Bioavailability assessment
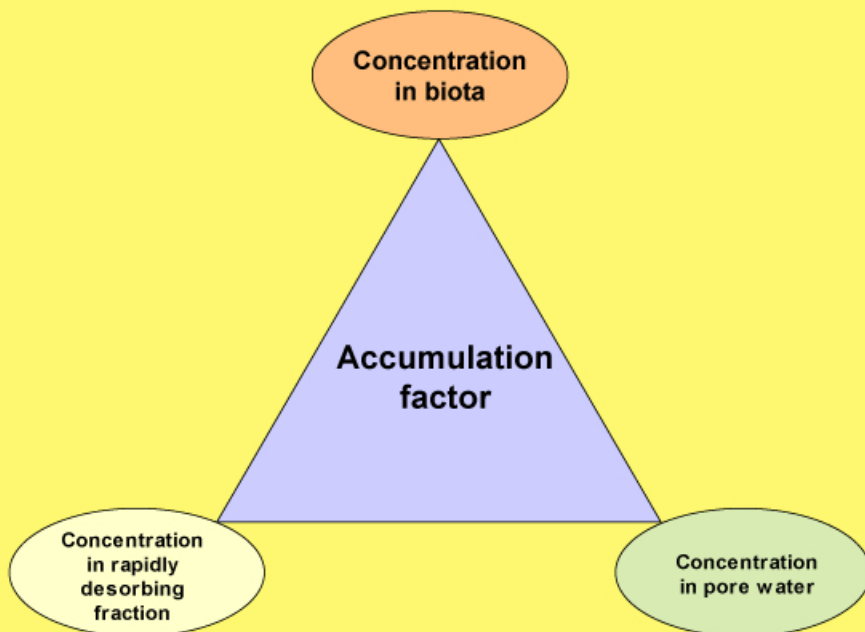# of sediment-associated organic compounds
through desorption and pore-water concentration

by
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Bioavailability assessment of sediment-associated organic compounds through desorption and pore-water concentration

ACADEMIC DISSERTATION

To be presented, with the permission of the Faculty of Biosciences of the University of Joensuu, for public criticism in the Auditorium C2 of the University, Yliopistokatu 4, on 15th August, 2008, at 12 noon

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Determining the bioavailability of sediment-associated compounds is an essential but difficult part of the modern environmental risk assessment process. The Equilibrium partitioning theory (EqP) is commonly used to describe the bioavailability of sediment-associated chemicals. EqP assumes the distribution of the hydrophobic organic chemicals to be in thermodynamic equilibrium between the lipids of the organisms (C_l), the pore water and the organic carbon in the sediment ($C_{s,OC}$). However, recent studies have shown that the total concentration in sediment organic carbon (OC) is not the fraction that causes the actual risk to the environment.

The general aim of this thesis was to use different approaches to estimate the bioavailability of sediment-associated hydrophobic contaminants. Bioaccumulation was measured by exposing oligochaetes (*Lumbriculus variegatus*) to sediment-spiked model compounds. The desorption kinetics of these chemicals were measured in sediment-water suspensions using Tenax® extraction, and freely dissolved pore water concentrations (C_w) were measured using the polyoxymethylene (POM) solid phase extraction method. The major hypothesis was that the rapidly desorbing fraction (F_r) of chemicals or chemical concentration in C_w can give a more precise estimate of the bioavailable fraction than can total chemical concentration in the sediment OC. Further, F_r or C_w concentrations were used alternatively to estimate biota-sediment accumulation factors. The second major hypothesis was that organisms' behaviour (feeding rate or sediment ingestion) can modify the chemical exposure to such an extent that the steady-state tissue residues are not accurately estimated by the traditional EqP approach nor by the F_r or C_w-revised models.

Numerous environmental factors (temperature, chemical contact time, chemicals present in the sediment), chemical and sediment properties (amount and quality of organic carbon) modify bioavailability of model compounds, but this change in bioavailability is partially based on the changes in desorbing fractions. However, bioavailable fraction can not be solely interpreted by reference to the size of the desorbing fraction. Further, F_r did not totally describe the bioavailable fraction of "superlipophilic" polychlorinated dibenzo(*p*)dioxins and -furans, polychlorinated diphenyl ethers in field-contaminated sediments. In addition, the organisms' sediment ingestion may modify the bioavailable fraction in a way that is not taken into account in the traditional EqP approach or in desorption and C_w-revised models. Regardless of this, this study strongly supports the equilibrium theory, if sequestration is taken account. As C_w is affected by sequestration, the bioaccumulation of model compounds can successfully be described as a partitioning process between C_w and organisms. Further, the bioavailability estimate of $BSAF_{POM}$ based on C_w was successfully used as surrogates for actual bioavailability estimates (BSAF). The results indicate that C_w can give a better estimation for the bioavailable fraction than do total concentration and thus could improve the realism of site-specific ecological risk assessment.

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ABBREVIATIONS

BAF	bioaccumulation factor
BC	black carbon
BCF	bioconcentration factor
BDE-47	tetrabrominated diphenyl ether
BDE-99	pentabrominated diphenyl ether
BSAF	biota-sediment accumulation factor
$BSAF_{Fr}$	biota-sediment accumulation factor estimate revised with the rapidly desorbing fraction
$BSAF_{POM}$	biota-sediment accumulation factor estimate based on the freely dissolved aqueous concentration in pore water
$BSAF_{Tenax}$	biota-sediment accumulation factor estimate based on the desorption modeling
CB	chlorobenzene
CP	chlorophenol
CV	coefficient variation
C_w	concentration in pore water
$C_{s,OC}$	chemical concentration in organic carbon
dw	dry weight
ESB	equilibrium partitioning benchmark
EqP	equilibrium partitioning theory
F_r	rapidly desorbing fraction
F_{sl}	slowly desorbing fraction
F_{vs}	very slowly desorbing fraction
HOC	hydrophobic organic chemical
K_{Lipid}	lipid-water partition coefficient
K_{OC}	organic carbon-water partitioning coefficient
K_{OW}	octanol-water partitioning coefficient
K_p	POM-water partitioning coefficient
k_r	rapidly desorbing rate constant (h^{-1})
k_s	slowly desorbing rate constant (h^{-1})
k_{vs}	very slowly desorbing rate constant (h^{-1})
LSC	liquid scintillation counter
Lw	lipid weight
MW	molecular weight
OC	organic carbon
PAH	polyaromatic hydrocarbon
PCB	polychlorinated biphenyl
PCDD/Fs	polychlorinated dibenzo-*p*-dioxins and furans
PCDEs	polychlorinateddiphenyl ethers
POM	polyoxymethylene
SPME	solid phase microextraction
TCDD	tetrachlorinated dibenzo-*p*-dioxin
ww	wet weight

CONTENTS

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following articles or manuscripts, which are referred in the text by the Roman numerals (I-IV). Some unpublished results are also presented.

I   Sormunen, A.J., Leppänen, M.T. and Kukkonen, J.V.K.: Examining the role of temperature and sediment – chemical contact time on desorption and bioavailability of sediment -associated tetrabromo diphenylether and benzo(*a*)pyrene. Manuscript submitted to *Ecotoxicology and Environmental Safety*.

II   Sormunen, A.J., Leppänen, M.T. and Kukkonen, J.V.K.: Desorption and bioavailability of spiked pentabromo diphenyl ether and tetrachlorodibenzo-*p*-dioxin in contaminated sediments. Manuscript submitted to *Archives of Environmental Contamination and Toxicology*.

III   Sormunen, A.J., Leppänen, M.T. and Kukkonen, J.V.K. 2008: Influence of sediment ingestion and exposure concentration on the bioavailable fraction of sediment-associated tetrachlorobiphenyl in Oligochaetes. *Environmental Toxicology and Chemistry*, 27: 854-873.

IV   Sormunen, A.J., Koistinen, J., Leppänen, M.T. and Kukkonen, J.V.K. 2008: Desorption of sediment-associated polychlorinated dibenzo-*p*-dioxins, dibenzofurans, diphenylethers and hydroxydiphenyl ethers from contaminated sediment. *Chemosphere* 72: 1-7

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I participated in the design of all the studies and was mainly responsible for the laboratory work, data collection, the data analysis and preparation of the manuscripts. The processing of the articles was carried out in collaboration with co-authors.

1. INTRODUCTION

During the last hundred years, human society has produced and released numerous synthetic chemicals into our environment. These chemicals have been introduced into the environment accidentally, due to the use of chemicals, or as a component of various materials. There are at present over 100,000 synthetic chemicals in daily use, and the number is increasing continuously (Schwarzenbach et. al. 2003). As a final point, high concentrations of these hydrophobic chemicals can be found in aquatic environments, especially in the sediments. While tightened regulations have reduced the amount of compounds released into the environment, past discharges have resulted in substantial concentrations of such chemicals remaining on lake and river bottoms with concentrations potentially several orders of magnitude higher than in overlying waters (Ingersoll, 1995). Although some fractions of these chemicals are tightly sorbed to sediment, they may still be available for biota (Ingersoll, 1995). For example, organisms living in contaminated sediment may accumulate high body burdens by ingesting sediment particles (Kukkonen and Landrum, 1995), and after consumption of these organisms by predators, transfer chemicals to upper level of the food chain. The sediment that was once thought of as a sink for the disposal of unwanted organic chemicals is now identified as a source of toxic compounds (Gess and Pavlosthahis, 1997).

Sediment is generally a mixture of materials and can be relatively heterogeneous in terms of its physical, chemical, and biological characteristics. Sediments are composed of four main components. The largest volume is occupied by pore water, which fills the spaces between sediment particles and usually accounts for over 50% of surface sediments. The inorganic phase includes the rock and shell fragments and mineral grains that have resulted from the natural erosion of terrestrial material. While organic matter occupies a small volume,

it represents an important component as a result of its influence on the sorption and bioavailability of many organic contaminants. Finally, anthropogenically derived materials include contaminated materials (Power and Chapman, 1992). As a result of this process, some sediments accumulate sufficient concentrations of harmful materials that they are said to be contaminated sediments, which are defined as sediment-containing chemical substances at concentrations that pose a known or suspected threat to environmental or human health (Ingersoll, 1995).

Ecological risk assessment is used to determine which sediments meet the above criterion. This process includes hazard identification, characterisation of exposure and effects, and risk characterisation and management (Figure 1). Several methods or techniques have been introduced and used for sediment assessment. Available methods include direct measurement of contaminants, toxicity tests, various biomarkers, measurement of tissue residues, the microcosm test, in situ toxicity testing etc (Adams et al., 2005). Currently the challenging part of this process is the assessment of chemicals' bioaccumulation potential (exposure). Most approaches to risk estimation have utilised total contaminant concentrations in sediments. However, the total concentration does not provide a representative estimate for the actual risk to the environment (Cornelissen et al., 2001). A more accurate approach is to use the chemical concentration in sediments that are readily available for transport and uptake by organisms (Alexander, 2000). Yet, the major challenge has been how to accurately predict the bioaccumulation of sediment-associated chemicals in sediment-living organisms. So far, in most European countries, bioavailability assessment is not included in their risk assessment process for contaminated sediment (Den Besten et al., 2003). In Finland, bioavailability estimation has been incorporated into risk assessment for the River Kymijoki sediments (Verta et al., 1999) and tributyltin-contaminated sediments (Ympäristöministeriön työryhmä 2006; Vahanne et al., 2007).

ECOLOGICAL RISK ASSESSMENT
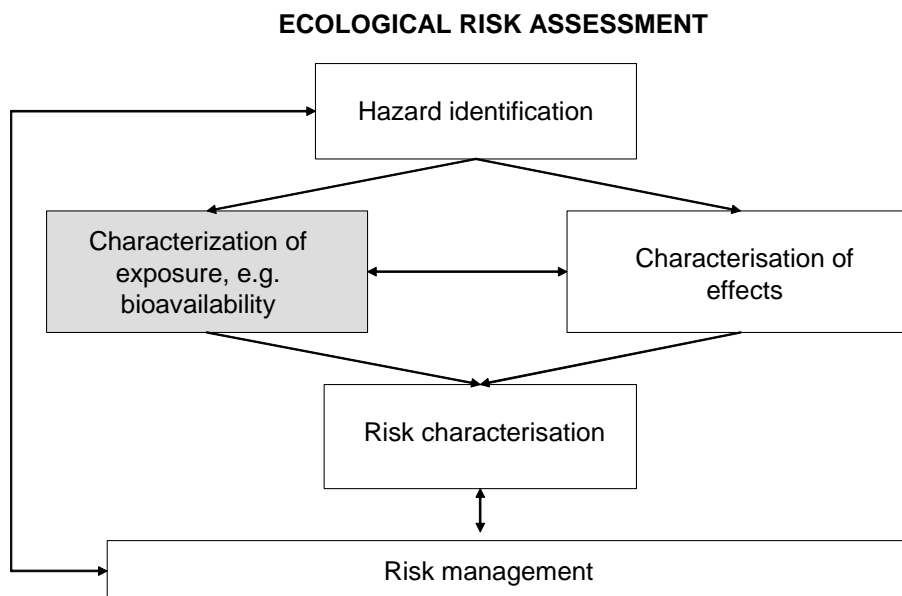
Figure 1. Ecological risk assessment process (adapted and modified from Suter, 1997).

