

Models of the Distribution of Persistent Organic Pollutants in the Marine Environment

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Doctoral Thesis

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Till alla

Sätt siffror på verkligheten, räkna och se var du hamnar
T. Hammar, Länsstyrelsen Kalmar

Abstract

Persistent organic pollutants (POPs) is a group of chemicals that are toxic, undergo long-range transport and accumulate in biota. Due to their persistency the distribution and recirculation in the environment often continues for a long period of time. Thereby they appear virtually everywhere within the biosphere, and poses a toxic stress to living organisms. In this thesis, attempts are made to contribute to the understanding of factors that influence the distribution of POPs with focus on processes in the marine environment. The bioavailability and the spatial distribution are central topics for the environmental risk management of POPs. In order to study these topics, various field studies were undertaken. To determine the bioavailable fraction of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated naphthalenes (PCNs), and polychlorinated biphenyls (PCBs) the aqueous dissolved phase were sampled and analysed. In the same samples, we also measured how much of these POPs were associated with suspended particles. Different models, which predicted the phase distribution of these POPs, were then evaluated. It was found that important water characteristics, which influenced the solid-water phase distribution of POPs, were particulate organic matter (POM), particulate soot (PSC), and dissolved organic matter (DOM). The bioavailable dissolved POP-phase in the water was lower when these sorbing phases were present. Furthermore, sediments were sampled and the spatial distribution of the POPs was examined. The results showed that the concentration of PCDD/Fs, and PCNs were better described using PSC- than using POM-content of the sediment. In parallel with these field studies, we synthesized knowledge of the processes affecting the distribution of POPs in a multimedia mass balance model. This model predicted concentrations of PCDD/Fs throughout our study area, the Grenlandsfjords in Norway, within factors of ten. This makes the model capable to validate the effect of suitable remedial actions in order to decrease the exposure of these POPs to biota in the Grenlandsfjords which was the aim of the project. Also, to evaluate the influence of eutrophication on the marine occurrence PCB data from the US Musselwatch and Benthic Surveillance Programs are examined in this thesis. The dry weight based concentrations of PCB in bivalves were found to correlate positively to the organic matter content of nearby sediments, and organic matter based concentrations of PCB in sediments were negatively correlated to the organic matter content of the sediment.

Table of Contents

Abstract	1
Table of Contents	3
List of Papers	4
Introduction	5
Background	5
Phase Partitioning	6
Emissions and Sources	12
Transport and Reaction	14
Multimedia Mass Balance Fate Models	18
Aims of the Papers	19
Discussion	22
Acknowledgements	26
References and Notes	27

List of Papers

This doctoral thesis is based on the following four papers, which are referred to by their roman numerals:

I Persson NJ, Axelman J, Broman D. 2000. Validating Possible Effects of Eutrophication Using PCB Concentrations in Bivalves and Sediment of the US Musselwatch and Benthic Surveillance Programs. *Ambio* 29: 246-251.

II Persson NJ, Gustafsson Ö, Bucheli TD, Ishaq R, Næs K, Broman, D. 2002. Soot-Carbon Influenced Distribution of PCDD/F in the Marine Environment of the Grenlandsfjords, Norway. *Environ Sci Technol* 36: 4968-4974.

III Persson NJ, Gustafsson Ö, Bucheli TD, Ishaq R, Næs K, Broman D. Distribution of PCN, planar PCB, and other POPs together with Soot Carbon and Organic Matter in the Marine Environment of the Grenlandsfjords, Norway. *Manuscript*.

IV Persson NJ, Cousins IT, Gustafsson Ö, Molvær J, Næs K, Broman D. Modelling the Fate of Polychlorinated Dibenzo-*p*-Dioxins and Dibenzofurans outside a large Emission Point Source in the Grenlandsfjords, Norway. *Manuscript*.

Introduction

When research on toxic pollutants is focussed on consequences for a whole ecosystem, it is commonly referred to as ecotoxicology. This is a very broad field of science where issues such as uptake and effects in organisms, as well as distribution and residence time of the pollutants in the physical environment are studied in many different ways. The fundamental question to answer is whether ecosystems are harmfully disturbed when polluted by toxicants. To answer this important question, quantitative understanding of the pollutants behaviour within ecosystems is essential, and therefore researchers develop methods to manage this.

One class of environmental toxic pollutants is the persistent organic pollutants (POPs, see Jones and de Voogt, 1999) among which can be found the polychlorinated biphenyls (PCBs), the polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs, "dioxins"), and the polychlorinated naphthalenes (PCNs). The PCBs and PCDD/Fs cause adverse effects in organisms (van den Berg et al 1998, SAB 2001), which is reason enough for studying them. Furthermore, the various isomers (210 PCBs, 212 PCDD/Fs and 75 PCNs) have relatively different physico-chemical properties (Mackay et al 1992), and they also behave differently in the environment. This wide span of properties and behaviour offers researchers a good opportunity to study if and how such factors are related. In this thesis such relations are studied, with emphasis on the POPs partitioning between water and particles, and also on their geographical distribution in the marine environment. The aim of the thesis is to contribute to the quantitative understanding of why POPs distribute the way they do in the marine environment.

Background

Literally, distribution means spread of matter, and in this thesis the main focus is set on POPs, organic matter and soot. As outlined by Wania and Mackay (1999) the way POPs spread in the environment can be described by four building blocks of information which are; emission, phase partitioning, transformation and transport. These topics are briefly discussed in the following sections. In addition, some discussions on the quantitative description of the POPs distribution using mass balance models are presented.

Phase Partitioning

Pollutants like PCBs, PCNs and PCDD/Fs are hydrophobic which means that they have low solubility in water. They are also lipophilic i.e. they have high solubility in lipids (Sangster 1997). As a result, in the marine environment these POPs will preferentially associate to particles. This occurs because the particles typically contain spaces and surfaces filled and coated with phases that in important aspects resembles lipids. Into and at the surface of these phases the POPs sorb or like it better than in the water phase (Luthy et al 1997).

The partitioning of POP molecules between the freely dissolved phase and various types of solid phases (e.g. particles) is one aspect of chemical speciation, and this has major influence on the uptake of POPs in marine organisms and food webs (Hamenlink et al 1994, Muir et al 1992, Servos et al 1992b). Generally, it is found that only the dissolved phase is small enough to pass biological membrane and thereby be taken up by the organisms. The chemical speciation is also of importance for the fate and transport of the POP in the marine environment, e.g. for the processes determining degradation (Friesen et al 1996), sedimentation (Broman et al 1989, Servos et al 1992a), and volatilisation (Lohmann et al 2000, Wania et al 1998). Further aspects on the chemical speciation were given by Gustafsson and Gschwend (1997a), who discussed properties of aquatic colloidal matter and implications for the fate of pollutants attached to it.

