Sorption of Micropollutants to Natural Aquatic Particles

CENTRALE LANDBOUWCATALOGUS
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SORPTION OF MICROPOLLUTANTS TO NATURAL AQUATIC PARTICLES

Sorptie van microverontreinigingen aan natuurlijke aquatische deeltjes

PROEFSCHRIFT

ter verkrijging van de graad van doctor
in de landbouw- en milieuwetenschappen,
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WAGENINGEN

The research described in this thesis was carried out at the Department of Nature Conservation, Water Quality Management Section, Wageningen Agricultural University, P.O. Box 8080, 6700 DD, Wageningen, The Netherlands.

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STELLINGEN

1. De door Gschwend en Wu gehanteerde uitdrukking voor de partitiecoëfficiënt van hydrofobe microverontreinigingen (Kp^{true}) is onjuist.
   Gschwend P.M. and S.C. Wu, (1985), Environ. Sci. Technol., 19:90-96, dit proefschrift

2. Bij het gebruik van distributie- of partitiecoëfficiënten in waterkwaliteitsmodellen wordt de rol van variaties in de sediment- of zwevend slib-samenstelling ten onrechte buiten beschouwing gelaten.
   dit proefschrift

3. Bij de interpretatie van desorptiesnelheidsconstanten voor verschillende adsorbentia houden Autenrieth en DePinto ten onrechte geen rekening met verschillen in gas debiet en vaste stof/vloeistof ratio.
   Autenrieth R.L and J.V. DePinto, (1991) Environ. Toxicol. Chem., 10:857-872.

4. Het gebruik van de evenwichts-partitie benadering voor hydrofobe organische microverontreinigingen in waterkwaliteitsmodellen is vaak onterecht.

5. De biologische beschikbaarheid van microverontreinigingen wordt teveel gezien als een stofeigenschap.

6. De door Seedorf en Assmann ingevoerde aanduiding "sterol carrier protein-x" voor het 58 kDa grote eiwit dat de gehele sequentie van sterol carrier protein-2 bevat is misleidend zolang het vermogen van deze eiwitten om sterolen te binden niet is aangetoond.
   Seedorf U. and G. Assmann, (1991), J. Biol. Chem., 266:630-636.

7. In een land waar kerk en staat gescheiden zijn, dient het gelijkheidsbeginsel te prevaleren boven de vrijheid van godsdienst.

8. Het belang van vakpublicaties ten opzichte van publicaties in internationale tijdschriften wordt onderschat.

9. Publicaties in *The Journal of Irreproducible Results* dienen in een beoordeling van onderzoekskwaliteiten buiten beschouwing te worden gelaten.

10. Het doorgaans ovationele applaus na concerten doet vermoeden dat de blijdschap over de afloop groter is dan die over de kwaliteit van het gebodene.

11. Tuinieren is natuurbeheer en andersom.

12. De verplichting tot het leveren van stellingen voor het verkrijgen van de doctorsgraad dient te worden afgeschaft.

Stellingen behorende bij het proefschrift van A.A. Koelmans:
Sorption of micropollutants to natural aquatic particles.
Wageningen, 11 februari 1994

to boldly go were no one has gone before..

Aan mijn ouders
Voor Bernadette

CONTENTS

Chapter 1

SORPTION OF MICROPOLLUTANTS TO NATURAL AQUATIC PARTICLES: INTRODUCTION AND OVERVIEW

SORPTION OF MICROPOLLUTANTS TO NATURAL AQUATIC PARTICLES: INTRODUCTION AND OVERVIEW

1.1 Introduction

As great advances in chemical technology have been made throughout the world in the last decades, increasing concentrations of chemical substances originating from industrial sources and other human activities have been detected in air, water and soil. The elevated concentrations and subsequent bioaccumulation of many substances, have given rise to environmental and ecotoxicological effects, not only in industrial regions but also on the global commons, such as the Antarctic, the Arctic, and remote nature reserves [1].

A number of hydrophobic organic compounds (HOCs) and heavy metals are implicated in environmental contamination. Because these pollutants occur in the environment at relatively low concentrations, they are commonly referred to as micropollutants. The fate of micropollutants in lakes or rivers depends on physical transport, physico-chemical distribution, and transformation processes. Characteristics of the aquatic system as well as the properties of the chemical in question determine the rate and extent of general processes like transport by air and water flows, sedimentation, resuspension, evaporation or (photo)-chemical degradation [2,3]. Another important process is sorption to aquatic particles: sediments or particles in the water column, which is the subject of this thesis. Here, the general term *sorption* refers to all processes which cause the removal of a chemical species from an aqueous solution to a contiguous solid phase [4].

Suspended and settling particles have been recognized as important scavengers for organic and inorganic micropollutants [5,6]. As such, they have strong influence on the residence times and geochemical cycling of these substances [7]. Several sediment trap and suspended solid studies have demonstrated that the vertical flux of particulate matter is one of the most important natural removal mechanisms for organic and inorganic contaminants [5,6,8,9]. These studies also show that among the constituents of settling materials in lakes, planktonic particles and detritus are the dominant vectors for trace metals and hydrophobic organic compounds. Besides an effect on transport processes, accumulation in settling solids also affects the bioavailability of micropollutants: the extent to which a contaminant is accumulated determines the concentration in solution and, consequently the potential for transport in the water column or uptake by organisms.

1.2 Purpose of this thesis

The purpose of the work described in this thesis was to investigate the equilibrium and kinetics of sorption of HOCs and heavy metals to natural aquatic particles such as sediments and suspended solids. Special attention was paid to the role of phytoplankton and detritus in the scavenging of micropollutants.

To allow the possible validation of laboratory results, the study consisted of laboratory sorption experiments, as well as the interpretation of field data. The research was performed in the framework of an assessment of management strategies for protection of Lake Volkerak/Zoom by the Dutch Institute for Inland Water Management and Wastewater treatment (RIZA). Therefore, natural adsorbents and field data from Lake Volkerak/Zoom were used. When necessary, experimental conditions were attuned to the conditions in the lake.

In the following paragraphs of **Chapter 1**, an overview of the literature on micropollutant sorption to sediments and phytoplankton is given. The aspects of sorption which are not well documented and are the subject of this research, are identified. **Chapter 2** describes a study on the relationship between adsorbent characteristics and contaminant concentrations for settling and suspended solids in Lake Volkerak/Zoom. A set of field data obtained in a routine monitoring program, was interpreted using statistical techniques. A selection of sediment and suspended solids samples obtained in this program, was used for sorption studies in the laboratory (**Chapters 3 - 5**).

A problem in the determination of HOC distribution coefficients in the laboratory is the impossibility to separate the solid phase completely from the aqueous phase [10]. To obtain meaningful distribution coefficients the influence of this artefact must be quantified (**Chapter 3**). In **Chapter 4** the relationship between suspended solid characteristics and distribution coefficients for cadmium and a chlorobenzene congener is described. **Chapter 5** focuses on the HOC desorption kinetics for the same type of particles.

Because planktonic particles and detritus are a constituent of natural suspended solids, the results reported in the chapters 2 - 5 also allow the evaluation of the role of phytoplankton as scavengers of micropollutants. Further, several aspects of biosorption to algae, were explored in detail by laboratory experiments with algal cultures (**Chapters 6 - 8**).

In **Chapter 6** the temperature dependency of the bioconcentration factor (*BCF*) of some chlorobenzene congeners for phytoplankton is discussed. When phytoplankton decomposes, this concentration factor may change. The influence of decomposition on chlorobenzene (bio)sorption characteristics, and the differences between algae, detritus and sediments is described in **Chapter 7**. Measurements on the influence of chlorinity and algal decomposition on distribution coefficients for three heavy metals are presented in **Chapter 8**.

1.3 Sorption of HOCs to sediments

Reviews on HOC sorption to sediments were published by Karickhoff [11], Weber and Miller [12,13] and Brusseau and Rao [14,15]. Sorption of organic micropollutants to natural aquatic particles depends on both sorbent and sorbate properties. Because natural particles are heterogeneous, probably the most important sorbent characteristic is their chemical phase composition. Typically, sediments contain mineral phases such as clays, quartz, feldspars, amorphous aluminosilicates, iron- and manganese (hydr-)oxide coatings, carbonates, and organic matter originating from decomposed animal, plant, algal and bacterial remains, or the aggregation of lower molecular weight organics [16].

Equilibrium sorption of HOCs has been found to vary with contaminant hydrophobicity, as parameterized by the octanol-water partition coefficient K_{ow} or aqueous solubility, and is commonly considered as a partitioning process in which the sorbate permeates into the three-dimensional network of the sorbent organic matter [15,17]. Among others, particularly Chiou [18,19] and Karickhoff [11,20] provided evidence for the equilibrium partitioning model: (a) the linearity of sorption isotherms over a wide concentration range; (b) the existence of an inverse, linear relationship between solute aqueous solubility and partition coefficient; (c) a low and exothermic heat of sorption; (d) the absence of competitive sorption when solutes are present in mixtures, and (e) the linear relationship of the partition coefficient with the organic matter content of the solids. The partitioning model implicitly assumes that HOCs have equal affinities for all particulate organic matter and that sorption rates are rapid, and has been able to explain a large amount of data for sorption of hydrophobic (nonionic) organic contaminants by a wide variety of natural sorbents. However, in several situations the equilibrium concept fails to describe experimental and field data on sorption of HOCs. First, limitations arise when organic matter fractions are so small that partitioning no longer dominates over sorption to the mineral constituents [11,21]. Second, in aquatic systems sorption may not be at equilibrium which was demonstrated in several recent studies (e.g. [22,23]). Sorption kinetics is found to be slower for more hydrophobic compounds [14,24-27] and may have time scales of months to years [25,27]. Recent work of Brusseau and co-workers [17] provided strong evidence that intraorganic matter diffusion is the responsible process for retarded sorption. Third, laboratory partition coefficients vary with the solid/water ratio [28-32]. One plausible explanation is the experimental artefact of incomplete phase separation. As ideally partition coefficients are measured with regard to pure water, in practise dissolved organic matter and non-separable particles (e.g. colloids) remain in the aqueous phase and increase the apparent solubility of the chemical in consideration [10,33-36]. As a result, partition coefficients are underestimated. The extent of underestimation is dependent on sorbate and non-separable phase properties and on the sediment/water ratio (**Chapter 3**). The mobilization of HOCs due to binding to humic or colloidal materials is not only encountered in the laboratory, but is operative in natural aquatic or soil systems as well [37-42]. Besides incomplete phase separation, other mechanisms are likely to contribute to the variation of the partition coefficient with the sediment/water ratio, such as: particle induced desorption [32], changes in solids aggregation or chemical reactions such as mineral dissolution or precipitation [43]. Fourth, several studies have shown that different types of organic matter have different partition coefficients (K_{oc}) [44-49]. In these studies, sediments or soils of different origin are compared. However, it is not clear whether and to what extent mineralization of fresh biogenic material from one source, changes the partition coefficient (**Chapter 7**)

1.4 Biosorption of HOCs to phytoplankton

The biosorption of HOCs to phytoplankton was reviewed more than ten years ago by Butler [50] and Baughman and Paris [51], and more recently by Swackhamer and Skoglund [52]. Usually the extent of biosorption at equilibrium is quantified by the bioconcentration factor *BCF* which is the ratio of sorbed and dissolved states of the hydrophobic chemical. The *BCF* is often normalized to the fraction lipid in the cells, analogous to the carbon normalized water-particle partition coefficient, K_{oc}. As for sediments, in many studies equilibrium biosorption of HOCs to phytoplankton has been found to vary linearly with contaminant hydrophobicity, as parameterized by the octanol-water partition coefficient K_{ow} [51-57]. Mainly because of this observation biosorption to phytoplankton or to microorganisms is generally considered a partitioning process. However, in these studies, equilibration times typically were several hours, linear relationships of $\log K_{ow}$ versus $\log BCF$ had slopes less than one, and mostly chemicals with $\log K_{ow} < 7$ were used [52]. In recent work of Swackhamer et al [58,59] increasing slopes of $\log K_{ow}$ versus $\log BCF$ plots with equilibration time (up to 20 days) and a lack of consistent $\log K_{ow}$-$\log BCF$ relationships for $\log K_{ow} > 7$ were reported for a suite of 40 polychlorobiphenyls (PCB). This suggests that in many studies equilibrium may not have been reached and that HOC uptake, at least for the more hydrophobic HOCs, is slower than commonly assumed. The slow approach to equilibrium may partially result from algal growth. Rhee [60] studied uptake of a PCB in continuous cultures (turbidostat) and found steady state cellular PCB concentrations after 4 - 6 days, at growth rates of 0.2 -

0.6 d^{-1}, which confirms the slow approach to steady state. Another approach may be to test the log*BCF* - logK_{ow} linearity at low-growth conditions (**Chapter 6**). Further support for the partitioning model are the linear biosorption isotherms reported by several authors [61,62] and the absence of competition effects [63]. Data on isotherm linearity are somewhat conflicting because some other authors report non-linear sorption [64]. This may be caused by the contribution of other sorption mechanisms than partitioning. According to Wang [65], for HOCs with $K_{ow} < 1000$ a Langmuir type surface sorption may become significant. Another explanation for non-linear isotherms is incomplete equilibrium.

Several researchers compared live with dead microbial biomass to asses the possible role of active processes in the bioaccumulation. They found that biosorption is the same on live and dead cells [51,66], or somewhat greater on dead cells [67] or somewhat greater on live cells [68]. However, most of them conclude that uptake is a passive process [52]. The greater sorption on dead cells is explained from greater loss by excretion by live cells, or by cellular alterations by the killing of the cells.

Also data on the organic matter pool responsible for HOC uptake are conflicting. Several authors report that biosorption is a partitioning process to the lipid fraction of the cells [66]. In other studies *BCF* values showed no or poor correlation with lipid content [59,62,69]. Autenrieth and DePinto [62] studied the relationship between *BCF* and lipid content as well as organic carbon fraction and found no significant correlation in either case. This is probably caused by experimental artifacts such as incomplete equilibrium or differences in lipid composition, or by the contribution of other organic matter fractions than lipid.

For the analogous HOC partitioning between water and fish, and water-octanol, a significant temperature dependency was found by Opperhuizen [70]. For sediment to water partition coefficients, literature data are somewhat conflicting. Horzempa et al. [71] found increased sorption of a PCB at increasing temperatures. Szecsody et al [72] found decreased sorption of chlorobenzenes to a model soil with increasing temperatures. In a more recent study, no significant variation of sorption of chlorobenzenes with temperature was found [73]. The question is whether the way in which the partitioning of these pollutants to algal organic matter responds to temperature changes, is similar to fish-fat or, on the other hand similar to sediment-type organic matter (**Chapter 6**).

Several authors suggest a two-step uptake mechanism with a fast initial sorption to the surface, followed by slower uptake in the cells [52,62,67]. However, to date, detailed studies on biosorption and desorption kinetics for phytoplankton are scarce and fragmentary. Tsezos and Bell [67] tried to find evidence for the uptake mechanism by comparing the HOC content of cell walls to that of whole cells which were at sorption equilibrium. Because the cell walls accounted for 16-49% of the total amount of sorbed HOC they conclude that besides the walls, other cellular components contribute to the biosorption process. This was confirmed by Herman and co-workers who studied HOC distribution over cell walls, microsomes and whole cells [57]. However, HOC distributions at equilibrium do not provide information on uptake mechanism. Better support for the two-step mechanism comes from studies in which fast initial, followed by slower sorption is observed from uptake or depuration experiments (e.g. [52,62]). Experiments by Lederman and Rhee [69] showed different initial uptake rates for cells that were treated differently, which indicates that surface type is important in the initial stage of sorption [52]. Whereas most studies used batchwise equilibration and phase separation by filtration or centrifugation, Autenrieth and DePinto [62] were the first to study desorption from phytoplankton with a gas purge method. They interpreted the desorption data in terms of an empirical first order two-compartment model. Although their results support the plausibility of a two-step desorption mechanism, a mechanistical approach allowing the calculation of rate constants which can be compared for different sorbents (e.g. algal species, sediments, detritus) is to be preferred (**Chapter 7**).

1.5 Sorption of HOCs to suspended and settling solids

In many aquatic systems, suspended or settling solids are complex mixtures of planktonic particles, detritus and/or resuspended sediments. Several authors report on differences between sorption to sediments as compared to biosorption to phytoplankton or on simultaneous competitive sorption to phytoplankton and sediments. Powers et al [74] and Nau-Ritter et al [75,76] exposed phytoplankton cells to PCB contaminated sediments and mineral particles, and reported PCB transfer from particles to water and subsequently to the phytoplankton cells. Autenrieth and DePinto [62] performed competitive sorption tests in which a hexachlorobiphenyl originally sorbed to sediments was released to be taken up by algae. Weber and co-workers [68] report larger K_p values for algae and bacteria than for sediments. Organic carbon normalised partition coefficients (assuming a 40% carbon content for algae) were about equal. Oliver [23] compared K_{oc} values for suspended solids and algae which were calculated from field samples. For PCBs with $\log K_{ow} > 5.5$, he found algal K_{oc} values one order of magnitude higher than those for suspended solids, assuming a 50% organic carbon content for the algae. It must be noted that field data often do not refer to sorption equilibrium, and that sorption equilibration time may be different for algae than for sediments. Smets and Rittmann [64] studied trichloroethene ($\log K_{ow} = 2.88$) sorption to algae. They compared their *BCF* values on a dry weight basis, with organic matter normalised partition coefficients (K_{om}) which where calculated using empirical $\log K_{om}$-$\log K_{ow}$ relationships reported by other researchers, using other methods. The values for the algae were one order of magnitude higher than those for sediment or soil organic matter. Although these studies prove the sorption potential of algae and suggest that K_{oc} differences between sedimentary organic matter and planktonic organic matter may exist, the results are difficult to interpret as long as different (non)equilibrium situations, or results obtained with different methods are compared, or as long as organic carbon content is estimated instead of measured. We are not aware of any previous studies on HOC sorption to suspended solids containing planktonic particles (**Chapter 4, 5**) or on the effect of decomposition of phytoplankton on sorption characteristics (**Chapter 7**).

Besides sorption equilibrium, kinetics are different for different particle types. Autenrieth and co-workers [62] found hexachlorobenzene desorption from a sediment to be slower than from phytoplankton. In another study [77], Autenrieth et al report differences in PCB desorption kinetics among sand, bentonite, activated carbon and waste activated sludge. The microorganisms released PCB much slower than sand and bentonite. Such studies show the characteristics of desorption for the different particle types. However, because particles often exist in the water column as complex mixtures or aggregates, measurements on the desorption from natural suspended solid mixtures may yield useful information (**Chapter 5**).

1.6 Sorption of heavy metals to sediments

The sorption of heavy metals to sediments was reviewed by Honeyman and Santchi [78], to soils by Evans [79] and to organic matter by Sposito [80], and for all these sorbent types by Birkett and co-workers [81]. The surfaces of sediments contain sites that are neutral, negatively or positively charged. Adsorption of trace metals to sediments may involve complexation reactions with the surfaces of mineral and organic constituents. Besides, metals may be retained by precipitation reactions resulting in secondary mineral phases. If the adsorption proceeds beyond the formation of a monolayer, then the distinction between adsorption and precipitation is less clear. Hydrolyzable elements such as the transition metals and the rare earths, can form inner sphere complexes with oxides, oxyhydroxides, and hydroxides, and thus are very strongly held to sediments through ligand exchange reactions [79]. Complexation with organic matter is important for metals that form strong associations with oxygen and sulphur atoms, such as most hydrolyzable metals. In general, natural adsorbents are heterogeneous and contain adsorption sites with a continuous distribution of sorption affinities [78,82,83].

Sorption to sedimentary surfaces is often described on a molecular level with models as the surface complexation model (SCM) [78,84,85] or the surface precipitation model (SPM) [86-88]. Although these models successfully describe metal sorption to model phases over wide concentration ranges, to date, the applications of this type of models have been restricted to model phases such as metal oxides. In contrast, Oakley et al [89] and Davies-Colley [90] have presented a simple model for the distribution of a trace metal among a number of phases comprising an aerobic sediment. Mathematically, the model is identical with those of complexation and distribution of soluble trace metals among dissolved ligands. It is assumed that parameters such as chlorinity, pH, pE and ionic strength are constant so that conditional equilibrium constants can be used. It is also assumed that the adsorption of the trace metal has only negligible effect on the total concentration of available surface sites. In that case, precipitation and competition between different trace metals can also be neglected, and instead of the site concentration, the fixed concentration of the solid phase can be used. Finally, it is assumed that all sedimentary phases behave independently. According to the model, the distribution of a metal over the different phases of a sediment or suspended particle is a function of the abundance of that phase and its binding ability. According to the literature, the relevant adsorbent characteristics for heavy metal sorption are the contents of organic matter (e.g. phytoplankton), manganese (hydr)oxides, iron (hydr)oxides and clays [89-95]. However, the applicability of Oakley's approach to field data has not been tested (**Chapter 4**).

1.7 Biosorption of heavy metals to phytoplankton

Biosorption of heavy metals to algae, or generally aquatic microorganisms were reviewed by Wood and Wang [96] and Sigg [97]. As for HOCs, for live phytoplankton usually the bioconcentration factor is used to express the extent of biosorption. In general, the distribution between sorbed and aqueous states is considered as the result of active (metabolic energy-driven) uptake processes into the cells, and binding to cell surfaces [96-98]. The first mechanism is considered unique for live cells, whereas surface adsorption also occurs to dead cells or cell debris. Surface adsorption may be a first step in the eventual total uptake.

Some trace metals are essential for the organisms because they have some biological function. For these elements elaborate transport mechanisms have evolved which are specific and carefully regulated by the cell. Many of the same elements are toxic at higher concentrations and therefore homeostatic mechanisms maintain a proper balance for biological function [96,99]. This means that the stoichiometric composition of algal cell material for the major elements (C, N, P, O, H) may be extended to essential trace metals [6,9]. However, nonessential elements may be mistaken as micronutrients by the cell. A description of the biochemistry or molecular mechanisms is beyond the scope of this introduction, we mention only a general model for uptake [96,97], in which special ligands (often proteins) synthesized by the cell, form high stability complexes with the metal. One type of ligands carries the metal through the cell membrane, while another type binds the metal to the cell surface, or forms a complex in the cell interior. The uptake is further actively regulated by concentration gradients that are established through the complexation reactions, or by energy-coupled channels and pumps. The accumulation of the trace metal by the cell is not at equilibrium, because metabolic activity is responsible for the synthesis of the ligands, as well as the energy-driven channels and pumps. Many chemical parameters influence the metal uptake, e.g. charge, ionic radius, preference for the coordination of metals to certain organic ligands (as expressed by stability constants), coordination geometry or available concentration of ligands and metals in solution. The latter factor is influenced by pH and pE.

Binding of metals to the cell surface is considered through coordination with ligands at the cell surface, such as amino, carboxylic or hydroxo groups [97,100,101]. The surface complexation can be described in a similar fashion as for metal binding to mineral surfaces. Factors that influence the surface complexation are the surface type of the cells, which may depend on the life stage of the cells, the metal type, pH and Eh, and the aqueous speciation of the metal in consideration. Probably because of the many factors involved, metal biosorption is very different among metals and species [102-104]. Because various functional groups have different affinities for the binding of metal ions and thus different stability constants, the affinity spectra approach [105-107] may give the best description of metal binding tendency. The concepts of coordination chemistry have been found to apply to binding to algae. Several researchers found the selectivity of the algal surface for metal ions to vary with the Irvin-Williams order of complexation constants [108]. Fisher [109] successfully correlated metal concentration factors for phytoplankton with solubility products of metalhydroxides.

1.7 Sorption of heavy metals to suspended and settling solids

As is suggested by the model of Oakley [89], sorption to natural suspended and settling solids can be considered as sorption to several competing phases. The relative importance of the phases in the uptake of metals is determined by their abundance and affinity for the metal. Many authors report on the scavenging and solid phase speciation of metals in aquatic systems [16]. Because of the many differences in the characteristics of the aquatic system, such as particle type, flow conditions, pH, pE or temperature, generalisations are not straightforward. Conflicting data have been reported regarding to the relative importance of cadmium adsorption by organic material in soils and sediments ([95] and references therein). Shafer [8] and Sigg [6,9] found algal matter to be the most important carrier for heavy metals in lakes. Davies-Colley [90] reported an important role of organic matter for Cu in marine sediment, but not for Cd. Rauret et al [110] also reported an important role of organic matter for Cu in river sediment, but not for Pb. This means that the fate modeling for a metal like cadmium should not be based on literature data only, but must be supported by data obtained from the system in consideration (**Chapter 4**).

Relatively few studies provide data on the role of detritus as compared to live algae in the scavenging of heavy metals. Fisher and Wente [111], studied the accumulation and subsequent release under dark conditions of metals from marine phytoplankton. They found significant differences in the time course of metal:dry weight ratios for different metals and species. Lee and Fisher [112] studied the degradation and release rates of carbon and metals from phytoplankton debris. They also found that release rates were very different for different metals. For some metals, the release was much slower than the release of C (the mineralization rate), so that for these metals settling of detritus will be an important transport process, while for other metals rapid recycling can be expected. However, their approach did not allow the calculation of equilibrium distribution coefficients for detritus. The question whether distribution coefficients change when phytoplankton mineralizes is very relevant for modeling purposes (**Chapter 8**).