1.1. Equilibrium partitioning approach and desorption-revised theory

During the past few decades, significant research efforts have been focused on improving the accuracy of bioavailability estimates. The most frequently used theory for predicting the bioavailability of organic chemicals to biota is the Equilibrium Partitioning theory (EqP theory) (Shea, 1988; Di Toro et al., 1991). The EqP theory assumes distributions of hydrophobic organic chemicals to be in thermodynamic equilibrium between the lipids of the organisms, the pore water and the organic carbon (OC) of the sediment, and that the partitioning via passive diffusion between the lipids and OC results in a more or less constant value. Theoretically, this value is independent of sediment type, species, temperature, exposure concentration or hydrophobicity of the compounds. When the partition coefficient between sediment and biota is known, the total concentration in sediments (nmol g^{-1} OC) can be used to provide an estimate of the concentration in exposed organisms (nmol g^{-1} lip). The use of EqP has reduced the variation in biota-sediment accumulation factors (BSAFs), but significant unexplained variation still exists (Tracey and Hansen, 1996; Wong et al., 2001).

Some variation in BSAF values may derive from sediment properties, e.g. the heterogeneous nature of OC (Bucheli and Gustafsson, 2000; Rockne et al., 2002). Sediment organic matter is generally grouped into an amorphous or expanded "soft rubbery" carbon phase (humic acid, fulvic acid, humin, polysaccarides, lipids, proteins, lignin) and a condensed or "hard glassy" carbon phase (soot, char, kerogen) (Weber and Huang, 1996; Luthy et al., 1997; Cuypers et al., 2002; Jonker et al., 2003; Ehlers and Loibner, 2006). Thus organic matter typically contains several

domains or constituents, each with different sorption activities (Cuypers et al., 2002).

The bioavailability of sediment-associated contaminants should therefore relate more closely to the fraction of the total chemicals in the sediment that can readily be released to the water phase, rather than to the total concentration in the organic carbon. Usually, this can be described by two parameters: by directly measuring the freely dissolved chemical concentration in pore-water (C_w) (Jonker and Koelmans, 2001) or by estimating the concentration in the sediment that is available for release to the water phase (e.g. rapidly desorbing fraction) (Cornelissen et al., 2001; ten Hulscher et al., 2003). Several sampling methods have been developed to measure these releasable concentrations. For example, a reference phase, such as polyoxymethylene (POM), polydimethylsiloxane (PDMS), low density polyethylene (LDPE) or TENAX can be introduced into a water/sediment suspension and the solution shaken for an extended period of time, a process that allows the reference phase to accumulate the released contaminants (Mayer et al., 2000; Jonker and Koelmans, 2001; Cornelissen et al., 2001; ten Hulscher et al., 2003; Booij et al., 2003; Rusina et al., 2007). From the measured uptake by the reference phase, either the C_w after equilibrium is estimated (e.g. POM extraction), or some measure of the readily desorbed fraction is obtained (e.g. TENAX extraction). Both of those can be used to estimate the bioavailable fraction of sediment-associated contaminants. For example, after measuring the freely dissolved pore water concentration of hydrophobic organic chemicals, the body residues of sediment dwelling organisms can be estimated on the basis of C_w and bioconcentration factors (BCF) (Kraaij et al., 2003). Alternatively, several investigators have recently attempted to explain the bioavailability of chemicals using their desorption behaviours (e.g. Kraaij et al., 2001; Leppänen et al., 2003; ten Hulscher et al., 2003; You et al., 2006). Often the desorption of contaminants from sediment has been seen as a diffusion limited process,

occurring either through the organic matter matrix or through and along the walls of narrow intraparticle pores (Figure 3) (Carroll et al., 1994; Pignatello and Xing, 1996). Probably organic matter diffusion or intraparticle diffusion operates simultaneously, but the relative importance of each depends on the sediment properties (Pignatello and Xing, 1996). However, desorption of contaminants from the sediments can be divided into two or three distinct fractions (rapid, slowly and very slowly desorbing fractions) with different desorption rate constants (e.g. ten Hulscher et al., 1999; Leppänen et al., 2003). Recent studies have shown a relationship between the rapidly desorbing fraction (F_r) and the BSAFs, a finding which has led several researchers to agree that F_r offers a more accurate estimate of the bioavailable fraction than the total concentration in sediment or in sediment organic carbon (e.g Cornelissen et al., 2001; Kraaij et al., 2002a; ten Hulscher et al., 2003; You et al., 2006). The desorption refined EqP-theory appears to successfully estimate bioaccumulation potentials (Kraaij et al., 2002a; Kraaij et al., 2003) and also helps to understand the mechanisms involved in the bioavailability of sorbed contaminants.

However, animal behaviour or feeding may add an additional factor that may significantly influence the bioavailable pool and cannot be explained by equilibrium partitioning, desorption, pore water concentration or sediment properties. For example, the gut fluids may enhance the dissolved chemical concentration in the gut (Voparil et al., 2004; Weston and Mayer, 1998), which can increase the uptake rate and may even lead to biomagnification (Gobas et al., 1993). Further, the hydrophobicity of a chemical may affect the uptake route of contaminants. Pore water is an important accumulation route for compounds with an octanol-water partitioning coefficient (log K_{OW}) < 5 (Thomann et al., 1992), while for more hydrophobic compounds the importance of ingested material increases (Leppänen and Kukkonen, 1998b).

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1.2. Objectives and hypotheses

This thesis describes the POM and Tenax extraction methods for the estimation of releasable concentrations of hydrophobic organic contaminants and discusses their validity for estimating the bioavailability of sediment-associated compounds in different circumstances (Table 1). In order to achieve the aim, studies with laboratory-spiked sediments were used to elucidate the mechanisms behind the bioavailability process. Further, the desorption extraction method was also applied to field-contaminated sediments, and the resulting data were considered in combination with the earlier observed bioavailability estimates. The overall goal is to attain a more precise bioavailability estimate of sediment-associated chemicals and increase the accuracy of the risk assessment process.

1. The main hypothesis was that F_r and C_w can provide more precise estimates for the bioavailable fraction than total chemical concentrations in the sediment organic carbon. More specifically, it was hypothesised that temperature, contact time between chemicals and sediment, sediment properties, chemicals present in sediments, and chemical concentrations modify desorption, but the change in bioavailability is actually based on changes in the desorbing fractions (articles I, II, III). These data were used to determine the accuracy with which the concentration in the sediment that is available for release to the water phase (F_r) or C_w can be used to predict the bioaccumulation factors of sediment-associated hydrophobic compounds.

2. The second major hypothesis was that organisms' feeding behaviour (measured as feeding rates or sediment ingestion) can modify the chemical exposure to such an extent that the steady-state tissue residues are not accurately estimated by the traditional EqP approach or by F_r or C_w-revised models (articles I, II, III).

3. Finally, based on the desorption data, the bioaccumulation potential of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), diphenylethers (PCDEs) in contaminated field sediments was evaluated, and desorption kinetics were applied to estimate the bioavailability of these compounds in contaminated river sediment (article IV).

Table 1. The main themes of the study.

	BaP	PBDEs	PCB-77	PCDD/F/Es
Factors that modify the desorption and bioavailability of sediment associated chemicals				
Aging	I	I		
Temperature	I	I		
Concentration			III	
Sediment properties		II	III	II
Feeding behaviour of worms	I	I, II	III	
Desorption and bioavailability	I	I, II	III	II, IV
The freely dissolved pore water concentration and bioavailability			III	
Desorption and bioavailability in field-contaminated sediments				IV

2. MATERIALS AND METHODS

2.1. *Lumbriculus variegatus* as a test organism

Sediment provides a habitat for many benthic organisms, such as oligochaete species. Oligochaetes occur in marine, estuarine, freshwater and terrestrial environments (Martin et al., 2008). About two-third of the almost 1700 valid aquatic oligochaetes described inhabit freshwaters (Martin et al., 2008). The freshwater oligochaeta, *Lumbriculus variegatus,* occurs in shallow oxygen rich oligotrophic or mesotrophic waters throughout the Northern Hemisphere (Dermott and Munawar, 1992) and can also be found in shallow waters in Southern and Central Finland (Laakso, 1967). These organisms are quite tolerant of changes in temperature, dissolved oxygen, and pH (Phipps et al., 1993). Oligochaetes feed on organic material in the aerobic subsurface sediment and egest onto the sediment surface, hence recycling deposited material (Phipps et al., 1993; Leppänen and Kukkonen, 1998b). Aquatic oligochaetes also perform important ecological functions; they impact on sediment structure and water-sediment exchanges and are important in aquatic food chains (Martin et al., 2008).
Lumbriculus variegatus is the common organism for testing bioaccumulation in freshwater systems (Leppänen, 1999; ASTM, 2004). It has been used in toxicity testing for over 20 years (Bayley and Liu, 1980). *L. variegatus* meets most of the criteria for an ideal test organism. They are easy to culture and handle, have adequate tissue mass for chemical analyses, tolerate a wide range of sediment physiological characteristics, have low sensitivity to contaminants associated with sediments, are amenable to long-term exposures without feeding, attain steady state rapidly, are in direct contact with sediment, are ecologically important, and have a broad geographical distribution (Phipps et al., 1993; Brunson et al., 1998; ASTM, 2004). Standard guides have been published for conducting bioaccumulation studies with *L. variegatus* (ASTM, 2004).

2.2. Model compounds

Radiolabelled (^{14}C or ^{3}H) chemicals were used as model compounds (Figure 2, Table 3). If very high concentrations were needed, both labelled and non-labelled were used in a known ratio (article III). The overall, concentrations used in experiments were intended to resemble those found in field-collected samples (Table 2). The studied chemicals are members of a broader chemical class termed polycyclic organic compounds. All the chemicals are bioavailable for aquatic organisms and thus can lead to biomagnification in food chains. Further, occurrence of these persistent organic compounds is not limited to industrialised areas, but rather have been found throughout a wide geographical area and are present in a large number of terrestrial and aquatic species (de Wit, 2002; Ueno et al., 2005).

Table 2. Exposure concentration for model compounds used in laboratory tests and concentrations found in field-collected sediment samples. OC denotes organic carbon.

| | Exposure concentration in laboratory | | | Concentration found in field-collected samples | |
	$nmol\ g^{-1}$ OC	$ng\ g^{-1}$ dry weight		$ng\ g^{-1}$ dry weight	Reference
BaP	6.5-8.5	12-16	BaP	314-1355	Harkey et al., 1995
BDE-47	33-36	32-35	BDE-47	368	Allchin et al., 1999
BDE-99	0.9-1.3	37-45	BDE-99	898	Allchin et al., 1999
TCDD	3.8-6.9	90-114	PCDD/Fs	193000	Malve et al., 2003
PCB-77	12-30000	70-220 000	PCBs	33000	Sivey & Lee 2007

2.1. Polyaromatic hydrocarbons

The polycyclic aromatic hydrocarbons (PAHs; e.g. benzo(*a*)pyrene) represent a widespread class of environmental pollutants. Possible sources of PAHs are petroleum production, forest fires or combustion of organic material (Baumard et al., 1998). The general toxicity of PAHs varies substantially and depends on the specific compound, the organisms exposed and the environmental conditions. Many organisms can metabolise and detoxify certain PAHs, but some of these biotransformed compounds also pose a carcinogenic or mutagenic risk (Rand et al., 1995). The sediment-associated PAHs can remain unchanged for years, thus constituting a potential long-term source for ecological uptake (Landrum, 1989).

2.2. Polybrominated diphenylethers

Polybrominated diphenylethers (PBDEs; e.g. 2,2',4,4'-BDE-47 = BDE-47 or 2,2',4,4',5-PBDE = BDE-99) are used as flame retardants in plastics, textiles and electronic equipment. PBDEs are very similar in structure to polychlorinated biphenyls (PCBs). PBDEs potentially involve 209 different congeners, varying in both number and position of bromination (Birnbaum and Staskal, 2004). Bioaccumulation of PBDEs has been reported across a range of organisms and geographic locations (e.g. Hale et al., 2001; Mancester-Neesvig et al., 2001; Ikonomou M.G. et al., 2002b). For example, PBDE concentrations in Arctic ring seals have continued to increase exponentially in a similar proportion to worldwide commercial PBDE production (Ikonomou M.G. et al., 2002a). Concentrations up to 47 000 ng g^{-1} lipid have been reported in freshwater fish (Hale et al., 2001). PBDEs have been found in human adipose tissue (Fernandez et al., 2007) and milk (Ohta et al., 2002). Animal studies have shown that PBDEs can cause thyroid hormone disruptions, neurobehavioural deficits, and possibly cancer (Birnbaum and Staskal, 2004; McDonald, 2002). However, the toxicity of PBDEs is still not well understood (Zhao et al., 2008). The use of flame retardants has increased over the last 30 years (Birnbaum and Staskal, 2004), but nowadays tightening legislation has set requirements for the marketing of products containing these substances. For example, the European Union has banned the use of BDE-99 since 2004 (European Union Directive 2003/11).