In nature one strongly sorbing phase for POPs is the organic matter (OM, Note 1). This has been shown in studies with water solutions equilibrated with particles from soils and sediments. The content of organic carbon (OC), serving as a measure of the OM, was then shown to be the primary property of the particle determining the partitioning (Karickhoff et al 1979, Karickhoff et al 1981). From such experiments, a linear relation was found to describe the distribution of POPs between the particle and the dissolved phases. This relation was determined at concentrations around 50 % of the compounds aqueous solubility (Karickhoff 1979, Karickhoff et al 1981), <60-90% (Chiou 1983)), which for extrapolations to the natural environment is a quite high range for many compounds. The solid-water phase distribution coefficient K_d ($L_{\text{water}}/\text{kg}_{\text{dw solid}}$) according to such relations is:

$${}^{OMP}K_d = f_{OC} \cdot K_{OC} = \frac{C_s}{C_w} \quad (1)$$

Where K_{OC} is the organic carbon – water partition coefficient (L_{water}/kg_{OC}), f_{OC} is the fraction organic carbon in the solid phase ($kg_{OC}/kg_{dw \text{ solid}}$), C_s is the particle associated concentration ($mol/kg_{dw \text{ solid}}$) and C_w the truly dissolved concentration (mol/L_{water}).

Stated with thermodynamics, a system of a hydrophobic POP in two phases (of equal volumes) e.g. water and a lipid (Note 2) will have lower free energy when the POP molecules are mainly distributed into the lipid phase. This reflects the findings that hydrophobic POPs spontaneously partition from water into fatty phases like for instance the lipids, and reach much higher concentrations there than in the water.

The K_d in Equation 1 can be converted to a mole fraction based ("unitless") partition coefficient (K'). This K' can be shown to be a function of the difference between the partial molar excess free energy ($(\delta G/\delta n)_{P,T}$, Note 3 and 4) of the POP molecules in the water and those in the solids. The change in partial molar free energy in each phase (the POPs in the solids, and the POPs in the water) is defined as the chemical potential (μ in J/mol) of the POP in that specific phase. At equilibrium the chemical potential of the POP in the solids and the chemical potential of the POP in the water are equal. In addition, the total free energy of the system is as minimized as it can get by means of only redistributing the POP between the phases. Chemical potential is consequently a criterion for equilibrium. Net diffusion of POPs between phases (water/air, particles/water etc.) will take the direction from high to low chemical potential. This is of interest when estimating transport of POPs in the environment. An analogue expression to chemical potential is fugacity (f , in Pa). For reasons described in Mackay (1979), Mackay and Paterson (1981, 1982), and summarised in Mackay (1991), fugacity is a more useful criteria for equilibrium, than chemical potential, when POPs are considered. Simply stated, fugacity equals molar concentration (mol/m^3) divided by the parameter Z (in $mol \cdot Pa^{-1} \cdot m^{-3}$). This is called the fugacity capacity, and it describes the capacity of a phase to contain a POP at a certain fugacity in the phase. The fugacity capacity is thus a function of phase properties, and the physico-chemical properties of the POP. For water in the marine environment, containing suspended particles, the fugacity capacity can be calculated as:

$$Z_{bulkwater} = Z_{water} + Z_{particle} \cdot VF_{particle} \quad (2)$$

Where Z_{water} , is the fugacity capacity of the pure water, and Z_p is the fugacity capacity of suspended particles, and $VF_{particles}$ is the volume fraction of suspended particles in the water. The $Z_{particles}$ is thus essentially a function of the partition coefficients for the sorbing phases the particle contains, e.g. organic carbon and soot carbon.

The K_{OC} parameter (Equation 1) for PCB and PCDD/F is frequently estimated by empirically derived relations to their hydrophobicity, commonly expressed as the octanol-water partitioning coefficient (K_{OW} , Sangster 1997). Examples of such an empirical relation were recently presented by Seth et al (1999) who found that K_{OC} equals $0.35K_{OW}$ with 95% confidence interval a factor 2.5 in either direction. Their relation was based on studies with particles of somewhat varying sizes. In the study by Karickhoff et al (1981), the relation was found to be $K_{OC} = 0.41K_{OW}$ (with a factor 2 variation) and this was valid for the fine sized ($<50 \mu m$) fraction of sediment particles. In theory, at equilibrium K_{OC} for particles of different sizes should be equal if dependent on OC content alone. However, in a recent review of K_{OC} for dissolved organic carbon (DOC) (Burkhard, 2000) a lower capacity of DOC was found, $K_{DOC} = 0.08K_{OW}$. The 95 % confidence limits in this relation was however a factor 20 in either direction, indicating that in general the sorbing capacity of DOC is not clearly distinguishable to that of OC in larger particles. Burkhard (2000) noted that the huge variation could be an indication that the hydrophobicity of the POPs was not the only parameter influencing their association with DOC. Chiou et al (1983) investigated experimentally the equilibrium partitioning of chlorobenzenes and PCBs between soil organic matter and water. They also derived a theoretical expression for the partition coefficient (K_{OM}), with which the combined contribution of aqueous insolubility (γ_w) and incompatibility in the polymeric soil organic matter (γ_{OM}) could be compared. It was concluded that γ_w was the major factor, and the γ_{OM} was significant but of secondary importance to the K_{OM} . Since natural organic matter has a variable composition (Hedges and Oades 1997), one could expect its capacity to sorb a POP molecule to vary somewhat. And indeed, some studies have indicated that the composition of the OM (e.g. the C:N ratio) in aquatic particles seem to influence the degree of POP

association to particles (Koelmans et al 1997), as well as the uptake in organisms fed with contaminated OM of varying composition (Gunnarsson et al 1999). Furthermore, equilibrium concentrations are not instantaneously established between water and OM. Studies on the kinetics of sorption and desorption of POPs to particles have revealed that the particle size and content of more condensed OM influence the time to reach equilibrium. To understand such observations, the effective diffusivity of the POP as a function of sorbate (particles) size, porosity and composition is usually considered (Cornelissen et al 2000, Pignatello and Xing 1996, Valsaraj and Thibodeaux 1999).

In the water column, a significant portion of the particles is living plankton. Swackhamer and Skoglund (1993) argued that plankton can grow at a faster rate than the POPs are sorbed on/at the plankton, and that this results in a non-equilibrium situation that can last for long periods (notably during spring blooms). Stange and Swackhamer (1994) gave additional explanations to this phenomenon. They calculated that binding to DOC in the surrounding water could explain much of the apparent non-equilibrium, but not all.