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Chapter 2

MICROPOLLUTANTS IN SUSPENDED SOLIDS OF LAKE VOLKERAK/ZOOM: SEASONALITY AND TRENDS

A.A. Koelmans, W. Makatita, F. Gillissen and L. Lijklema

LIST OF ABBREVIATIONS

DDT = dichloro-diferyl-trichloroethane (insecticide)
CF = continuous flow centrifuge sample
CHL = chlorophyll
COD = chemical oxygen demand
ECD = electron capture detector
GC = gas chromatograph
HCB = hexachlorobenzene
HCBD = hexachlorobutadiene
HCH = hexachlorocyclohexane
HEPO = heptachloroepoxide (insecticide)
HEPTA = heptachlore (insecticide)
HOC = hydrophobic organic chemicals
IC = inorganic carbon, carbonates
ICP-AES = inductively coupled plasma atomic emission spectroscopy
K_{ow} = octanole to water partition coefficient
LOI = loss of ignition
OC = organic carbon
OM = organic matter
PAH = polyaromatic hydrocarbons
PCB = polychlorobiphenyls
QCB = pentachlorobenzene
ST = sediment trap sample

Sampling points:
DM = Dintel River
HD = Hollandsch Diep inlet point
VZ3 = location 3 in Lake Volkerak/Zoom
VZ7 = location 7 in Lake Volkerak/Zoom

MICROPOLLUTANTS IN SUSPENDED SOLIDS IN LAKE VOLKERAK/ZOOM: SEASONALITY AND TIME TRENDS

Abstract- This study describes the 1987 - 1992 time variation of the bulk chemical composition, levels of heavy metals, polychlorobiphenyls and pesticides in suspended and settling solids in Lake Volkerak/Zoom. The relations between solids characteristics and pollutant concentrations in the particles were investigated using correlation and factor-analysis. Heavy metals, except manganese, were associated with clay content of the particles and with organic carbon (OC). OC was mainly determined by phytoplankton growth. Manganese as well as hydrophobic compounds (HOCs) were correlated with OC only. Clay and associated heavy metal content, and organic matter and associated HOC content, showed negative trends on all locations, and a seasonality due to dilution by algal biomass. This dilution also resulted in a lowering of OC normalised HOC concentrations. Settling particles showed higher clay content and higher C/N elemental ratios than suspended solids which points to a larger degree of mineralization. Settling particles had also 1.3 to 6.8 times higher OC normalized HOC concentrations. This may be explained by the different character of the organic matter, by biomagnification or the smaller impact of growth dilution for settling solids.

INTRODUCTION

In aquatic systems, the cycling of heavy metals and hydrophobic organic compounds (HOCs) is often dominated by resuspension, sedimentation and horizontal transport of sediments. The close relationship between pollutant fate and sediment transport is mainly caused by the strong tendency of many pollutants to accumulate in particulate materials. The extent of this accumulation, and the accumulation rate are highly dependent on suspended solid composition. The composition is influenced by several chemical and biological processes which show a strong seasonality. Many laboratory sorption studies address the influence of adsorbent properties on sorption phenomena. In these studies the processes occur under controlled conditions which allows the variation of one factor while the others are kept constant. However, the results obtained under typical laboratory conditions should always be compared with those obtained in field studies.

This study concerns the temporal and spatial variation of heavy metal, arsenic, polychlorobiphenyl (PCB) and pesticide levels in suspended and settling solids in a freshwater lake and its inflows and relates this variation to changes in particle composition. All data were obtained in a routine monitoring program. The primary aim of this program was to determine concentration levels and trends in the framework of an assessment of management strategies for protection of the lake. The pollution status and the implications for the water quality management have been described recently [1]. A secondary aim of the program, which is the main subject of this paper, was to investigate the relationship between adsorbent properties and pollutant concentrations. In data interpretation special attention was paid to: (a) the relative importance of the different geochemical phases responsible for pollutant scavenging, (b) the effect of organic matter type on sorption of hydrophobic chemicals, and because of the expected eutrophication of the lake (c) the role of phytoplankton. A five year set of suspended solid data for four locations, sampled monthly with continuous flow centrifuges and sediment traps, was examined using statistical techniques.

MATERIALS AND METHODS

Study area

The study area was the new Lake Volkerak/Zoom (The Netherlands) which came in to being in 1987 as a result of a dam closure. After a desalination period of about a year, the previously estuarine section of the Eastern Scheldt has turned into a stagnant freshwater lake. Since then, this lake has mainly been fed by small tributary rivers and by water suppletion from the Rhine/Meuse system. Because of the damming, North Sea water no longer dilutes the incoming river water and concentrations of heavy metals and organic pollutants have increased [2]. It was expected that without preventive measures, the ecosystem would be dominated by phytoplankton [3], and that sediments and organisms would become contaminated.

Lake Volkerak/Zoom consists of two parts: Lake Volkerak in the north, and Lake Zoom which is located in the south (Figure 1). The two lakes are connected by a channel, the Eendracht and form one water system. Morphological data are shown in Table 1. At the northwest of the lake, water from the Hollandsch Diep enters the system. This water is a 3:1 mixture of Rhine/Meuse water and is the most important source of micropollutants. Also at the northwest of the lake, two tributary rivers: Dintel and Vliet drain freely into the northwest of Lake Volkerak and are an important source of fresh water. The Dintel is strongly fed by rainfall and is the second important source of micropollutants. Other sources of pollutants may be atmospheric deposition and shipping.

Sampling and sample storage

Suspended solids were collected monthly in the Hollandsch Diep (HD), the Dintel (DM), Lake Volkerak (VZ3) and Lake Zoom (VZ7), between october 1987 and december 1992 using continuous flow centrifuges (Pennwalt, AS 16). The water was centrifuged at a speed of 1000 l/h and 15000 rpm (13200 g). Teflon sheets were attached to the inner surface of the centrifuge in order to prevent contamination with metals from the walls. The centrifuge samples were immediately frozen, freeze dried and stored at -18 °C. In three of the five years (from april 1989 to december 1991) settling particles were also sampled monthly at locations VZ3 and VZ7 with sediment traps. Six 60 cm long

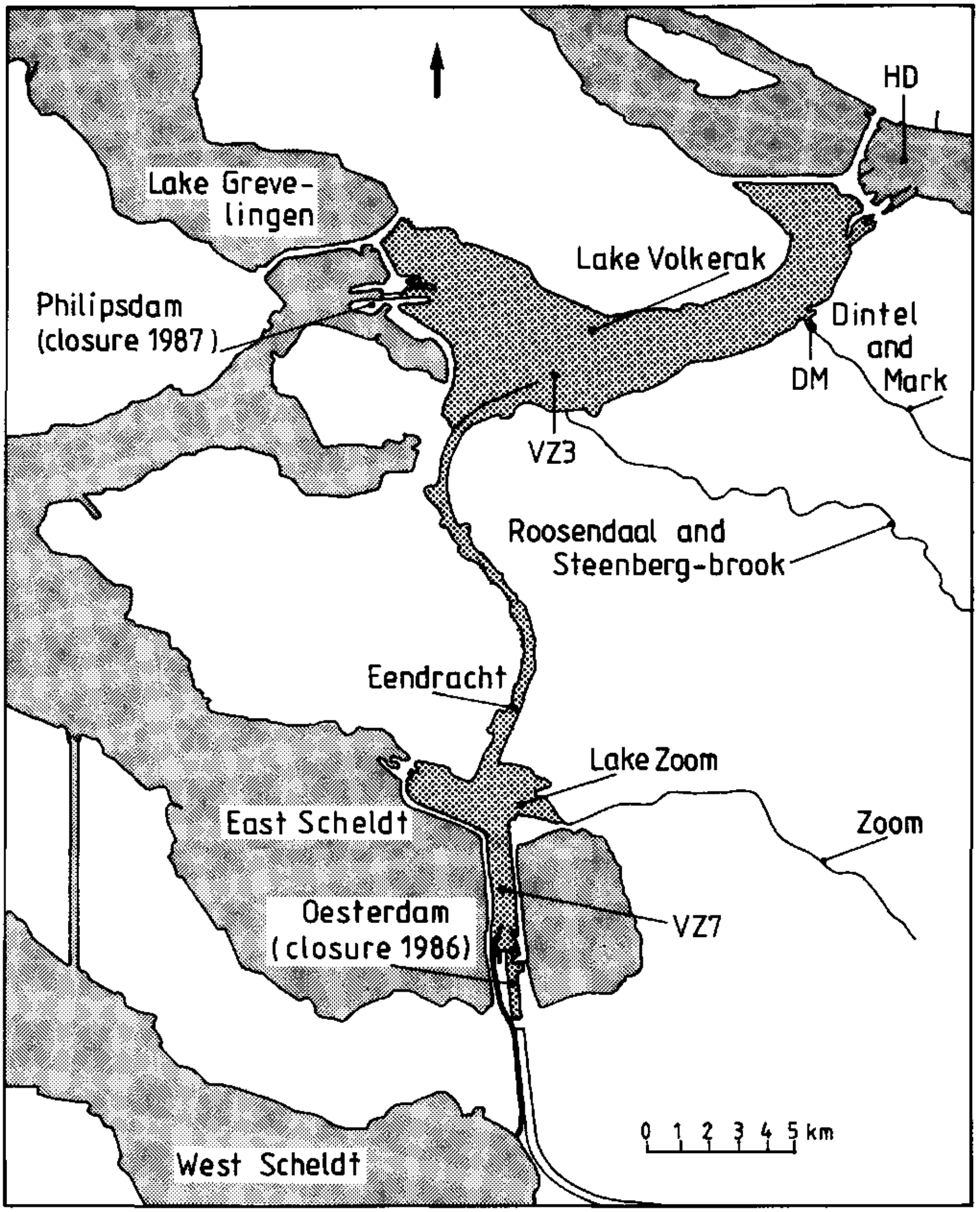

Fig. 1: Lake Volkerak/Zoom and the sampling locations HD, DM, VZ3 and VZ7.

cylindrical traps with $\phi = 6$ cm, collected sufficient material for the subsequent analysis. To minimize the collection of resuspended material, the traps were located 1 m above the bottom sediment. For VZ3 and VZ7 these depths were 7 m and 19 m respectively. The exposure time of the traps was two weeks. After collection of the traps and transport to the laboratory, the suspended material was allowed to settle for 24 hours at 4°C before the overlying water was removed by a siphon. Sediment trap samples were immediately frozen, freeze dried and stored at -18°C.

TABLE 1:
Morphography of Lake Volkerak/Zoom

		Lake Volkerak/Zoom	Lake Zoom
Surface area	(km^2)	45.7	15.5
Volume	(m^3)	238×10^6	80×10^6
Mean depth	(m)	5	6
max. depth	(m)	24	20

Data were taken from [2].

Analysis of settling and suspended solids

All determinations were carried out using freeze dried and homogenized sample material. Total organic carbon (OC) and carbonates (IC) were measured independently with the method described by Begheijn [4]. Loss of ignition (LOI) was measured by heating at 600°C for 3 h. Chemical oxygen demand (COD) was measured as oxidizability by $K_2Cr_2O_7$. Chlorophyll-a (CHL) was extracted with ethanol (80 % V/V) and measured on a Beckman DU-64 spectrophotometer. Total nitrogen and phosphorous were measured after destruction with a mixture of H_2SO_4, Se, salicylic acid and H_2O_2 at elevated temperature on a Skalar San-plus autoanalyzer. The particle size fraction $< 16 \mu m$ was measured with the conventional pipette analysis. The elements Al, As, Cd, Cr, Cu, Fe, Hg, Pb, Mn, Ni, Sc and Zn were extracted from the samples using a HNO_3/HCl digestion mixture. Digestion was at 100°C for three hours. Concentrations in the extracts were measured with ICP-AES (Sc) graphite-furnace-AAS (Cd), flame-AAS (Fe, Mn), the hydride generation technique (As) and the cold vapour technique (Hg). Polychlorobiphenyls (PCB) and organochlorinepesticides were extracted with acetone by repeated vigorous shaking and ultrasonication. Extracts were mixed with diethyl-ether and washed several times with water to remove the acetone. The combined diethyl-ether extracts were dried with sodiumsulphate and concentrated with a Kuderna Danish apparatus to a volume of 5 ml, and subsequently to 1 ml under a flow of clean nitrogen. The extracts were cleaned by passage over a column of deactivated alumina and used for

GC-ECD analysis. A Hewlett-Packard 5890 double column gas chromatography system equipped with two ^{63}Ni electron capture detectors (ECD) was used in chlorobenzene quantisation. Congener separation was accomplished with 50 m, 0.25 i.d., HP Ultra 1 (0.5 μm film thickness) and Ultra 2 (0.33 μm film thickness) columns.

Data analysis

In this study, pollutant concentrations are evaluated for their variation in time and space and for their relationship to particle characteristics. To study variation in time and space, differences in sorption affinity among the particles should be eliminated. This was done by correcting the pollutant concentrations for differences in suspended solid composition. For the heavy elements, the affinity for the particulate material is determined by a few geochemical phases which are mainly associated with the clay minerals [5,6]. Consequently, the metal concentrations can be normalised by division by the clay content. A good alternative which is used in this study, is division by the content of the conservative element scandium [7,8], which is positively correlated with the clay fraction and can be determined relatively easy. For the study of heavy element concentrations in relation to adsorbent characteristics, the original (not normalised) data were used. Ideally, data on the aqueous phase concentrations should be included in the interpretation, but these data were not available. The affinity of suspended solids for HOCs is determined by the organic matter content of the particles [9]. In a recent review of Perlinger and Eisenreich [10] an organic carbon fraction of 0.001 is mentioned as the critical value needed for the partitioning process to dominate over sorption to mineral surfaces. The particles in our study had OC fractions larger than 0.05. Therefore, the contribution of inorganic constituents was considered negligible and HOC concentrations were normalised to organic carbon content. Consequently, the normalised data can be interpreted as concentrations in the organic matter. Because solid components other than organic matter were considered irrelevant, only the OC normalised data were interpreted.

The time series of individual variables were tested for normality (skewness and kurtosis values), seasonality and trend using the software package WQSTAT [11]. For all variables, a distribution significantly different from the normal distribution was found. Therefore, only non-parametric tests were used. Before testing for seasonality, the linear trend was removed using the Sen slope estimate. Subsequently, seasonality was tested on quarterly data using the Kruskall-Wallis test for equal medians among three or more groups of data. The time series of monthly data were tested for trend using the non parametric Kendall tau test. The advantages of the Kendall tau test are that it is applicable to small datasets ($n < 60$) for which normality can not be proven, and that it is relatively insensitive to outliers and missing values [12]. For time series with significant seasonality, the seasonality was removed prior to trend analysis, by subtracting the seasonal means from each data point. The majority of these deseasonalized datasets were not distributed normally either. Correlation and factor analysis were performed using the statistical software package STATGRAPHICS. Correlation analysis was performed using the nonparametric Pearson rank procedure. Standardized factor analysis was performed using Varimax rotation. Other rotation methods (Equimax, Quartimax) were tested but did not yield extra information relevant for the interpretation of the results. To be strictly applicable, the dataset must meet several assumptions of the factor analysis model, primarily that the variables have normal distributions and be uncorrelated. For applications involving statistical testing of hypotheses, the assumptions must be met rather well. However, for the merely descriptive purposes as in this study, larger departures from data structure are tolerable ([13] and references therein).

The type of statistical analysis performed to describe the relationships among the measured variables typically yields rather extensive numerical results. For completeness, most results are tabulated and included in this paper. However, in the following sections only the most relevant observations are considered and a full discussion of all figures is avoided.

RESULTS AND DISCUSSION

Characteristics of suspended and settling solids

The characteristics measured and used for the particles in this study were the concentrations of the major mineral and organic phases measured as total Al, Fe, Mn, chlorophyll, LOI, IC, OC, N and P, the variables indicative for clay content: $\% < 16\mu m$, Al and Sc and the derived molar based elemental ratios: OC/N, OC/P, Fe/P and N/P. The 1987 - 1992 time variations of the most important mineral and organic phases of the suspended solids sampled with centrifuges for the four locations are given in Figure 2. Following van Eck [14] who studied the geochemistry of the Hollandsch Diep in the late seventies, it was assumed that Al is present as Al_2O_3, Fe as Fe_2O_3, Mn as MnO_2, OC as organic matter (OM) with an OM/OC ratio of 2.5, and IC as $CaCO_3$. The weight percentages were calculated using the elemental concentrations and the molar weight for each phase. The difference between the sum of these phases and 100% is mainly explained by the presence of the oxides SiO_2, TiO_2, MgO, K_2O and Na_2O which were not measured in this study, and formally by the trace amounts of metals and HOCs. LOI, being the total amount of carbon dioxide and water liberated from organic matter, carbonates and clays after heating, is not a separate phase and is therefore not included in the construction of Figure 2. For a more detailed description of the mineralogy of the particles found in the study area, we refer to the study by van Eck [14]. The graphs in Figure 2 show a low contribution of organic carbon in winter, whereas the relative contribution of the mineral phases is large. Although formally no conclusions can be drawn about causality, it seems clear that algal growth is the main factor explaining the observed seasonality.

Correlation analysis

The results of the correlation analysis of suspended solid characteristics are presented in Table 2. The analysis shows a strong inverse correlation of the fraction $<16\mu m$, Al and Sc with OC, N and chlorophyll, which confirms the role of algal growth. Generally Sc, Fe and the $<16\mu m$ grain size fraction are positively correlated, which supports the assumptions underlying the heavy metal normalisation procedure. The fraction $<16\mu m$ is not always correlated. This may be due to a lack of available data. Manganese is not correlated with Sc, Fe and the fraction $< 16\mu m$ (VZ3, VZ7), or negatively correlated (HD, DM). In the latter case Mn is positively correlated with CHL, N, OC and to a lesser extent with P.

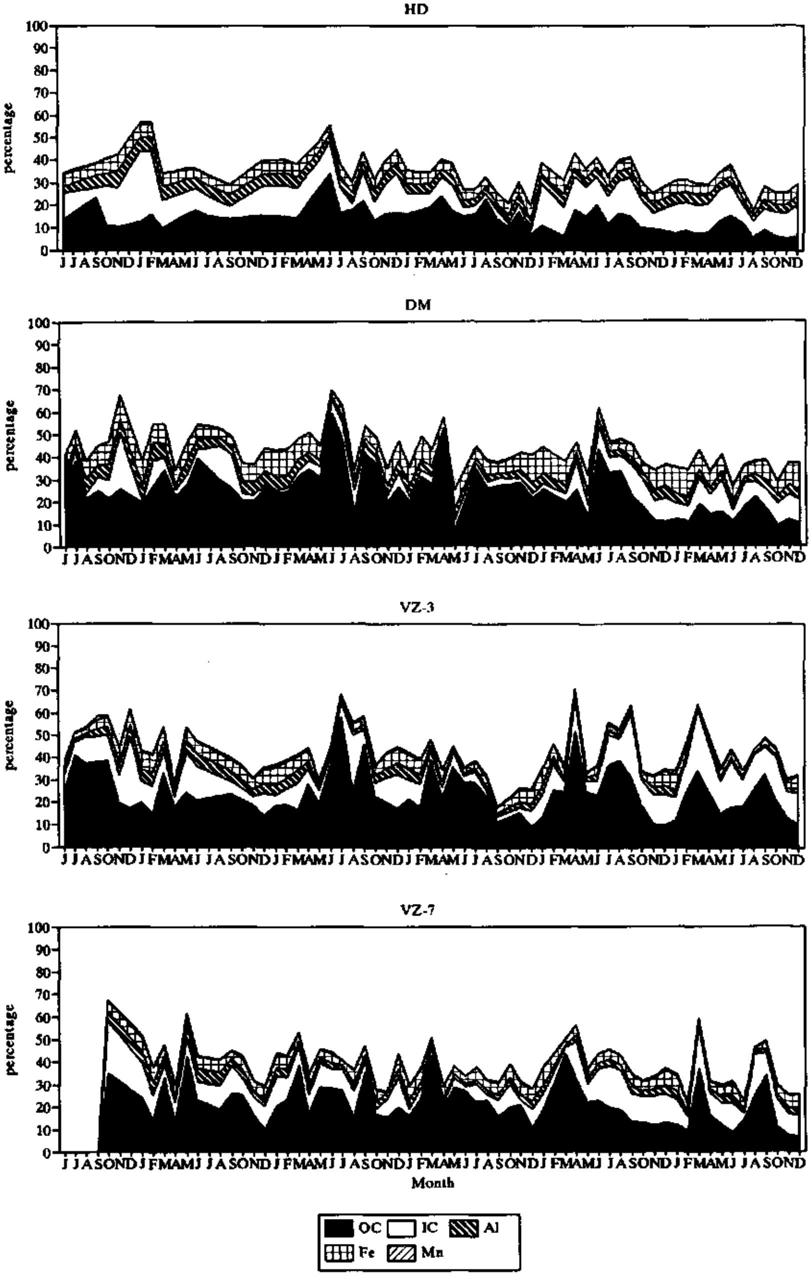

Fig. 2: The June 1987 - December 1992 time variation of the most important mineral and organic phases comprising the suspended solids sampled with centrifuges for four locations in Lake Volkerak/Zoom.

TABLE 2: Pearson rank correlations

	<16	OC	IC	Al	As	Cd	Cr	Cu	Fe	Hg	Pb	Mn	Ni	Sc	Zn	P	N	CHL	OC/N	
		Suspended solids at DM																		
		0.375	-.318	**0.608**	**0.489**	**0.661**	**0.423**	**0.599**	0.280	**0.597**	**0.503**	**-.393**	0.335	**0.355**	**0.397**	0.027	-.318	-.284	**0.622**	<16
			-.267	**-.252**	0.233	0.175	-.097	-.064	**-.373**	0.234	-.176	0.229	**-.301**	**-.432**	**-.361**	0.142	**0.460**	**0.522**	**0.383**	OC
				-.179	-.191	**-.457**	-.107	**-.365**	**-.249**	-.234	-.165	0.137	0.053	-.118	-.116	-.176	0.241	0.248	**-.471**	IC
					0.581	**0.638**	**0.716**	**0.831**	**0.696**	**0.311**	**0.792**	**-.754**	**0.550**	**0.805**	**0.671**	0.156	**-.576**	**-.618**	**0.423**	Al
						0.426	**0.522**	**0.551**	0.115	**0.359**	**0.493**	**-.380**	**0.259**	**0.334**	0.176	0.172	-.035	-.297	**0.301**	As
Suspended solids at HD							**0.429**	**0.775**	**0.515**	**0.337**	**0.447**	**-.581**	0.184	**0.339**	**0.387**	0.028	**-.369**	-.459	**0.598**	Cd
OC	-.215							**0.573**	**0.444**	**0.311**	**0.691**	**-.452**	**0.505**	**0.533**	**0.478**	0.238	**-.439**	**-.548**	**0.394**	Cr
IC	0.660	-.087							**0.686**	**0.387**	**0.722**	**-.707**	**0.434**	**0.697**	**0.568**	0.160	**-.543**	**-.837**	**0.514**	Cu
Al	**0.405**	0.006	**0.364**							**0.050**	**0.591**	**-.751**	**0.504**	**0.728**	**0.777**	0.203	**-.748**	**-.677**	**0.426**	Fe
As	0.032	0.169	**0.293**	**0.431**							0.207	-.102	0.105	0.187	-.049	0.040	-.017	-.066	**0.257**	Hg
Cd	0.041	**0.320**	**0.334**	**0.629**	**0.501**							**-.530**	**0.634**	**0.747**	**0.633**	0.232	**-.484**	**-.575**	**0.396**	Pb
Cr	0.299	0.054	0.207	**0.638**	**0.462**	**0.571**							**-.365**	**-.569**	**-.672**	-.057	**0.642**	**0.799**	**-.485**	Mn
Cu	0.079	0.091	-.201	**0.312**	**0.298**	**0.331**	0.213							**0.577**	**0.531**	0.057	**-.430**	-.471	0.130	Ni
Fe	**0.364**	**-.263**	**0.320**	**0.697**	0.149	**0.408**	**0.400**	0.232							**0.697**	0.148	**-.605**	-.177	**0.304**	Sc
Hg	-.232	0.146	-.224	0.166	**0.296**	**0.389**	0.154	**0.629**	-.060							0.155	**-.618**	**-.703**	**0.345**	Zn
Pb	0.238	0.024	0.133	**0.661**	**0.463**	**0.522**	**0.629**	**0.555**	**0.558**	**0.295**							-.049	0.152	0.108	P
Mn	**-.387**	**0.483**	-.146	**-.611**	-.047	-.233	**-.383**	-.132	**-.705**	-.031	**-.461**							**0.882**	**-.061**	N
Ni	0.286	-.122	**0.356**	**0.589**	**0.413**	**0.392**	**0.365**	**0.312**	**0.640**	0.154	**0.492**	**-.444**							-.407	CHL
Sc	**0.504**	-.242	**0.274**	**0.732**	**0.354**	**0.257**	**0.366**	**0.297**	**0.662**	0.013	**0.588**	**-.499**	**0.476**							
Zn	**0.381**	**-.352**	0.178	**0.413**	**0.404**	0.245	**0.490**	**0.371**	**0.500**	0.220	**0.614**	**-.481**	**0.402**	**0.544**						
P	**-.410**	**0.551**	-.093	-.224	0.139	0.128	**-.381**	0.143	**-.375**	0.232	-.213	**0.585**	**-.265**	-.212	**-.316**					
N	**-.512**	**0.497**	-.147	**-.516**	0.025	-.125	**-.463**	-.117	**-.691**	0.088	**-.486**	**0.854**	**-.433**	**-.471**	**-.478**	**0.744**				
CHL	**-.604**	**0.743**	0.081	-.272	0.121	**0.654**	-.120	-.281	**-.429**	-.062	-.367	**0.703**	-.108	-.132	**-.493**	**0.733**	**0.753**			
OC/N	**0.400**	**0.258**	0.058	**0.597**	0.121	**0.452**	**0.628**	0.221	**0.540**	0.098	**0.610**	**-.554**	**0.335**	**0.354**	**0.305**	**-.354**	**-.671**	-.282		

