carbon in OM). This value is 22-fold greater than measured feed concentrations of PCB-153 (Easton et al., 2002; Jacobs et al., 2002), and 12-fold greater than that our estimated concentrations for salmon feces.

5. Discussion

Theoretical predictions of solid-water partitioning coefficients (K_d, the ratio of solid-phase concentration to aqueous concentration) are usually based on the hydrophobicity of the chemical (K_{OW}), the organic carbon content of the solid phase, and an estimate of the affinity of natural organic carbon for hydrophobic chemicals (e.g., Mackay, 1982; Seth et al., 1999). Field observations, however, frequently report apparent K_d values greatly in excess of what would be predicted by theory (e.g., Bucheli and Gustafsson, 2001 and references therein). This disparity is usually blamed on an underestimation of the affinity of the solid phase for these chemicals (e.g., Gustafsson and Gschwend, 1999; Jonker and Koelmans, 2002), an explanation that continues to rely on the assumption that chemical distribution processes are at equilibrium.

We have shown here that competing kinetics in real systems can produce a state of persistent disequilibrium, preventing organic chemicals from ever reaching thermodynamic equilibrium on ecologically relevant time scales (cf. Skoglund et al., 1996 and Schulz-Bull et al., 1995 for similar arguments regarding sorption kinetics). This mechanism could explain why equilibrium models fail to predict the very high sediment-water partitioning coefficients commonly observed in the field. Our hypothesis also provides a satisfying explanation (Fig. 1) for the observation that K_d often tends to increase with particle age (Baker et al., 1991; Koelmans et al., 1993, 1997; Axelman et al., 2000; Epplett et al., 2000; Gobas and MacLean, 2003).

In organically enriched systems, especially, rapid OM decomposition is a viable alternative explanation for apparently high values of K_d. Our models predict moderate levels of diagenetic magnification (two- to four-fold) across a wide range of realistic parameter values, and rather higher DMFs for very labile OM in systems with low burial rates (long residence times, e.g., deep ocean environments). It is also important to note that OM is rarely buried forever. It is common practice for fish farms to alternate fallow periods with their production cycles, for example. Buried OM will be re-exposed during a fallow period as surface sediment decomposes and the sediment redox profile returns to normal (e.g., McGhie et al., 2000). This re-exposed material will then resume the process of diagenetic magnification, effectively sliding to the left along one of the curves in Fig. 2. DMFs that emerge on the time scale of entire production-fallow cycles may therefore be even higher than predicted by our steady-state model.

The key assumption in this hypothesis is that the process of OM decomposition does not itself accelerate desorption kinetics. As decomposition proceeds, the volume of OM declines, and so the average distance a molecule must travel to escape the OM matrix declines. This might well relax to some extent the

internal resistance to diffusion that seems to be the basis of slow-desorption kinetics. It is also possible, however, that OM decomposition processes will even further retard desorption kinetics. Bacteria use extracellular enzymes to cleave and solubilize biopolymers (lipids, carbohydrates, proteins), releasing a layer of charged and polar chemical fragments at the boundary of the neutral bulk OM (Dassonville and Renault, 2002). The resulting cloud of charged fragments will present a barrier to diffusion of hydrophobic molecules, especially if the labile OM is interspersed with an inorganic or recalcitrant matrix. The relative importance of these two phenomena (volume depletion and polar-layer resistance) will determine whether k_{D2} increases or decreases as decomposition proceeds. If extensive decomposition does enhance desorption kinetics (i.e., k_{D2} increases as F_1 and F_2 decline), our models will tend to overestimate DMFs for longer residence times. The DMF for a given chemical will then be better predicted by shifting to progressively faster-k_{D2} curves as residence time increases (e.g., shifting from the $k_{D2} = 10^{-4}$ curve to 10^{-3} and 10^{-2} as k_B declines to the left of Fig. 2).

The DMF models presented here are based on concentrations of POPs in bulk OM. More relevant to sediment-dwelling biota, however, is the fugacity of these chemicals (Mackay, 1991), and it is likely that fugacity is magnified to an even greater extent than the concentration. The gastrointestinal magnification model for biomagnification in fish (Gobas et al., 1999) makes the observation that the most easily digested fractions of OM are also those with the highest sorption affinity for hydrophobic organic chemicals. Digestive processes selectively deplete these fractions of the diet, reducing the overall fugacity capacity (Z) of the gut contents much more rapidly than the volume or OM content, and therefore increasing the fugacity of chemical in the resulting material ($f = C/Z$) much more rapidly than volume depletion increases the concentration. The result is a doubling of chemical concentration in feces over that in the ingested material, but a more than seven-fold increase in fugacity. We suggest that similar processes are likely at work in sediment. As decomposition depletes the most labile fractions of OM, the overall Z of the OM declines, producing a disproportionate increase in f.

The predictions of our models have implications for chemical fate modelling and risk assessment in a wide variety of aquatic environments. In systems with rapid OM-cycling kinetics, the widely held assumption of equilibrium partitioning is inappropriate (Swackhamer and Skoglund, 1993; Cheng et al., 1995) and models based on this assumption will make poor predictions. A recognition of the dynamic nature of the OM matrix, incorporating relationships such as those described in this paper, will permit a better understanding of chemical fate in organically enriched systems.

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