Bucheli and Gustafsson (2000) showed that polycyclic aromatic hydrocarbons (PAH) have very high affinity to soot carbon (SC), which is a highly condensed sub fraction of the organic carbon. Soot carbon seems to be present in most marine and aquatic particles (Gustafsson et al 2001), and it has been suggested to increase their sorbing capacity. Earlier, Gustafsson et al (1997c) proposed an extension of the organic matter-partitioning model to account for both organic matter and soot carbon binding.

$$K_d = K_{POC} \cdot f_{POC} + K_{SC} \cdot f_{SC} = \frac{C_s}{C_w} \quad (3)$$

Here f_{SC} is the fraction soot carbon in the particles ($\text{kg}_{SC}/\text{kg}_{dw \text{ solid}}$) and K_{SC} the soot carbon – water partition coefficient ($\text{L}_{\text{water}}/\text{kg}_{dw \text{ solid}}$). If the product $f_{SC}K_{SC}$ gets sufficiently large, this will lower estimates of the dissolved phase (fugacity) in the marine environment. Knutzen (1995) and also Paine et al (1996) suggested that exposure effects of PAH to biota were overestimated due to PAH association to pitch or coke particulates. It will further influence estimates of rates for abiotic processes where speciation is involved (see above). Mechanistic studies

(Bucheli and Gustafsson 2000 a, Accardi-Dey and Gschwend 2001, Neue and Rudolph 1993) have additionally indicated that sorption of planar POPs to SC is an adsorption process, i.e. that the surface areas of the SC and the POPs interact. Gustafsson and Gschwend (1997b) actually speculated that the strong sorption of PAH to SC occurs due to inter-molecular forces established by geometrically π -cloud overlapping, resembling fusion. Such an adsorption mechanism is different from organic matter partitioning where the POPs are thought to dissolve in the organic matter and get absorbed within it. Indeed, if adsorptive SC association of POPs was significant, one would expect the binding capacity of SC at high concentration of POPs to level off, since the surface available for adsorption would be occupied by other POPs. Such a competitive sorption would be reflected in the linearity of the K_d . Accardi-Dey and Gschwend (2001) formulated this concentration dependence as:

$$K_d = K_{POC} \cdot f_{SC} + K_{SC} \cdot f_{SC} \cdot C_w^{n-1} = \frac{C_s}{C_w} \quad (4)$$

Where the exponential term $n-1$ scales the concentration dependence. In this case, the n factor originates from assumptions of Freundlich sorption isotherms where $n = 1$ gives no dependency at all and $n < 1$ describes a saturation of binding sites for higher C_w . One complicating practical aspect with Equation (4) is that it takes numerical iteration to solve for the C_w term. This may severely increase the computation time when applied in e.g. multimedia models, where the equation has to be solved many times for a multiple of compartments (see Paper IV). Also, additional information on the value of the n term is needed to solve for the dissolved phase. Finally, the choice of what dissolved concentration to relate the concentration dependence to may not always be obvious if many compounds are present at very different concentrations in a system. In Paper IV we chose to use Equation (3) instead of (4) in order to avoid these complications.

A crucial question yet awaiting to be finally answered is whether the association of POPs and SC in the environment results from the POPs being trapped within SC already when released (emitted), which for POPs produced in combustion processes (e.g. PAH and PCDD/Fs) would not seem unlikely (cf. Weber et al 2001, Musdalslien et al 1998). This would also give strong correlations of POPs and SC, and observed

partition coefficients above predicted from OM partitioning (as seen in e.g. Paper II and III). Given what has been discussed above, there are different ways to validate whether POPs are permanently occluded within the SC phase or whether they undergo active partition to the SC surface. Observations of concentration dependent (non-linear) K_d in sorption studies would support a surface partition mechanism. The degree of POP molecules coverage for SC surfaces (on particles) in the environment, compared to the degree of coverage in the emission sources will also be of interest, since higher coverage in the environment would indicate that further uptake of POPs had occurred in the environment, i.e. active partitioning to the SC. Finally, if permanent occlusion of POPs within the SC phase was the case, one would expect very similar POP-profiles in particles in emissions and those found in the environment. These profiles would thereby not necessarily vary with physico-chemical properties of the POPs. Theoretically derived K_{SC} for PAH together with measured f_{SC} of suspended particles (Næs et al 1998) have given better accordance of predicted versus observed K_d . Their improved predictions of observed K_d in the environment with the SIC model thus speak against occluded POPs. Since PCDD/F-molecules are planar like the PAHs, one could expect a similar binding mechanism. In Paper II and III, we investigated the relative importance of SC and OC for the phase distribution of POPs in the marine environment of a Norwegian fjord system, the Grenlandsfjords.

There are numerous descriptions on how to parameterize the distribution of pollutants between the various phases of a water volume (e.g. Voice and Weber 1985, Pankow et al 1991, Schwarzenbach et al 1993). Based on such literature and what has been discussed above, the total fugacity capacity of a bulk water volume could be expressed as:

$$Z_{bulkwater} = Z_{water} + Z_{DOM} \cdot VF_{DOM} + Z_{POC} \cdot VF_{POC} + Z_{SC} \cdot VF_{SC} \quad (5)$$

Where Z_{DOM} is fugacity capacity of dissolved organic matter (DOM), VF_{DOM} is the volume fraction of DOM in the water, and Z_{POC} , Z_{SC} , VF_{POC} , VF_{SC} are the analogues for particulate organic matter and soots respectively. In Paper IV, we use this equation in a fugacity based multimedia model of the fate of PCDD/Fs in a marine environment.

The phase partitioning of POPs is also influenced by the temperature of the system. For most POPs, the distribution is shifted to the more condensed phase at low temperatures. Shiu and Ma (2000a, 2000b) have gathered experimental data on the temperature dependence of phase distribution of a large number of different POPs. They found that usually a linear relationship of $\ln K$ versus the reciprocal absolute temperature (T in K) apply within an environmentally applicable range of temperatures (5-50 °C). The slope of such a line is related to the enthalpy of phase change for the process studied, e.g. fusion of a liquid. This makes assumptions of constant enthalpy of phase change valid (e.g. for vaporisation ΔH_{vap} , for fusion of liquids ΔH_{fus} , for sublimation ΔH_{sub} in kJ/mol). One interesting aspect of this temperature dependence of phase partitioning processes, is that it may significantly influence how semi-volatile POPs distribute throughout the global environment (Wania and Mackay 1993, Wania and Mackay 1996, Wania et al 1998).