TABLE 2 (continued): Pearson rank correlations for suspended solids at VZ3 and VZ7

Suspended solids at VZ3

	OC	IC	Al	As	Cd	Cr	Cu	Fe	Hg	Pb	Mn	Ni	Sc	Zn	P	N	CHL	OC/N
<16	-.330	-.219	0.708	0.493	0.444	0.453	0.583	0.700	0.116	0.640	0.164	0.414	0.712	0.544	-.470	-.497	-.050	0.581
OC		-.092	-.324	-.157	-.224	-.114	-.406	-.593	-.217	-.304	-.365	-.321	-.389	-.303	0.591	0.653	0.392	-.013
IC			0.111	-.145	-.052	-.042	-.233	.055	-.167	-.065	-.001	0.244	0.087	0.019	-.015	0.043	-.142	-.196
Al				0.790	0.532	0.656	0.629	0.862	0.307	0.705	0.192	0.473	0.920	0.518	-.536	-.709	-.382	0.653
As					0.528	0.698	0.602	0.736	0.545	0.582	0.173	0.530	0.750	0.373	-.376	-.639	-.077	0.711
Cd						0.465	0.493	0.574	0.262	0.462	0.182	0.389	0.517	0.492	-.295	-.344	-.261	0.236
Cr							0.522	0.586	0.345	0.587	0.090	0.469	0.551	0.380	-.213	-.476	-.449	0.537
Cu								0.704	0.311	0.666	0.329	0.439	0.672	0.499	-.328	-.569	-.099	0.440
Fe									0.361	0.732	0.385	0.623	0.892	0.654	-.632	-.847	-.466	0.605
Hg										0.181	0.132	0.363	0.344	-.010	-.258	-.394	-.050	0.338
Pb											0.312	0.453	0.716	0.718	-.386	-.542	0.029	0.477
Mn												0.333	0.222	0.352	-.131	-.185	-.015	-.079
Ni													0.527	0.495	-.162	-.393	-.426	0.313
Sc														0.536	-.610	-.738	-.221	0.656
Zn															-.290	-.393	-.227	0.283
P																0.714	0.141	-.419
N																	0.596	-.728
CHL																		-.360

Suspended solids at VZ7

	<16	OC	IC	Al	As	Cd	Cr	Cu	Fe	Hg	Pb	Mn	Ni	Sc	Zn	P	N	CHL
OC	-.411																	
IC	0.021	-.114																
Al	0.376	-.197	0.190															
As	0.276	0.142	0.047	0.609														
Cd	-.028	0.040	0.101	0.361	0.261													
Cr	0.293	0.012	-.015	0.545	0.589	0.366												
Cu	0.254	-.366	-.039	0.540	0.236	0.011	0.284											
Fe	0.426	-.441	0.081	0.715	0.320	0.206	0.313	0.667										
Hg	0.185	0.218	-.181	0.316	0.486	0.138	0.306	0.047	0.080									
Pb	0.189	-.108	0.060	0.577	0.418	0.306	0.430	0.612	0.518	0.288								
Mn	0.109	-.173	0.103	0.240	0.097	0.286	0.207	0.364	0.279	0.039	0.495							
Ni	0.164	-.148	0.121	0.341	0.202	0.132	0.232	0.462	0.382	0.266	0.688	0.314						
Sc	0.408	-.324	0.190	0.865	0.407	0.130	0.365	0.644	0.701	0.188	0.580	0.165	0.444					
Zn	0.311	0.026	0.167	0.432	0.212	0.228	0.237	0.371	0.378	0.005	0.697	0.306	0.460	0.440				
P	-.142	0.479	-.130	-.429	-.157	-.011	-.217	-.472	-.643	0.246	-.185	-.106	-.027	-.408	-.104			
N	-.455	0.628	0.006	-.570	-.298	-.050	-.330	-.579	-.692	-.047	-.340	-.209	-.212	-.578	-.052	0.701		
CHL	-.300	0.491	-.177	-.518	-.250	-.193	-.421	-.492	-.632	0.211	-.162	-.144	-.055	-.432	-.206	0.578	0.677	
OC/N	0.161	0.173	-.139	0.539	0.566	0.131	0.479	0.314	0.393	0.421	0.365	0.085	0.204	0.441	0.117	-.319	-.589	-.409

TABLE 2 (continued): Pearson rank correlations for settling solids at VZ3 and VZ7

Settling solids at VZ3

OC	IC	Al	As	Cd	Cr	Cu	Fe	Hg	Pb	Mn	Ni	Sc	Zn	P	N	CHL	OC/N	
	0.196	0.065	-.056	-.078	-.051	-.088	-.249	0.046	-.205	-.330	0.061	-.074	-.033	0.076	0.347	0.135	0.181	OC
		-.383	-.089	-.271	-.351	-.353	-.496	-.073	-.140	-.084	-.061	-.386	0.063	0.128	0.458	0.408	-.084	IC
			0.605	0.162	0.413	0.477	0.730	0.188	0.262	0.285	0.311	0.849	0.119	0.204	0.104	-.223	-.113	Al
				-.096	0.501	0.314	0.438	-.094	0.384	0.110	0.347	0.395	-.044	0.029	0.123	-.236	-.132	As
					0.249	0.455	0.230	0.309	-.114	0.285	0.261	0.202	0.464	-.030	-.112	-.412	0.073	Cd
						0.606	0.594	0.046	0.437	0.105	0.472	0.557	0.354	-.105	-.335	-.032	0.171	Cr
							0.676	0.274	0.232	0.469	0.623	0.449	0.604	0.283	-.212	-.233	-.037	Cu
								0.220	0.327	0.531	0.273	0.718	0.276	0.176	-.379	-.256	0.103	Fe
									-.273	0.264	0.310	0.123	0.038	0.385	0.294	0.292	-.234	Hg
										0.027	0.068	0.413	0.363	-.116	-.054	0.106	-.131	Pb
											0.149	0.177	0.202	0.443	-.120	-.299	-.002	Mn
												0.291	0.546	0.278	0.191	0.152	-.289	Ni
													0.207	0.139	-.151	-.046	-.013	Sc
														0.152	-.012	0.228	-.064	Zn
															0.117	-.110	0.035	P
																0.259	-.808	N
																	-.201	CHL

Settling solids at VZ7

	OC	IC	Al	As	Cd	Cr	Cu	Fe	Hg	Pb	Mn	Ni	Sc	Zn	P	N	CHL	OC/N
IC	-.019																	
Al	-.127	-.463																
As	0.059	-.544	0.485															
Cd	0.142	-.226	0.312	0.504														
Cr	0.236	-.159	0.651	0.427	0.096													
Cu	0.459	-.476	0.515	0.243	0.595	0.373												
Fe	-.422	-.234	0.676	0.946	-.025	0.295	0.063											
Hg	0.087	-.458	0.490	0.940	0.326	0.442	0.350	0.373										
Pb	0.117	-.733	0.817	0.259	0.410	0.317	0.650	0.300	0.312									
Mn	-.024	-.505	0.523	0.469	0.345	0.463	0.392	0.364	0.475	0.117								
Ni	0.081	-.029	0.132	0.177	-.104	0.196	-.126	0.121	0.302	0.243	0.144							
Sc	-.146	-.511	0.864	0.477	0.246	0.563	0.530	0.550	0.492	0.700	0.490	0.177						
Zn	0.150	-.519	0.086	-.201	0.318	0.043	0.386	-.296	0.262	0.300	0.315	0.420	0.053					
P	0.880	-.651	0.667	0.359	0.359	0.667	0.821	0.359	0.287	0.667	0.051	-.205	0.821	-.359				
N	0.714	0.071	-.700	-.900	-.900	0.000	-.200	-.900	-.894	-.700	-.500	0.100	-.400	-.100	0.578			
CHL	0.771	-.371	0.500	-1.00	-.500	-.500	1.000	-.500	-1.00	0.500	-.500	-1.00	0.500	-.500	0.975	0.900		
OC/N	-.167	-.452	0.700	0.900	0.900	0.100	0.200	0.900	0.671	0.700	0.700	-.400	0.600	-.500	-.121	-.762	-.800	

Between 4/89 and 12/92 for location VZ3 and VZ7, settling particles were collected with sediment traps. The correlation analysis for the resulting datasets shows a smaller number of significant correlations due to the smaller size of the dataset. Manganese is positively correlated with iron (VZ3) and at VZ7 with Al and Sc. For the rest, the correlations confirm the general pattern for the suspended solids on the same locations.

The difference in the behavior of manganese between VZ3 and VZ7 on one hand and HD and DM on the other is illustrated in Figure 3 which shows a reversed seasonality for the locations in the lake as compared to those in the inlet rivers. For the seasonality of Mn for HD and DM with high levels in summer, several explanations may be given. First, the seasonality may be caused by the enhanced oxidation of dissolved manganese at higher temperatures in summer. This explanation was also given by Van der Weijden and

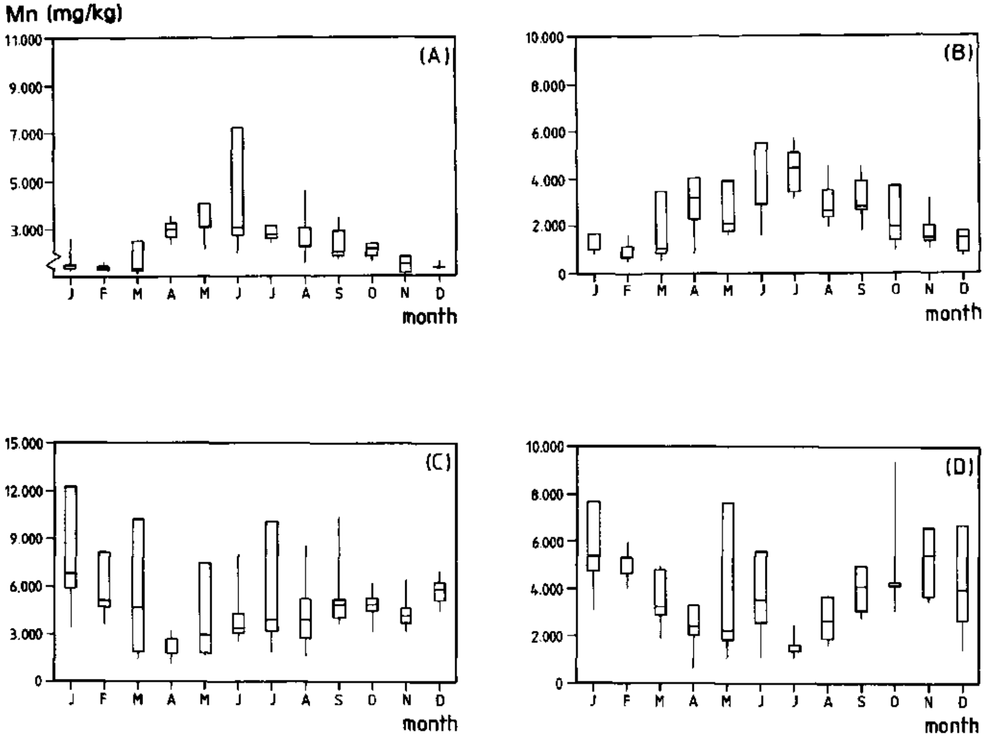

Fig.3: Box and whisker plot for detrended monthly manganese concentrations in suspended solids sampled at the locations: HD (A), DM (B), VZ3 (C) and VZ7 (D). The central box covers the middle 50% of the data values, between the lower and upper quartiles. The "whiskers" extend out to the extremes, while the central line is at the median.

Middelburg [15] who found the same seasonality for suspended solids in the Rhine between 1975 and 1984. Second, as was suggested by van Eck [14] for Mn behavior in the Hollandsch Diep, Mn may be proportional to Fe in the form of metal coatings, or to chlorophyll due to the precipitation of MnO_2 or $MnCO_3$ because of a high pH and oxygen saturation during primary production. Third, Mn seasonality with maxima in summer may originate from the reduction of solid manganese oxides in the deeper parts of the lake during oxygen depletion in summer, a subsequent upward Mn^{2+} flux and reprecipitation in the oxic upper water layers [16,17]. Van Nes and Smit [18] who studied some chemical characteristics of Lake Volkerak/Zoom in 1987 and 1988, reported oxygen depletion at depths > 10 m. At VZ3 and VZ7 the maximum Mn concentrations are measured on the winter samples, so the seasonality is reversed. We assume that the precipitations mentioned above also may occur at these locations but that they are more than compensated by dilution with planktonic particles. However, insufficient data are available to distinguish unambiguously among the possible processes.

Trend analysis

Most of the time variation and differences between locations which can be seen in Figure 2 and 3, are supported by the statistical tests for time variation and the median values as presented in Table 3. In this table for each variable, the median, the Sen slope of the linear trend line, the significance level of the quarterly Kruskall Wallis test for seasonality and the number of measurements, is given for the four locations.

The unidirectional seasonality in LOI, OC, COD, CHL and N originates from algal growth. For Sc and Al a seasonality opposed to that for OC is found which can be explained by simple dilution of clay particles. Seasonality for the $< 16\mu m$ fraction is less significant. This is probably caused by the limited size and relatively large number of missing values for this variable. An important observation is the significant negative trend found for Sc and Al on all locations. In the beginning of our time series in 1988 and 1989, rainfall was below average. Afterwards, as discharge increases, the contribution of clay particles containing Sc and Al to the total suspended matter may have decreased because of the increased resuspension of coarser material. This may explain the observed trend for these metals. Because Sc has a negative trend, the trends found for the normalised metal concentrations have more negative slopes than those for the absolute concentrations. Normalisation of Al to Sc removes the seasonality, but a significant negative trend in Al/Sc remains. Further, the fractional trend in Al/Sc calculated as the Sen slope divided by the median, is identical on all locations. This means that Al decreases faster in time than Sc, which suggests a shift in the mineralogical composition of the clay particles with the change in flow regime. Another process which may be considered is the dissolution of aluminiumoxides as a result of acidification [19,20].

TABLE 3: Seasonality and time trends

	Median	Sen slope	Per	N
$\% < 16\mu m^{(a)}$				
HD	68.700	0.0667	(2)	30
DM	57.150	-2.3800 (3)		32
VZ3	44.700	-2.1400		19
VZ7	52.750	-6.5000	(1)	22
LOI$^{(a)}$				
HD	21.000	0.0500	(1)	54
DM	32.300	-1.188 (3)	(3)	61
VZ3	37.800	1.6817 (2)	(2)	63
VZ7	27.700	-0.150	(1)	59
OC$^{(a)}$				
HD	5.910	-0.7800 (3)	(3)	54
DM	9.685	-1.1400 (3)	(1)	62
VZ3	9.150	-0.5503 (3)	(3)	60
VZ7	7.910	-0.9675 (3)	(1)	59
COD$^{(b)}$				
HD	24.550	0.3125 (1)	(1)	30
DM	42.050	-1.8000	(3)	38
VZ3	41.467	3.9000 (1)	(3)	35
VZ7	34.800	4.7750 (1)		34
IC$^{(a)}$				
HD	11.900	0.6375	(1)	54
DM	5.4500	0.7500 (3)		60
VZ3	9.9200	0.9200 (2)		61
VZ7	9.6350	0.4050		58
P$^{(a)}$				
HD	0.4050	-0.0100 (1)	(2)	54
DM	0.9630	-0.0317 (3)		59
VZ3	0.5200	0.0083	(1)	57
VZ7	0.4050	0.0100		58
N$^{(a)}$				
HD	1.0400	0.0300	(3)	54
DM	2.0600	-0.0217	(3)	59
VZ3	2.8000	0.2450 (3)	(3)	57
VZ7	1.9400	0.2167 (3)	(2)	58
CHL$^{(b)}$				
HD	410.0			17
DM	921.0	-14.000	(1)	17
VZ3	2220.0			7
VZ7	848.0			16
OC/N$^{(c)}$				
HD	5.455	-0.8200 (3)	(1)	54
DM	5.410	-0.5900 (3)	(3)	59
VZ3	4.220	-0.5970 (3)	(1)	56
VZ7	4.735	-0.8500 (3)		58
OC/P$^{(c)}$				
HD	32.25	-4.3330 (3)		54
DM	25.60	-1.3330 (1)		59
VZ3	45.05	-3.5330 (3)		56
VZ7	52.30	-7.3000 (3)		58
N/P$^{(c)}$				
HD	5.650	0.2375 (3)	(3)	54
DM	4.370	0.1355	(3)	59
VZ3	11.300	0.9402 (3)	(3)	57
VZ7	10.900	0.3525 (1)		58
Fe/P$^{(c)}$				
HD	4.470	-0.0217	(3)	54
DM	3.087	0.0608	(3)	59
VZ3	3.130	-0.2900 (2)	(3)	57
VZ7	4.805	-0.2350		58
LOI/OC$^{(c)}$				
HD	3.775	0.5650 (3)		54
DM	3.395	0.3700 (3)		62
VZ3	3.615	0.3740 (3)		60
VZ7	3.720	0.5200 (3)		59
Absolute metals				
Al$^{(b)}$				
HD	23950	-1845 (3)	(3)	54
DM	22400	-1850 (3)	(3)	62
VZ3	15400	-2647 (3)	(3)	63
VZ7	16100	-2033 (3)		59
As$^{(b)}$				
HD	20.62	-2.34 (2)		54
DM	26.28	-4.70 (3)		62
VZ3	15.35	-3.65 (3)	(2)	62
VZ7	14.80	-4.10 (3)		59
Cd$^{(b)}$				
HD	5.37	-0.900 (3)		54
DM	2.38	-0.450 (3)	(3)	62
VZ3	1.15	-0.125 (3)	(3)	60
VZ7 ^{stap}	0.70	-0.125 (3)		53

(a) %; (b) mg/kg; (c) dimensionless ratio;

(1)=$p<0.20$, (2)=$p<0.10$, (3)=$p<0.05$

TABLE 3 (Continued)

	Median	Sen slope	Per	N
Cr$^{(b)}$				
HD	98.25	-18.00 (3)		54
DM	62.00	-8.00 (3)		62
VZ3	69.00	-18.00 (3)		62
VZ7	46.00	-11.00 (3)		59
Cu$^{(b)}$				
HD	105	-3.00 (3)	(3)	54
DM	78.5	-7.75 (3)	(3)	62
VZ3	34.0	-3.00 (3)	(3)	63
VZ7	31.0	-1.00		58
Fe$^{(b)}$				
HD	36000	-925 (3)	(3)	54
DM	53750	-367	(3)	62
VZ3	29400	-2775 (3)	(3)	63
VZ7	34700	-950 (2)	(1)	59
Hg$^{(b)}$				
HD	1.20	-0.100 (3)	(1)	54
DM	0.40	-0.050 (3)		62
VZ3	0.50	-0.033 (3)	(1)	63
VZ7	0.30	-0.050 (3)		59
Pb$^{(b)}$				
HD	159.3	-9.50 (3)	(3)	54
DM stap	78.0	+0.875	(3)	62
VZ3	68.0	-10.50 (3)	(3)	62
VZ7	45.0	-3.50 (3)	(3)	59
Mn$^{(b)}$				
HD	2080	+42.0	(3)	54
DM	2142	+225 (3)	(3)	62
VZ3	4500	+282 (2)	(1)	63
VZ7	3690	+24	(3)	59
Ni$^{(b)}$				
HD	50	-1.33 (2)	(1)	54
DM	58.5	+0.667		62
VZ3	40.0	-0.625	(3)	63
VZ7	35.0	0.00		59
Sc$^{(b)}$				
HD	5.342	-0.07	(3)	54
DM	4.625	-0.0375	(3)	62
VZ3	3.660	-0.3825 (3)	(3)	63
VZ7	3.860	-0.2133 (3)		59

(a) %; (b) mg/kg; (c) dimensionless ratio

	Median	Sen slope	Per	N
Zn$^{(b)}$				
HD	835	+2.50	(3)	54
DM	641	+1.75	(3)	62
VZ3	335	-4.33	(3)	63
VZ7	228	-2.33	(3)	59
Normalised metals				
Al/Sc$^{(c)}$				
HD	4340	-322.0 (3)		54
DM	5010	-373.3 (3)		62
VZ3	4300	-330.0 (3)		63
VZ7	4010	-343.3 (3)		59
As/Sc$^{(c)}$				
HD	3.83	-0.395		54
DM	5.83	-0.855 (3)		62
VZ3	4.88	-0.500 (3)		62
VZ7	4.28	-0.740 (3)		59
Cd/Sc$^{(c)}$				
HD	0.968	-0.1297 (3)		54
DM	0.591	-0.0748 (3)		62
VZ3	0.319	+0.0078	(2)	60
VZ7 piek	0.195	-0.0297 (3)		53
Cr/Sc$^{(c)}$				
HD	19.4	-3.567 (3)		54
DM	13.9	-1.765 (3)		62
VZ3	17.5	-3.450 (3)		62
VZ7	11.4	-2.045 (3)		59
Cu/Sc$^{(c)}$				
HD	19.9	-0.533	(3)	54
DM	17.9	-1.425 (3)		62
VZ3	9.31	+0.264 (1)		63
VZ7	7.88	+0.445 (3)		58
Fe/Sc$^{(c)}$				
HD	6380	-147.5 (1)	(1)	54
DM	11400	-182.5 (3)	(1)	62
VZ3	8530	+ 75.0 (1)		63
VZ7	8350	+386.7 (2)		59
Hg/Sc$^{(c)}$				
HD	0.249	-0.0175 (3)	(2)	54
DM	0.095	-0.0050 (3)		62
VZ3	0.144	+0.0059 (2)		63
VZ7	0.086	-0.0113 (3)		59

(1)=$p<0.20$, (2)=$p<0.10$, (3)=$p<0.05$

TABLE 3 (Continued)

	Median	Sen slope	Per	N
Pb/Sc$^{(c)}$				
HD	30.85	-2.02 (3)	(3)	54
DM $^{\text{stap}}$	17.80	-0.70 (1)		62
VZ3	19.40	+0.15		62
VZ7	11.45	-0.28	(3)	
Mn/Sc$^{(c)}$				
HD	396.5	+15.5	(3)	54
DM	458.0	+45.0 (3)	(3)	62
VZ3	1280.0	+258.3 (3)		
VZ7	864.0	+69.8 (3)	(1)	
Ni/Sc$^{(c)}$				
HD	9.559	-0.425 (3)		54
DM	13.10	+0.033	(1)	62
VZ3	11.80	+1.113 (3)	(1)	63
VZ7	9.120	+0.560 (3)	(1)	59
Zn/Sc$^{(c)}$				
HD	157.5	+2.20 (1)	(1)	54
DM	138.0	+2.75		62
VZ3	105.0	+10.6 (3)		63
VZ7	56.7	+4.3 (3)	(2)	59
Organic pollutants (OC normalised)				
PCB28$^{(d)}$				
HD	337.5	35.5	(3)	50
DM	23.7	-1.44		45
VZ3	59.7	-4.28 (1)	(3)	45
VZ7	51.8	+0.24		37
PCB52$^{(d)}$				
HD	331	19.17	(3)	47
DM	42.6	-0.9		35
VZ3	44.6	-4.40 (3)		31
VZ7	34.2	-0.75		23
PCB101$^{(d)}$				
HD	500	54.67 (2)	(2)	49
DM	74.3	2.42		47
VZ3	68.95	-12.5 (3)	(3)	42
VZ7	38.50	-4.0667 (1)		31
PCB118$^{(d)}$				
HD	434	17.35	(1)	41
DM	60.05	2.125		48
VZ3	59.4	-0.50	(1)	35
VZ7	34.10	-2.875		30

(b) mg/kg; (c) dimensionless ratio; (d) μg/kg

	Median	Sen slope	Per	N
PCB138$^{(d)}$				
HD	707	0.00	(1)	49
DM	115	1.5		47
VZ3	122	-13.167 (2)	(3)	44
VZ7	71.20	-10.817 (3)		37
PCB153$^{(d)}$				
HD	531	-2.00		45
DM	115	3.75		46
VZ3	111	-13.75 (3)	(3)	39
VZ7	45.35	-7.025 (3)	(1)	38
PCB180$^{(d)}$				
HD	405.5	-16.0 (1)	(3)	48
DM	83.55	4.34	(3)	52
VZ3	62.40	-8.769 (3)	(3)	49
VZ7	52.2	-5.931 (1)		48
α-HCH$^{(d)}$				
HD	108	+60.3 (3)	(1)	26
DM	21.7	0.00	-	7
VZ3	35.65	-		10
VZ7	35.3	6.867		8
β-HCH$^{(d)}$				
HD	105	-42.0		42
DM	49.2	7.242		8
VZ3	49.6	-15.05 (2)	(2)	25
VZ7	28.5	-4.433		15
γ-HCH$^{(d)}$				
HD	97.25	-5.875 (2)		42
DM	61.65	3.775		48
VZ3	66.6	3.883		50
VZ7	51.75	7.533 (3)		46
HEPTA$^{(d)}$				
HD	109.5	-20.8 (1)	(1)	28
DM	47.10	9.375		15
VZ3	54.3	-6.62		23
VZ7	43.75	1.663		14
HEPO$^{(d)}$				
HD	273	46.625 (3)		39
DM	46.10	11.65 (3)		27
VZ3	48.2	9.28	(3)	33
VZ7	39.3	-7.70		18

(1)=$p<0.20$, (2)=$p<0.10$, (3)=$p<0.05$

TABLE 3 (Continued)

	Median	Sen slope	Per	N
ALDRIN(d)				
HD	165.5	-44.67 (1)		24
DM	45.5	-16.88		15
VZ3	85.25	0.0875		20
VZ7	64.30	+1.70		12
DIELDRIN(d)				
HD	120.5	-38.45 (3)	(1)	40
DM	102	0.18		49
VZ3	75.85	-7.75 (2)	(3)	40
VZ7	45.0	0.725	(1)	35
ENDRIN(d)				
HD	225.5	-36.5		36
DM	43.2	0.20		31
VZ3	44.35	-7.507		26
VZ7	39.50	+2.69		17
ISODRIN(d)				
HD	63.8	-21.525		19
DM	35.58	15.55		12
VZ3	37.9	+14.55 (1)		16
VZ7	31.10	-0.717		9
DDD44(d)				
HD	187	-5.1875		48
DM	121	-2.40		49
VZ3	64.7	-3.9	(2)	33
VZ7	26.5	-1.125	(1)	27
DDE44(d)				
HD	262	+37.15 (3)	(1)	41
DM	136	5.65	(3)	53
VZ3	72.85	2.865	(3)	38
VZ7	71.9	-5.463		41
DDT24(d)				
HD	143	+1.00	(1)	41
DM	20.9	4.215		27
VZ3	47.0	21.65 (2)		22
VZ7	20.9	-5.217	(1)	13
DDT44(d)				
HD	281	-45.275		41
DM$^{\text{piek}}$	113	13.125 (3)	(3)	49
VZ3	73.35	+3.30	(1)	34
VZ7	103.75	16.985 (3)		26

(b) mg/kg; (c) dimensionless ratio; (d) μg/kg

	Median	Sen slope	Per	N
HCB(d)				
HD	507	-78 (3)	(1)	47
DM	21.7	0.02		38
VZ3	43.30	-8.482 (3)		37
VZ7	26.55	-0.75		34
HCBD(d)				
HD	112.5	-16.85 (2)	(3)	36
DM	70.8	-25.3		17
VZ3	112	-10.4		16
VZ7	76.3	-33.05 (3)	(1)	17
QCB(d)				
HD	259	-28 (2)	(2)	41
DM	23.3	0.933	(1)	23
VZ3	38.65	-18.30 (3)	(1)	34
VZ7	47.95	-7.37 (3)		24

(1)=$p<0.20$, (2)=$p<0.10$, (3)=$p<0.05$

However, the variations in pH (not reported in this paper) are too small to explain the observed trend.