2.3. Polychlorinated hydrocarbons

Polychlorinated biphenyls (PCBs; e.g. 3,3'4,4'-tetrachlorobiphenyl = PCB-77) belong to the group of halogenated compounds that have a high toxicity and bioaccumulation potential. The amount of PCB produced worldwide is estimated at about 1.3 million tonnes (Breivik et al., 2007). Polychlorinated biphenyls and related compounds enter the environment during the production of chemicals, as byproducts in industrial manufacturing processes, and by combustion (Kjeller and Rappe, 1995; Braune and Simon, 2003). PCBs have been detected in a range of environmental systems: for example, concentrations of PCB-77 up to 400 pg g^{-1} lipids have been found in the muscle of skipjack tuna collected form Asian offshore (Ueno et al., 2005) and sediment concentrations of total PCBs up to 33 μg g^{-1} dw in heavily contaminated Lake Hartwell, South Carolina (USA) (Sivey and Lee, 2007). PCBs and related compounds can be found in the human tissues as well (Hays and Aylward, 2003). A variety of adverse effects, including neurotoxicity, carcinogenicity and suppression of the immune system have been reported to result from elevated levels of PCBs in organisms (Chu et al., 2001; Knerr and Schrenk, 2006). As a result of the risks these chemicals pose, international agreements now prohibit or restrict production of these compounds, and emission rates have been reduced.

Another example of the group of chlorinated compounds is polychlorinated dioxins (PCDDs) (e.g. 2,3,7,8-TCDD). PCDDs enter the environment during the production of chemicals and by combustion (Kjeller and Rappe, 1995; Braune and Simon, 2003), and

they have a global distribution in the environment (e.g. Kjeller and Rappe, 1995; Braune and Simon, 2003; Ueno et al., 2005; Wan et al., 2005). Human industrial activity produced a sharp rise in releases of PCDDs and related compounds during the middle decades of the 20th century (Hays and Aylward, 2003). For example, concentrations up to 230 pg/g for 2,3,7,8-TCDD have been found in herring gulls lipids (Kannan et al., 2001).

Table 3. Physico-chemical properties of model compounds. Log K_{OW} denotes the octanol-water partitioning coefficient.

Chemical	Abbreviation	Molecular formula	Molecular weight[a] (g/mole)	Log K_{ow}	Molar volume[a] (cm^3/mol)	Aqueous solubility[a] (mg/L)
Benzo(a)pyrene	B*a*P	$C_{20}H_{12}$	252	6.2 (5.8-7.9[a])	262.9	$4.0*10^{-5}$ - $6.0*10^{-3}$
Tetrabromodiphenyl ether	2,2',4,4'-BDE (BDE-47)	$C_{12}H_6Br_{4O}$	485	6.8 (5.8-7.0[b])	288.8	$1.5*10^{-3}$ - $1.1*10^{-2}$
Pentabromodiphenyl ether	2,2'4,4',5-BDE (BDE-99)	$C_{12}H_5Br_{5O}$	564	7.3 (6.4-8.4[b])	312.1	$9.0*10^{-7}$ - $2.4*10^{-3}$
Tetrachlorobiphenyl	3,3',4,4'-CBP (PCB-77)	$C_{12}H_6Cl_4$	295	6.4 (6.0-6.8[a])	268.2	$5.5*10^{-4}$ - 0.175
Tetrachlorodibenzo(*p*)dioxin	2,3,4,7-TCDD	$C_{12}H_4Cl_4O_2$	322	6.96[c] (5.3-8.9[a])	260.6	$7.9*10^{-6}$ - $1.6*10^{-2}$

[a]MacKay et al. 2006
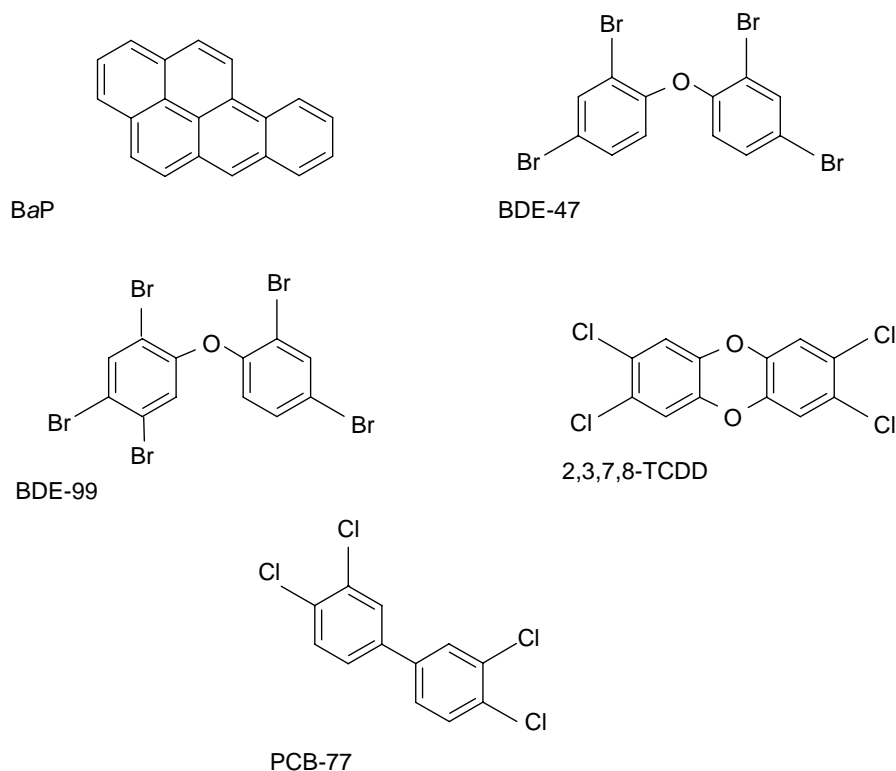[b]Braekevelt et al. 2003
[c]Paasivirta et al. 1999

Figure 2. The chemical structure of model compounds.

2.3. Sediments

2.3.1. Sampling sites of test sediments.

Two sediments samples (S1, S2) from a contaminated area of the River Kymijoki are known to have shown elevated concentrations of PCDDs, PCDFs and PCDEs and chlorophenols (CPs) (Koistinen et al., 1995; Verta et al., 1999; Lyytikäinen et al., 2003b) as a result of pulp mill and wood industry effluents. Concentrations up to 193 000 ng g^{-1} have been reported for PCDD/Fs in the dry sediment taken from the most contaminated area (Malve et al., 2003). While current loading has been reduced considerably, the surface sediments still contain 24-66% of the maximum concentrations in the 1960-70s (Isosaari et al., 2002). Lake Ketelmeer (S3) is also highly polluted with elevated concentrations of polycyclic aromatic hydrocarbons (PAHs) (25 μg g^{-1} dry weight=dw) (Cornelissen et al., 2004b), polychlorinated biphenyls (PCBs) (~0.3 μg g^{-1} dw) (Cornelissen et al., 2001), and chlorobenzenes (CBs) (~2 μg g^{-1} dw) (ten Hulscher et al., 1999).

Sediment S4, S5 and S6 are assumed to be clean sediments because they were collected from known unpolluted areas with only low atmospheric contamination prevailing. The concentrations of PAHs and PCBs in oligotrophic Lake Höytiäinen (S6) are very low or below detection limit (Ristola et al. 1996; Ristola et al., 1999). Low levels of PAHs were measured in the sediments of Lakes Kuorinka (S5) (0.2 μg g^{-1} dw) and Mekrijärvi (2 μg g^{-1} dw) (Cornelissen et al., 2004b). The trace amounts of chemicals are not expected to have an influence on the experiment. Lake Mekrijärvi is characterised by a high content of organic matter and humic substances (Leppänen and Kukkonen, 1998a). In experiment II, the sediments from Lakes Mekrijärvi and Höytiäinen (1:3) were blended together to obtain a clean reference sediment (S4) with a similar organic carbon content to that of the sediment samples from contaminated sediments S1, S2 and S3 (article II).

In the laboratory all the sediments were sieved (1mm) to remove large particles and debris. The sediments were thoroughly characterised including determinations of dry weight (dw), particle size, and organic carbon (OC) and nitrogen (N) (Table 4).

Table 4. Characteristics of sediments used in the experiments. Dry weight (dw, %), organic carbon (OC % of dw), nitrogen (N, % of dw), carbon to nitrogen (C/N), black carbon (BC % of dw) and the smallest particle size fraction % (< 20 μm) of the test sediments. * denotes a contaminated sediment sample.

Code	Sediment	dw (%)	OC (%)	N (%)	C/N	BC (%)	Particle size < 20 μm	Details	article
S1	Site Keltti	24±1	6.7	0.33	20.3	0.27	53±1	The River Kymijoki, Finland *	II,IV
S2	Site Lopotti	22±0.4	5.8	0.35	16.6	0.30	64±8	The River Kymijoki, Finland *	II
S3	Lake Ketelmeer	38±0.5	6.7	0.28	23.9	0.72 [a]	49±5	Sedimentation area of The River Rhine, the Netherlands *	II
S4	Reference	13±0.4	7.8	0.41	19.0		61±2	3:1 mixture of Lakes Mekrijärvi and Kuorinka, Finland	II
S5	Lake Kuorinka	20±0.1	1.8	0.07	25.7	0.15 [a]	60±2	Finnish Lake	I,III
S6	Lake Höytiäinen	48±0.4	3.0	0.23	13.0	0.11 [a]	82±2	Finnish Lake	III

[a] Cornelissen et al., 2004b

2.3.2. Spiking of sediment

The model chemicals dissolved in acetone were added drop-wise to the sediment while mixing (4h) with a rotating metal blade (article I, II) or adding chemicals to quartz sand, allowing the acetone solvent to evaporate and then rotating with a metal blade (article III).

The contact time between the sediment and the chemicals varied from 2 weeks to 24 months. Chemical analyses (tissue, Tenax, and sediments) were performed using a Liquid Scintillation Counter (LSC) (Wallac Finland Oy, Turku, Finland).

2.4. Desorption experiments

Desorption kinetics were measured by the Tenax® (mesh size 60-80; 177-250 μm, Chrompack, the Netherlands) extraction method. Briefly, spiked or contaminated sediment (4 g), Tenax (0.2 g) and artificial freshwater (48 ml) were constantly shaken in 50 ml glass tubes. Further, mercury chloride (50 mg/L) was added to inhibit microbial activity. The Tenax samples were replaced with a fresh portion (Tenax beads floated on top and the sediment sank to the bottom) at predetermined time points. The collected Tenax sample was extracted once with acetone (5 ml) and three times with hexane (5 ml). The extracted samples were concentrated to 2-3 ml by evaporation, 12 ml of LSC cocktail (UltimaGold^{TM}, Packard Bioscience, Groningen, the Netherlands) was added and the vials were mixed cautiously. Radioactivity was counted on the next day by LSC. At the end of the desorption experiment, the sediments were centrifuged (30 min, 672 g), and the water and sediment samples were analysed for mass balances.

Nonlinear regressions were performed using Scientist (MicroMath 2.01, Scientific Software, Salt Lake City, UT, USA) or GraphPad Prism 4 (GraphPad Software, Inc. San Diego, CA, USA). The time frame of the desorption experiments was long enough for triphasic desorption modelling (Cornelissen et al., 1997b; Cornelissen et al., 2001). The triphasic model gave a high average coefficient of determination (average 0.998) in all experiments. The model divides the chemical into three pools with different desorption rates:

$$S_t / S_0 = F_r e^{-k_r t} + F_{sl} e^{-k_{sl} t} + F_{vs} e^{-k_{vs} t} \qquad [1]$$

In the model, $S_t(t)$ and $S_0(0)$ are the total amounts of sediment organic carbon sorbed chemical (nmol g^{-1} OC) at the start (0) and at time t (h). F denotes the size fraction of the chemical in rapidly (F_r), slowly (F_{sl}), and very slowly (F_{vs}) desorbing fractions at time zero, and k (h^{-1}) is the corresponding rate constant. The model assumes that there is no significant re-adsorption into the sediment.

2.5. POM experiment

The polyoxymethylene (POM) solid phase extraction method was used to analyse chemical concentration in pore water (Jonker and Koelmans, 2001). Briefly, 50 ml glass bottles filled with artificial freshwater, POM plates (0.11-0.115 g), and spiked sediment samples (3 g) were vertically shaken (6 rpm) at 20 °C for 60 days. Mercury chloride (50 mg/L) was added to inhibit microbial activity. The POM strips were then removed and extracted 5 times with 3 ml hexane. Hexane washing was used for POM extraction until 5% or less of radioactivity was left in the POM strips. After the mixing period, the POM plates were washed and radioactivity was counted by LSC as described above for the Tenax samples (see above).