Phase partitioning seem to be a very important block of information to understand how POPs distribute in the marine environment. But obviously, pollutants must be released into the environment before they start partitioning between phases. Knowledge of their sources and how they are emitted is therefore of great interest.

Emissions and Sources

The release of pollutants from industries or other sources is called emissions. There are many aspects of how to express emissions, e.g. in terms of emission flux (E_{flux} in e.g. $\text{kg}\cdot\text{h}^{-1}\cdot\text{m}^{-2}$), or as a flux integrated over a given area to give emission rate (E_{rate} in e.g. $\text{kg}\cdot\text{h}^{-1}$). From a grid-perspective (i.e. for many equally sized smaller areas), the emission flux of POPs varies spatially, and is high close to point (distinct) sources such as an industry. Other POPs may have multiple sources, and thereby show a more geographically diffuse emission flux. Man-made pollutants are termed anthropogenic in order to distinguish them from natural sources which for some POPs (e.g. the PAHs) also are significant.

The main sources of PCDD/F are commonly combustion related (Alcock et al 2001). The mechanism of formation varies, but usually two main types are distinguished based on the type of reactants involved, the *de novo* synthesis from macromolecular carbon structures, and the precursor synthesis from small organic molecules (Addink and Olie 1995). This

distinction has however been subjected to criticism by Lenoir et al (1998). For municipal waste incineration and metallurgical processes, *de novo* synthesis of PCDD/Fs, PCNs, co-planar PCBs and other POPs, have been shown to be of significance (Sakai et al 1996, Ilino et al 1999, Buekens et al 2001, Weber et al 2001). This is a mechanism of oxidative breakdown and transformation of macromolecular carbon structures (soots) to yield smaller aromatic compounds. In the experiments by Sakai et al (1996), the coplanar PCBs were also found to be formed through the precursor mechanism by dimerization of chlorobenzenes. In the Grenlandsfjords samples (Papers II-IV) the typical *de novo* PCDD/F profile, i.e. high degree of low chlorinated and low degree of high chlorinated POPs (Sakai et al 1996, Ilino et al 1999, Buekens et al 2001, Weber et al 2001), is not observed. Instead the PCDFs with the highest degree of chlorination dominate the pattern. Also the fullchlorinated PCB congener 209 dominate the PCB pattern in the Grenlandsfjords. The type of magnesium fabrication used in the Grenlandsfjords, has unintentionally generated PCDD/Fs, PCNs, PCBs and other chlorinated POPs as by-products through a yet non-documented mechanism (anonymous), although some studies exist (Oehme et al 1989, Musdalslien et al 1998). It is however clear that the amount and type of reduced carbon source (coal or pet coke) used in the production strongly influenced the amount of chlorinated POPs produced (anonymous, Musdalslien et al 1998).

In addition to the anthropogenic sources for the PCDD/Fs, some natural sources are reported to exist. One interesting recent discovery by Hayward et al (1999) was that Ball clays contain relatively high concentrations, e.g. 0.7 and 21 ng/g dw of 2378-TCDD and OCDD respectively, in addition to an unusual composition with levels of PCDDs 100-1000 times higher than the PCDFs. According to Ferrario et al (2000), ball clay is the type of clay used for sanitary ware and pottery production. Ball clays with this PCDD/F pattern have been found in both European and American mines (Hayward et al 1999, Ferrario et al 2000). How these Ball clay PCDD/Fs were formed seems to be unknown. Recently, Müller et al (2002), found a PCDD/Fs pattern similar to that of the Ball clays of Ferrario et al in sediments outside Hong Kong.

Historically, the PCBs and the PCNs were to a large extent produced commercially for a diverse set of applications. These include oils for electrical equipments, softening and flame retarding agents in plastics, sealants and paints (clf. PCBs: Brevik et al 2002a, b; Lang 1992, Tanabe

1988; clf PCNs: Brinkman and Reymer 1976, Yamashita et al 2000). Much of this commercially produced PCBs and PCNs are still in use and generates diffuse emissions to the environment.

In Paper IV we described the emissions of PCDD/Fs from a point source with respect to temporal variability over a historically long time. We investigated the resulting geographical distribution resulting from scenarios of different emission rates through the history. In Paper II and III, we briefly discussed the influence of the formation mechanism for PCDD/Fs, PCNs and other POPs on their geographical and phase distribution in a recipient water.

Once the POPs are formed and emitted, or also if they already reside in the natural environment, they will be subjected to forces that act to transport them throughout the environment, or even destroy them. The understanding of how POPs distribute in the marine environment therefore demand knowledge of these transport and reaction-processes.

Transport and Reaction

When for example river-water polluted with POPs move, the pollutants follow. This is called advective transport, and is perhaps the most obvious transport-mechanism for pollutants. Advective transport of POPs also occurs when e.g. polluted air masses move (wind), or when polluted animals, e.g. a contaminated salmon, swim around (Ewald et al 1998, Wania 1998). However, since the POPs are partitioned between the particles and the aqueous dissolved phase, not all POPs in the water will move in the same direction. Particle-bound pollutants tend to settle through the water column onto the bottom and become incorporated into the sediments (Broman et al 1989, Servos et al 1992b, Gustafsson et al 1998). Since a large fraction of the total inventory of POPs in a water column are bound to particles, it is important to understand the transport dynamics of the particles. Thus, one important aspect is the particle's content of phases capable of sorbing the POPs, such as organic matter and soots.

Much of the organic matter produced in surface waters, and brought into the water by exchange with the surroundings, will eventually start sinking towards the bottom sediments. A multitude of factors influences what will sink and what will not. The gravitational force drags particles denser

than water towards the bottom, but also small- and large-scale turbulence in the water will influence the transport of particles and to some extent bring them closer to the bottom. Since the turbulence in a water column, in turn, is influenced by factors such as winds and stratification of the water (Lund-Hansen et al 1994), these factors also have impact on the sedimentation rate. In the marine and aquatic environment OC containing particles have a continuous spectra of size and density, and as discussed by Gustafsson and Gschwend (1997), the combined effect of such properties most likely determines what type of particles sink (gravitoids), and what will remain floating (colloids). The sedimentation flux of particulate organic matter varies substantially with season in temperate regions such as Scandinavia (e.g. Kankaanpää et al 1997, Heiskanen and Leppänen 1995). This variation is mainly driven by the seasonally variable particle generation flux from carbon fixating pelagic algae.

Some particles that settle at the bottom sediment become resuspended into the water column. Therefore, in the water close to the bottom, a certain fraction of the particles are of resuspended origin. The gross sedimentation refers to the total load of particulate deposition to the sediments. By net sedimentation, the gross sedimentation minus resuspension is meant. This is conceptually illustrated in Figure 1.