A significant negative trend is also found for OC. This may also be caused partially by the changing flow regime and the dilution with coarser particles containing less organic carbon. Further, algal growth was much stronger in 1988 than in the years thereafter [3], which also explains the negative trend.

IC was expected to vary because of the pH variations induced by the dynamics of algal growth. However, when calcite precipitation is coupled to OC production, the nett effect on their respective weight fractions may be small.

The seasonality of P is less significant than seasonality for OC. Apparently, the variation in phosphorus content is not determined only by OC seasonality. P may appear in various chemical forms, whith different mobility, which is also affected by pH and Eh. Besides a constituent in algal material, P species adsorb to iron- and aluminium--(hydr)oxides [21]. Significant seasonalities are also found for the N/P, Fe/P, and OC/N atomic ratio. For the OC/P ratio, no seasonality is found. These ratios may be compared to the stoichiometry for algal material at optimal growth conditions according to Redfield [22]: $(CH_2O)_{106}(NH_3)_{16}H_3PO_4$, or the stoichiometry for minerals containing iron and/or phosphates. The N/P ratio is highest in summer with values close to 16 which is the Redfield ratio for phytoplankton. However, on the average, the N/P ratio is lower than is to be expected from Redfield's ratios for organic material. This is also the case for the OC/P ratio which is approximately 2 - 4 times lower than the Redfield ratio of 106. This indicates the presence of inorganic phosphates either bound in allochthonous minerals, such as apatite, or in coprecipitates with calcite [23]. The Fe/P ratios of 3 to 5 are a little higher than the ratios of 1 to 3 found by Sigg et al in Lake Zurich [17] and are too large to be accounted for only by biological binding. Morel and Hudson [24] report a Fe/P ratio of 0.01 for marine algae. In a recent study [25], Veen estimates a Fe/C ratio of 9×10^{-5} for phytoplankton in the fresh Lake Maarsseveen. With the theoretical OC/P ratio of 106, this would also result in an Fe/P ratio of approximately 0.01 for freshwater algae. The higher Fe/P ratios are probably explained by the presence of Fe as small particles of iron oxide or as coatings on other particles. The seasonality of Fe/P on location VZ3 is given in Figure 4 as an example. The Fe/P ratio has its minimum in summer on all locations studied. This can be explained from an increase in biologically bound P and a simultaneous dilution of particulate iron in summer. The possible relationship between total P content and the abundance of the P related phases aluminium(hydr)oxides, iron(hydr)oxides and algal matter were further explored using multiple regression calculations (Table 4). The calculations were based on the linear model:

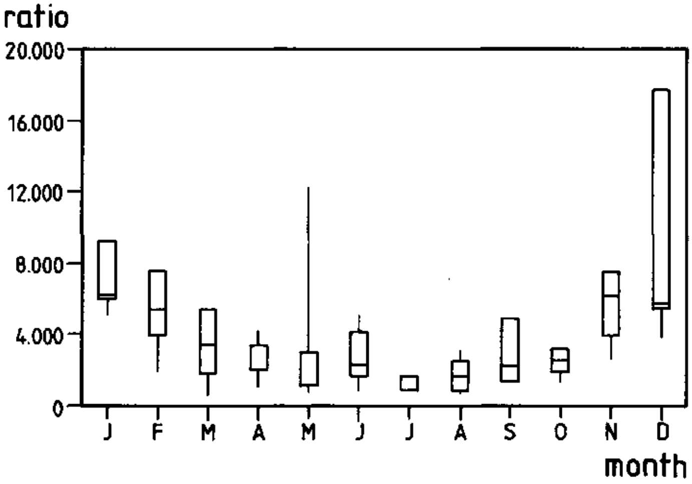

Fig. 4: Box and whisker plot for detrended monthly elemental Fe/P atomic ratios for suspended solids sampled at locations VZ3. For explanation of Box and Whisker plot see Figure 3.

$$P=a + b \times OC + c \times Al + d \times Fe \qquad (1)$$

in which:

P	=	total phosphorous content (mg/kg)
OC	=	organic carbon content (mg/kg)
Al	=	total aluminium content (mg/kg)
Fe	=	total iron content (mg/kg)
a, b, c, d	=	regression coefficients

The variables *Fe*, *Al* and *OC* were not a priori forced into the model. A stepwise variable selection procedure was followed, in which variables were added one at a time as long as they added significantly to the model. The results of the calculations are listed in Table 4. The selection of significant variables appears to be quite different for the four locations. Apparently, some variables had a small range or too much random error to contribute significantly to the model. Another possibility is the different adequacy of the model as condensed in equation 1 for locations having different phosphorous chemistry, or correlations among the 'independent' variables. The latter is certainly the case for Al and Fe, which are significantly correlated (Table 2). Consequently, the Al and Fe terms in

Table 4 may be interpreted as nested (Al+*n*Fe) terms. P appears to be positively related to organic carbon, and negatively to Al and Fe. The OC coefficients for HD and VZ3 are 0.0230 and 0.0244 respectively. From these coefficients, molar based OC/P ratios for organic matter related phosphorous of 112 (HD) and 106 (VZ3) were calculated. The agreement of these values to the Redfield ratio strongly suggests that the OC related phosphorous on HD and VZ3 is caused by biological uptake only, and not by other processes indirectly related to photosynthesis, such as phosphate(co)precipitation. The inverse relationship with Al and Fe probably originates from the same dilution process responsible for the observed seasonality. For DM a very constant P content is found. In contrast to the other locations, DM represents a relatively turbulent river where vigorous photosynthesis is restricted and inorganic phosphate dominates.

TABLE 4:

Multiple regression results for phosphorous as independed variable.

location	Selected model[(a)]	N	P-value
HD	$P = (2980 \pm 400) + (2.30 \pm 0.66) \times 10^{-2} \times \mathbf{OC}$	54	0.0009
DM	$P = (9880 \pm 450)$	59	0.0000
VZ3	$P = (4440 \pm 790) + (2.44 \pm 0.50) \times 10^{-2} \times \mathbf{OC} - (7.7 \pm 2.6) \times 10^{-2} \times \mathbf{Al}$	57	0.0000
VZ7	$P = (9160 \pm 640) - (0.14 \pm 0.019) \times \mathbf{Fe}$	58	0.0000

(a) P= phosphorous content (mg/kg), OC= organic carbon content (mg/kg), Al= total aluminium content (mg/kg), Fe= total iron content (mg/kg). Final models were selected using the stepwise variable selection procedure available in STATGRAPHICS.

OC/N ratios vary between 4 and 20 (Table 3). The lower values of 4 - 6 are found in spring and summer and are typical for fresh phytoplankton. The higher OC/N ratios of 10-20 are found in winter and are typical for more degraded and humic types of organic material [26]. However, most samples have ratios in between and are composed of mixtures of algal debris and resuspended sediments of various degrees of mineralization. The variation in OC/N ratio illustrates the large changes in organic matter type throughout the year.

Settling versus suspended solids

Between 4/89 and 12/92 for location VZ3 and VZ7, settling particles were collected with sediment traps. For every month that the solid characteristics were measured in suspended particles (centrifuge) as well as in settling particles (sediment trap), the ratio was calculated between the sediment trap value (ST) and the centrifuge value (CF). ST and CF value were always measured within the same month, so it can be assumed that the concentrations of relevant components in the aqueous phase were similar. The averaged ST/CF ratios are listed in Table 5.

TABLE 5:
Comparison of solid characteristics, metal, PCB and pesticide concentrations between settling solids and suspended solids. Solids were collected at location VZ3 between 4/89 and 12/92.

Variable	ST/CF ratio ± s.d.	N	Variable	ST/CF ratio ± s.d.	N
		Solid characteristics			
OC	0.63 ± 0.29	37	OC/N	2.26 ± 1.37	23
IC	1.45 ± 1.02	38	OC/P	1.06 ± 0.68	23
P	1.00 ± 1.13	23	N/P	0.53 ± 0.27	23
N	0.36 ± 0.21	23	Fe/P	2.73 ± 2.09	23
Sc	1.64 ± 0.69	39	-		
Al	1.65 ± 0.75	39	Al/Sc	1.01 ± 0.15	39
Fe	1.54 ± 0.66	39	Fe/Sc	0.96 ± 0.15	39
Mn	0.84 ± 0.61	39	Mn/Sc	0.53 ± 0.26	39
		Trace elements			
As	1.59 ± 1.24	29	As/Sc	1.01 ± 0.54	29
Cd	2.07 ± 3.50	32	Cd/Sc	1.20 ± 1.67	32
Cr	1.26 ± 0.62	37	Cr/Sc	0.84 ± 0.46	37
Cu	1.46 ± 1.22	39	Cu/Sc	1.02 ± 1.15	39
Hg	1.41 ± 1.81	39	Hg/Sc	0.88 ± 1.22	39
Pb	1.50 ± 0.54	29	Pb/Sc	1.01 ± 0.27	29
Ni	1.18 ± 0.47	39	Ni/Sc	0.79 ± 0.36	39
Zn	1.47 ± 0.75	37	Zn/Sc	1.01 ± 0.73	37
	Polychlorobiphenyls (a) and pesticides (OC normalised)				
PCB28	3.15 ± 2.46	16	ALDRIN	1.85 ± 1.00	7
PCB52	5.18 ± 3.59	4	DIELDRIN	4.90 ± 7.33	8
PCB101	5.11 ± 5.36	8	ENDRIN	3.33 ± 4.59	11
PCB118	1.58 ± 0.80	9	ISODRIN	1.54 ± 0.32	2
PCB138	3.10 ± 2.30	9	DDD44	2.80 ± 1.58	5
PCB153	1.96 ± 1.29	9	DDE44	2.46 ± 1.87	5
PCB180	2.32 ± 1.51	13	DDT24	0.73 ± 0.00	1
ß-HCH	1.34 ± 0.46	4	DDT44	3.73 ± 2.97	13
γ-HCH	1.55 ± 1.19	13	HCB	6.77 ± 7.15	7
HEPTA	1.78 ± 0.75	5	HCBD	1.81 ± 1.08	11
HEPO	1.41 ± 0.32	2	QCB	4.81 ± 8.08	18

(a) PCB numbers refer to IUPAC PCB congener numbers

The number of ratios for each variable (N) varies because of missing ST and/or CF values. It appears from this comparison that sediment traps collect particulate material with lower OC and larger IC and clay content. This is caused by the slower settling of phytoplankton cells, which results in a larger contribution from eroded clays and resuspended sediments to the settling flux, and/or by degradation of organic material in the sediment traps which were deployed for 14 days. The latter process is supported by the OC/N ratios, which are a factor 2.3 higher for the settling solids (Table 5). Another explanation was suggested by Baker and co-workers [27] who also found lower organic content and higher OC/N atomic ratios in settling solids relative to suspended solids, in Lake Superior (U.S.A.). They explained the higher OC/N ratios of settling material by assuming that the settling material consists of faecal pellets and large amorphous aggregates which have a larger degree of mineralization. Van Son [28] found an increase in OC/N ratio with depth for settling particles in a bay of Lago Maggiore (Italy). Obviously, a significant part of the degradation of algal material occurs during settling in the water column in these lakes. For Fe also a ST/CF ratio >1 is found which follows from its relation with the clay fraction. Mn is the only metal for which an average ST/CF ratio <1 is found. This may be explained by some association with organic matter [6], or by possible anaerobic conditions in the sediment trap which causes reduction of Mn oxides and subsequent mobilization of Mn^{2+} [16].

Heavy metals and arsenic

For the study of metal speciation in heterogeneous natural particles such as sediments or suspended solids, several approaches may be followed. The first is based on thermodynamic calculations and was proposed by Oakley [29]. His approach requires thermodynamic data which are mostly not available, and does not consider the interaction between solid phases. A second approach applied frequently is that of sequential extraction as described by Tessier [30]. However, this method is time consuming and may suffer from a non-predictable redistribution of metals during the extractions [31,32]. Therefore, the information provided with sequential extraction procedures is difficult to interpret and always remains operationally defined. The third approach which was followed in this study and which is also frequently encountered in literature [15,33,34], is the measurement of total elemental content, and the use of statistical techniques to find relationships among the variables. This method is very useful for the analysis of large datasets which are obtained in routine water quality monitoring programs. It should be kept in mind that only indirect information is obtained and that no conclusions can be drawn about causality. We applied correlation analysis, trend analysis and factor analysis to our heavy metal data and solid characteristics.

Correlation analysis

For all locations, most heavy metals and arsenic are positively correlated, and are correlated with the parameters representing the clay fraction $<16\mu m$, Sc and Al (Table 2). The same variables are negatively correlated with CHL, OC, N and P. In contrast, Mn is correlated positively with CHL, OC, N and P at HD and DM, as was discussed in the previous section. Some metals seem to have a lower number of significant correlations such as Hg and As, which may be caused by the more complex chemical speciation of these elements.

Trend analysis

Trend analysis for the absolute metal contents shows negative slopes for almost all metals. Significant positive trends ($p<0.20$) are only found for Mn on locations DM and VZ3. This general decrease in metal content is partially explained by the decrease in clay and organic matter content which was discussed in the previous section. Consequently, normalisation to Sc yields much less negative trends as can be seen from Table 3. Another explanation may be the increase in chloride concentration of about 30% from 1988 to 1991 [35] which may lead to a mobilization of metals. Because the normalisation to Sc roughly compensates for differences in sorption affinity of the particles, the normalised metals more closely reflect the long term changes in pollution level of the aqueous phase. Accordingly, it can be concluded that for example pollution with Zn at HD, with Hg, Ni and Zn at VZ3, and with Cu, Ni and Zn at VZ7 has significantly increased. An overview of all significant ($p<0.20$) positive trends for the pollutants investigated in this study, is given in Table 6.

TABLE 6:
Summary of significant ($p<0.20$) positive trends in normalized metal and HOC concentrations

location	metal trends	HOC trends
HD	Zn	PCB-101, α-HCH, HEPO, DDE44
DM	Mn	HEPO, DDT44
VZ3	Cu, Fe, Hg, Mn, Ni, Zn	ISODRIN, DDT24
VZ7	Cu, Fe, Mn, Ni, Zn	γ-HCH, DDT44

Factor analysis

Besides correlation analysis, factor analysis was applied to the data set for each location, to grasp the relationships among variables. Factor analysis finds linear combinations (factors) of the original variables that are best linear descriptors of the full set of variables. Essentially, in our analysis only factors with at least two significant variables (factor loading > 0.5) are selected for the final model. For centrifuge samples from the locations HD, DM, VZ3 and VZ7, 65-70% of the total variance is explained by four factors which are quite similar for the four locations (Table 7). The fourth factors for DM and VZ7 had only one factor loading > 0.5, but were included to enable comparison with the other locations. For all locations a first factor describes 30-40% of the variability with high positive loadings on $<16\mu m$, Al, Cr, Fe, Pb, Sc, Zn and OC/N, and negative loadings on N and CHL. This bipolar factor may be interpreted as "clay", which binds a large fraction of the metals present and is diluted by phytoplankton growth. Because the highest clay fractions are found in winter when the contribution of fresh phytoplankton with a low OC/N ratio is low, also OC/N loads positively on this factor. The second factor seems to be an organic matter factor, with loadings of OC, and/or CHL, P and N. Some metals load on factor 1 or 2, or both, such as Cd, As, Pb and Cu. This may be explained by significant scavenging of these metals by organic matter, which may occur to a different extent for different metals. Several authors report differences in binding strength of heavy metals to planktonic particles [36,37,38,39,40]. Despite of the different experimental conditions, methods and algae used in these studies, the order in binding strength is very similar. Usually, Cd, Cu and Pb are among the metals with the highest binding constants, which agrees to our factor analysis results. The third and the fourth factor differ for the four locations and are therefore difficult to interpret. For the sediment traps on locations VZ3 and VZ7 (Table 8) similar first two factors are found. However, for the traps at both locations, Mn loads positively on the first factor. For the carbonates (IC) no significant role as a carrier for heavy metals is indicated. Factor analysis results of other studies can be compared to ours. Van der Weijden [15] found very similar factors relating heavy metal concentrations with clay and organic matter content of suspended solids in the Rhine. Sigg [17] who studied heavy metals on settling solids, had no data on clay content but measured a close relation between heavy metal and organic matter content. In both studies calcite did not correlate with any of the heavy metals studied, which confirms our findings.

Settling versus suspended solids

As described in the previous section, between 4/89 and 12/92 on location VZ3, settling solids were collected with sediment traps. For each metal the ratio was calculated between the sediment trap measurement (ST) and the centrifuge measurement (CF) in the same month. The averaged ST/CF ratios for the trace metals are listed in Table 5. Except Mn, the settling solids are enriched in all metals to the same extent as the conservative elements Al and Sc. Normalization of the metals to Sc removes most of the differences between sediment trap and centrifuge samples, especially for Al, As, Cu and Fe.

TABLE 7: First 4 factor loadings for heavy metals and arsenic in solids sampled with centrifuges.

HD Factor:	1	2	3	4
%var(a):	35.1	16.6	10.0	6.4
<16μm	0.57	x	x	0.67
OC	x	0.70	x	x
IC	x	x	-0.58	x
CHL	x	0.89	x	x
Al	0.87	x	x	x
As	x	0.62	x	x
Cd	x	0.67	x	x
Cr	0.72	x	x	x
Cu	x	x	0.66	x
Fe	0.86	x	x	x
Hg	x	x	0.84	x
Pb	0.74	x	x	x
Mn	-0.72	x	x	x
Ni	x	x	x	-0.59
Sc	0.77	x	x	x
Zn	0.64	x	x	x
P	x	0.59	x	x
N	-0.76	x	x	x
OC/N	0.66	x	x	x

DM	1	2	3	4
	37.6	13.1	10.1	7.2
<16μm	0.60	x	x	0.56
OC	x	-0.80	x	x
IC	x	x	x	x
CHL	-0.79	x	x	x
Al	0.91	x	x	x
As	x	-0.56	x	x
Cd	0.63	x	x	x
Cr	0.57	x	x	x
Cu	0.76	x	x	x
Fe	0.81	x	x	x
Hg	x	x	x	x
Pb	0.68	x	x	x
Mn	-0.80	x	x	x
Ni	x	x	x	x
Sc	0.79	x	x	x
Zn	0.68	x	x	x
P	x	x	x	x
N	-0.79	x	x	x
OC/N	x	x	-0.60	x

VZ3 Factor:	1	2	3	4
%var(a):	40.2	11.2	8.5	7.5
<16μm	0.75	x	x	x
OC	-0.51	x	0.60	x
IC	x	0.52	x	x
CHL	x	-0.82	x	x
Al	0.90	x	x	x
As	0.81	x	x	x
Cd	0.62	x	x	x
Cr	0.58	x	x	x
Cu	x	-0.56	x	x
Fe	0.97	x	x	x
Hg	x	x	x	x
Pb	0.74	x	x	x
Mn	x	x	-0.67	x
Ni	x	x	x	x
Sc	0.91	x	x	x
Zn	0.63	x	x	-0.50
P	-0.58	x	x	-0.53
N	-0.82	x	x	x
OC/N	0.73	x	x	x

VZ7	1	2	3	4
	31.6	13.7	9.0	7.9
<16μm	x	x	x	x
OC	x	0.70	x	x
IC	x	x	x	x
CHL	-0.69	x	x	x
Al	0.88	x	x	x
As	0.63	x	x	x
Cd	x	0.66	x	x
Cr	0.54	x	x	x
Cu	0.65	x	x	x
Fe	0.77	x	x	x
Hg	x	x	0.70	x
Pb	0.73	0.56	x	x
Mn	x	x	x	x
Ni	0.52	x	x	x
Sc	0.88	x	x	x
Zn	x	x	-0.52	x
P	x	x	x	x
N	-0.65	0.60	x	x
OC/N	x	x	x	0.52

(a) percentage of total variability explained.

TABLE 8: First five factor loadings for heavy metals and arsenic in solids sampled with sediment traps.

VZ3	Factor:	1	2	3	4	5
	%var(a):	24.8	13.9	12.6	10.0	7.9
OC		x	x	x	x	-0.52
IC		-0.60	x	x	x	x
CHL		-0.53	x	x	x	x
Al		0.74	x	x	x	x
As		0.59	x	x	x	x
Cd		x	x	x	x	x
Cr		0.68	x	x	x	x
Cu		x	x	0.77	x	x
Fe		0.89	x	x	x	x
Hg		x	x	x	0.70	x
Pb		0.51	x	x	x	0.64
Mn		0.52	x	x	0.64	x
Ni		x	x	0.77	x	x
Sc		0.79	x	x	x	x
Zn		x	x	0.52	x	x
P		x	x	0.50	x	x
N		x	0.85	x	x	x
OC/N		x	-0.76	x	x	x

VZ7	1	2	3	4	5
	35.3	22.3	11.4	9.8	8.8
OC	x	-0.61	x	x	0.54
IC	-0.73	x	x	x	x
CHL	x	-1.19	x	x	x
Al	0.87	x	x	x	x
As	0.87	x	x	x	x
Cd	0.57	x	x	x	0.69
Cr	0.74	x	x	0.50	x
Cu	0.67	-0.56	x	x	x
Fe	0.82	x	x	x	x
Hg	0.53	0.54	x	x	x
Pb	0.72	x	x	0.51	x
Mn	0.62	x	x	x	x
Ni	x	x	0.80	x	x
Sc	0.86	x	x	x	x
Zn	x	x	0.85	-0.62	x
P	0.62	-0.87	x	x	x
N	x	-0.79	x	x	x
OC/N	0.90	x	x	x	x

(a) percentage of total variability explained.

Organic pollutants

For the organic pollutants correlation- trend- and factor analysis were performed and settling solid data were compared with suspended solid data. In all calculations organic carbon normalised concentrations were used. Correlation analysis showed significant positive correlations between most pollutant concentrations. This is caused by the fact that the compounds share the physico-chemical mechanism of hydrophobic partitioning. Because of space economy and because the information obtained from correlation analysis and factor-analysis was very similar, also between the locations, this section focuses on the trend analysis, the comparison of the two particle types, and factor-analysis for location VZ3.