The organic carbon-water partitioning coefficient (K_{OC}) was determined using the mass balance equation (Jonker and Koelmans, 2001):

$$K_{OC} = \frac{1}{M_{OC}} \left(\frac{K_p Q_{tot}}{C_p} - M_p K_p - V_w \right) \qquad [2]$$

Where; M_{OC}, Mp, and V_w are the masses of sediment OC (g), POM (g) and the volume of water (ml). Q_{tot} is a total amount of chemical (nmol) in a system, K_p is the POM-water partitioning coefficient for the chemical according to (Jonker and Koelmans, 2001) and C_p is the chemical concentration in POM (nmol g^{-1}). For the unpublished (Figure 9) data, K_p was determined by rotating POM plates (0.110-0.115 mg) in artificial freshwater ($K_p = C_p/C_{water}$) until equilibrium was reached. Using the assumption inherent in the EqP theory, the concentration of hydrophobic organic chemicals in the pore water and organic carbon are in equilibrium, and the freely dissolved chemical concentration in pore water is related to the chemical concentration in OC. In this way the freely dissolved concentration can be calculated.

$$C_w = \frac{C_{s,OC}}{K_{OC}} \qquad [3]$$

2.6. Bioaccumulation experiments

Test organisms (*Lumbriculus variegatus)* were exposed through the sediments in order to assess bioaccumulation. After the equilibrium period, spiked sediments (30 g wet weight) were added to 50 ml glass beakers (exposure unit). Aerated artificial freshwater (pH 6.0) was added cautiously on top of the sediments to avoid sediment disturbance. After a two-day settling period, five test organisms were placed in each beaker. The oxygen concentration in the overlying water was measured at the beginning and the end of the experiment, but no aeration was provided.

After exposure, the triplicate exposure units were randomly selected for analysis. The worms were sieved from the sediment and purged in clean artificial freshwater for 6 h (Mount et al., 1999). The worms were then blotted dry, weighed, and placed in LSC vials with 1 ml of tissue solubiliser (Lumasolve ®). On the next day, 12 ml of LSC cocktail (UltimaGold) was added. The vials were shaken cautiously and radioactivity was counted by LSC. Chemical concentrations in the worms were normalised to lipid content at each sampling point. The lipids were analysed from control organisms using a gravimetric method with chloroform: methanol: water (2:1:0.5; v:v:v) extraction (Parrish, 1999).

The feeding behaviour of the worms was followed during the whole tests by collecting faecal pellets with a pipette from the sand surface. The produced pellets were dried, weighed and the feeding rate was calculated as an average egesting rate (mg dry faeces wet worm $^{-1}$ h^{-1}).

In addition, it was easy to take advantage of the ability of *L. variegatus* to regenerate body segments in order to estimate the uptake rate only from pore water, since worms without heads do not ingest sediments (Leppänen and Kukkonen, 1998b; article III). Briefly, five knife-truncated test organisms (worms without head segments) were placed in a similar experimental unit in three replicates.

2.6.1. Bioaccumulation factors

A two-compartment kinetics model (Landrum, 1989) was used to model bioaccumulation (Sigma Plot 8.0, SPSS Corporation, Chicago, IL, USA).

$$C_l(t) = \left(\frac{k_s * C_{s,OC}}{k_e}\right)\left(1 - e^{-k_e t}\right) \qquad [4]$$

Where $C_l(t)$ refers the concentration of the chemicals in the biota (nmol g^{-1} lipid) at time t, $C_{s,OC}$ is the initial chemical concentration in the sediment (nmol g^{-1} OC), k_s is the uptake clearance coefficient from the sediment (g^{-1} OC g^{-1} lipid h^{-1}), and k_e is the elimination rate constant of the chemical (h^{-1}). This equation requires that the $C_{s,OC}$ remains unchanged.

Differences in bioavailability were measured by calculating accumulation factors (BAF) based on the concentration in organisms (C_a) and sediment (C_s):

$$BAF = \frac{C_a}{C_s} = \frac{pmol\ g^{-1}\ fresh\ wt}{pmol\ g^{-1}\ dry\ wt} \qquad [5]$$

or BSAF based on uptake and elimination rate constants.

$$BSAF = \frac{k_s}{k_e} = \frac{nmol\ g^{-1}\ Lipid}{nmol\ g^{-1}\ OC} \qquad [6]$$

2.6.2. Revised bioaccumulation factors

Desorption modeling can be employed to estimate the bioavailable fraction and a revised accumulation factor can be calculated (Kraaij et al., 2002a). For example, a rapid fraction corrected estimate can be presented:

$$BSAF_{Fr} = \frac{k_s}{k_e} * F_r \qquad [7]$$

Further, BSAFs can also be alternatively estimated on the basis of the extent of rapid desorption (BSAF$_{Tenax}$) (Oen et al., 2006).

$$BSAF_{Tenax} = \frac{K_{Lipid}}{K_{OC}} * F_r \qquad [8]$$

where K_{Lipid} is the lipid-water partitioning coefficient (g^{-1}) and can be approximated as equal to the octanol-water partitioning coefficient (K_{OW}) values (Di Toro et al., 1991). K_{OC} is the organic carbon-water partitioning coefficient and for many non-polar contaminants, it can be estimated with sufficient accuracy from their octanol-water coefficient (Chiou et al., 1998). Thus K_{OC} for PAHs was obtained from log K_{OC} = 0.98 * log K_{OW} − 0.32 and for substituted aromatic compounds from log K_{OC} = 0.74 * log K_{OW} + 0.15 (Schwarzenbach et al., 2003).

On the other hand, BSAFs can be estimated on the basis of C_w (BSAF$_{POM}$). The bioconcentration factor was based on equation log BCF = 1.01 * log K_{OW} − 0.07 (Kraaij et al., 2003).

$$BSAF_{POM} = \frac{BCF * C_w}{C_{s,OC}} \qquad [9]$$

3. STATISTICS

Biota-sediment accumulation factors based on accumulation kinetics (k_s/k_e) were tested by the Z-test procedure (Bailer et al., 2000) (article I, III). The differences in egestion rates were measured using univariate repeated measures analyses of variance (Green, 1993; Paine, 1996) (articles I, III) or basic ANOVA using SPSS 11.0, SPSS Corp. Chigago, IL, USA (thesis). In the repeated measures analyses of variance test, the sphericity assumption of the test was checked by Mauchly's test. If the test was significant, Huynh-Feldt epsilon adjustment to the degrees of freedom was used. The Games-Howell (G-H) or least significant difference (LSD) multiple comparison test was applied for pairwise comparisons. The factorial ANOVA was used for comparing the bioavailability between the chemicals and sediments (article II). The basic ANOVA was used for comparing the means of lipids during the experiment (articles I, II, III). In basic ANOVA, Levene's test was used to check the homogeneity of variances, and the Games-Howell post hoc test or Tukey's multiple comparison was used for pairwise comparisons. Pearson correlation analysis (P) was performed for linear regression (article I). The modeling of desorption resulted in simultaneous estimation of six parameters from the desorption-time profile. Entire desorption curves of different data sets were compared by means of an F-test (GraphPad Prism 4, GraphPad Software, Inc., CA, USA) (article I, II). Statistical significance was set at 0.05 for all tests.
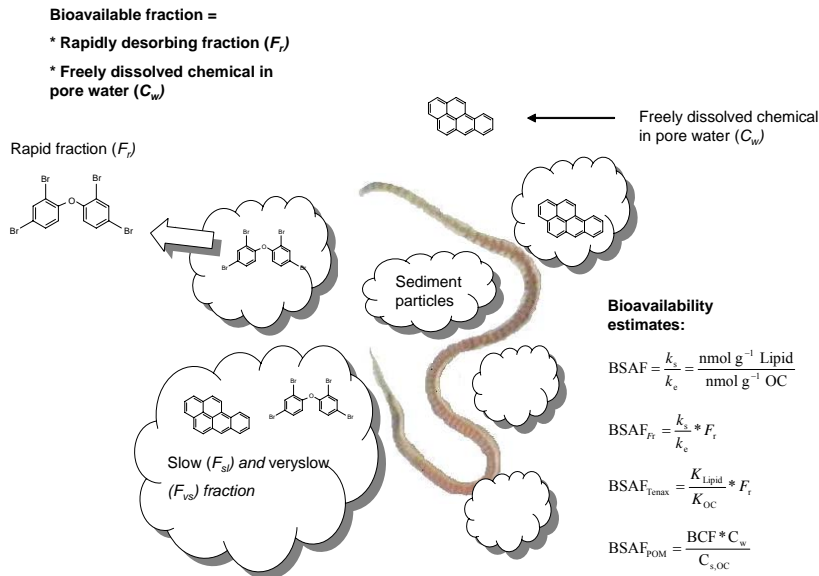
Figure 3. Conceptual structure of sediment, giving an idea of different approaches used in this thesis to study bioavailability. Biota-sediment accumulation factors (BSAFs) are based on uptake and elimination rate constants (equation 6). $BSAF_{Fr}$ represent the desorption-revised bioavailability estimates (equation 7). $BSAF_{Tenax}$ (equation 8) and $BSAF_{POM}$ (equation 9) represent the estimates for bioavailability based on the rapidly desorbing fraction (F_r) or the freely dissolved pore water concentration (C_w), respectively. K_{Lipid} is the lipid-water partition coefficient and can be approximated as equal to the octanol-water partition coefficient (K_{OW}) values (Di Toro et al., 1991). K_{OC} is the organic carbon-water distribution coefficient and can estimated on the basis of K_{OW} (log K_{OC} = 0.98 log K_{OW}– 0.32 for B*a*P, log K_{OC} = 0.74 * log K_{OW} + 0.15 for substituted aromatic compounds) (Schwarzenbach et al., 2003). Bioconcentration factor (BCF) was estimated on the basis of K_{OW} (log BCF = 1.01 * log K_{OW} – 0.07 (Kraaij et al., 2003).

4. RESULTS AND DISCUSSION

4.1. *Factors that modify desorption and bioavailability*

4.1.1. Sediment characteristics

Hydrophobic organic chemicals (HOC) have great affinity to sediment particles, and one of the most essential factors affecting the environmental fate of sediment-associated chemicals is the sorption-desorption processes. It is therefore essential to take some sediment biogeochemical characteristics into account in desorption and bioaccumulation studies.

Particle size

The particle size can have significant effects on the partitioning of chemicals because hydrophobic organic compounds do not distribute homogeneously in sediments (e.g. (Borglin et al., 1996; Kukkonen and Landrum, 1996; Millward et al., 2001; Rockne et al., 2002; Tye et al., 1996). In general, the organic carbon partitioning coefficient (Koc) increases as particle size decreases. In the present sediments the majority of compounds were associated with the smallest particle size

fraction (< 20 μm) (Table 5). The reason for this is that most of the organic matter resides in this small particle-size fraction (Kukkonen and Landrum, 1996) and where the particle surface area to volume ratio is the highest (Tye et al., 1996). It should be noted that the distributions among small particles may still differ between compound classes, e.g. PAHs and PCBs (Kukkonen and Landrum, 1996) or when the contaminant concentration changes (Kukkonen and Landrum, 1994). In the experiments conducted here, varying the chemical concentration was not found to alter the PCB distribution among the particle size fractions, even though very high concentrations were used (article III). Further, no relationship between desorption parameters and particle size distribution was found either. The data in the literature are conflicting on this topic. Some studies have shown greater desorption in the fine fractions (Ghosh et al., 2001; Shor et al., 2003) while others have not observed any particle size dependence (Cornelissen et al., 1999). Thus the connection between desorption and particle size fraction is not clear for all chemicals or sediments either.

Further, it should be noted that particle size distribution may influence the bioaccumulation of sediment-associated compounds if selective feeding of benthic organisms exists. Even though *L. variegatus* generally ingest particles below 100 μm (Lawrence et al., 2000), the worms might concentrate on the best suitable diet, i.e. the fraction of the very finest particles where most of the organic matter and hydrophobic compounds reside (Kukkonen and Landrum, 1994; Kukkonen and Landrum, 1996; article III), and this might increase the amount of chemical concentration in pellets (article I). Thus, selective feeding may also explain the negative correlation between feeding rate and chemical concentration in faecal pellets during the experiment (article I). At the start the worms' diets may include the finest, most suitable particle fraction (low feeding rate) and in the later stages of the experiment (high feeding rate) (> 100 h), all particles small enough to fit the worms' mouth may also make a contribution to the diet, and as a consequence, the chemical concentration in pellets decreases.

However, as generally accepted, organic matter, often expressed as organic carbon (OC), plays an important role in overall sorption (Schwarzenbach et al., 2003), and thus a comprehensive understanding of desorption requires more attention to organic matter structure and properties.

Table 5. Distribution of chemicals in different size classes of sediment particles. Pentabromodiphenyl ether (BDE-99) and tetrachlorodibenzo(*p*)dioxin (TCDD) chemical distribution is expressed as % in various sediments. Tetrachlorobiphenyl (PCB-77) distribution is presented in two different concentrations for the sediments S5 and S6.