In a study by Pejrup et al (1996), during stratified water column conditions, the fraction resuspended matter of the gross sedimentation flux decreases exponentially from the bottom and upwards. The implication of this for POC fluxes was that under stratified conditions essentially no POC was resuspended more than 6 to 10 m above the bottom in a shallow bay such as the one investigated (Åhus Bight, Denmark). One other situation where the water column was mixed was also observed. This was encountered when the water column had vertically homogenous temperature and salinity. Thereby it became unstable, and storm winds could mix the water and cause resuspended matter to be distributed throughout the water column. In Paper IV we modeled how PCDD/Fs were distributed in a Norwegian fjord. The water column of these commonly become stratified for long periods of time. We assumed this stratification influenced how the PCDD/Fs were distributed throughout the fjord area, and accordingly we divided our model into vertically separate layers. This is illustrated in Figure 2, and elaborated below.

In addition to particle driven transport, POPs also move due to Brownian motion, i.e. the movement all matter/molecules undergo when the temperature is above the point of absolute zero (0 K). This gives rise to diffusive transport, which move POPs very slowly. But this can still be of importance, e.g. when pollutants vaporise from a water surface into the air, or across an imagined sediment-water interface (Figure 1). Transport of POPs from sediment to water is of great concern since it is suspected that historically polluted sediments may act as a source to the overlying water column (Larsson 1985, Larsson et al 1990), thereby prolonging the exposure of biota, long after emissions are stopped. The key processes that determine the transport of POPs over the sediment-water interface are (a) the sedimentation and resuspension of particles, (b) the diffusive movement of the POPs and also POPs attached to dissolved organic matter. In systems where oxygen is present, benthic animals such as worms, bivalves, and molluscs increase the mixing of the particles with the associated pollutants. Such bioturbation generally increases the transfer of pollutants over the sediment-water interface (Gilek et al 1997, Schaffner et al 1997). These key processes transporting POPs across the sediment-water interface are illustrated in Figure 1.

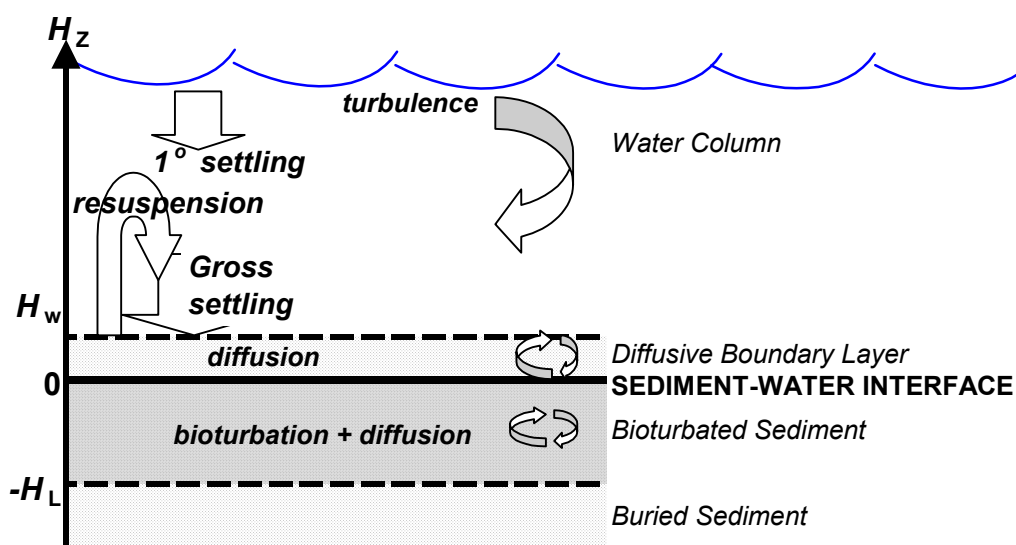


Figure 1. The sediment-water interface and the key processes determining the release flux of POPs from contaminated sediments to overlying waters.

The marine environment also receives POPs through wet- and dry deposition to the water-surface, and by diffusive vapour exchange

between air and water (Wania et al 1998). In Paper I and IV, the influence of all possible transport processes for the marine distribution of POPs are discussed from different perspectives. In Paper IV particular focus is set on the sediment-water transfer. Since the study area has been subjected to orders of magnitude higher emission rates in the past, sediments are likely to act as a source to the water column.

Persistent organic pollutants react only very slow in the natural environment. Reported half life times of the PCDD/Fs are 10 - 300 years in sediments, and 3-40 for PCBs (Sinkkonen and Paasivirta 2000, Mackay et al 1992). Half-life data is sometimes based on observations of declining concentrations in a natural system, e.g. a dated sediment core sample. Such data is subject to changing emission and other variable factors, and hence the decline may sometimes be caused by other processes than actual reaction. On the scale of the total biosphere, other loss mechanisms may be more important than reaction of the POPs, e.g. permanent burial in sediments (Axelman and Broman 2001, Jönsson et al 2002). Crosby (1971) found that negligible degradation of 2378-TCDD occurred in soil and suspensions. Friesen et al (1996) studied the aquatic photochemistry of 2,3,7,8-tetrachlorodibenzofuran and 2,3,4,7,8-pentachlorodibenzofuran in in-situ experiments in humic lake water with the sun as irradiation source. By interpreting mass-spectrometric data they concluded that reductive dechlorination, C-O cleavage, and hydroxylation all play a role in the photolytic transformation of PCDFs and the dibenzofuran nucleus in natural water. Both congeners experienced enhanced degradation rates in the humic lake water, with very low half-lives of 1.2 and 0.19 days, respectively. In Paper IV we initially tested the influence of such extreme half life data on our model-predicted concentrations in the fjord system. This had very little, or even no significant influence. The total reaction rate of a POP in the marine environment is a function of the reaction rate in both the water and the sediment, which may vary depending on what mechanisms causes the reaction. Hence the understanding the spatial distribution is relevant for to estimate this.

In order to quantitatively describe transport and reaction process, Mackay (1979, 1991) introduced a parameter called the *D*-value (in $\text{mol}\cdot\text{Pa}^{-1}\cdot\text{h}^{-1}$). These *D*-values can be derived for any type of process, and the relative magnitude of *D*-values for different processes, gives an immediate insight to which will be of importance. Multiplying the *D*-values with the fugacity of the POP in the phase or compartment gives an expression of

rate (i.e. $Df = R$ in $\text{mol}\cdot\text{h}^{-1}$). This is an interesting expression when formulating a mass balance.