Trend analysis

Data on median concentrations, trends and seasonality are presented in Table 3. Generally, concentrations are highest on location HD followed by DM, VZ3 and VZ7. The higher concentrations at HD do not result in positive trends at the locations downstream (VZ3 and VZ7). As compared to the metals described in the previous section, the number of significant trends for the OC normalised data is smaller (Table 3). Most of the significant Sen slopes are negative. This corresponds to the fact that the pollution of the Rhine and the Meuse decreased gradually after the early seventies [41]. Significant positive trends are found only for a few cases, and are summarized in Table 6. Altogether, the data indicate a decrease in the HOC levels in Lake Volkerak/Zoom and the sources. Seasonality is less obvious than for the heavy metals. When seasonality is present, the lower concentrations are found in summer, due to the dilution of sorbed HOCs with newly generated planktonic particles.

To test differences in partitioning behavior of the HOCs on the four locations in this study, the PCB congener distribution was considered in detail. Essentially, the distribution of the HOCs over space and time is a function of the location of the sources, the physical/chemical properties of the chemicals and the hydrodynamics of the aquatic system(s) in consideration. HOCs may enter the lake from several sources or from nonpoint sources such as urban runoff and atmospheric deposition, in which case it is very difficult to distinguish between the processes. To test the influence of different partitioning behavior of HOCs, only compounds having an identical source function (location and source strength) should be compared. For instance, in case of one well defined source, compounds that exhibit a greater tendency to partition into sediments or suspended solids are less likely to be desorbed and thus would be found at greater distances from the source than those that sorb less strongly [42]. Important sources of PCBs are the Hollandsch Diep and the Dintel [2], both located at the northeast of the lake system. Insufficient data are available to quantify the contribution of air-water exchange of PCBs to the overall lake mass balance. However, Achman and co-workers [43] have shown recently that the air-water exchange of PCBs did not change the congener distribution in Lake Michigan significantly. Assuming that this is also the case for Lake Volkerak/Zoom and the supplying waters, we used solid phase congener distributions to evaluate the contribution of physical properties to the solid-water exchange of PCBs. Figure 5 shows the PCB congener distribution based on average values for the four locations HD, DM, VZ3 and VZ7. It appears that all seven PCBs studied have a very similar sequence for the locations HD, DM and VZ3, despite the geographic differences among these locations and the wide $\log K_{ow}$ range of 5.67 to 7.36 [44]. For VZ7 which has the greatest distance to the source, the pattern is slightly different but no clear shift towards the more hydrophobic congeners is found. We explain the somewhat diverging behavior of the PCBs at location VZ7 from the lower concentrations, resulting in more non-detects, lower accuracy and more error in the data. In Figure 6, the fractional contributions of PCB-153 and PCB-180 to the total PCB concentration in suspended solids sampled on location VZ3, are plotted as a function of the sampling month. Multiple data points for a certain month correspond to the different years in which sampling took place. Figure 6 illustrates that the congener distributions show no significant seasonal or linear variation in time. Apparently, the PCBs are all sorbed strongly enough to merely represent the time averaged hydrodynamic processes in the lake.

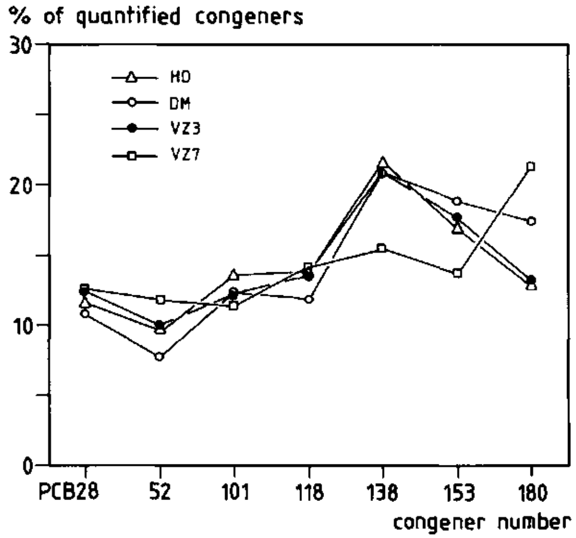

Fig. 5: PCB congener distribution for the locations HD, DM, VZ3 and VZ7.

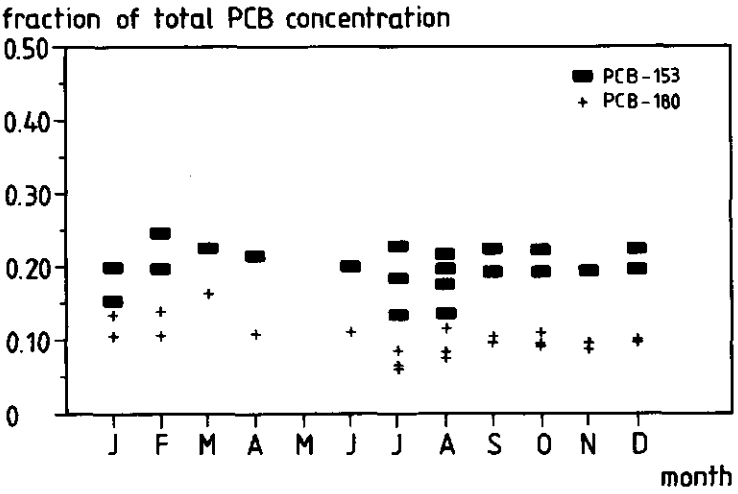

Fig. 6: The fractional contributions of PCB-153 and PCB-180 to the total PCB concentration in suspended solids sampled on location VZ3, plotted as a function of the sampling month.

Comparison of settling and suspended solids

Sediment trap PCB and pesticide concentrations were compared to suspended solid PCB and pesticide concentrations in a similar manner as was described for the solid characteristics and metal concentrations in the previous section. Hydrophobic organic compounds have been found to adsorb completely to the organic content of the particles [9,10]. By using the organic carbon normalised concentrations in this comparison, differences in organic carbon content of the two types of particles should not play a role. Our ST/CF ratios were calculated from data obtained in the same month, and in most cases in the same two-week period. Assuming that aqueous PCB and pesticide concentrations were approximately constant in these two-week periods, the equilibrium partitioning concept predicts identical OC normalized concentrations. A significant finding of this study is the elevated PCB and pesticide concentration on solids settling through the water column at locations VZ3 and VZ7 of Lake Volkerak/Zoom. As shown in Table 5, the concentrations in the settling solids on location VZ3 are on the average 1.3 to 6.8 times higher than concentrations in suspended solids. On location VZ7 (data not shown) less data were available, but the results confirm those for location VZ3. Higher PCB and PAH concentrations in settling solids were also reported by Baker and co-workers [27] in Lake Superior. However, their comparison was between suspended solids sampled one to two years later than their settling solids which makes the interpretation of their observations rather questionable. Several factors may explain the observed differences. First, differences in geometry of the organic matter particles may result in different sorption kinetics. The organic matter particles are generated in the water column by biotic production and are simultaneously exposed to aqueous HOC concentrations. To explain the differences between suspended and settling solids from uptake kinetics, the settling particles should be closer to equilibrium because they have the higher HOC concentrations. In previous studies on sorption kinetics for mineralizing phytoplankton [45,46], the release and uptake kinetics for detritus was found to be faster than for intact cells. Further, when the particles are living phytoplankton cells, growth causes a dilution of the chemical concentration in the cells [46,47], which might be the dominating process causing lower concentrations. When kinetics play a role, also some correlation of the ST/CF ratio with hydrophobicity as quantified by $\log K_{ow}$ might be expected. Sorption and bioaccumulation kinetics have been found to be slower for more hydrophobic compounds [9,47]. However, no significant correlation was found ($p=0.50$, Pearson correlation on ranks). Second, in our study (Table 5) as well in the report of Baker et al [27], a higher OC/N ratio was observed for the rapid settling particles. Regardless of the shape and origin of the particles, this indicates a difference in organic matter type which is probably related to the degree of mineralization. Pavoni et al [48] determined the PCB content of algae in the Lagoon of Venice (Italy) in fresh algal fronds (water surface) and old fronds (bottom). PCB concentrations in the older and decomposing algae were approximately 4.5 times higher than those in the fresh algae. In the laboratory, OC/N ratios for decomposing phytoplankton [45,46] and soils and sediments [49,50] have been found to correlate positively with organic carbon normalized partition coefficients for HOCs. This correlation is usually explained from differences in the adsorbent's average polarity as quantified by the OC/N or OC/(O+N) atomic ratio. Third, the vertical particle flux may be dominated by zooplankton faecal pellets and amorphous "marine snow". Baker et al [27] suggested that these biogenic particles may have acquired PCBs and pesticides through the process of biomagnification which explains the higher concentration levels.

Factor analysis

The factor analysis was performed using all pollutant data for location VZ3, including the sediment trap data. All available variables that provide information on particle and organic matter type were included. The results (Table 9) show 4 factors which explain 65.8% of total variance. The first factor explains 40.9% of the variance and has high negative loadings on all PCBs and most pesticides, Al and Sc, and positive loadings on OC, COD, N and LOI. This means that the pollutant concentrations in organic matter are correlated and that they are low in particles containing much organic matter. The first correlation originates from the similar chemical behavior of these chemicals.

TABLE 9: Factor loadings for organic carbon normalised PCBs and pesticides (VZ3)

Factor:	1	2	3	4
%var$^{(a)}$:	40.9	8.9	8.2	7.8
OC	0.74	x	x	x
COD	0.69	-0.64	x	x
IC	x	x	x	x
Al	-0.66	x	x	x
Sc	-0.76	x	x	x
P	x	-0.62	x	x
N	0.77	x	x	x
OC/N	x	x	x	0.51
OC/P	x	x	x	x
N/P	x	x	x	x
LOI	0.75	x	x	x
PCB28	-0.86	x	x	x
PCB52	-0.79	x	x	x
PCB101	-0.82	x	x	x
PCB118	-0.68	x	x	x
PCB138	-0.73	x	x	x
PCB153	-0.70	x	0.81	x
PCB180	-0.66	x	x	x
α-HCH	-0.93	x	-0.78	x
β-HCH	-0.84	x	x	x
γ-HCH	-0.80	x	x	x
HEPTA	-0.79	-0.50	x	x
HEPO	-0.89	x	x	x
ALDRIN	-0.64	x	x	0.55
DIELDRIN	-0.65	x	x	x
ENDRIN	-0.63	x	x	x
ISODRIN	-0.85	x	x	x
DDD44	-0.68	x	x	-0.64
DDE44	-0.71	x	x	x
DDT24	x	x	-0.70	x
DDT44	-0.78	x	x	x
HCB	-0.80	x	x	-0.52
HCBD	x	x	x	x
QCB	-0.87	x	x	x

(a) percentage of variance explained

The second observation may be caused by the significant seasonality found for organic carbon (Table 3), combined with the difference between suspended and settling solids. Generally, the particles rich in organic matter are the spring and summer particles when primary production is significant. Simple dilution may cause lower pollutant concentrations in these particles. Among these particles, the ones collected with centrifuges will have the higher OC content and the lower OC normalized PCB and pesticide concentrations because of the reasons described above.

CONCLUSIONS

In this study, correlations among the concentrations of constituents of suspended and settling solids were discussed. The results indicate that in the Hollandsch Diep and Lake Volkerak/Zoom phosphorous chemistry is influenced by photosynthesis, whereas in the Dintel, inorganic phosphate control dominates. Most heavy metals are correlated with clay and/or organic carbon content of the particles, and exhibit similar variation in time. Clay and most associated heavy metals showed negative trends on all locations, and a strong seasonality due to dilution by algal biomass. Exceptions were Mn and Hg. The behavior of Mn is complex and seems partially related to primary production but cannot be explained unambiguously from the available data. No correlation of heavy metals with carbonate content was found. HOCs were correlated with organic matter, which was governed mainly by primary production. In periods of algal growth, also organic carbon normalised HOC concentrations were lowered by dilution.

Settling particles showed a larger clay content and a larger degree of mineralization of the organic matter fraction as quantified by OC/N elemental ratios than suspended solids sampled simultaneously. The settling particles had also 1.3 to 6.8 times higher organic carbon normalised HOC concentrations. This difference suggests that HOCs in settling solids are closer to equilibrium and/or that variations in organic matter type significantly influence the sorption equilibrium constant K_{oc}. Regardless of which process is dominant, the variation in OC normalised HOC concentrations illustrates the shortcomings of the constant K_{oc} approach in many pollutant transport models. PCB congener distributions in the suspended solids were very constant in space and time. This means that differences in partitioning kinetics do not play a role.

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Chapter 3

SORPTION OF 1,2,3,4-TETRACHLOROBENZENE TO SEDIMENTS: THE APPLICATION OF A THREE PHASE MODEL

A.A. Koelmans and L. Lijklema

based on:

A.A. Koelmans, and L. Lijklema. 1989. Sorption of chlorobenzenes to sediments and suspended solids in Lake Volkerak/Zoom: the application of a three phase model. *Abstracts*, SETAC 10th Annual meeting, Toronto, Canada

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NOMENCLATURE

A = wetted inner surface of container (cm^2)
C = amount of test compound sorbed to container walls (g)
C_a = sediment concentration (g/ml)
D = amount of dissolved test compound (g)
DOC = Dissolved Organic Carbon (or third phase organic carbon, or total organic carbon) concentration in the aqueous phase after phase separation.
f_{oc}^{a} = the fraction organic carbon for the entire adsorbent.
f_{oc}^{i} = fraction organic carbon of organic matter type 'i' (g/g)
f_{oc}^{N} = fraction organic carbon for the non separable fraction of the sediment
K^C = constant for the aqueous phase and container wall (g/cm^2)
K_{oc}^{i} = organic carbon normalised sorption constant for organic matter type 'i'
K_{oc}^{N} = organic carbon normalised sorption constant for the non separable sediment fraction
K_{oc}^{obs} = 'observed' organic carbon normalised sediment to water-plus-third phase sorption constant
K_{oc}^{S} = organic carbon normalised sorption constant for the separable sediment fraction
K_{oc}^{true} = organic carbon normalised sediment/water sorption constant
K_{ow} = 1-octanole to water partition coefficient
K_p^{ASE} = 'True' HCB partition coefficient, corrected according to the Gschwend and Wu model and apparent solubility enhancements
K_p^{DOC} = 'True' HCB partition coefficient, corrected according to the adapted model and DOC measurements.
K_p^{N} = equilibrium constant for the aqueous and non-separable phase
K_p^{obs} = 'observed' sediment to water-plus-third phase sorption constant
K_p^{S} = equilibrium constant for the aqueous and separable phase
K_p^{true} = true sediment-water sorption constant
N = amount of test compound sorbed to the non-separable sediment fraction (g)
NSP = non separable particles
P^{glass} = composite variable accounting for sorption to container walls, equal to: $P^{glass}=A\times K^C/(f_{oc}^{a}\times Qa)$
Qa = total amount of sediment (g)
q^N = amount of non-separable sediment (g)
q^S = amount of separable sediment (g)
S = amount of test compound sorbed to the separable sediment fraction (g)
T = total amount of test compound (g)
V_w = weight of the aqueous phase (g)

Greek
α = non-separable sediment weight fraction
β = the weight fraction of the adsorbents carbon that is present in the form of dissolved organic carbon

SORPTION OF 1,2,3,4-TETRACHLOROBENZENE TO SEDIMENTS: THE APPLICATION OF A SIMPLE THREE PHASE MODEL

Abstract- The partition coefficients for 1,2,3,4-tetrachlorobenzene to three sediments were measured at different sediment to water ratio's with a batch equilibration method. The measured concentration dependency was described by a simple three phase model. A characterisation of the non separable fraction showed that the composition of this fraction varied significantly with sediment concentration. Despite of this variation, the three phase model used one organic carbon normalised sorption constant for the particulate organic matter (logKoc= 4.26) and one for the organic matter in the non separable fraction (logKoc= 3.90). Apart from incomplete phase separation, a major part of the concentration dependency originated from the adsorption of test compound to the container walls, so a correction for this phenomenon was included in the model. Validation of the model with literature data on HCB sorption confirmed the adequacy of the model

INTRODUCTION

In aquatic systems, the fate of hydrophobic organic compounds (HOCs) is controlled to a major extent by sorption processes. To quantify the sorption equilibrium, commonly the sorption coefficient, being the ratio of the sorbed and dissolved pollutant concentration, is used [1,2]. Several studies showed a decreasing apparent partition coefficient with increasing adsorbent concentration [3,4,5]. In the past decade, this phenomenon has been the subject of many further investigations. A major explanation has been the incomplete separation of the aqueous and solid phase in batch equilibration experiments [5,6]. In those studies, the part of the sediment remaining in the aqueous phase after centrifugation or filtration, is referred to as the 'third phase'. However, because the non separable material is poorly defined and not a true chemical phase, the term 'non separable particles' (NSP) will be used throughout this paper. Because of the presence of NSP in the aqueous phase, aqueous HOC concentrations are overestimated and the partition coefficients underestimated. A recent study [7] indicates, that besides this experimental artefact, also interparticle interactions, failure to reach equilibrium, volatilization, degradation of the chemical and sorption to glass may contribute to the observed concentration dependency of the partition coefficient. Besides glass, also the use of Teflon in liners and stir bars might contribute to adsorption losses.

To obtain true partition coefficients, independent of particle concentration, adapted experimental methods have been used. These include prewashing the sediments, more stringent centrifugal conditions [5], alternative methods to *determine* the true aqueous concentration such as the use of the gas purge technique [7,8] and reversed-phase separation [7,9], or methods to *estimate* true aqueous concentrations e.g. on the basis of apparent HOC solubility enhancements [10]. The disadvantage of prewashing is, that a part of the original adsorbent as present on the sampling location, is removed. Because washing with water is an extraction with a polar solvent, probably the more hydrophillic constituents of the organic matrix are removed. Centrifugation reduces the non-separable particle concentration, but it is not sufficient for extreme hydrophobic compounds and is not suitable for large volumes. The gas purge technique, the method of reversed-phase separation and corrections using the apparent solubility enhancements in water containing NSP are useful but are too complicated and time consuming to be used on a routine basis. A drawback of using solubility enhancements is that corrections are based on concentrations in HOC saturated aqueous phases, which is problematical for hydrophobic compounds [10].

Another possibility is the use of an arithmetical correction procedure to calculate the 'true' partition coefficient from the results of batch equilibration experiments which are relatively easy to perform.

Such a procedure was proposed and tested with experimentally determined partition coefficients, and with literature sorption data. Partition coefficients were measured at various solid to water ratios for three sediments of different composition. The objectives were to test the model underlying the correction procedure, to gain insight in the origin and nature of the third phase and to apply the method to the characterisation of hydrophobic sorption for a large number of adsorbents in the framework of another study [11].

EQUILIBRIUM SORPTION MODEL

Gschwend and Wu [5] described pollutant speciation as a three-phase equilibrium. Their model was developed to explain the sediment concentration dependency of partition coefficients obtained from batch experiments. The concept is also applicable to natural systems where besides discrete particles also organic matter in dissolved or colloidal form is present.

We changed this model, by using a different equilibrium equation and by including sorption to container walls, and applied it to sediment suspensions with varying solid to water ratios.

In any experimental system the total amount of test compound equals the amount dissolved and the amount sorbed to the phases present:

$$T=D+S+N+C \qquad (1)$$

$T=$ total amount of test compound (g)

$D=$ amount of dissolved test compound (g)

S=	amount of test compound sorbed to the separable sediment fraction (g)
N=	amount of test compound sorbed to the non-separable sediment fraction (NSP-fraction) (g)
C=	amount of test compound sorbed to the container walls (g)

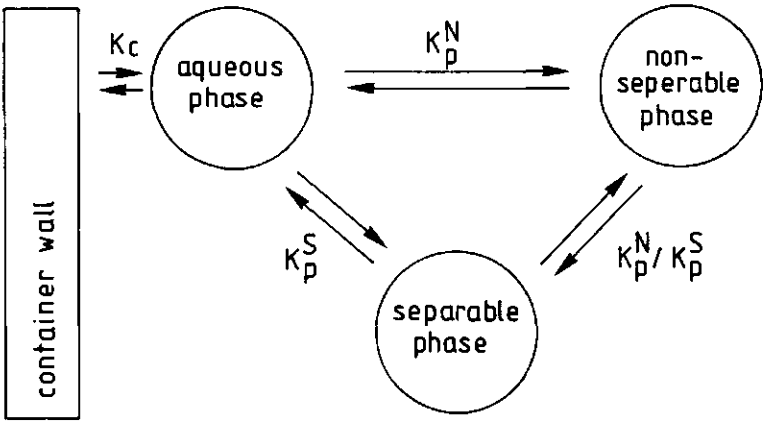

Fig. 1: Schematic representation of a three phase system with sorption to container walls.

Thermodynamically meaningful equilibrium constants as shown in Figure 1 for interactions between phases, can be defined as:

$$K_p^N = \frac{N/q^N}{D/V_w} \tag{2}$$

$$K_p^S = \frac{S/q^S}{D/V_w} \tag{3}$$

q^S and q^N can be written as fractions of the total amount of adsorbent, Qa, according to:

$$q^N + q^S = Qa \tag{4}$$

$$q^N = \alpha \times Qa \tag{5}$$

$$q^S = (1-\alpha)Qa \tag{6}$$

and: K_p^N = equilibrium constant for the aqueous and non-separable phase (g/g)
K_p^S = equilibrium constant for the aqueous and separable phase (g/g)
q^N = amount of non-separable sediment (g)
q^S = amount of separable sediment (g)
α = non-separable sediment-fraction (g/g).
V_w = weight of the aqueous phase (g)

For the adsorption to the container walls, a constant relating the dissolved concentration to the amount adsorbed to the surface can be defined [12,13]:

$$K^C = \frac{C/A}{D/V_w} \tag{7}$$

In which: K^C = constant for the aqueous phase and container wall (g/cm^2)
A = wetted inner surface of the container (cm^2)

Analysis of the aqueous phase, yields $(D+N)$ and if T is known, $(S+C)$ can be calculated by difference. The *observed* partition-coefficient is given by:

$$K_p^{obs} = \frac{(S+C)/Qa}{(D+N)/V_w} \tag{8}$$

and Qa = total amount of sediment (g)
V_w = total amount of water (g)

Elimination of S, C, D and N in equation (8) using the equations (2), (3) and (7), followed by substitution of q^N and q^S using (5) and (6) results in:

$$K_p^{obs} = \frac{K_p^S(1-\alpha) + (f_{oc}^a P^{glass})}{1+\alpha K_p^N C_a} \tag{9}$$

In which C_a is the sediment-concentration (g/ml), and P^{glass} is a composite variable equal to $A \times K^C/(f_{oc}{}^a \times Qa)$, which is defined for convenience. The conditional coefficient K_p^{obs} reflects the distribution of the pollutant between aqueous phase plus colloids, and the settleable particles, but it is not a sediment-water partition coefficient. In a natural system e.g. a river or a lake, P^{glass} would be zero and K_p^{obs} would represent the distribution between the total concentration in the water column and the concentration in the settling particles or sediments. Because hydrophobic chemicals bound to colloids are transported as being dissolved, K_p^{obs} as defined in equation (8) is a useful parameter in models describing the fate of micropollutants. Aggregation and settling of destabilized colloids in the presence of larger particles may, however, rapidly remove the pollutants under favourable hydrodynamic and chemical conditions.

In the model of Gschwend and Wu, a 'true' sorption coefficient relating sorbed concentrations to the real dissolved concentrations, is defined as:

$$K_p^{true} = \frac{S/q^S}{D/V_w} = K_p^S \tag{10}$$

Thus the third phase is not taken into account as a part of the adsorbent. This simplification is not allowed when the fraction sediment organic matter that is transferred to the aqueous phase in colloidal form is large, or the affinity of the test compound for that material is high, or both. We believe that principally *all* phases should be taken into account and that an alternative formulation for K_p^{true} should be used. Karickhoff [1] suggested that the total partition coefficient of a sediment that consists of N different types of organic material should be calculated according to:

$$K_p = \sum_i^N K_{oc}^i \times f_{oc}^i \tag{11}$$

with $f_{oc}^{\ i}$ = fraction organic carbon of organic matter type 'i' (g/g)
$K_{oc}^{\ i}$ = organic carbon normalised sorption constant for organic matter type 'i'

In our conception, the original sample is split up due to the agitation and centrifugation procedure, so two adsorbent types are distinguished. Based upon equation (11) the theoretically correct expression for the sorption coefficient for the *total* adsorbent, is:

$$K_p^{true} = \frac{(N+S)/Qa}{D/V_w} = \alpha K_p^N + (1-\alpha)K_p^S \tag{12}$$

Combination of (9) and (12) gives:

$$K_p^{true} = K_p^{obs}(1+\alpha K_p^N C_a) + \alpha K_p^N - (f_{oc}^a \times P^{glass}) \tag{13}$$

Based upon this equation, corrections to the observed values can be made. Unfortunately α and K_p^N are unknown and are likely to vary with sediment concentration. This problem can be solved by switching to organic carbon normalised coefficients as in equation (11) and by using the total organic carbon concentration in the aqueous phase TOC (g/g). Although colloidal organic particulates contribute to TOC, usually the abbreviation 'DOC' (dissolved organic carbon) is used for aqueous phase organic carbon, which yields:

$$DOC = f_{oc}^{N} \times \alpha \times C_a \tag{14}$$

Using (11) and (14), (12) can be rewritten as:

$$K_{oc}^{true} = \beta K_{oc}^{N} + (1-\beta) K_{oc}^{S} \tag{15}$$

in which ß = the fraction of the adsorbents' carbon that is present in the form of DOC in the aqueous phase, equal to: ß = DOC/($f_{oc}{}^{a} \times Ca$), and $f_{oc}{}^{a}$ = the fraction organic carbon for the entire adsorbent.