Particle size	S1 BDE-99	S2 BDE-99	S3 BDE-99	S4 BDE-99	S5 PCB-77 kons I	S6 PCB-77 kons I
<20 μm (%)	70	63	93	74	90	69
20-37 μm (%)	7	9	2	6	4	5
37-63 μm (%)	5	9	1	5	2	7
63-125 μm (%)	9	10	1	8	1	6
125-400 μm (%)	8	9	2	6	3	12
>400 μm (%)	2	1	0	0	0	2
	TCDD	TCDD	TCDD	TCDD	PCB-77 kons VI	PCB-77 kons VI
<20 μm (%)	92	99	94	96	98	95
20-37 μm (%)	2	1	1	1	1	1
37-63 μm (%)	1	0	1	1	1	1
63-125 μm (%)	1	0	1	2	0	2
125-400 μm (%)	3	0	3	1	0	2
>400 μm (%)	1	0	0	0	0	0

Organic matter

The sediment organic matter is the most essential constituent for the chemicals' sorption/desorption behaviour, and a consensus exists that organic matter is a predominant sorbent of hydrophobic organic compounds (Schwarzenbach et al., 2003; Birdwell et al., 2007), except for sediments with very low OC, very low moisture content or relatively high clay content (Pignatello et al., 2006). Further, increased OC of sediment can decrease the bioavailability of hydrophobic compounds (Park and Erstfeld, 1999; Mäenpää et al., 2003). Based on the present data, no very clear trends can be presented. A wider range in the OC of the sediment could potentially help to identify a relationship between OC content and desorbing parameters. Despite this, the F_r showed a decreasing trend with increasing OC in sediments (r^2=0.47), even though the tested sediments showed minor variation in OC (article II). Earlier published data show conflicting information; some studies have shown a negative correlation between organic matter concentration and the extent of desorption (Cornelissen et al., 1998; Shor et al., 2003), while some others have not found any relationship with desorbing parameters (Cornelissen et al., 2000; Kukkonen et al., 2003). However, the amount of OC in sediment may not alone explain the chemicals' partitioning behaviour in the sediment matrix, and thus the quality aspect of OC should also be taken into consideration.

As mentioned earlier, the complex nature of organic material is well known, and organic material may contain several domains or constituents, each with different sorption activities. For example, much focus has been assigned to the role of black carbon (BC) in the environmental behaviour of chemicals. In general, BC comprises about 9% of the total organic carbon in aquatic sediments (median value of 300 sediments) (Koelmans et al., 2006). The BC has appeared to be a strong sorbent for PAHs (Jonker and Smedes, 2000; Jonker and Koelmans, 2002; Lohmann et al., 2005), PCBs (Jonker and Koelmans, 2002;

Cornelissen et al., 2004a), and polychlorinated dibenzo-*p*-dioxins and -furans (Bärring et al., 2002), as well as PBDEs (Bärring et al., 2002). In the present sediments the S3 has the highest BC content (0.7% of dw ~ 10% of the OC) compared to the other sediments (Table 4). However, no definitive conclusion was found based on the quality of the organic matter either. Further, the adsorption sites in BC could be occupied by native compounds (article II) and need to be discussed.

Chemical present in sediments

Model compounds in contaminated sediments (S1, S2, S3) had a higher F_r compared to the reference (S4) with atmospheric input only indicating possible competition for sorption sites by native compounds (article II). This may also contribute to the higher chemical outflux ($F_r * k_r * C_{s,OC}$) from contaminated sediments compared to that from S4 (article II). Multiple chemicals present in sediments may compete for the highest energy binding sites in the organic material and thus accelerate desorption (White and Pignatello, 1999; Weber et al., 2002; Zhao et al., 2002). When this sorption capacity is filled, any excess contaminants will bind to lower energy sites and thus desorb more rapidly. For example, it has been estimated that about 50% of these adsorption sites in the very slowly desorbing domain of the Lake Ketelmeer sediment were not directly accessible to phenanthrene due to the presence of native compounds (van den Heuvel and van Noort, 2003). The chemical data collected in the present study are not sufficiently extensive to draw more detailed conclusions, given the possibility that concentrations of native compounds may vary widely within a site. However, it is reasonable to suspect that chemicals present in the sediment may also affect the outcome of test.

4.1.2. Chemical properties

Planarity and size of molecules

Chemical planarity or size of molecules may partly explain the desorption rates of organic chemicals (article I, II). Desorption rates have been used to imply the binding strength of chemicals (Greenberg et al., 2005). For example, the relatively constant desorption rate of BaP in different treatments may be taken to suggest that sorption/desorption behaviours are driven by compound properties (article I). It has been suggested that sorption can occur either by physical adsorption on a surface or by partitioning into an organic matter fraction (absorption) (Pignatello and Xing, 1996). On this basis, one explanation could be that planar BaP is able to penetrate into the organic matter (high F_{vs}), and slowly desorbing fractions are not in direct contact with water (Cornelissen et al., 1997a, article I), and as a result, diffusion from the remote sites of organic matter is smaller (lower k_r, k_s, k_{vs}) compared to non-planar BDE-47 (article I). By contrast, BDE-47 with a more complicated structure is adsorbed on the surface of solid material (higher F_r) and molecules are in direct contact with water and do not encounter such stronger diffusion-related retardations and thus can be desorbed more easily than BaP. On the other hand, planar BaP can more readily access the narrow sites from which desorption is retarded compared to BDE-47. Earlier published data has showed that planar compounds have smaller F_r compared to non-planar compounds (Lamoureux and Brownawell, 1999; van Noort et al., 2002).

Further, planar compounds have a capability to interact via efficient π-π bonds with the aromatic constituents of the sediment, interactions that increase the resistance to desorption (Bucheli and Gustafsson, 2001). The other interactions potentially available for neutral organic compounds (van der Waals, dipole-dipole, hydrogen bonding) are common to both adsorption and partitioning (Pignatello and Xing, 1996), but these aromatic interaction are stronger than those for non-covalent interactions. The very tight interaction (high F_{vs}) between the sediment particles and BaP can also be seen in lower bioavailability estimates (k_s, BSAF) compared to BDE-47. Therefore, the sediments may contain matrices to which various compounds can attach preferentially.

In addition, the size of molecules, expressed as molecular volume (cm^3 mol^{-1}) (Table 3), may help to explain the different desorption rates of various chemicals. Large chemicals, such as BDE-47 and BDE-99, diffuse more slowly through the organic matter matrix or through micropores compared to smaller chemicals, such as BaP or TCDD (article I, II). This explanation has previously been presented for sediments spiked with CBs, PCBs and PAHs (Carroll et al. 1994; Cornelissen et al., 1997b; Birdwell et al. 2007). On the other hand, increasing molecular size is closely related to the chemical's lipophilicity and needs to be discussed on the basis of the present data.

Lipophilicity

A chemical's lipophilicity, expressed as K_{OW}, represents an essential factor regarding the chemical's desorption behaviour (article IV). Higher log K_{OW} values evidently leads to higher binding affinity, and thus slower desorption is seen for more chlorinated and hence more lipophilic PCDDs, PCDFs and PCDEs. The rapidly desorbing fraction also decreased with the increasing lipophilicity of various congeners of PCDDs, PCDFs, and PCDEs (article IV). Earlier studies have shown a similar correlation between K_{OW} and F_r for CBs, PCBs and PAHs in laboratory-contaminated sediments (Cornelissen et al., 1997b) as well as CBs in field-contaminated sediments (Gess and Pavlosthahis, 1997). Thus the various diffusion limitations of different chemicals appear to have an important function in defining a contaminant's behaviour in sediments (Pignatello and Xing, 1996). Further, the contaminant's molecular size, lipophilicity and conformation and sediment characteristics have a role in the bioavailability of sediment-associated PCDDs,

PCDFs and PCDEs (Lyytikäinen et al., 2003a). In general, the extent of both desorption from sediments and bioavailability to organisms decrease as the lipophilicity of a compound increases. On the other hand, increases in lipophilicity often occur in combination with an increase in the steric dimensions of the molecules, which in turn may hinder the passage of the contaminants through the membranes into the organisms (Opperhuizen et al., 1985).

4.1.3. Environmental factors

Temperature

Temperature is the evident physicochemical factor that affects chemical and biological processes in aquatic life, especially in boreal waters, where seasonal variations are large. It has been reported that increasing temperature can reduce sorption coefficients (Koc) (ten Hulscher and Cornelissen, 1996), increase desorption fractions and rates (Piatt et al., 1996; Cornelissen et al., 1997a; ten Hulscher et al., 2004), increase uptake rate constants (Gerould et al., 1983; article I) and bioconcentration factors (Honkanen et al., 2001) or biota-sediment accumulation factors (Leppänen et al., 2003).

In the present study the decreasing temperature clearly shifted desorption towards the more desorption-resistant fraction (F_{vs}) (article I). For most compounds, sorption coefficients (Koc) increase with decreasing temperature (ten Hulscher and Cornelissen, 1996; Schwarzenbach et al., 2003; Pignatello et al., 2006), thus fewer molecules are available for the loosely bound fraction and F_{vs} tends to increase at low temperatures. Possibly this might indicate an increase in the number of higher energy sites as temperature decreases. This observation may be attributed to the finding that the F_{vs} state is energetically more favourable than the F_r or F_{sl} compartment (ten Hulscher et al., 1999; Vrind et al., 2006). It is also possible that higher temperatures alter the structure of organic material and enhance diffusion from the sites

of slow desorption (from the deeper part of organic matter). For example, increasing temperature may increase the mobility of macromolecules in the organic material and thus change the sorption/desorption behaviour of chemicals (Pignatello et al., 2006). Evidence for this has been reported for synthetic organic polymers as well as for natural organic material (Leboeuf and Weber, 2000).

Although changing the temperature had general effects on desorption, there were also chemical-specific impacts. One example of this in the current study was that increasing temperature increased the desorption rate (k_r) of BDE-47, but not that of BaP (article I). It was speculated earlier that BaP may be absorbed (high F_{vs}) in the organic matter fraction, while the BDE-47 may be situated on the surface of solid material (high F_r). Thus molecules adsorbed on the surface of solid material are in direct contact with water and do not encounter such strong diffusional retardations. According to the Langmuir adsorption theory, adsorption decreases with an increase in temperature (Langmuir, 1916) and molecules adsorbed earlier on surfaces tend to desorb more at elevated temperatures. Based on this assumption, desorption rates of BDE-47 could be affected more by temperature compared to BaP.

In the data presented here, increasing temperature clearly accelerated the uptake (k_s), but it did not clearly affect steady-state tissue concentrations (article I), a result in accordance with the equilibrium partitioning theory. The one evident explanation for increased chemical uptake at higher temperatures may be the increased activity or feeding rate of organisms (article I). More active organisms can be expected to intake larger volumes of pore water and ingest larger masses of contaminated sediment compared to less active organisms, two changes expected to increase k_s values. Thus, the k_s determined at room temperature may not be applicable at lower temperatures when uptake rates are of interest.

Ageing

The prolonged contact time between chemical and sediment increased the desorption-resistant fraction (F_{vs}) of chemicals, decreased desorbing rates (k_r, k_{sl}, k_{vs}) and to some extent also bioavailaibility (BSAFs, k_s) (article I). The very slowly desorbing fraction (F_{vs}) was very high in aged field sediments, too (article IV). These results accord well with earlier reports that increased contact time decreases the rapidly desorbing fraction (Borglin et al., 1996; Cornelissen et al., 1997b; Kraaij et al., 2002b; ten Hulscher et al., 2005), desorption rates (Borglin et al., 1996; ten Hulscher et al., 2005), uptake rate constants (k_s) (Loonen et al., 1997; Kukkonen and Landrum, 1998; Leppänen and Kukkonen, 2000; Schuler and Lydy, 2001), and biota-sediment accumulation factors (Loonen et al., 1997; Kraaij et al., 2002a) for several compounds and may cause the reduced uptake at higher trophic levels (Moermond et al., 2007).

It is reasonable to suppose that with time the chemical can attach more closely to the organic carbon of the sediments. However, so far there is no very clear physical-chemical explanation for the observed increase in the desorption-resistant compartment with ageing of the sediment. If rapidly desorbing sites in the sediment particles come to be filled first, the remaining chemicals have to find more slowly desorbing sites. The presence of the very large F_{vs} may be caused by the presence of different (denser) regions in the organic carbon of the sediment particles, from which "trapped" contaminants cannot be easily desorbed (ten Hulscher et al., 1999). As mentioned earlier, the sorbed state (F_{vs}) could be thermodynamically more favourable, and chemicals gradually find these favourable sites. On the other hand, it has been suggested that the F_r is the outer sphere of the organic matter and the F_{sl} is associated with amorphous organic matter, whereas the F_{vs} is associated with microcrystalline organic matter (e.g BC) (Cornelissen et al., 1997a). Alternatively it is suggested that the F_r is associated with inorganic material (Weber and Huang, 1996). However, the sorption domains of other than sediment organic material have been considered a negligible factor for hydrophobic organic compounds (Birdwell et al., 2007). Overall, these explanations again assume that there are several domains for sorption in the sediments (Weber et al., 1992; Xing et al., 1996; Huang and Weber, 1997; Xing and Pignatello, 1997; Chiou and Kile, 1998).