Multimedia Mass Balance Fate Models

In Papers I and IV, we used computerized calculation models in trying to simulate results seen in field data. The models were of a type commonly called multimedia mass balance models (Mackay 1991). Briefly, such models predict POPs concentrations in various compartments (media) of the natural environment. These predictions are calculated from a set of assumptions on the emissions, phase partitioning, transport and reaction, i.e. the four building blocks of information. The assumptions are described mathematically by mass balance equations, which strictly speaking are the model.

Models like these are formulated differently depending on what questions are studied (for an overview see Wania and Mackay 1999). In Paper I we studied the effects of eutrophication on the distribution of PCBs in the coastal environment. Eutrophication has been defined as increased input rate of nutrients to an ecosystem (Nixon 1990). Nixon actually suggested that since it is tricky to know this, the primary productivity of organic matter could be a more useful definition. In an eutrophic system many particle fluxes, e.g. sedimentation and phytoplankton growth are sped up (Wassman and Tamminen 1999), which in turn influence the POPs wash out from the water column (Broman et al 1989) as well as the uptake of the POPs in plankton (Dachs et al 1999, Dachs et al 2000, Swackhamer and Skoglund 1993). Furthermore, since the water column may be expected to become partially depleted of POPs due to sedimentation, the fugacity gradient from air to water could increase, and consequently increase the air to water transport. More possible interaction effects of eutrophication on the behaviour of POPs in the marine environment are outlined by Gunnarsson et al (1995). In order to quantitatively understand the combined effect of such interactions, it is practical to use an automated calculation tool that integrates all effects. The coastal zone model for POPs used in Paper I (CoZMo-POP, Wania et al 2000) and model in Paper IV (DIG, Dioxins In Grenland model) accounts for all processes that we assumed influenced the POPs behaviour in the environment. Most notably, one would expect the processes related to the fluxes of particles to influence the behaviour of the POPs in the coastal environment.

The basic concept of the CoZMo-POP and the DIG models is that they assume that a homogenous distribution of a POP within each separate media is established instantaneously. The model then calculates fugacity and fugacity-capacity for the POP in various medias using the mass-balance equations. The f and Z are finally converted into concentrations, amounts and process fluxes, which together with the residence time of the POP, are the main outputs.

Truly, the outputs from these types of models can seem very ambiguous. Great uncertainties commonly exist already in the "four building blocks" (see above), e.g. for transport dynamics of water, transport dynamics for particulate organic matter, degradation rates and the description of phase partitioning. Still these models are an integrated synthesis of what is believed to be relevant current knowledge for the topic studied. Depending on what questions are studied, different model validations would be appropriate (see Wania and Mackay 1999). As mentioned above, in Paper I we validated the model simulation outputs with observed correlations from a database study. We then focussed on the model outputs on a qualitative trend-scale, i.e. behaviour of the POPs for different scenarios of organic matter-dynamics. In Paper IV we validated the model predicted concentration of PCDD/Fs in water and sediment with observed concentrations from the field. We also validated the model-predicted solid-water phase distribution coefficient with observed data.

Ultimately, models like these, or any type of model predicting the same type of results, i.e. spatial and temporal distribution, and bioavailability of POPs in the environment, seem to be powerful research tools to answer the important questions in the ecotoxicological field of research.

Aims of the Papers

The papers on which this thesis is based, all concern the environmental distribution of POPs. One aim in common is to study if the distribution of the POPs in the marine environment follows the distribution and fluxes of sorbing bulk phases, e.g. organic matter and soots. In addition, the influence of emission scenarios are investigated and discussed.

In Paper I we investigated field data from an extensive database (NOAA, 1998), and sought for trends in how the trophic status affects PCB concentrations in sediments and bivalves. We started by defining a parameter describing the trophic status of the system. We wanted the parameter to be continuous, so that linear regression of PCB concentrations could be undertaken. Since such a parameter was difficult to find, we used the total organic carbon content of sediments in the systems (TOC_{sed}). Our first hypothesis ($^{sedimentOC}H_0$) was that organic matter normalised PCB concentration in sediments was unaffected by the trophic status of the coastal system they were sampled in. Thus, if there was a positive relation, we could expect both PCB and TOC to originate from land run-off. This in turn would result in very varying PCB compositions and concentrations, since hot-spot contamination could be co-varying with the TOC_{sed} parameter. A positive relation would therefore disqualify the TOC_{sed} parameter for any further studies. Our second hypothesis ($^{bivalve}H_0$) was that PCB concentration in bivalves was unaffected by trophic status (TOC_{sed}). This was of great interest, since other studies had revealed a negative relation between dry weight based POPs concentration in plankton and fish, respectively, and the trophic status of the system (Taylor et al 1991). The third hypothesis ($^{BAF \& f_{wc}}H_0$ (denoted H_0 for Qs, Paper I) was that identical PCB profiles in systems of different trophic status should be seen if no interaction between eutrophication and contamination occurred in the environment. In essential that the relative concentrations for PCBs with different physico-chemical properties should be unaffected by the trophic status (e.g. bivalves concentrations of tri- and penta-chlorinated PCBs, Equation 6 and 7, below). Absence of such trophic status-dependent profile differences in bivalves, we argued, could only be established if bioaccumulation factors (BAF , water to bivalve, Equation 6-7 below), and PCB fugacities in the water column (f_{wc}) for different PCB homologues were equally, or not at all affected by trophic status. This difference was calculated for matched pairs of PCB concentrations in the bivalves. The difference we called Q (*quotients*, calculated as a logarithmic difference, Equation 8).

$$^{triCB}C_{bivalve} = ^{triCB}f_{wc} \ ^{triCB}BAF \quad (6)$$

$$^{pentaCB}C_{bivalve} = ^{pentaCB}f_{wc} \ ^{pentaCB}BAF \quad (7)$$

$$Q = \log ^{pentaCB}C_{bivalve} - \log ^{triCB}C_{bivalve} \quad (8)$$

We then investigated if these Q_s had linear regression on the TOC_{sed} variable.

In Paper II we tested the hypothesis that observed elevated partitioning of PCDD/Fs to particles in the marine environment was caused by interaction with highly aromatic soot particles (Gustafsson et al 2001) in addition to the bulk organic matter. We investigated if such an efficient interaction may be similar to what has recently been shown to occur for PAHs (Bucheli and Gustafsson 2001, Accardi-Dey and Gschwend 2001). Our hypothesis was validated by measuring the distribution of PCDD/F, soot carbon, and organic carbon in the marine environment of the Grenlandsfjords, Norway. This was a good system for this investigation, because of its relatively high PCDD/F contamination, allowing easier detection and hence more detailed data.