An important assumption in the Gschwend and Wu model, is that the different K_{oc}'s are independent of the sediment to water ratio. It can be seen from equation (15) that therefore, the magnitude of the variable ß must be independent on the sediment to water ratio. This is only possible if the DOC in the aqueous phase after phase separation is proportional to the sediment to water ratio C_a; a condition which should be tested.

Also using (11) and DOC $= f_{oc}{}^{N} \times \alpha \times C_a$, equation (13) can be rewritten to yield an equation for organic carbon based partition coefficients:

$$K_{oc}^{true} = K_{oc}^{obs}(1 + DOC \times K_{oc}^{N}) + \beta K_{oc}^{N} - P^{glass} \tag{16}$$

Equation (16) shows that the measurement of DOC and $K_{oc}{}^{obs}$ at varying sediment to water ratios, allows the calculation of $K_{oc}{}^{true}$ and $K_{oc}{}^{N}$, when the organic carbon content of the entire sediment $f_{oc}{}^{a}$, 'K^{C}' and 'A' are known. In an experimental set up where glass sorption plays no role, e.g. when $K_{oc}{}^{obs}$ is calculated from HOC concentrations directly measured in solid and aqueous phase, 'C' in equation (1), and consequently, P^{glass} in equation (16) become zero. For the Gschwend and Wu model, an analogous derivation which is given in [5], yields:

$$K_{oc}^{true} = K_{oc}^{obs}(1 + DOC \times K_{oc}^{N}) \tag{17}$$

Comparison of (16) and (17) shows that the Gschwend and Wu model underestimates $K_{oc}{}^{true}$ with a factor [$ß \times K_{oc}{}^{N}$]. Consequently, when this term is large, the model is inadequate in estimating $K_{oc}{}^{true}$. Equation (16) can also be written in a linearized form:

$$\underbrace{K_{oc}^{obs} - P^{glass}}_{Y} = -\underbrace{DOC\times\left[K_{oc}^{obs}+\frac{1}{C_a\times f_{oc}^{a}}\right]}_{X}\times K_{oc}^{N} + K_{oc}^{true} \tag{18}$$

When the terms marked 'X' and 'Y' are plotted, theoretically a straight line with slope 'K_{oc}^{N}' and constant 'K_{oc}^{true}' results. An alternative method is to express K_{oc}^{obs} as a function of C_a and to estimate K_{oc}^{true} and K_{oc}^{N} directly from the measurements with a non linear curve fitting technique. This analysis has been tried out for 1,2,3,4-tetrachlorobenzene and three lake sediments.

EXPERIMENTAL

Chemicals

All water used in the sorption experiments was distilled water. Organic solvents (acetone and 2,2,4-trimethylpentane) were obtained from Promochem (nanograde). 1,2,3,4-Tetrachlorobenzene (Dr.S. Ehrenstorfer, 98%) was used without further purification.

Sediments

Sediments were sampled by the Dutch Institute for Inland Water Management and Waste Water Treatment, and delivered frozen and dried at 105 °C, or freeze-dried (Table 1). Organic carbon contents were determined according to the wet oxidation method described by Begheijn [14]. Data about grain size were provided by the Dutch Institute for Inland Water Management and Waste Water Treatment. The results of the characterisation of the sediments are shown in table 1. The three sediments differ significantly in organic carbon content and grain size.

TABLE 1:
Sediment characteristics.

	SEDIMENT 1$^{(a)}$	SEDIMENT 2$^{(b)}$	SEDIMENT 3$^{(b)}$
$f_{oc}$$^{(a)}$	0.0386 ± 0.0021 (n=5)	0.0146 ± 0.0014 (n=2)	0.001 ± 0.0005 (n=3)
$\% < 16\mu$	30	> 45	< 5

(a) freeze dried; (b) oven dried

Batch equilibration protocol

Teflon-lined bottles with volumes between 500 ml and 10 l were filled with sediment (0.3 g to 40 g) to obtain a sediment concentration range of 0.03 - 80 g/l. A 1,2,3,4-tetrachlorobenzene (TeCB) spike-solution of approximately 2000 μg/l was prepared in a closed gas-purge system as described elsewhere [11]. In this apparatus the transfer of TeCB from the solid to the dissolved phase takes place via the gas phase. The TeCB solution was used to spike the sediment suspensions in such a way, that aqueous phase concentrations after equilibration were approximately 20 μg/l. Equilibration for bottles smaller than 1000 ml was for 24 hours on a shaking machine. Larger bottles were agitated for 24 hours using magnetic stirrers. Prior experiments showed that equilibrium was achieved within 10 hours. All experiments were performed at room temperature. The sediment phase was separated from the water phase by centrifugation at 2000 g for 20 minutes.

Analysis of test compounds and characterisation of supernatant

The supernatants were extracted (1:1 V/V) with 2,2,4-trimethylpentane and subsequently analyzed for the test compound with capillary gas chromatography (HP 5890) with electron capture detection, using external standards. The chromatograms showed no signs of lower substituted chlorobenzene congeners, indicating that biodegradation did not occur.

Blank runs were made without sediment, to asses losses of the test compound to container walls. From these experiments, a sorption-constant as defined by equation (4), of 0.27 g/cm2 was calculated. This value was used in the sorption-model and reflects the affinity of the test compound for the combination of glass walls and Teflon liners and stir bars. DOC-measurements were performed on a Dohrmann DC-180 TOC-analyzer and on an OIC model 700 TOC-analyzer. Detection limits were 0.5 ppm and 0.06 ppm respectively. Reproducibility was better than 2% (relative standard deviation, n=6). Carbon standards of 5.00, 10.0 and 100.0 ppm C were made with potassium hydrogenphtalate in Barnstead Nanopure water. For the sediment with 0.1 % organic carbon content (sediment 3), DOCs could only be detected at high sediment-concentrations (2 samples). The beam attenuation factor at 360 nm was measured on a Cecil Instruments CE 272 spectrophotometer with a 4 cm cuvette. For sediment 1, 270-900 nm beam attenuation spectra were measured for three batches with adsorbent concentrations of 0.1, 1.5 and 80 g/l respectively, on a Beckman DU-64 spectrophotometer with a 5 cm cuvette. Although formally beam attenuation factors were measured, the more common term *absorbance* will be used throughout this paper. NSP-concentrations for sediment 1 were determined by drying known weights of supernatant (up to 400 g) at 105 °C in preweighed beakers.

RESULTS AND DISCUSSION

Characterisation of non separable particles

The logarithms of DOC-measurements and sediment concentrations are shown in Figure 2. It appears that the concentration of organic carbon in the supernatant is not fully proportional to the sediment concentration. This was also found by Voice *et al.* [15] and Servos *et al.* [7]. This means that ß as in equation (15) decreases with increasing sediment concentration. However, in the range up to ≈5 g/l the deviation from linearity is limited. Solid concentrations in aquatic systems are generally below this value [16] which justifies the use of equation (15). The DOC measurements were successfully fitted to the linearized form of the equation:

$$DOC = a \times [C_a]^b \tag{19}$$

with;

Sediment 1:	$a = 3.9\times10^{-4}$	$b = 0.76$	$r^2 = 1.00$	(n=9)
Sediment 2:	$a = 1.2\times10^{-4}$	$b = 0.75$	$r^2 = 0.99$	(n=4)
Sediment 3:	$a = 0.9\times10^{-4}$	$b = 1$		(n=2)

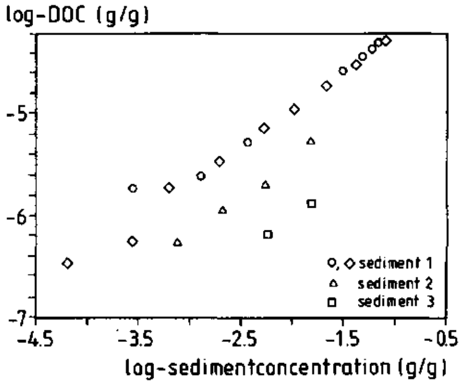

Fig. 2: DOC-measurements for the sediments studied. Measurements for sediment 1 are in duplicate

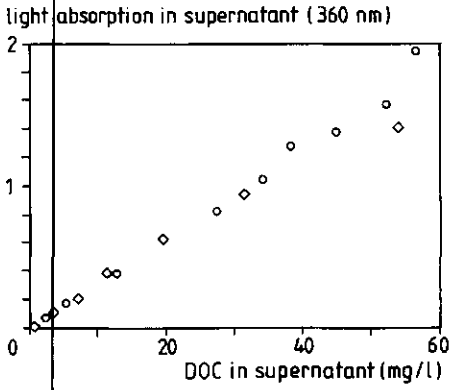

Fig. 3: Light absorption at 360 nm (×0.25 cm^{-1}) as a function of DOC for sediment 1.

For sediment 1, a linear relationship between light absorption at 360 nm and DOC is shown in Figure 3. This relationship can be used as a cheaper alternative to DOC measurements, or to estimate DOC-values below the DOC detection-limit. For the same sediment, the 270-900 nm adsorption spectra of the third phase, normalised to DOC for three sediment to water ratio's are depicted in Figure 4. When the normalisation is performed correctly and the nature of the third phase material is independent of its concentration, the three spectra should match completely. However, the DOC-normalised extinctions increase with DOC concentration. Several characteristics of the spectra were used to examine the constancy of NSP composition. At a wavelength of 272 nm (A_{272}), the differences in extinction are the most significant due to the smallest relative error. The absorptivity at 272 nm reflects absorbance of π-π^* transitions in substituted benzenes and most polyenes and has been related to the aromatic content of isolated soil humic acids [17]. Furthermore, K_{oc} values for pyrene were found to be proportional to A_{272} [17]. Another relevant parameter is the ratio of the extinctions at 465 and 665 nm (E_4/E_6), which was found to decrease with increasing particle size at constant pH [18]. From the three spectra, E_4/E_6 ratio's of 5.0, 4.1 and 3.2 were calculated for the supernatants of the 0.1, 1.5 and 80 g/l batches respectively. Although these ratio's have limited significance as a result of the inaccurate extinction measurements, especially at 665 nm, the general trend suggests that the non separable phase at high sediment concentrations, consists of larger particles than at lower sediment concentrations. Apparently, the third phase organic material has different properties at different sediment concentrations.

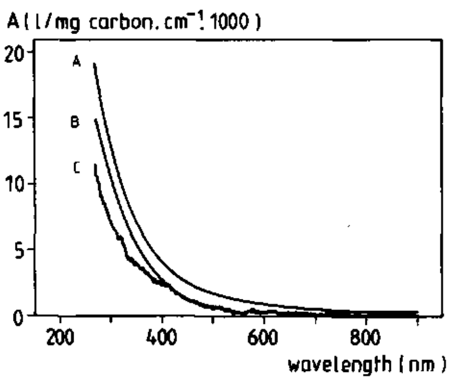

Fig. 4: Absorption spectra for third phase material obtained from sediment 1 at 80 (A), 1.5 (B) and 0.1 (C) g/l.

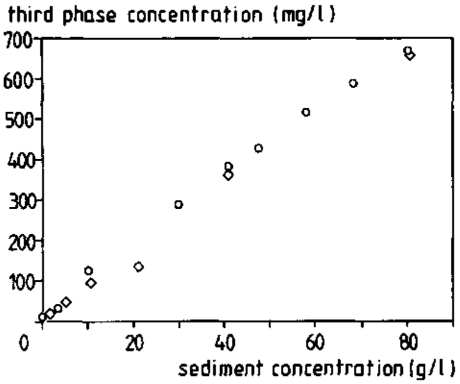

Fig. 5: Concentration of non-seperable phase as a function of sediment concentration for sediment 1.

For sediment 1, the NSP-concentration is plotted against the sediment concentration, in Figure 5. The relationship seems linear, except at high sediment concentration. Also for this sediment, the relationship between DOC and third phase concentration is plotted (Figure 6). This curve suggests a decrease of f_{oc}^N at higher sediment-concentrations.

For example at a NSP concentration of 100 mg/l, the DOC is 10 mg/l, yielding a foc^N of 0.1. At a NSP concentration of 600 mg/l, f_{oc}^N decreased to 0.083.

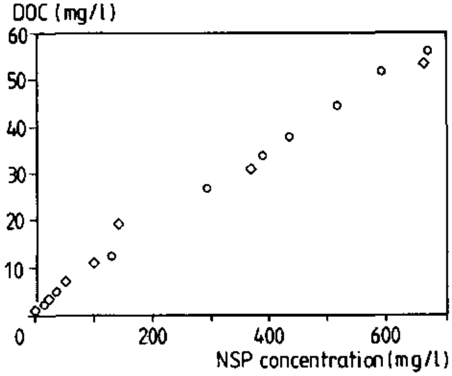

Fig. 6: DOC as a function of the concentration of non-separable phase for sediment 1.

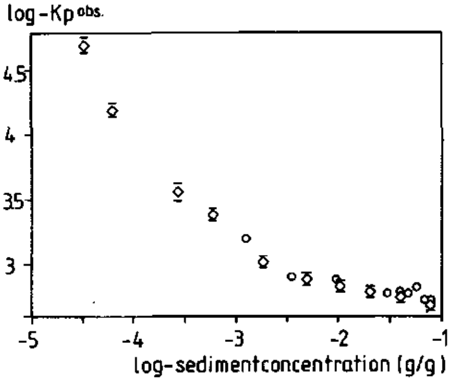

Fig. 7: Observed partition coefficients as a function of sediment concentration for duplicate experiments with sediment 1.

Model validation using experimentally determined TeCB partition coefficients

The observed partition coefficients are plotted as a function of sediment concentration in Figure 7 for duplicate experiments with sediment 1. The reproducibility is good. The observed partition coefficient increases strongly at low sediment concentrations. For one series of measurements also the standard deviation, calculated with the Gauss-equation for propagation of errors, is shown.

The results were fitted to the non-linear model as condensed in equation (16). The best fit was obtained by minimizing the residual sum of squares by trial and error. For the whole dataset a value for K_{oc}^{true} of 18×10^3 and a value for K_{oc}^N of 8×10^3 were obtained. The results of the model fit are depicted in Figure 8 and are quite satisfactory, despite the fact that the DOC is not fully proportional to the sediment concentration and that the third phase composition is not constant.

Karickhoff [19] derived an empirical relationship between K_{oc} and the octanol to water partition coefficient K_{ow}:

$$LogK_{oc} = LogK_{ow} - 0.36 \tag{20}$$

With a logK_{ow} for 1,2,3,4-tetrachlorobenzene of 4.635 [20], equation (20) yields a logK_{oc} value of 4.28. The value of K_{oc}=18000 (logK_{oc}= 4.26) for the bulk organic matter is in good agreement with this value.

Apart from the K_{oc} values, the model is very sensitive to K^C and the organic carbon content. The fit for sediment 3, for example, improves significantly when a foc value of 0.05 is used (Figure 9). Uncertainties in the measured foc value for this sediment are of the same magnitude as this difference. For the combination of 1,2,3,4-tetrachlorobenzene and the sediments studied, the contribution of the third phase to the concentration dependency is significant, but smaller than the contribution of the sorption to the container walls.

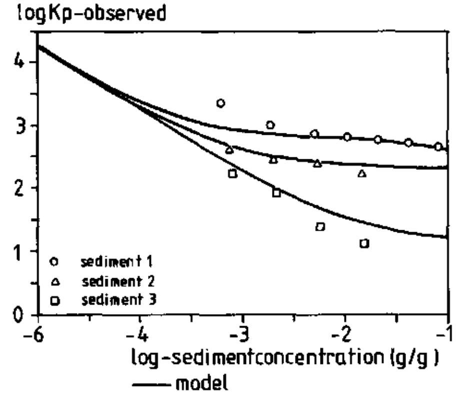

Fig. 8: Measurements of Kp^{obs} as a function of sediment concentration and model calculations for the three sediments studied. Koc^{true}= 18000, Koc^{N}= 8000.

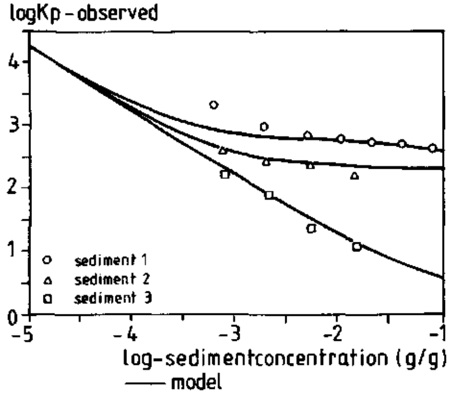

Fig. 9: Model fit as shown in figure 8, illustrating the effect of a small change in the foc for sediment 3, with 0.1 % organic carbon content.

The results for sediment 1 were also fitted to the model using equation (18) and linear regression. The linear relationship between 'Y' and 'X' (see eqn. 18) and the model parameters are shown in Figure 10 and Table 2 respectively. It appears from Table 2 that the model is highly significant. Because of the different estimation method used, the values for K_{oc}^{true} $(20 \pm 1.2) \times 10^3$ and K_{oc}^{N} $(5.8 \pm 1.8) \times 10^3$ are slightly different.

According to the model results, the K_{oc} for NSP-organic carbon is lower than the K_{oc} for the whole organic phase present in the sediment. Lower K_{oc} values for sorption to DOM, compared to K_{oc} values for particulate organic matter from sediments, were also found for chlorobenzenes and for PCBs [21]. This supports the idea that third phase material contains a more hydrophillic part of the total organic phase, having a lower affinity for hydrophobic compounds.

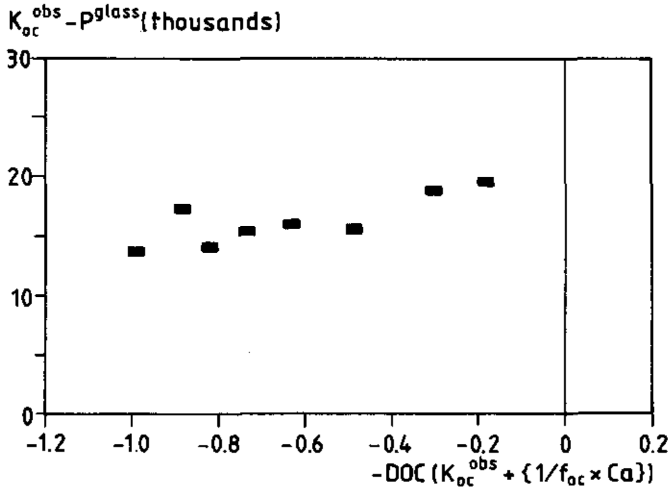

Fig. 10: Linear relationship between 'Y' and 'X' (eqn. 18), for TeCB sorption to sediment 1.

TABLE 2:

Parameter estimates and analysis of variance for the linearized model (equation 18) applied to sorption data for 1,2,3,4-tetrachlorobenzene.

Parameter	Estimate	SE	T-value		P
K_{oc}^{true}	19897	1231	16.2		0.00000
K_{oc}^{N}	5792	1801	3.2		0.01822
		Analysis of variance			
Source	Sum of squares	DF	Mean square	F-ratio	P
Model	1.90×10^7	1	1.90×10^7	10.3	0.01822
Error	1.10×10^7	6	1.83×10^6		

$r^2 = 0.633$

The concentration dependency is the greatest for sediment 3, which has a very low organic carbon content. For this sediment *relatively* the largest amount (up to 15%; $\beta = 0.15$) of the original particulate organic carbon is released to the supernatant. Probably the tendency of particulate organic matter to dissolve or to break up into colloidal particles is influenced by the saturation level of the aqueous phase. In addition, the tightness of packing might play a role, resulting in an easier release for sandy sediments. In recent, similar experiments of Schrap and co-workers [10] with Oostvaardersplassen (The Netherlands) sediment, at low solid/water ratios even 33% of the particulate organic carbon ($\beta=0.33$) was transferred to the supernatant. We conclude that for these values of β, the Gschwend and Wu model is not applicable.

Model validation using literature data on hexachlorobenzene (HCB) sorption to sediment

In a recent study, Schrap and co-workers [10] determined hexachlorobenzene partition coefficients (K_p^{obs}) at varying sediment concentrations with a batch method. Phase separation was accomplished by centrifugation, and HCB was measured in sediment and aqueous phase. To quantify the effect of incomplete phase separation, the supernatants were used for measurement of DOC and apparent solubility enhancements caused by NSP. Corrections were calculated using the original Gschwend and Wu model [5] (eqns. 10, 17). In this section the data of Schrap et al are used to validate our model. Further, our correction procedure using DOC and the adapted model, is compared with the procedure followed by Schrap et al. The data provided by Schrap et al are listed in Table 3. Sediment was obtained from the Oostvaardersplassen (The Netherlands, $f_{oc}=0.025$), the test compound was a more hydrophobic chlorobenzene congener than TeCB (HCB, $\log K_{ow}=5.731$ [20]), and HCB was determined in aqueous and solid phase, so sorption to container walls was insignificant ($P^{glass}=0$).

The data from Schrap were transformed according to equation (18). K_{oc}^{true} and K_{oc}^{N} were estimated using linear regression and are shown Table 4. The significance of the regression is similar to the one for 1,2,3,4-tetrachlorobenzene described in the previous section. With a $\log K_{ow}$ of 5.731 for HCB, equation (20) yields a K_{oc} of $10^{5.37}$, which is a little higher than the measured K_{oc}^{true} value of $10^{5.14}$. As for 1,2,3,4-tetrachlorobenzene, the K_{oc} for NSP-organic carbon is lower than the K_{oc} for the whole organic phase. However, the difference between K_{oc}^{true} and K_{oc}^{N} is much larger. One explanation may be the difference between the sediments as well as between the experimental methods used. Another explanation may be the fact that the DOC values were too high, as was reported by Schrap [10]. As can be seen from equation (18), this results in an underestimation of K_{oc}^{N}. It must be noted that in contrast to K_{oc}^{N}, the estimate for K_{oc}^{true} is not influenced by systematic errors in the DOC determinations. This is an advantage of the linearized model. From the results listed in Table 4 we conclude that our model is also adequate in describing HCB sorption to the Oostvaardersplassen sediment.

TABLE 3:
Model parameters calculated using literature data for hexachlorobenzene sorption to sediments at varying solid/water ratios.

data provided by Schrap et al [10]				This study
C_a g/ml	K_p^{obs} l/kg	DOC g/ml	$K_p^{\mathrm{ASE},(a)}$	$K_p^{\mathrm{DOC},(b)}$
2.5×10^{-4}	3250	1.1×10^{-5}	6500	3890
1.0×10^{-3}	3200	1.4×10^{-5}	6720	3670
2.0×10^{-3}	2830	1.8×10^{-5}	6510	3310
6.3×10^{-3}	2700	3.3×10^{-5}	7560	3460
1.0×10^{-2}	2100	4.8×10^{-5}	6930	2950
2.5×10^{-2}	1600	1.0×10^{-4}	8320	2920
5.0×10^{-2}	1400	2.0×10^{-4}	11900	3690
		Average:	7780	3410
		%s.d.:$^{(c)}$	± 25%	± 11%

(a) 'True' HCB partition coefficient, corrected according to the Gschwend and Wu model and apparent solubility enhancements [10], (b) 'True' HCB partition coefficient, corrected according to the adapted model and DOC measurements. (c) relative standard deviation, n=7.

Table 3 also shows the HCB partition coefficients corrected by Schrap on the basis of solubility enhancements and the Gschwend and Wu model (K_p^{ASE}), together with values (K_p^{DOC}) which we calculated from K_p^{obs}, f_{oc}^{a}, DOC and our estimate for K_{oc}^{N} (Table 4) according to equation (16). The K_p^{DOC} values have less less trend and variation than the K_p^{ASE} values. Because the corrections are meant to yield a constant K_p we conclude that our method is better. One explanation for the more constant K_p^{DOC} values as compared to the K_p^{ASE} values is the different model used. Following Gschwend and Wu, Schrap et al do not take the change in particulate organic carbon content into account. This results in an underestimation of K_p^{ASE} with magnitude $[f_{oc}^{a}\times\beta\times K_{oc}^{N}]$. Because in the experiments by Schrap et al, ß increases with decreasing solid/water ratio, the K_p^{ASE} values show a trend. Another explanation may be the lesser accuracy of solubility measurements compared to DOC measurements. DOC values can be measured on a routine basis using sophisticated TOC analyzers, whereas solubility measurements require complicated and time consuming experimentation. Another striking observation is the relatively high average K_p^{ASE} as compared to the average K_p^{DOC}. Schrap et al also note that their K_p^{ASE} values are high, and explain this from non-ideal behavior of HCB at saturation level resulting in an overprediction of the actual solubility enhancement during the sorption experiment.