A decline in bioavailability with ageing may be associated with a more compact interaction between chemicals and sediment particles, making a chemical less available to biota after the ingestion of soil particles (Conrad et al., 2002). The gut fluids are not able to break this interaction, yielding higher chemical concentration in faecal pellets and possibly explain the lowered uptake rate pellets in the treatments with long contact time (article I). Additionally, the uptake rates may decrease due to the smaller chemical concentration in the pore waters.

4.1.4. Organisms' behaviour

To conclude the present data, increasing feeding rate (FR) clearly accelerates uptake, but does not have a clear effect on BSAF values (article I, II). In the sediments used here, the feeding activity of *L. variegatus* expressed as egestion rate varied, depending on the sediment's properties (Figure 4). One reason for higher feeding activity in the sediment S5 compared to other sediments ($F_{5,12} = 154$, $p < 0.01$) could be the lower nutritional value (C:N ratio) (Figure 4, Table 4). The C:N ratio in sediment can be considered to be a general indicator of the nutritional value of organic matter (Cammen, 1982). If it is assumed that the maximum C:N ratio that will provide an adequate diet for benthic organisms is 17 (Russel-Hunter, 1970), then the sediment's S3 and S5 are the most unsuitable diet for *L. variegatus*. Further, in the sediments with low organic matter content (e.g. S5), organisms have to pass more material through the gut to meet their energy needs (Leppänen and Kukkonen, 1998a). Thus more active organisms should encounter more contaminants in pore water or accumulate

more chemicals from the gut. An additional confounding factor relevant to sediment (e.g. S3) is that high concentrations of chemicals presents in the sediments may have caused adverse living conditions and thus may have reduced the worms' feeding activity.

Instead, the present data confirm earlier published data in that sediment ingestion has an important role in the bioaccumulation process (Leppänen and Kukkonen, 1998b). Ingestion of sediment clearly increased the uptake (k_s), steady-state concentration of PCB-77 and BSAFs compared to non-feeding *L. variegatus* (article III). Bioaccumulation routes include uptake from pore water and overlying water through the body wall and respiratory surfaces or through ingestion of contaminated sediment particles (Power and Chapman, 1992; Kukkonen and Landrum, 1996) and thus the potential digestive exposure of chemicals can be much greater than that predicted on the basis of the traditional EqP-theory (Voparil et al., 2004). The present study shows that pore water is not the only uptake route, since ingesting worms had access to an additional bioavailable chemical fraction (article III). Earlier, it has been suggested that initial uptake of B*a*P is from absorption across the body wall, but with increasing time and feeding activity, sediment ingestion becomes the major source of B*a*P

for polychaeta (Weston et al., 2000). Therefore, processes in the organism's gut may result in a different bioavailable fraction than expected on the basis of desorption studies if the digestive fluids in the organisms modify desorption. Thus under these circumstances the actual bioavailable fraction would differ from the rapidly desorbing fraction or freely dissolved pore water concentration in pore water. However, the effect of the processing of sediments through the guts of organisms is unknown, but appears to increase the desorption of the chemicals. For example, the gut fluids may enhance the dissolved chemical concentration in the gut (Gobas et al., 1993; Mayer et al. 1996, Weston and Mayer, 1998; Millward et al., 2001; Voparil et al., 2004; Mayer et al. 2007), which can increase the potential for bioaccumulation or toxicity. Further, these effects may differ depending on the chemical structure. In an experiment in which contaminated sediment was extracted with the digestive fluid of polychaete, desorption of PCBs was higher compared to that of PAHs (Weston and Maruya, 2002). Thus, sediment ingestion may modify the bioavailable fraction in ways that cannot entirely be explained by equilibrium partitioning models or desorption-revised models either.
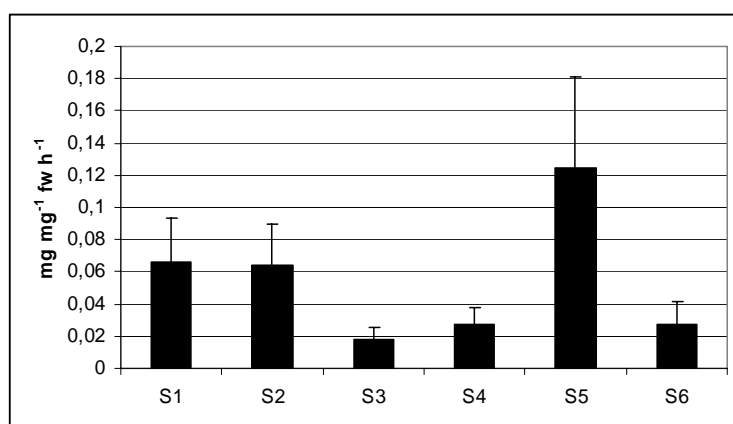

Figure 4. The mean egestion rate of *L. variegatus* in various test sediments at 20 ºC (mg pellet mg^{-1} fw h^{-1}) during the exposure period with standard deviations ($n = 8$).

4.2. Desorption as a factor explaining bioavailability

The data from all laboratory work in the present study ($r^2 > 0.28$) (articles I-III) added to similar data from Great Lake area sediments ($r^2 > 0.55$) (Kukkonen et al., 2004) confirm that the rapidly desorbing fraction (F_r) of chemicals play a significant role in explaining BSAF values (Figure 5). Also, the outflux of chemicals from the sediment particles in the rapid fraction ($F_r * k_r * C_{s,OC}$) and inflow of chemicals ($k_s * C_{s,OC}$) into organisms support the argument that desorption plays a role in the bioaccumulation process (Figure 6). Further, the finding that F_r had a relationship with the K_{oc} (based on POM analyses) (article III) indicates that F_r is mainly responsible for the chemical concentration in pore water (assumed bioavailable fraction), and it should also be possible to explain variation in biota-sediment accumulation factors by differences in desorbing fractions.
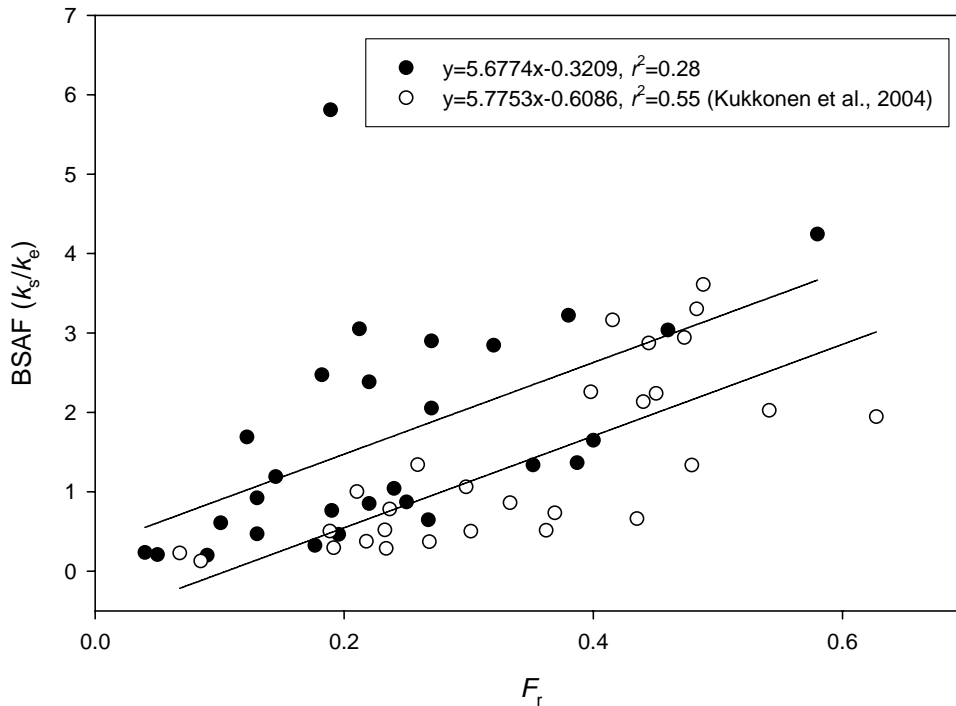

Figure 5. The relationship between biota sediment accumulation factors (BSAF) calculated using kinetics based on equation 2 and rapidly desorbing fractions (F_r) in various sediment treatments with several organic compounds. Solid symbols represents all data included in this thesis and open symbols represent data obtained from Kukkonen et al. (2004). Lines correspondingly represent the linear regression to data.

In the present data, the biota-sediment accumulation factors showed high variation (BSAF; 0.21 – 5.8) depending on the chemical, treatment, or concentration (Table 6). Desorption-revised accumulation factors decreased variation between the chemicals, but still left some questions unexplained. For example, the lower bioavailability of BaP compared to that of BDE-47 can only to a certain extent derive from the desorption resistance of the BaP sorbed to the sediments (Table 6, article I). Further, rapidly desorbing fractions seems to explain better the bioavailable pool for TCDD compared to BDE-99 (Table 6, article II). Thus, for some chemicals or various circumstances, the slowly or veryslowly desorbing fraction may have a larger role when the organisms/sediment/pore water system has attained steady state (Leppänen et al., 2003; Kukkonen et al., 2004). Therefore, the assumed bioavailable chemical fraction (F_r) in the mixed system (Tenax tubes) may not describe fully the bioavailable fraction in stagnant sediments (worms) similarly for all chemicals. Further, as speculated earlier, processes in the organism's digestive track are not fully understood, and some processes may have chemical-specific effects (article I, II).

Despite this, in most cases desorption-revised estimates managed to reduce variation between the various chemicals, sediments or concentration treatments (Table 6, articles I, II, III). This can be seen as a smaller coefficient of variation (CV) when comparing actual BSAF and desorption-revised estimates (BSAF$_{Fr}$, BSAF$_{Fr+Fsl}$, BSAF$_{F99}$) (Table 6). Even though, the bioavailable fraction can not be solely presented by the size the desorbing fraction; including the desorbing fractions in risk assessment represents a step towards more accurate risk estimation of pollutants.

Table 6. Biota sediment accumulation factors (equation 6) and different desorbing fraction-revised bioaccumulation factors (equation 7). The details for various sediment treatments can be found in the original articles (S1-S4 article II, S5 article I, III, and S6 article III).

Article I	Sediment (treatment)	BSAF	BSAF$_{Fr}$	BSAF$_{Fr+Fsl}$	BSAF$_{F99}$		Sediment (treatment)	BSAF	BSAF$_{Fr}$	BSAF$_{Fr+Fsl}$	BSAF$_{F99}$
BDE-47	S5 (24 months 10°C)	3.0	6.6	4.2	5.3	BaP	S5 (24 months 10°C)	0.85	3.87	1.78	1.99
	S5 (24 months 20°C)	2.8	8.9	5.3	6.2		S5 (24 months 20°C)	0.47	3.62	1.43	1.80
	S5 (6 weeks 10°C)	4.2	7.3	5.2	6.7		S5 (6 weeks 10°C)	0.87	3.49	1.56	1.70
	S5 (6 weeks 20°C)	3.2	8.5	4.7	5.8		S5 (6 weeks 20°C)	0.92	7.10	2.37	3.13
	Average±SD	3.3±0.6	7.8±1.1	4.8±0.5	6±0.6		Average±SD	0.78±0.2	4.5±1.7	1.8±0.4	2.2±0.7
	CV	0.18	0.14	0.10	0.10		CV	0.26	0.38	0.22	0.32
Article II											
BDE-99	S1	3.1	14.5	8.2	9.2	TCDD	S1	2.4	10.8	7.5	8.5
	S2	2.2	22.0	7.9	5.1		S2	1.8	12.7	10.0	8.7
	S3	5.8	26.0	13.9	9.5		S3	2.8	10.4	6.8	6.8
	S4	1.7	13.0	6.8	4.3		S4	1.2	9.9	4.4	3.3
	Average±SD	3.2±1.8	18.9±6.2	9.1±3.2	7.1±2.7		Average±SD	2.3±0.8	11.0±1.2	7.1±2.3	6.8±2.5
	CV	0.56	0.32	0.35	0.38		CV	0.33	0.11	0.31	0.37
Article III											
PCB-77	S5 (Cons I)	1.37	3.50	1.9	2.29	PCB-77	S6 (Cons I)	1.65	4.12	2.6	3.15
	S5 (Cons II)	1.34	3.82	1.8	2.15		S6 (Cons II)	1.04	4.34	1.9	2.80
	S5 (Cons III)	0.65	2.40	1.4	1.73		S6 (Cons III)	0.76	4.02	1.8	2.54
	S5 (Cons IV)	0.46	2.32	1.4	1.73		S6 (Cons IV)	0.21	2.33	0.9	1.34
	S5 (Cons V)	0.32	1.80	1.1	1.42		S6 (Cons V)	0.21	4.19	1.6	2.49
	S5 (Cons VI)	0.61	6.09	3.8	4.47		S6 (Cons VI)	0.23	5.86	2.1	3.10
	Average±SD	0.79±0.44	3.3±1.5	1.9±0.98	2.3±1.2		Average±SD	0.68±0.59	4.1±1.2	1.8±0.56	2.6±0.67
	CV	0.57	0.46	0.51	0.51		CV	0.86	0.28	0.31	0.27