In Paper III we tested the same hypothesis as in Paper II, but for planar PCBs (pPCBs), PCNs, PAH and a few other POPs. A primary objective of Paper III was to significantly increase the number of available field data on the phase distribution of these POPs, especially for PCNs and pPCBs, against which hypotheses of governing processes could be tested. Another objective was to investigate if the previously observed elevated partitioning to soot containing solids only was valid for PCDD/Fs (Paper II), or whether it occurred also for a broader range of POPs. In addition the influence of formation of the POPs for the phase distribution was discussed.

In Paper IV we further tested the hypothesis that accounting for sorption to soot gave better prediction of environmental distribution of PCDD/Fs in the Grenlandsfjords. This we did by writing and running a multimedia model (Figure 2) with and without soot partition equations for the phase distribution. In addition, in order to examine the influence of historically polluted sediments on the present pollution level in the water column, we simulated the distribution of the PCDD/Fs resulting from different scenarios of historically emission rates. Based on the agreement of simulated versus observed concentrations, we wanted to investigate why the PCDD/Fs were distributed the way they are in the Grenlandsfjords today. The model was written also for the purpose of predicting future concentration and biotic exposure in the fjords.

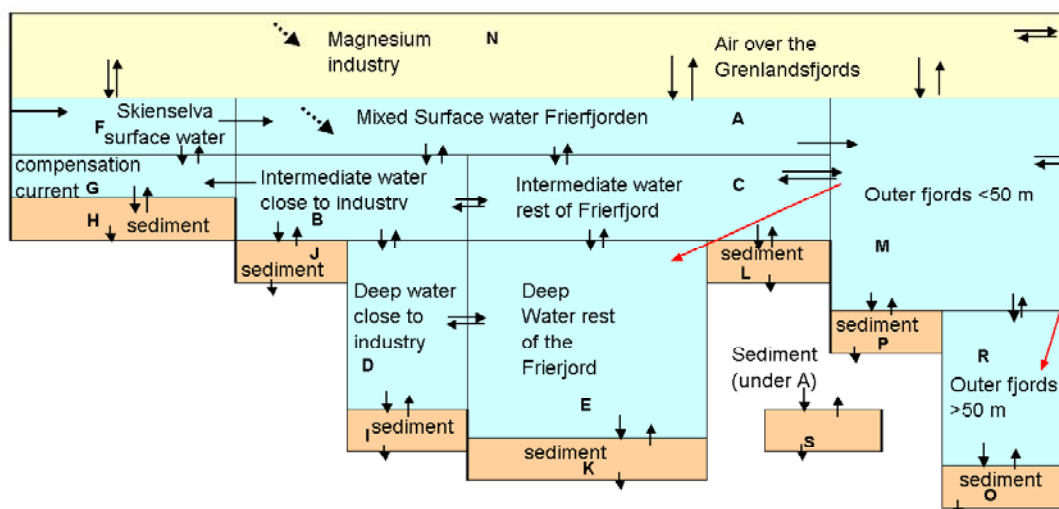


Figure 2. The compartments of the DIG model written for Paper IV.

Discussion

In Paper I we presented indications that the trophic status of a coastal area influences the concentrations and patterns of PCB in sediments and bivalves. Various such interactions were postulated since long (e.g. Gunnarsson et al 1995), but direct observations from the field are more difficult to prove due to the complexity of many processes occurring simultaneously. However, for small isolated Canadian lakes, a negative relation between aquatic organisms' dry weight concentration of POPs and trophic status of the lakes was observed by Taylor et al (1991) who explained this as a biomass dilution effect.

The first hypothesis in Paper I ($^{(\text{sedimentOC})}H_0$: "unaffected OC normalised PCB concentrations in sediments") was found true for most PCB homologue groups and also for one isomer (PCB 28) out of seven tested, since their OC normalised concentration in sediment was not correlated to the TOC concentration of the same sediment. For most PCB isomers and the di- and nona-homologue groups, however, there was a negative correlation. We interpreted this as if there were no co-emission of nutrients and PCB, e.g. from land runoff. We therefore felt we could continue with the other hypotheses. The second hypothesis ($^{(\text{bivalve})}H_0$:

"unaffected bivalves PCB concentration") was found false since in the field database, the dry weight based concentration of PCB (homologue groups) in bivalves had linear positive regression on the TOC_{sed} . We discussed possible mechanisms behind this positive relation, e.g. the food ration dependent apparent BAF for mussels found in studies by Björk and Gilek (1997), and the OM quality dependent BAF for invertebrates found in studies by Gunnarsson et al (1999). Regarding the last hypothesis of Paper I ($^{BAF \& f_{wc}} H_0$: "unaffected PCB profiles"), also this was found false since the difference of log penta homologues minus the logarithm of the lower chlorinated homologues (denoted $Q_{5/4}$, $Q_{5/3}$ and $Q_{5/2}$ respectively) in fact increased with trophic status. This showed that the PCB profiles in bivalves were not similar in systems of different trophic status.

We then questioned if these observations were in accordance with an expected generic behaviour of PCB in coastal marine environments under various trophic conditions. To answer that, we simulated the behaviour of PCB in coastal marine environments of various trophic conditions with the CoZMo-POP model (Wania et al 2000). The model predicted strongly decreased OC normalised sediment concentrations of PCB-118, but much less affected sediment concentrations for PCB-28, on a scale from oligo- to hypertrophic status. This was in qualitative agreement with the negative correlation seen for PCB-118 in the sediments, and the non-correlation for PCB-28. But for the water column the model predicted decreasing f_w of both PCBs on the scale from oligo- to hypertrophic status, which was not in accordance with increasing concentrations in the bivalves with TOC_{sed} . We speculated that this discrepancy originated from the fact that the CoZMo-POP model did not account for organic matter growth dynamics and/or partitioning of POPs to dissolved organic matter in the water column. We suggested that the profile differences could be established by increased sedimentation of organic matter in the water column in more eutrophic systems. This would affect PCB of different hydrophobicity differently. Di-, tri and tetra PCB-homologues have K_{OW} less than $10^{6.48}$ (Hawker & Connell, 1988) and these have by Swackhamer and Skoglund (1993) been shown to maintain equilibrium with pelagic algae under their active growth periods (e.g. spring blooms). They also found that PCB with higher K_{OW} did not reach equilibrium under active growth periods. For those, the field measured log BAF showed no correlation to log K_{OW} . An increased sedimentation flux of OC will undoubtedly increase the sedimentation rate of all PCBs. But PCBs with K_{OW} less than $10^{6.48}$ will thereby increase more than the more hydrophobic. We therefore argued that for a

given increase in sedimentation of organic matter, the depletion of the water-column for the less hydrophobic PCBs would be larger relative to the more hydrophobic. This would contribute to our finding, that in the bivalves $Q_{5/2}$, $Q_{5/3}$ and $Q_{5/4}$ correlated with the trophic status. It would also explain why the bivalves $Q_{5/6}$, $Q_{5/7}$, $Q_{5/8}$ and $Q_{5/9}$ versus trophic status were not correlated. However, today we question our explanation in Paper I, since the non-linearity of the apparent $BAF - K_{OW}$ relation for phytoplankton, has been partially explained as an artefact (Stange and Swackhamer, 1994, Koelmans et al 1999). They suggest this artefact is caused by an overestimation of the dissolved phase in the BAF estimate, resulting in lower BAFs. The overestimation was attributed to binding to colloids, which may not have been physically separated from the apparently dissolved phase in the experiments by Swackhamer and Skoglund (1993). We assumed this artefact influenced our observation also in our water column field studies in Paper II and III.