TABLE 4:
Parameter estimates and analysis of variance for the linearized model (equation 18) applied to sorption data for hexachlorobenzene obtained from Schrap et al [10].

Parameter	Estimate	SE	T-value		P
K_{oc}^{true}	136609	11843	11.5		0.00009
K_{oc}^{N}	8065	2086	3.9		0.01180
			Analysis of variance		
Source	Sum of squares	DF	Mean square	F-ratio	P
Model	4.02×10^9	1	4.02×10^9	15.0	0.01180
Error	1.35×10^9	5	2.69×10^8		

$r^2=0.749$

CONCLUSIONS

The concentration dependency of the 1,2,3,4-tetrachlorobenzene partition coefficient for three sediments with different organic carbon fractions and grain sizes can be described by a simple three phase model. The model is similar to the Gschwend and Wu model, but is based upon a different equation for the 'true' partition coefficient and includes a correction for sorption losses to the container walls.

It was shown that the nature of the non separable fraction in batch equilibration experiments, is dependent on sediment concentration. However, for the quantification of the sorption of TeCB, the use of one 'overall' organic carbon normalised sorption constant for the sediment organic matter and one for the organic matter in the non separable fraction was sufficient. The non separable colloidal phase has a lower K_{oc} value than the organic matter from the bulk sediment.

Besides validation with new experimental data, the model was tested on a literature data set for sorption of hexachlorobenzene to sediments at different solid/water ratios. The calculations confirm the conclusions mentioned above, and show that the effect of solid/water ratio could be quantified better using DOC measurements and the adapted model, than apparent solubility enhancements and the Gschwend and Wu model .

Although the adapted model needs validation with more sediments and HOCs, we conclude that the procedure proposed in this paper is a promising tool for correcting partition coefficients measured at varying sediment concentrations on a routine basis. The only requirements besides batchwise determination of K_p^{obs} values, are accurate measurements of DOC and the organic carbon content of the sediment, which are relatively easy to perform.

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Chapter 4

SORPTION OF 1,2,3,4-TETRACHLOROBENZENE AND CADMIUM TO SEDIMENTS AND SUSPENDED SOLIDS IN LAKE VOLKERAK/ZOOM

A.A. Koelmans and L. Lijklema

based on:
A.A. Koelmans and L. Lijklema. 1989. Sorption of 1,2,3,4-tetrachlorobenzene and cadmium to sediments and suspended solids in Lake Volkerak/Zoom. *Wat. Res.*, **26**:327-337.

SORPTION OF 1,2,3,4-TETRACHLOROBENZENE AND CADMIUM TO SEDIMENTS AND SUSPENDED SOLIDS IN LAKE VOLKERAK/ZOOM

Abstract- Sediment and suspended solid samples were collected from Lake Volkerak/Zoom in The Netherlands. The samples were used for the determination of 1,2,3,4-tetrachlorobenzene and cadmium sorption coefficients and for the determination of the concentrations of total iron, manganese, organic carbon, chlorophyll-a and scandium. Cadmium sorption coefficients were also determined for isolated suspensions of *Cryptomonas* spp. A statistical analysis of the results indicates that the sorption coefficients for tetrachlorobenzene are proportional to the organic carbon content, which is highly influenced by algal blooms. A similar analysis shows that cadmium is bound almost completely to the geochemical iron, manganese and organic phases, the first being exclusively associated with the clay fraction. Due to a decrease in relative clay content during algal blooms, a proportional decrease in the cadmium distribution coefficient was found. It was found that the data obtained from the statistical analysis are in good agreement with reported data for isolated model phases.

INTRODUCTION

In 1987, in The Netherlands, the previously estuarine Lake Volkerak/Zoom (Fig. 1) became stagnant and fresh as a result of a damming. Since that date, micropollutants transported by the rivers Rhine and Meuse are accumulating in this relatively clean area. This study addresses the measurement of sorption and distribution of micropollutants in the lake in the framework of an assessment of management strategies for protection of this lake.

In aquatic systems like Lake Volkerak/Zoom, suspended particles and sediments are the major compartments for organic micropollutants and trace metals. As a consequence, integral models for the behaviour of these compounds which are often used as a predictive tool in water quality management, should contain accurate descriptions of adsorption processes, valid for realistic conditions. Compared to the modelling of hydrophobic sorption equilibrium which is based upon the concept of phase partitioning to organic matter, the chemical modelling of heavy metal sorption is far more complex. Numerous laboratory studies address the effects of environmental conditions such as pH, ionic strength, complexing agents, competing surfaces, redox potential and sorbent concentration ([1] and references therein). However, low pH values, the use of buffers, high adsorbate concentration ranges, storage and preparation procedures that radically change the nature of the sample, or the use of isolated artificial model phases in such studies frequently limit the applicability of the results because they deviate significantly from natural conditions [2,3]. Furthermore, the role of algal blooms in the scavenging of micropollutants in lakes, is not well documented.

In this study, an attempt was made to measure and evaluate sorption coefficients for different natural particle types present in Lake Volkerak/Zoom, including algae, under realistic conditions. A second objective was the calculation of sorption parameters for the relevant geochemical adsorbent phases comprising the particles, and the comparison to literature values for isolated model phases.

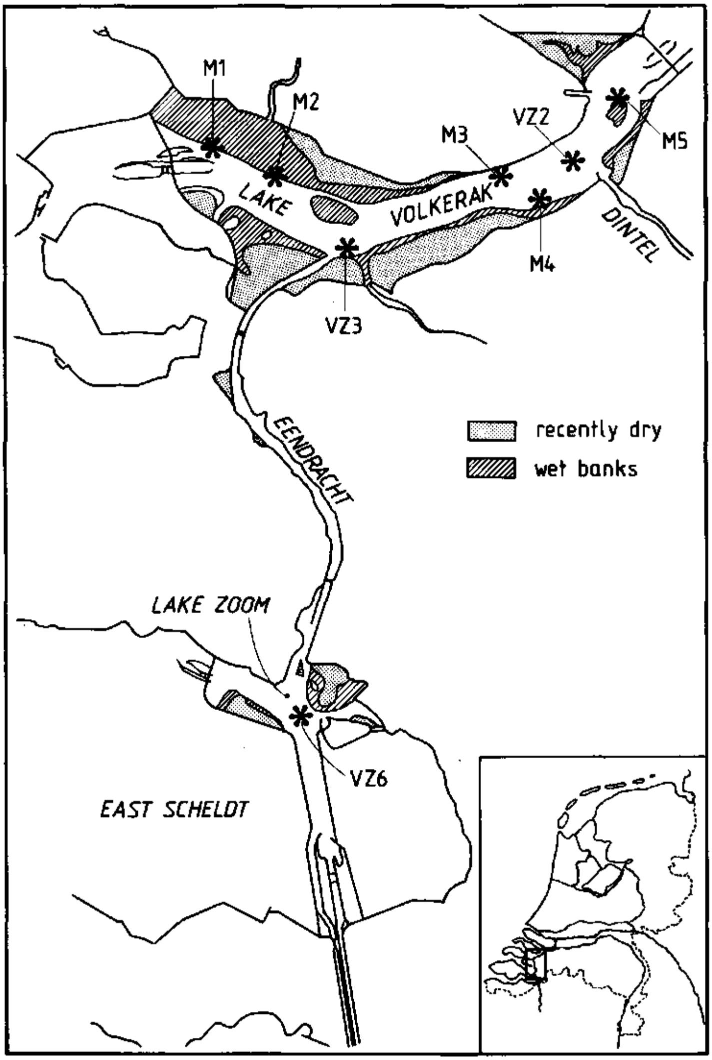

Fig. 1: Sampling locations M1, M2, M3, M4, M5, VZ2, VZ3, VZ6 and REF. Insert: location of Lake Volkerak/Zoom in the Netherlands.

RESEARCH PLAN

The sampling strategy was designed in such a way that a maximum variability of adsorbent characteristics would occur in samples taken from the same water body, including a period of algal growth.

The relevant adsorbent characteristics for the sorption of cadmium according to the literature are the contents of organic matter, manganese oxides, iron oxides and clays [2,4,5,6,7,8]. For 1,2,3,4-tetrachlorobenzene (TeCB), being a non-polar, non-reactive compound, only organic matter is relevant [9,10,11]. These geochemical phases were selected for this study and measured as total organic carbon, total manganese, total iron and total scandium respectively, the latter being proportional to the clay content [12]. Furthermore, the content of chlorophyll-a was included as a robust measure of the amount of phytoplankton.

The test compounds TeCB and cadmium were used in laboratory sorption experiments with suspended solids and sediments from the lake. Natural conditions were imitated by measuring at low concentrations (2-100 ppb), by not altering the samples in any way and, if necessary, by the use of fixed conditions such as pH (8.5), chlorinity (0.3 g/l) and temperature (14 °C). To be able to make a direct comparison between the laboratory and the natural system, cadmium sorption coefficients were also obtained from field data. Because cadmium sorption data for algae are scarce, sorption isotherms were also measured for a pure algal suspension.

The relationships between the sorption characteristics and the geochemical phase concentrations were evaluated by statistical analysis.

THEORY

Sorption of hydrophobic chemicals

For the description of the sorption of hydrophobic pollutants to sediments the concept of linear phase partitioning is widely accepted. At equilibrium, the concentration ratio between the two phases has a constant value, the dimensionless partition coefficient [9]:

$$Kp = C_s / C_w \qquad (1)$$

C_s (g/g) and C_w (g/l) are the concentrations of the hydrophobic chemical in the adsorbent phase and the aqueous phase respectively. Assuming that sorption takes place almost completely to the organic matter fraction:

$$K_p \approx f_{oc} \times K_{oc} \tag{2}$$

f_{oc} is the fraction organic carbon and K_{oc} is the carbon normalised sorption coefficient.

The organic matter is not a well defined chemical phase and has a heterogeneous nature. Recent studies show that significant differences in K_{oc} value can occur in different types of organic matter and that refinement of the K_{oc} approach is needed [13,14,15,16]. For example, differences are found between particulate and dissolved organic matter, or between materials at different degrees of mineralization [11,17]. The total partition coefficient of a sediment particle or a suspended particle that consists of 'N' types of organic matter can be described by [9]:

$$K_p^{total} = \sum_{i=1}^{i=N} K_{oc}^i \times f_{oc}^i \tag{3}$$

Sorption of cadmium

In the past decade, several models describing heavy metal sorption were developed. Oakley et al [2] have presented a simple model for the distribution of a trace metal among a number of phases comprising an aerobic sediment. Mathematically, the model is identical with those of complexation and distribution of soluble trace metals among dissolved ligands. It is assumed that parameters such as chlorinity, pH, pE and ionic strength are constant so that conditional equilibrium constants can be used. It is also assumed that the adsorption of the trace metal has only negligible effect on the total concentration of available surface sites. In that case, precipitation and competition between different trace metals can also be neglected, and instead of the site concentration, the fixed concentration of the solid phase can be used. Finally, it is assumed that all sedimentary phases behave independently. Based upon this model, Davies-Colley et al [6] derived an expression for the total distribution coefficient of a sediment comprised of N phases:

$$K_d^{total} = \sum_{i=1}^{i=N} K_d^i \times F^i \tag{4}$$

F^i = weight fraction of phase 'n'
K_d^i = conditional distribution constant of phase 'n' (l/g)

So, the distribution of a metal over the different phases of a sediment or suspended particle is a function of the concentration of that phase and its affinity for the metal.

EXPERIMENTAL

Sampling and sample storage

All sampling locations are indicated in Figure 1. Five bottom sediments were taken from Lake Volkerak/Zoom in May 1989 at places with different grain sizes. The sediments were sampled using a Seabed boxcorer, which is essentially a bottomless box. The box inserts in the bottom sediment by its own weight and is closed with a bottom plate. On board of the ship, the overlying water is removed and the 5 cm top layer is sampled.

Settling material was collected in May, August and November 1989, covering the period of algal growth, with sediment traps. Six 60 cm long cylindrical traps with $\phi = 6$ cm, collected sufficient material for the subsequent analysis. To prevent the collection of resuspended material, the traps were located 1 m above the bottom sediment. The exposure time of the traps was 2 weeks. After collection of the traps, the suspended material was allowed to settle for 24 hours before the overlying water was removed by a siphon.

In the same month and at the same location suspended solids were collected with industrial centrifuges (Pennwalt AS 16), as well. The water was centrifuged at a speed of 1000 l/h and 15000 rpm (13200 g). Teflon sheets were attached to the inner surface of the centrifuge in order to prevent contamination with metals from the walls. In the centrifuge, the water is continuously transported vertically. As a result, a gradient in grain size develops on the Teflon sheets. By scraping off several parts of the sheets, a 'fine', a 'coarse' and a 'total' sample were obtained.

In the laboratory, the samples were resuspended in two litres of fresh lake water, obtained from the centrifuge, and divided in eight representative subsamples with a Retsch suspension divider. One of the subsamples was used for the determination of dry weight and two subsamples were immediately frozen and stored at -18 °C and used later for the measurement of sorption characteristics. The rest of the material was freeze dried and subsequently used for the determination of sediment characteristics.

Sampling and determination of aqueous cadmium concentrations and environmental variables such as temperature, pH, O_2, conductivity, salinity and chlorinity of the lake water were performed by the Dutch Institute for Inland Water Management.

Sediment characteristics

Total organic carbon and inorganic carbon were measured independently with the method described by Begheijn [18]. Chlorophyll-a was extracted with ethanol (80 % V/V) and measured on a Beckman DU-64 spectrophotometer. Corrections for turbidity, coloured compounds and phaeophytins were made.

The (background level) metals Fe, Mn, Sc and Cd were extracted from the samples using a HNO_3/HCl digestion mixture. Digestion was at 100 °C for three hours. Concentrations in the extracts were measured with ICP-AES (Sc) graphite furnace AAS (Cd) and flame-AAS (Fe, Mn) using background correction.
For one of the sediment samples, the sediment characteristics were determined four times independently, to check the precision of the methods.

Tetrachlorobenzene sorption isotherms

Each of the samples was divided in four representative subsamples using the Retsch sample divider. Preweighed, glass stoppered, gas tight oxygen bottles with a volume of 300 ml were used. Sediment concentrations were ca. 1 g/l. Each set of subsamples was spiked with a different volume of a 2 mg/l 1,2,3,4-tetrachlorobenzene (TeCB) solution. These spike solutions of 1,2,3,4-tetrachlorobenzene (Dr.S. Ehrenstorfer, 98%) were prepared in Barnstead Nanopure water in a closed gas purge system (Fig. 2), in which the transfer of TeCB from the solid to the dissolved phase, takes place via the gas phase. The suspensions were equilibrated on a shaking machine in 17 hours at room temperature.

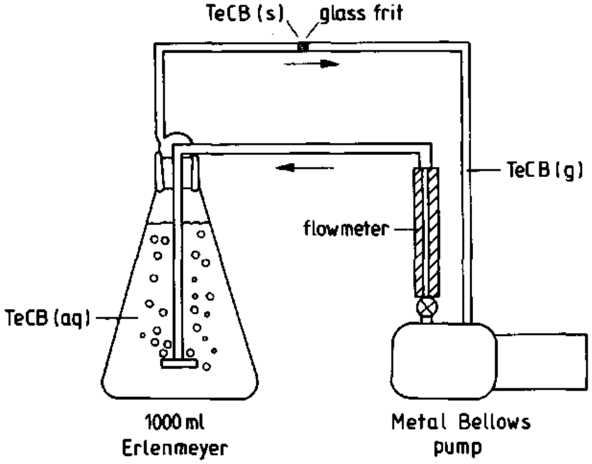

Fig. 2: Apparatus for the preparation of chlorobenzene solutions

Prior experiments showed that equilibrium was achieved within 10 hours and that losses caused by adsorption to the container walls, by volatilization and by biodegradation were negligible. The solid phase was separated from the aqueous phase by centrifugation for 30 minutes at 3000 g. Based upon Stokes law, this procedure yields a separation of particles of 0.45 μm with a density higher than 1085 kg/m^3. The weight of the solid phase was determined for each batch by drying at 105 °C till constant weight. The aqueous phase was extracted 1:1 with isooctane (Promochem, nanograde) and the extracts were analyzed together with diluted extracts of the spike solution on a Chrompack CP-9000 capillary gas chromatograph with ECD detection, using external standards. TeCB levels in the aqueous phase after equilibration were in the range of 8-160 μg/l. Concentrations in the solid phase were calculated from the initial concentration and the concentration after equilibration, by difference. Subsequently, K_p values were calculated from the slope of the linear plots of C_s versus C_w.

The supernatants were also analyzed for DOC on a Dohrmann DC-180 carbon analyzer, to check the efficiency of phase separation and to be able to correct the observed K_p values with the method described by Koelmans and Lijklema [19]. The measured DOC-levels however, turned out to be too low to make such a correction necessary.

Cadmium sorption isotherms

Because of a possible non-linearity of the cadmium sorption isotherms, at least 5 or 6 points should be measured. The division into more than 4 subsamples however, would result in very low sediment weights, causing poor reproducibility and inhomogeneous sample division. Hence, instead of batchwise equilibration, titration of the sediment suspensions was used. The major drawback of this method is a relatively short contact time between cadmium and the adsorbent.

The frozen samples were brought to a temperature of 4 °C and were suspended in fresh lake water in a 1.3 litre water cooled Teflon container, supplied with a gas inlet tube, Ross combi pH electrode, thermocouple and a Teflon magnetic stirring bar. To prevent mobilisation of sorbed cadmium by complexation with chloride, 10% KNO_3 was used as electrode filling solution, instead of 3 M KCl. The temperature was kept at 14 ± 0.1 °C with a thermostat. The pH of the solution was kept constant at a value of 8.5 ± 0.05 by purging the solution with an adjustable mixture of pure N_2 and 9:1 N_2/CO_2. The pH was measured continuously with an Orion SA-720 mV/pH meter. Small, but accurately known aliquots of a 10^{-4} M cadmiumnitrate solution (Merck, analytical grade) were added with time intervals of 60 minutes. Shortly before each addition, 25.00 ml of the suspension was sampled and centrifuged for 30 minutes at 3000g. The supernatants were acidified to pH=1 with nitric acid and subsequently analyzed for total cadmium on a Varian 300/400 atomic absorption spectrophotometer with background correction. The cadmium levels in the aqueous phase were in the range 1-100 μg/l. The concentration of adsorbed cadmium was calculated from the known total amount of cadmium added and the amount measured in the aqueous phase after equilibration. In these calculations, corrections were made for the change in suspension volume due to sampling. The background cadmium levels in the sediments and suspended solids were negligible (less than 2 ppm) compared to the amount of cadmium added in the laboratory.

The exact determination and isolation of the algal strains present in Lake Volkerak/Zoom was beyond the scope of this study. Therefore the cadmium sorption experiments with algae were performed with a mixed culture available in our laboratory in which *Cryptomonas* spp was the dominant species. Representative subsamples of the culture were used for determinations of dry weight. The suspensions were titrated as described above with a 10^{-4} M cadmium nitrate solution. The cadmium concentrations in the aqueous phase were measured without phase separation, with Differential Pulse Anodic Stripping Voltammetry using a Princeton PAR 174 A polarographic analyzer and a Metrohm 663 VA mercury electrode and with an Orion 94-48 cadmium selective electrode and an Orion 90-02 Ag/AgCl reference electrode connected to an Orion SA-720 pH/ISE meter. Cadmium additions were made with time intervals of 15 minutes, sufficient for the electrode responses to become stable. Polarographic measurements were made in 0.01 M KNO_3 buffered at pH=7.5 with trisbuffer, in a Teflon cell. Adsorbed amounts of cadmium were calculated from the added and measured amounts by difference. In the entire experimental procedure, no contact occurred between trace level cadmium solutions and glass, except for the pH electrode. Blank runs, without adsorbent, showed that losses to container walls were negligible. After use, Teflon and plasticware were thoroughly rinsed with nitric acid and subsequently with Barnstead nanopure water.

The K_d^{Cd} values were calculated from the slopes of the adsorption isotherms.

Statistical analysis

Correlation analysis, factor analysis and multiple regression calculations were performed with the statistical software package STATGRAPHICS. The variables used were the weight fractions of total Sc, Fe, Mn, Cd, organic carbon and chlorophyll-a and the experimentally determined distribution coefficients for tetrachlorobenzene (K_p^{TeCB}) and cadmium (K_d^{Cd}).

RESULTS AND DISCUSSION

The adsorbent characteristics and sorption coefficients are given in Table 1. The results of the duplicate measurements for sample REF are given in Table 2, showing a fairly good reproducibility. Representative selections of the TeCB and cadmium sorption isotherms are given in the Figures 3 and 4 respectively. The TeCB isotherms are essentially linear, suggesting a sorption mechanism of linear partitioning, irrespective of the nature of the sample. Occasionally, a single point deviates from the line. Presumably, this is caused by inhomogeneities in the samples due to small organisms.

Most of the cadmium isotherms also show linear distribution in the considered concentration range. However, in contradiction to the conventional concept of surface saturation, in some cases a slightly concave curve was found. This points to incomplete equilibration for data points at lower concentrations, and can be caused by the titration procedure used. Compared to K_d values calculated from field data in the literature, the K_d^{Cd} values in this study are relatively low. This may be caused by the higher sorbent concentrations [20,21] and to some extent to incomplete equilibration.

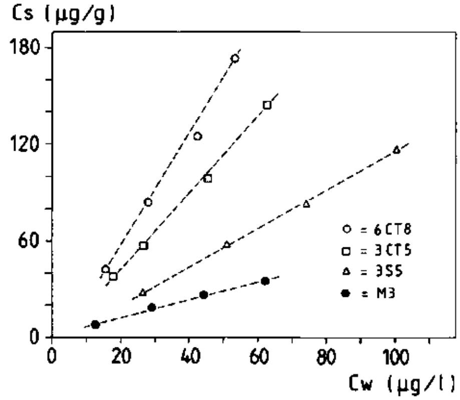

Fig. 3: 1,2,3,4-Tetrachlorobenzene adsorption isotherms for M3, 3S5, 3CT5 and 6CT8. For explanation of sample codes, see Table 1.

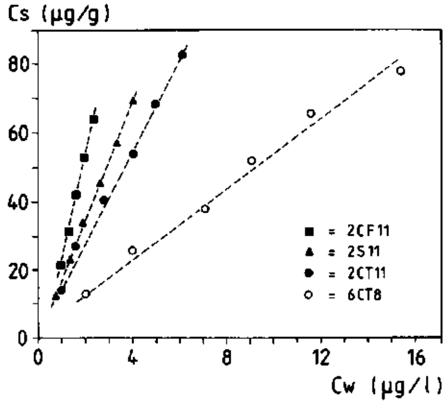

Fig. 4: Cadmium adsorption isotherms for 6CT8, 2CT11, 2S11 and 2CF11. For explanation of sample codes, see Table 1.

Correlation and factor analysis

The results of the correlation analysis are shown in Table 3. Correlations with a significance level smaller than 0.05 are underlined. Of the results of the factor analysis only a plot of the first two factor weights is given (Fig. 5). The complete dataset is available on request. It can be seen from the figure that the first factor is controlled by Sc, Fe and Cd, and in the opposite direction by chlorophyll. The second factor is mainly controlled by organic carbon, K_p^{TeCB} and Mn. The numerical factor analysis results reveal that these factors account for 82 % of the variance in the dataset. Although no conclusions can be drawn about causality, the clustering of Fe, Sc, Cd and K_d^{Cd} on one hand, and of organic carbon, chlorophyll and K_p^{TeCB} on the other, illustrates the relationships among these variables in each cluster.

Organic carbon and chlorophyll-a

Organic carbon and chlorophyll are highly correlated. It is obvious that the phytoplankton present in the samples gives a major contribution to the total carbon content, especially for the summer samples. In the fractionated summer samples,

chlorophyll contents were higher for the coarse fractions.
The following regression line was calculated:

$$chlor = 228.1 \times \%org.C - 718 \qquad r^2 = 0.692 \qquad (n=26) \tag{5}$$

chlor = chlorophyll content (mg/kg)
%org.C = percentage organic carbon.

From this equation a carbon to chlorophyll ratio of 30 was calculated.

Scandium, iron and manganese

Scandium and iron are highly correlated. The scandium content is proportional to the clay content, which acts as a substratum for iron oxides. Scandium is negatively correlated with chlorophyll. The reason for this, is the decrease in the scandium weight fraction in periods of algal growth.

The manganese content is highly correlated with iron, and to a lesser extent with scandium, illustrating the association with the clay fraction. Also, a certain relationship with organic carbon exists. Besides the binding to iron species, precipitation of MnO_2 or $MnCO_3$ caused by a pH increase due to primary production might play a role. The sediment samples M1 and REF contain relatively little manganese. These samples were taken from the deepest, probably frequently anaerobic, parts of the lake, where reduction and mobilization of manganese takes place.