BSAF(k_s/k_e) = Biota-sediment accumulation factor (nmol g^{-1} lipid / nmol g^{-1} OC)

BSAF$_{Fr}$ = Biota-sediment accumulation factor (nmol g^{-1} lipid / nmol g^{-1} OC * F_r)

BSAF$_{Fr+Fsl}$ = Biota-sediment accumulation factor (nmol g^{-1} lipid / nmol g^{-1} OC * ($F_r + F_{sl}$))

BSAF$_{99}$ = Based on the total fraction when 99.9 % rapidly desorbing fraction has been desorpted (nmol g^{-1} lipid / nmol g^{-1} OC * $F_{99.9}$)

Coefficient of variation is defined as the ratio of the standard deviation to the mean

For the risk assessment process, the magnitude of the F_r should be defined. In earlier studies, the fraction desorbed after 6 hours is about half of F_r (Cornelissen et al., 2001) or a 24-hour time site has been used to estimate the size of F_r (Shor et al., 2003). In the present thesis use of 24-hour estimate (y = 1.1615x - 0.0332, r^2=0.81) was better surrogate for F_r compared to the 6 hour estimate for spiked chemicals (y = 1.0758x + 0.0106, r^2=0.54) (data from articles I, II, III). Instead, for field contaminated sediments, the 6-hour (1.4772x+0.004, r^2=0.67) provided better surrogate than the 24-hour estimate (1.3591x+0.004, r^2=0.54) (data from article IV). However, some studies have shown that none of these two periods (6 or 24 h) were suitable surrogates for F_r (Kukkonen et al, 2004; De la Cal et al., 2008). Thus, for very accurate estimation, the complete curve of desorption should be determined. Table 7 provides an overview of the size of F_r measured in this study and obtained from the literature for some selected chemicals in the laboratory- and field-contaminated sediments. Even though, the F_r values obtained from the present study are in a similar category as those found in the literature in laboratory studies, some variation appears in the size of F_r, depending on the sediment, equilibrium time and chemical. In addition, desorption studies of field-contaminated sediments are still quite scarce. However, studies has shown already that chemical desorption from field-contaminated sediments may be substantially different from that predicted by spiked sediments (Table 7, articles II, IV). Thus, there is no single estimate for F_r that can be used for all risk assessment.

Table 7. Rapidly desorbing fractions (F_r) for the various organic contaminants measured in this study and obtained from the literature. Experiments with the Tenax extraction method and modelled with three-phase desorption kinetics are included in the table.

Laboratory spiked	F_r	Equilibrium time	Sediment sample description	Reference
BDE-99	0.11-0.21	6 weeks	Finnish lake, rivers and Dutch lake	article II
2,3,7,8-TCDD	0.12-0.27	6 weeks	Finnish lake, rivers and Dutch lake	article II
BDE-47	0.58	6 weeks	Lake Kuorinka, Finland	article I
BDE-47	0.46	24 months	Lake Kuorinka, Finland	article I
BDE-47	0.26	12 day	Spanish river	De la Cal et al., 2008
BDE-99	0.35	12 day	Spanish river	De la Cal et al., 2008
Benzo(a)pyrene	0.25	6 weeks	Lake Kuorinka, Finland	article I
Benzo(a)pyrene	0.22	24 months	Lake Kuorinka, Finland	article I
PCB-77	0.04-0.4	6 weeks	Lake Höytiäinen, Finland, various concentration	article III
PCB-77	0.1-0.39	6 weeks	Lake Kuorinka, Finland, various concentration	article III
Benzo(a)pyrene	0.16	7 months	Lake Höytiäinen, Finland	Leppänen and Kukkonen 2006
Benzo(a)pyrene	0.14	7 months	Lake Kuorinka, Finland	Leppänen and Kukkonen 2006
PCB-77	0.28	8 months	Lake Höytiäinen, Finland	Leppänen and Kukkonen 2006
PCB-77	0.22	8 months	Lake Kuorinka, Finland	Leppänen and Kukkonen 2006
PCB-28	0.15	2 day	Dutch Lake	ten Hulscher et al., 2005
PCB-28	0.02	6 months	Dutch Lake	ten Hulscher et al., 2005
Benzo(a)pyrene	0.19	3 months	Dutch Lake	Kraaij et al., 2002
Benzo(a)pyrene	0.28	32 months	Dutch Lake	Kraaij et al., 2002
PCB-77	0.42 (0.37-0.46)	2 months	American creek	Leppänen et. al., 2003
PCB-77	0.32 (0.23-0.45)	3,5 months	American lakes	Kukkonen et al., 2004
Field contaminated				
PeCDDs	0.015		Finnish river	article IV
HxCDDs	0.012		Finnish river	article IV
HpCDDs	0.011		Finnish river	article IV
OCDD	0.012		Finnish river	article IV
PeCDFs	0.013		Finnish river	article IV
HxCDFs	0.0075		Finnish river	article IV
HpCDFs	0.0077		Finnish river	article IV
OCDF	0.006		Finnish river	article IV
PCDEs	0.014		Finnish river	article IV
Benzo(a)pyrene	0.04		Dutch estuary	Kraaij et al. 2001
PCB-28	0.11		Dutch river	Cornelissen et al., 2001
PCB-101	0.18		Dutch river	Cornelissen et al., 2001
PCB-153	0.14		Dutch river	Cornelissen et al., 2001
PCB-138	0.10		Dutch river	Cornelissen et al., 2001
PCB-28	0.19		Dutch lake	Cornelissen et al., 2001
PCB-101	0.35		Dutch lake	Cornelissen et al., 2001
PCB-153	0.16		Dutch lake	Cornelissen et al., 2001
PCB-138	0.13		Dutch lake	Cornelissen et al., 2001
Benzo(a)pyrene	0.08-14		Dutch lakes and rives	Cornelissen et al., 2001
Benzo(a)pyrene	0.06(0.02-0.08)		Norwegian harbors	Oen et al., 2006

In addition, desorption-revised bioavailability estimates may have additional limitations for risk assessment. Firstly, desorption-revised BSAF (Equation 7) may not provide an exact estimate, if the solubility limit of chemicals is reached (arrow in Figure 6, article III). Secondly, the desorbing fraction (e.g F_r) estimated by Tenax does not represent the actual freely dissolved chemical concentration in pore water, because it includes both the freely dissolved chemicals fraction and the loosely attached chemical fraction in sediment particles. Thus depletive sampling (Tenax) is more likely to describe the fraction of contaminant that can be released from the sediment. Further, Tenax measurements cannot take account of the effects of feeding behaviour (ingestion of sediment) in the bioaccumulation process.
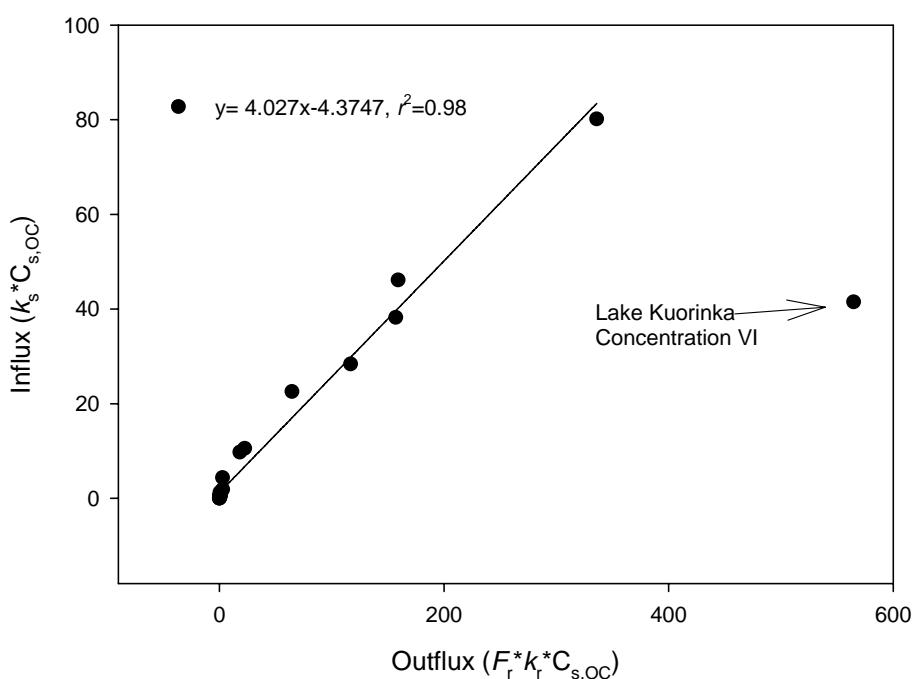
Figure 6. The relationship between flux out from the sediment in the rapidly desorbing fraction ($F_r*k_r*C_{s,OC}$) and flux into the organism ($k_s*C_{s,OC}$). Combined data from feeding *L. variegatus* in articles I, II and III are presented. Lake Kuorinka (concentration VI) is not included in the regression.

Bioaccumulation estimations based on desorption measurement (BSAF$_{Tenax}$)

In this study, desorption modelling was also employed to alternatively estimate the bioaccumulation factors (BSAF$_{Tenax}$) (Oen et al., 2006). However, BSAF$_{Tenax}$ estimates (Equation 8) underestimated the actual bioavailability of PCB-77 for feeding worms, but did indeed succeed in estimating bioavailability for non-feeding worms (Figure 7). This shows again that ingesting organisms evidently have an additional bioavailable fraction from ingested sediment particles. However, it is still uncertain how well the measured F_r represents the true bioavailable fraction in an unmixed system. On the other hand, BSAF$_{Tenax}$ recalculated with the rapid and slowly desorbing fraction ($K_{Lipid}/K_{OC}*F_r+F_{sl}$, r^2=0.23) or total desorbing fraction at the time point when 99.9% of the F_r has desorbed ($K_{Lipid}/K_{OC}*F_{99.9}$, r^2=0.34) did

not result in substantially improved predictions of the real BSAF values. Diffusion and desorption may differ in a very effectively mixed system (Tenax extraction) compared to an unmixed, whole-sediment bioaccumulation test. Also, the above-mentioned other disadvantages of the infinite-sink Tenax extraction method (a depletive method) can cause deviations between observed (BSAF) and estimated values (BSAF$_{Tenax}$). Further estimates for K_{OC} and K_{Lipid} may cause some inaccuracy in bioavailability estimates. Sediment properties affect K_{OC} values, and therefore K_{OC} values obtained from the literature should be used with caution. For example, literature-based K_{OC} values clearly overestimated the chlorobenzene concentration in sediment pore water in field-contaminated sediments (ten Hulscher et al., 1997). In addition the assumption that K_{Lipid} = K_{OW} may be incorrect.
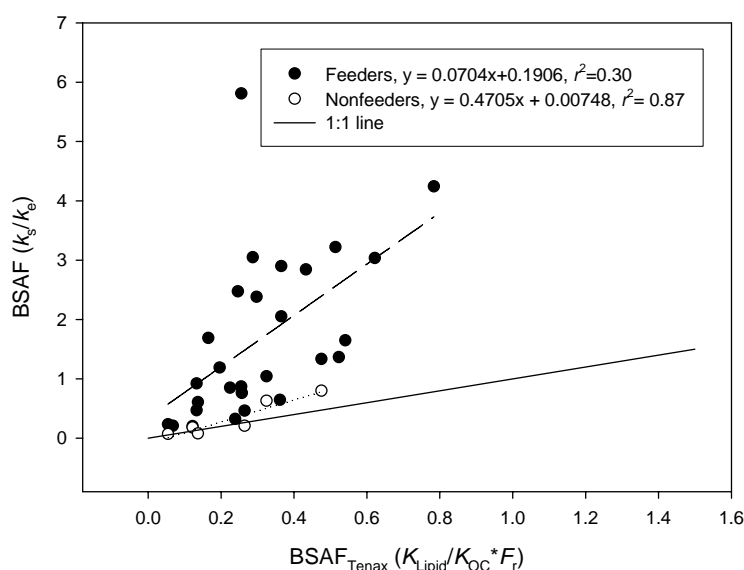

Figure 7. Actual BSAFs versus BSAFs estimated on the basis of extent of rapid desorption (F_r determined by the Tenax method), lipid-water partitioning coefficient (K_{Lipid}) and the organic carbon-water partitioning coefficient (K_{OC}). Symbols represent the combined data from articles I, II and III. The dash line (- - -) represents linear regression for feeding worms (closed symbol), the dotted line (⋯) represents linear regression for non-feeding worms (open symbol) and the solid line represents the 1 to 1 line.