In Paper II we presented indications that soot carbon influenced the distribution of PCDD/Fs in a marine environment. For suspended particles in the water column, the observed organic matter normalised partition coefficients $(K_{OC})_{obs}$, were significantly higher than predicted by the organic matter partitioning model. The $(K_{OC})_{obs}$ also showed a larger variation than expected if organic matter was the key sorbent in the particles. Furthermore we found that the geographical distribution of PCDD/Fs in sediments was generally better explained by the sediment content of soot than of organic matter. Finally we found that organic matter normalised concentration of PCDD/F isomers in particles increased by a factor 100 in a gradient from the surface water down to the sediments. This increase was larger than what could be expected from increase in PCDD/F fugacity estimated from measurements of the dissolved phase and temperature in the same vertical transect. With data on the fraction of soot and organic matter in the suspended particles, we also found a positive correlation of the SC:POC quotient to the factor underpredicted $(K_{OC})_{obs}$ as was expected from the soot inclusive partition model (Equation (3) section above). These four findings in Paper II indicated that the OMP model did not accurately describe the solid-water phase partition, and that organic matter was a less appropriate descriptor than soot for explaining the geographical distribution in the Grenlandsfjords.

In Paper III we found further evidence for that soots influence the distribution of POPs in the marine environment. Observed particle

associations of polychlorinated naphthalenes (PCNs) and three planar polychlorinated biphenyls (pPCBs) were found to poorly obey expectations from an organic-matter partitioning model, as we found for the PCDD/Fs in Paper II. We argued that the field observations were consistent with a soot carbon influenced distribution, since an unexpectedly high portion of the pollutants was particle associated. The factor under-predicted particle association, expressed as the ratio of observed over organic matter model predicted, had positive linear regression to the SC:POC (soot carbon: particulate organic carbon) ratio of the suspended particles. We also found that this factor under-prediction had linear regression to theoretical estimates of the soot-water distribution coefficient for the PCNs. In addition, the geographical distribution of surface sediments concentrations of PCNs and polycyclic aromatic hydrocarbons (PAH) were found to follow the sediments' content of soot stronger than the content of organic matter, a result we also found for the PCDD/Fs in Paper II. Regarding other persistent organic pollutants (POPs), i.e. octachlorostyrene, organochlorine pesticides, we saw no clear difference in the strength of correlations of the sedimentary concentrations of POPs to the sediments' soot or the organic matter. Mechanism possible of generating these type of observations were discussed, e.g. adsorption to soots and slow desorption of initially strongly particle bound POPs.

In Paper IV the formulation of a predictive fate model for polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) in the marine environment of the Norwegian Grenlandsfjords was described. Our model (DIG, Dioxins In Grenland), predicted concentrations, and the geographical distribution of PCDD/Fs, based on input information on emission and local hydrological and geochemical settings. By accounting for the combined sorptive capacity of particulate organic matter (POM), soot carbon (SC), and dissolved organic matter (DOM), improvements of both the phase- and the geographical distribution of the pollutants were achieved, relative to when soot carbon was not included. This was evaluated by comparing model simulations with and without soot partitioning. The soot inclusive calculations gave up to a factor 2000 better agreement for the solid - water phase distribution coefficients, relative to the organic matter model predictions. For the predicted concentrations of PCDD/Fs in the marine particles, factors of agreement between modelled and observed concentrations in the particles were best with the soot including model for the 2378-TCDD congener, but not for the OCDD and OCDF congeners. In the field study of Paper II, we

observed a vertical increase in the water column particulates PCDD/F concentrations. This trend was remodelled with the DIG-model in Paper IV, but only when account was taken to historically high emissions. With simulation runs using constant emissions at rates representative for the last ten years, present concentrations could not be remodelled for the sediments. Only by including historically high emission rates, the present pollution levels in this fjord system could be simulated with reasonable agreement to observed data. Generally our DIG model predicted the solids concentrations within less than a factor of ten throughout the Grenlandsfjords environment. It captured differences between pg/m^3 for the TCDD and ng/m^3 for the OCDD and OCDF. Finally, we concluded that much relevant information on the conditions affecting the fate of PCDD/Fs in the Grenlandsfjords are well known compared to other areas with respect to emissions, geochemical and hydrological settings. In spite of this, the simulations gave relatively high uncertainties and not always good agreement with observed levels and trends. Since this uncertainty must influence the risk associated with the pollution situation, this therefore indicated that much remain to be done within the research field of ecotoxicology.

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Note 1. Everywhere in the biosphere, organic matter is formed when living organisms of any kind grow. Many elements and compounds are incorporated into and synthesized within the organism during its growth, and those compounds containing reduced carbon are traditionally called organic (Solomons 1988). The size of organic matter entities in the marine environment thus spans from nano meters for single bio molecules, to many meters for e.g. blue whales. The elemental composition of OM can be measured chemically, and the three dominating constituents are always organic carbon (OC), organic nitrogen (ON), and phosphorous (P).

Note 2. Lipids are here defined as by Solomons (1988) i.e. components in plant or animal tissues extractable with nonpolar solvents. This definition is not based on similarities in chemical structures, and accordingly lipids includes a variety of compound groups such as fatty acids, neutral fats, phospholipids, waxes, terpenes, steroids etc.

Note 3. Partial molar free energy $((\delta g/\delta n)_{T,P})$, in units of J/mol), refers to the change of the phase's free energy as caused by changes in the number of moles of the compound only. Any additional changes due to changes of temperature and pressure is not included, hence the indices T and P.

Note 4. These thermodynamic entities are better described in text books such as Atkins (1990) and Warn (1969). Applications to environmental studies is discussed by e.g. Mackay (1991), Schwarzenbach et al (1993) and Sangster (1997).

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