Tenax applicability for measuring bioavailability in field-contaminated sediments

Desorption kinetics determined using the Tenax extraction method were also used to assess the bioavailable fraction in field-contaminated sediments from River Kymijoki sediments (S2) that had accumulated over the course of time, from years to decades (article IV). However, Tenax extraction (F_r ~1-8%) was not found to be a relevant estimate of the bioavailable fraction of "superlipohilic" PCDEs/Fs and PCDEs in field-contaminated sediment samples. The bioavailability estimates of PCDD/F/Es in the oligochaete based data set reported by Lyytikäinen et al. (2003b) had no connection with the rapidly desorbing fraction (article IV). On the other hand, there was a relationship between F_r and semi-permeable membrane device sediment accumulation factors (SSAFs) (article IV). This implies that animals may attain a steady state that does not reflect the exact desorbing fractions as observed previously with spiked PAHs and PCBs (Leppänen et al., 2003). On the other hand, it has been shown that both Tenax and solid phase microextraction (SPME) approaches were useful surrogates for bioaccumulation of PCB in contaminated field sediments (You et al., 2007), which indicates that bioaccumulation and desorption are related in contaminated sediments. This argument is also supported by a decreasing trend in accumulation in SPMDs (Lyytikäinen et al., 2003a) and a decreasing trend in desorption (article IV) with increasing lipophilicity of chemicals. However, it should be noted that the processes governing desorption and bioaccumulation in field-contaminated sediments may be even more complicated and can vary from site to site and from chemical to chemical within a site. Thus more work on the sorption-desorption kinetics of hydrophobic organic pollutants (e.g different chemicals, different sediments) is needed in order to determine clearly the connection between desorption and bioavailability in field circumstances.

4.3. Freely dissolved pore water concentrations as a factor explaining bioavailability

In this study, tissue concentrations of spiked PCB-77 for *L. variegatus* were quite predictable when based on freely dissolved pore water concentration (article III), which is in accordance with the equilibrium partitioning theory. This means that it should be possible to estimate steady-state hydrophobic organic chemical concentrations in sediment-inhabiting biota on the basis of chemical concentrations in pore water and bioconcentration factors (C_w*BCF) (Kraaij et al., 2003). At very high concentrations, however, the solubility limitations of chemicals may hamper prediction for tissue concentrations. The POM method (a non-depletive method) may underestimate bioavailable concentrations when sediments contain very high concentrations of chemicals with low solubility limits, because water solubility limits the freely dissolved chemical in pore water (Lake Kuorinka, arrow in figure 4 in the article III, arrow in figure 8). Further, the POM method does not take the organisms' feeding behaviour into account either. The observed high tissue concentration in S6 may be due to the organisms' active feeding behaviour (ingestion of sediment) compared to the tissue concentration predicted by freely dissolved pore water concentration (Lake Höytiäinen, arrow in figure 4 in the article III). The finding is especially noteworthy in the biomagnification process, when higher rates of dietary intake produces higher steady-state concentrations in the organisms that are essentially larger than would be predicted by uptake from water alone. Nevertheless, these findings do suggest that freely dissolved pore water concentrations can be seen as a successful, relatively easily defined parameter for the bioavailable compartment.

Bioaccumulation estimations based on freely dissolved pore water concentration (BSAF$_{POM}$)

The present results strongly support the notion that bioaccumulation factors of spiked hydrophobic compounds can also be estimated on the basis of freely dissolved aqueous concentrations. Calculated BSAF$_{POM}$ (Equation 9) slightly overestimated the actual BSAF for PCB-77 at various exposure concentrations (Figure 8). Instead, data based on PCB-77 and BDE-47 bioaccumulation studies with *L. variegatus* in various (n=20) river sediment samples from central Europe strongly support the equilibrium theory (Figure 9) (unpublished data). Thus the EqP theory successfully describes the bioavailability of sediment-associated hydrophobic compounds, if sequestration is taken account (Kraaij et al., 2003), because decline in bioavailability results from the compounds becoming sequestered. As pore water concentrations are affected by sequestration, the bioaccumulation can be described as a partitioning process between pore water and organisms. However, BCF obtained from the literature may cause some uncertainty in bioavailability estimates. Nevertheless, BSAF$_{POM}$ successfully served as a superior surrogate for bioavailability estimates than BSAF$_{Tenax}$ (Figures 7, 8, 9). As a result, the EqP theory might be also workable for risk estimation purposes.
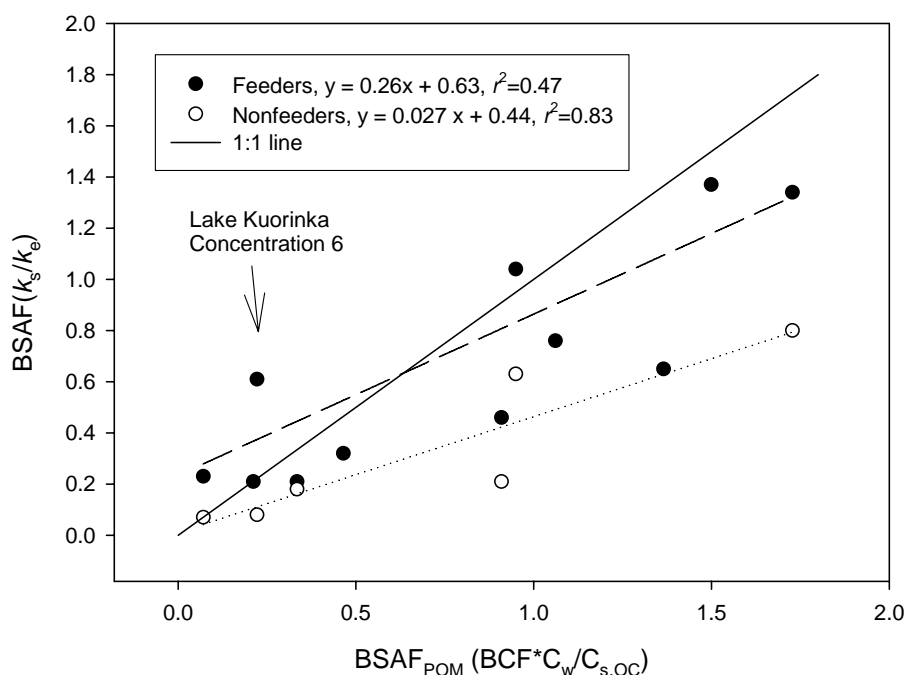
Figure 8. Actual biota-sediment accumulation factors (BSAF) for tetrachlorobiphenyl (PCB-77) based on uptake kinetics and BSAF$_{POM}$ estimated on the basis of freely dissolved aqueous concentration (determined using POM methods), bioconcentration factor (BCF) and organic carbon normalised chemical concentration (C$_{s,OC}$). Solid symbols represent feeding oligochaetes and open symbols represent the non-feeding oligochaetes in different exposure concentrations (data from article III). The dash line (- - -) represents linear regression for feeding worms (closed symbol), the dotted line (···) for non-feeding worms (open symbol) and the solid line represents the 1 to 1 line.
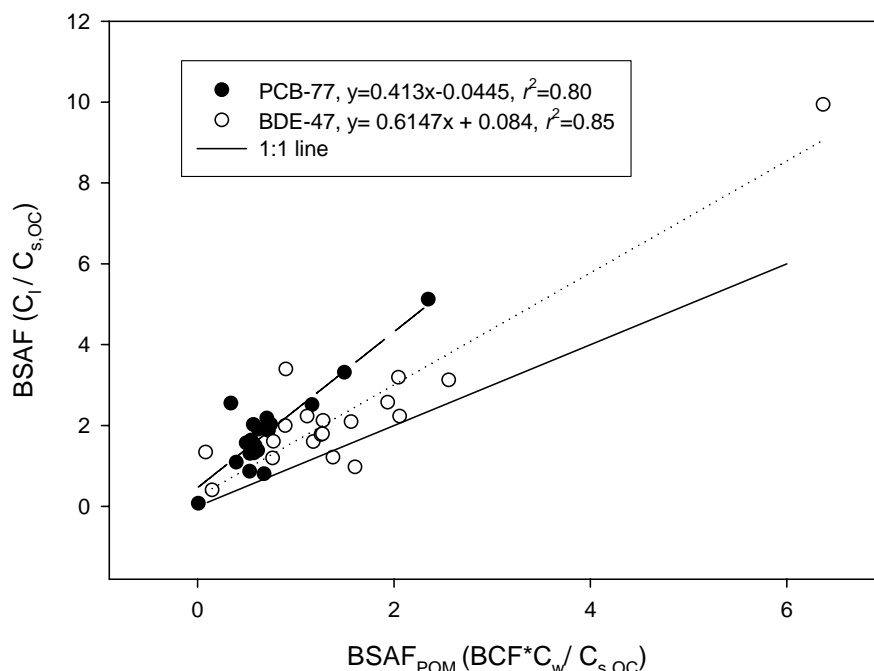
Figure 9. Actual biota-sediment accumulation factors (BSAF) based on concentration in organism (C_l) and sediment ($C_{s,OC}$) and BSAF$_{POM}$ estimated on the basis of the freely dissolved aqueous concentration (determined using the POM method), bioconcentration factor (BCF) and organic carbon normalised chemical concentration ($C_{s,OC}$) in 20 different sediments. Solid symbols represent tetrachlorobiphenyl (PCB-77) and open symbols represent tetrabromodiphenyl ether (BDE-47) exposed oligochaetes (unpublished data). The dash line (- - -) represents linear regression for PCB-77, the dotted line (···) for BDE-47 and the solid line represents the 1 to 1 line.

5. IMPLICATIONS FOR THE RISK ASSESMENT PROCESS

The findings of this thesis show that the measurement of the desorbing fraction (e.g. F_r) or freely dissolved concentration in pore water (C_w) can give a better estimation for the bioavailable fraction than does total concentration and thus could improve the realism of site-specific ecological risk assessment. Especially the equilibrium extraction methods (such as POM) appear to be useful and promising tools for ecological risk assessment. Based on present data, bioaccumulation can be determined mainly by pore water concentration and this supports the idea that the EqP theory might be applicable also for risk estimation purposes. For example, equilibrium partitioning benchmarks (ESB) are bulk sediment concentrations derived from the concentration in pore water and sediment organic carbon (Sample et al., 1998). Thus EqP can be used to calculate ESB toxicity units for assessing levels of contamination (USEPA, 2003). The sediment benchmarks are chemical concentrations in sediment that can be linked to adverse effects on benthic organisms and are helpful in determining whether contaminants in sediments require further attention. However, equilibrium passive samplers have been tested in field circumstances in only a few cases (Cornelissen et al., 2008). Thus, so far, inexpensive passive

sampling methods can be recommended for risk assessment of field-contaminated sediments in combination with real bioaccumulation studies in order to calibrate and verify results. Also further modifications of the models and techniques are still needed to improve understanding of a system where chemistry and biology interact. A recent application of equilibrium sampling devices is the introduction of the chemical activity concept (Reichenberg and Mayer, 2006). Theoretically, equilibrium sampling devices could be used to estimate chemical activities in sediment-animal systems, which would indicate the status of equilibrium in a given system.

6. CONCLUDING REMARKS

- Sediment and chemical properties affected the bioavailability of sediment-associated model compounds, but this can be to some extent be described by desorption-related phenomena. However, the bioavailable fraction can not be interpreted solely by reference to the size of the desorbing fractions (e.g. F_r).
- The freely dissolved aqueous concentrations seems to give a more precise estimate for the bioavailable fraction of various hydrophobic chemicals than the traditional total concentration in sediment and thus could improve the accuracy of the risk assessment process.
- The equilibrium extraction method based bioavailability estimate (BSAF$_{POM}$) was a successful approach to estimating observed BSAF.
- However the feeding behaviour (sediment ingestion) of worm may generate an additional bioavailable

fraction that cannot be predicted from the rapidly desorbing fraction or freely dissolved pore water concentration.
- Tenax extraction (F_r ~1-8%) did not prove a relevant estimate for the bioavailable fraction of PCDD/Fs and PCDEs in field-contaminated sediments.

Need for further investigations
- More work on the sorption-desorption kinetics of hydrophobic organic pollutants in field contaminated sediment are needed. For example, broader desorption data (e.g different chemicals and sediments) are needed to determine the connection between desorption and bioavailability in field circumstances.
- The relationship between freely dissolved chemical concentration and bioavailability should be investigated more thoroughly in field-contaminated sediments.
- The effect of processes in the digestive track of organisms on the bioaccumulation of sediment particle-associated contaminants should be studied. These processes appear to facilitate the release of contaminants from the sediment particles in chemical-specific ways.
- The link between environmental concentration and toxicity should be examined more thoroughly. For example, the applicability of passive sampling methods for measuring the toxicity of sediments should be explored.

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