TABLE 1:
Results of adsorbent characterization and sorption experiments.

sample-code(a)	chlor mg/kg	Sc mg/kg	%org.C	Fe g/kg	Mn mg/kg	Cd mg/kg	K_d^{Cd} l/kg	K_p^{TeCB} l/kg
2CF11	263	6.21	5.34	49.7	5470	2.08	30360	1287
2CF5	618	4.46	9.42	43.9	4880	1.48	8353	1124
2CF8	787	4.91	10.85	40.9	7650	1.90	14850	1319
2CG11	612	4.3	8.45	36.9	3650	1.55	15930	934
2CG5	2750	2.51	12.71	23.6	2130	0.85	5344	2196
2CG8	2140	3.6	9.85	30.0	4210	1.34	10810	2088
2CT11	487	4.58	6.30	38.9	3910	1.62	12830	1194
2CT5	2350	3.09	11.89	20.2	2890	1.06	11600	1591
2CT8	1280	4.25	10.05	36.0	6440	1.67	5322	1560
2S11	88	4.85	3.54	40.8	3260	1.61	17140	1110
2S5	1250	3	6.53	26.3	1180	1.21	2549	1000
2S8	231	4.96	6.19	38.2	2190	1.67	3823	882
3CT11	387	6.04	5.83	47.5	3740	1.15	17620	744
3CT5	2180	2.34	9.55	20.5	2970	0.71	5818	2354
3CT8	2470	3.07	10.66	24.6	3930	0.96	9686	2149
3S11	92	5.94	4.3	44.6	3520	1.10	17980	960
3S5	694	4.02	7.69	37.9	2560	1.08	11080	1192
3S8	343	4.31	6.72	37.8	3880	1.18	4562	1100
6CT8	2820	1.46	11.81	13.6	2930	0.59	5375	3022
6S8	220	3.79	7.94	34.1	2450	0.93	3896	1211
M1	94	4.31	2.62	32.0	600	0.71	(b)	434
M2	1	0.775	0.13	3.9	310	0.07	113.8	50
M3	11	5.32	2.33	39.5	3190	0.70	1527	543
M4	10	5.29	3.30	40.3	3670	1.62	1795	624
M5	10	3.22	1.46	22.4	1990	1.00	(b)	324
REF	64	5.2	3.86	38.6	770	1.56	5890	892

(a) first number= location (2=VZ2, 3=VZ3, 6=VZ6), last number= sampling month (5= May, 8= August, 11= November), C= centrifuge sample, F= fine fraction, G= coarse fraction, T= total sample S= sediment trap sample, M1 to M5 = bottom sediments, numbered arbitrary from 1 to 5, REF= bottom sediment used for reproducibility measurements; (b) erroneous results

TABLE 2:
Reproducibility of determinations.

Variable	sample	average	std.error	%std.error	n
Cd	REF	1.61 (mg/kg)	0.07	4	4
Fe	REF	38.6 (g/kg)	3.3	9	4
Mn	REF	769 (mg/kg)	15.3	2	4
Sc	REF	5.2 (mg/kg)	0.037	0.7	4
%org.C	REF	3.86 (%)	0.21	5	5
K_p^{TeCB}	REF	892 (l/kg)	108	12	4
$K_d^{Cd\,(a)}$	REF	1967 (l/kg)	343	17	2
$K_d^{Cd\,(a)}$	Cryptomonas	22000 (l/kg)	4000	18	2

(a) cadmium determined with DPASV

TABLE 3:
Spearman rank correlation coefficients (n=26).

	Chlorophyll	Sc	%Org.C	Fe	Mn	Cd	K_d^{Cd}
Sc	-.5017	<-- correlation coefficient					
	$\underline{.0121}$	<-- significance level, underlined for p<0.05					
%Org.C	.9328	-.4394					
	$\underline{.0000}$	$\underline{.0280}$					
Fe	-.3611	.9325	-.2971				
	.0710	$\underline{.0000}$	.1374				
Mn	.2999	.3789	.3641	.5173			
	.1338	.0582	.0687	$\underline{.0097}$			
Cd	-.0679	.5889	.0195	.6414	.5610		
	.7342	$\underline{.0032}$	.9223	$\underline{.0013}$	$\underline{.0050}$		
K_d^{Cd}	.1696	.3783	.1374	.4826	.4626	.3454	
	.4161	.0697	.5100	.0206	$\underline{.0265}$	.0977	
K_p^{TeCB}	.8637	-.4049	.8783	-.2561	.3867	.0168	.2226
	$\underline{.0000}$	$\underline{.0429}$	$\underline{.0000}$	.2004	.0532	.9332	.2857

Sorption of 1,2,3,4-tetrachlorobenzene

According to the statistical analysis, organic carbon and chlorophyll are the two master variables predicting the extent of hydrophobic partitioning of TeCB. Linear regression of the partition coefficient of TeCB and organic carbon (Fig. 6) yields:

$$K_p^{TeCB} = 175 \times \%org.C \qquad r^2 = 0.932 \qquad (n=26) \tag{6}$$

K_p^{TeCB} = the TeCB partition coefficient (l/kg)
%.org.C. = percentage organic carbon

This result is in good agreement with the concept of constant partitioning and appears to be valid also for settling particles with high phytoplankton contents. From the slope of Figure 6, a $\log K_{oc}$ value was calculated and compared to literature values in Table 4. The role of algal blooms on the scavenging of hydrophobic pollutants and the differences between the samples can be read from Figure 6. Typically, the sediments show coefficients in the range of 100-1000 (l/kg), the settling materials obtained with sediment traps and the suspended particles obtained in November show TeCB partition coefficients in the range 1000-1500 (l/kg), whereas the coefficients for the suspended solids sampled during the period of algal bloom are in the range of 1500-3000 (l/kg).
Finally, K_p^{TeCB} is significantly, negatively correlated with scandium. This inverse relationship originates from the strong decrease in scandium content in periods of algal bloom, as mentioned above.

Sorption of cadmium

Cadmium background level. The variation in cadmium background level is caused by the variation in aqueous phase cadmium concentration, by the variation in environmental conditions such as ionic strength, chlorinity and pH, by variation in the adsorbent's affinity for the metal and to some extent by random experimental error. Because of the relatively short sampling period and the relatively small size of the waterbody, all relevant environmental conditions and the cadmium concentrations in water (C_w) were considered to be constant. This important assumption was supported by the measurements of pH, salinity, and chlorinity during sampling (Table 5). As a consequence, the background cadmium levels in the solids 'Cd' can be interpreted as reflections of the adsorbent's affinity for cadmium, and can be used for the estimation of 'field data' distribution coefficients, through division by 'C_w'. Values for the cadmium concentration in the aqueous phase after filtration over 0.45 μm were close to the detection limit and therefore showed considerable scatter. From the measurements for the sampling locations VZ2 and VZ3, an avarage value of 0.05 ± 0.03 μg/l was calculated.

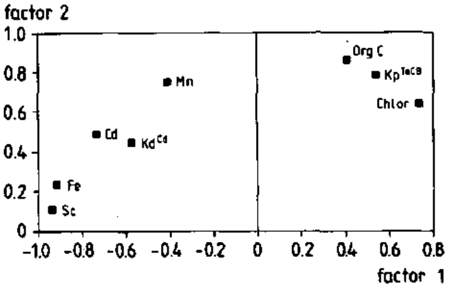

Fig. 5: Plot of first two factor weights.

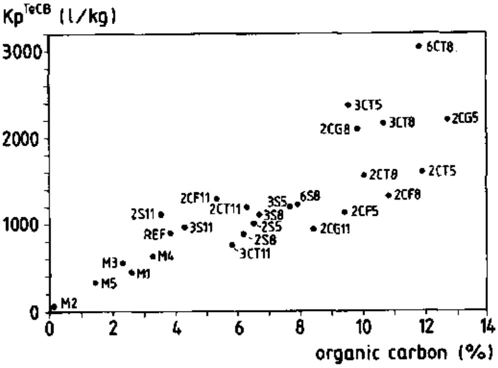

Fig. 6: Partition coefficients for TeCB as a function of the percentage organic carbon. For explanation of sample codes, see Table 1.

TABLE 4:
Sorption coefficients for chlorobenzenes.

compound	$\log K_{ow}$(a)	$\log K_{oc}$(b)	$\log K_{oc}$(c)	$\log K_{oc}$(d)	$\log K_{oc}$(e)	$\log K_{oc}$(f)
1,2,3-TCB	4.139	3.78	3.47		3.77	
1,2,3,4-TeCB	4.635	4.28	3.83	4.5	3.98	4.24
QCB	5.183	4.82	4.22	5.7	4.49	
HCB	5.731	5.37	4.62	5.8		

(a) octanol/water partition coefficient, slow stirring method, de Bruijn et al [22]
(b) $\log K_{oc} = \log K_{ow} - 0.36$, batch experiments, Karickhoff [23]
(c) $\log K_{oc} = 0.72 \times \log K_{ow} + 0.49$, batch experiments, Schwarzenbach et al, [24]
(d) phytoplankton/zooplankton > 0.5 μm, field data, Oliver [17]
(e) reference sediment, batch experiments, this study
(f) samples Lake Volkerak/Zoom (slope Figure 6), this study

The background level is highly correlated with scandium, iron and manganese. These findings illustrate the role of manganese- and iron-oxides as substrates for cadmium sorption and the association of these substrates with the clay particles, the latter being characterised by scandium. Although the importance of organic matter as a carrier for metals is thought to be high by many investigators, in this case no correlation was found between cadmium and organic carbon or chlorophyll.

TABLE 5:
Environmental variables Lake Volkerak/Zoom.

Month/location	Temp. (°C)	pH	Cl^- (mg/l)	Salinity (promille)
May				
VZ2	17.8	8.50	265	0.48
VZ3	16.5	8.60	290	0.50
August				
VZ2	20.1	8.48	280	0.51
VZ3	20.1	8.56	299	0.54
VZ6	20.8	8.73	507	0.92
November				
VZ2	8.3	8.16	295	0.53
VZ2(a)			289	
VZ3	8.2	8.30	347	0.62

(a) after transport to the laboratory, titrimetric.

Cadmium distribution coefficients. The experimentally determined distribution coefficients show correlations with iron, manganese and to a lesser extent with scandium and the background cadmium level. The latter correlation is moderate, suggesting some deviation from the realistic sorption process, during the titration. It appears that sediment and sediment trap samples have relatively low K_d^{Cd} values. These samples contain the more mineralised and 'packed' organic phases resulting in a certain degree of aggregation, opposed to the centrifuge samples in which the organic material is present in the form of loosely bound algae or algal debris. Together with the short equilibration time this may have resulted in some kinetic constraints.

Multiple regression calculations. To interpret the results in terms of the model of Oakley [2] as condensed in equation (4), multiple regression calculations were performed with the background cadmium level and K_d^{Cd} as dependent variables, respectively. Secondly, regression calculations were performed including the interaction terms $Fe \times Mn$, $Fe \times f_{oc}$ and $Mn \times f_{oc}$, to test the assumption of independency of the variables and to improve the models empirically. The variables organic carbon (f_{oc}), iron (Fe) and manganese (Mn) were entered as dimensionless weight fractions (1 % = 0.01, 1 mg/kg = 10^{-6}).

The results for the model of Oakley are presented in Table 6. The regression model for the background cadmium level is highly significant and can be written as:

$$Cd\ (mg/kg) = \begin{array}{l} + 1.071 \times fraction\ org.C \\ + 25.80 \times fraction\ Fe \\ + 76.11 \times fraction\ Mn \\ + 0.030 \end{array} \tag{7}$$

With the measured cadmium concentration in the lake ($\approx$ 0.05 μg/l), 'field data' distribution coefficients for the different phases were calculated from these regression coefficients. The values are compared to results of Davies-Colley et al [6] in Table 7. Davies-Colley et al determined distribution coefficients for synthetic ferrihydrite as a function of salinity. Based upon their measurements, an estimation for our experimental conditions was made by extrapolation to a salinity of 0.5 promille (Fig. 7).

Apart from the lower significance levels, the results for the distribution coefficients obtained from laboratory experiments (K_d^{Cd}) are similar to those for the background cadmium level. The model can be written as:

$$K_d^{Cd} = \begin{array}{l} + 11 \quad \times 10^3 \times fraction\ org.C \\ + 260 \ \ \times 10^3 \times fraction\ Fe \\ + 1100 \times 10^3 \times fraction\ Mn \\ - 3982 \end{array} \tag{8}$$

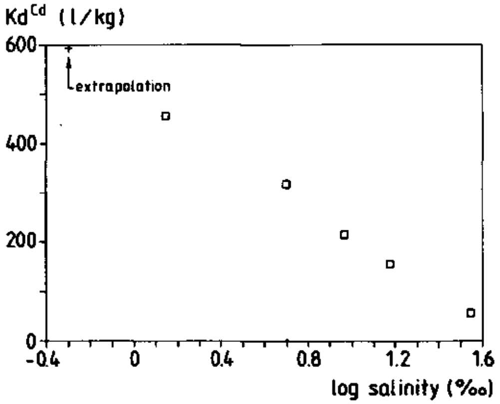

Fig. 7: K_d^{Cd} for synthetic ferrihydrite as a function of salinity. ◻, Data from Davies-Colley et al [6]; +, extrapolation to S= 0.5 promille.

The coefficients can be interpreted directly as distribution coefficients. Replacement of organic carbon as the independent variable by the chlorophyll weight fraction results in a slightly better model fit: P= 0.0259 instead of P= 0.0345. Also in Table 7, the coefficients obtained from this regression calculation are compared to literature values and to our laboratory results for *Cryptomonas* spp. In the calculation of the algae's distribution coefficient, an organic carbon content of 50%, and the measured carbon to chlorophyll ratio of 30, was used.

TABLE 6:
Results of multiple regression calculations according to the model of Oakley.

Background Cadmium level (mg/kg) (n=26).

Independent variable	coefficient	std.error	t-value	significance level
Constant	0.030	0.244	0.1242	0.9023
Fraction org. C	1.071	2.108	0.5082	0.6164
Fraction Fe	25.80	6.960	3.7072	0.0012
Fraction Mn	76.11	49.89	1.5256	0.1414

Variance analysis: F-ratio= 12.930, P-value= 0.0000

Experimentally determined cadmium distribution coefficients K_d^{Cd} (n=24)

Independent variable	coefficient	std.error	t-value	significance level
Constant	-3982.4	5754.5	-.6921	0.4969
Fraction org. C	10808	47816	0.2260	0.8235
Fraction Fe	261011	153024	1.7057	0.1035
Fraction Mn	1099294	1087993	1.0104	0.3244

Variance analysis: F-ratio= 3.499, P-value= 0.0345

TABLE 7:
Cadmium distribution coefficients K_d^{Cd} (l/g)

	Davies-Colley		This study					
			(5)	(6)	(7)	(8)	(9)	(10)
Organic matter (as C)	17[1]		21	11				
Iron oxides (as Fe)	130[2]	600[4]	520	260	350			
Manganese oxides (as Mn)	1500[3]		1500	1100	900			
Algae (dry weight)					25	31	22	22

1 Davies-Colley et al [6]; humic material from estuarium sediment, pH= 6-8.5, Cl^-=5g/l
2 Davies-Colley et al [6]; synthetic ferrihydrite, pH= 6-8.5, Cl^-= 5g/l
3 Davies-Colley et al [6]; synthetic birnessite, pH= 6-8.5, Cl^-=5g/l
4 Davies-Colley et al [6]; synthetic ferrihydrite, pH= 8.5, extrapolated to Cl^-= 0.3 g/l (Fig. 7)
5 this study; multiple regression Cd= f(Fe, Mn, f_{oc}), pH=8.5,Cl^-= 0.3 g/l
6 this study; multiple regression K_d^{Cd}= f(Fe, Mn, f_{oc}), pH=8.5, Cl^-= 0.3 g/l
7 this study; multiple regression K_d^{Cd}= f(Fe, Mn, chlor), pH=8.5, Cl^-= 0.3 g/l
8 this study; *Cryptomonas* spp, ionselective electrodes, pH=7.5
9 this study; *Cryptomonas* spp, polarography, pH= 7.5
10 Conway and Williams [25]; *Asterionella formosa*

TABLE 8:
Results of multiple regression calculations with empirical models.

Background cadmium level (mg/kg) (n=26)

independent variable	coefficient	std.error	t-value	significance level
constant	0.054	0.190	0.2841	0.7788
fraction Fe	29.36	5.309	5.5299	0.0000
fraction Mn × fraction org.C	719.7	296.7	2.4259	0.0235

Variance analysis: F-ratio= 20.533, P-value= 0.0000

Experimentally determined cadmium distribution coefficients K_d^{Cd} (n=24)

independent variable	coefficient	std.error	t-value	significance level
constant	3304.1	3175.5	1.0405	0.3112
fraction org. C	2.659×10^5	1.185×10^5	2.2438	0.0370
fraction Mn	-9.549×10^6	3.875×10^6	-2.4642	0.0234
fraction Fe × fraction Mn	2.832×10^8	9.433×10^7	3.0027	0.0073
fraction Fe × fraction org.C	-6.655×10^6	3.584×10^6	-1.8568	0.0789

Variance analysis: F-ratio= 4.830, P-value= 0.0074

In Table 8 the best emperical models including interaction terms are presented. For the background cadmium level the alternative model yields only a minor improvement and has the form:

$$\begin{aligned} Cd\ (mg/kg) = \\ &+ 29.36\times fraction\ Fe \\ &+ 719.7\times fraction\ Mn\times fraction\ org.C \\ &+ 0.054 \end{aligned} \tag{9}$$

This model suggests in addition to the correlation analysis that the variables Mn and Org.C are somewhat correlated. However, this model is not much different from the first one listed in Table 6. This can be shown by considering the role of the variable fraction Org.C. This variable has an average value of 0.068 and is relatively insignificant in the first model (equation 7). When the average value is entered in equations (7) and (9) the equations become very similar.

For the experimentally determined distribution coefficients, only the use of Mn, f_{oc} and the interaction terms Fe×Mn and Fe×f_{oc} as independent variables (Table 8) yields a serious increase in model fit: P= 0.0074 instead of P= 0.0345. The Fe×Mn term is the most significant in this extended model:

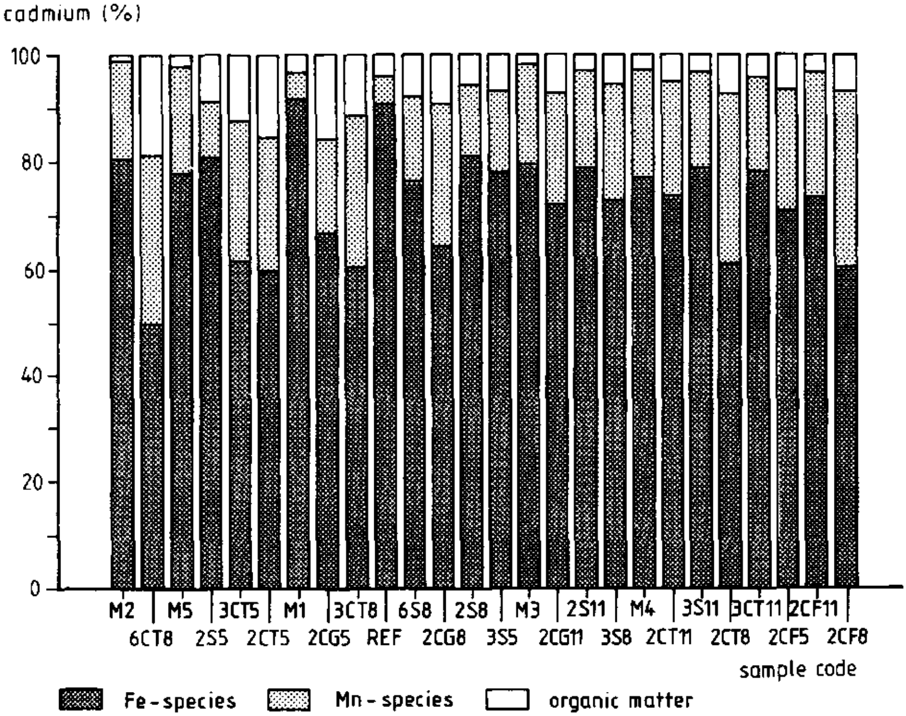

Fig. 8: The speciation of cadmium over competing sediment surfaces in percentages. The samples are ordered at the *x*-axis by increasing background cadmium level. For explanation of sample codes, see Table 1.

$$
\begin{aligned}
K_d^{Cd} = \; & \\
& + 2.66 \times 10^5 \times \textit{fraction org.C} \\
& - 9.55 \times 10^6 \times \textit{fraction Mn} \\
& + 2.83 \times 10^8 \times \textit{fraction Fe} \times \textit{fraction Mn} \\
& - 6.66 \times 10^6 \times \textit{fraction Fe} \times \textit{fraction org.C} \\
& + 3304
\end{aligned} \tag{10}
$$

Most likely, the experimentally determined distribution coefficients do not refer to sorption equilibrium. The accessibility of certain sorption reservoirs for cadmium is probably influenced by the presence of others. As a result, the degree of equilibration is dependent of the sample composition and the structure of the particles. The model of Oakley, being an equilibrium model, is not adequate in this case.

Despite of the uncertainties in the regression coefficients, especially for organic carbon and chlorophyll, and of the fact that different algal types are compared, the figures in Table 7 are in good agreement. It appears that the affinity of cadmium is the highest for the manganese oxides, followed by the iron species and organic matter. The relative importance of a phase as a carrier for cadmium however, is also determined by the weight fraction of that phase in the adsorbent. Using the coefficients of the first model in Table 6, the contribution of the phases was evaluated and depicted in Figure 8. The highest percentage is bound to the iron oxides, followed by the manganese oxides and organic matter. The latter contributes only for 5 to 10%, and for a single sample (6CT8) rich in phytoplankton, for 20%.

CONCLUSIONS

This study proves the important role of algal blooms in the fate of TeCB and shows the diversity in sorptive properties of different sorbent types that can be found in lakes similar to Lake Volkerak/Zoom, for TeCB and cadmium.

The TeCB sorption capacity of suspended solids and sediments is almost completely governed by the formation and degradation of organic matter, and shows a K_p range of 100-3000 (l/kg). The organic matter concentrations are strongly influenced by algal blooms, and therefore may vary seasonally. Because of their similarity in sorptive behaviour, this conclusion is also valid for many other classes of hydrophobic compounds.

It appears that the model of Oakley is accurate in describing the background cadmium levels and the derived equilibrium distribution coefficients in the study area. For the coefficients obtained with laboratory experiments, the fit is only reasonable but can be improved empirically by including interaction terms. 50-90% of the sorption of cadmium takes place on iron oxides, 5-30% on manganese oxides and the rest (less than 20%) on organic matter and other adsorbing phases. The *affinity* of cadmium is highest for the manganese species (K_d^{Cd}= 1100-1500 l/g), followed by the iron species (K_d^{Cd}= 260-520 l/g and organic matter (K_d^{Cd}= 11-21 l/g). In spite of the fact that organic matter is present in high weight fractions, especially in the suspended particles in summer, its role as a carrier for cadmium is unimportant and it acts mainly as a diluting phase.

Due to the role of the clay particles as a substratum for the manganese- and iron-species and to some extent for organic matter, the clay content as characterised by the scandium content is a usable indirect predictor for cadmium binding properties of the adsorbents. The scandium content shows an inverse relationship with the organic carbon (or chlorophyll) content and consequently with the TeCB sorption coefficients, due to algal growth. For this reason the scandium content turns out also to be an indirect predictor for binding properties of hydrophobic chemicals.

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Chapter 5

DESORPTION OF CHLOROBENZENES FROM NATURAL SUSPENDED SOLIDS AND SEDIMENTS

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based on:

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DESORPTION OF CHLOROBENZENES FROM NATURAL SUSPENDED SOLIDS AND SEDIMENTS

Abstract- The desorption of chlorobenzenes from heterogeneous suspended solid mixtures and sediments at nonequilibrium conditions was investigated, using a gas purge method. This technique offers the possibility to measure equilibrium and rate data from adsorbent suspensions, without phase separation. The desorption patterns were interpreted and fitted in terms of multiple box models. The results show that when the equilibration time for sediment suspensions contaminated in the laboratory is longer, desorption is slower. At nonequilibrium conditions, the more hydrophobic chlorobenzenes are released faster than the less hydrophobic ones.

For ten suspended solid samples the model parameters were related to adsorbent characteristics, such as organic matter-, phytoplankton- and clay content by means of correlation analysis, and compared to similar desorption data for algal cultures obtained in earlier studies in our laboratory. It was found that all desorption data could be described with a two-compartment desorption model. The partition coefficient was proportional to the content of organic matter, which in turn was mainly determined by the concentration of phytoplankton in the samples. The desorption rate was positively correlated with the phytoplankton content as well. This suggests that phytoplankton cells form an easily accessible fraction of the total adsorbent.

INTRODUCTION

Contaminated suspended solids and sediments can act as a source of hydrophobic organic compounds (HOC) to aquatic ecosystems. The extent of sorption and the desorption rate are important for the transport and bioavailability of such compounds. Whereas many studies address the differences in sorptive behavior between different HOC congeners (e.g., quantitative structure activity relationship studies), studies that consider particle mixtures are scarce. Such mixtures often contain phytoplankton, detritus, and resuspended sediments. For these types of particles, sorption equilibrium and desorption rate data are available from the literature: e.g., dissolved organic matter [1], phytoplankton [2,3], sediments [4,5,6,7,8]. In previous studies, we measured chlorobenzene desorption characteristics of pure suspensions of *Scenedesmus* spp [9] and *Anabaena* spp (Koelmans, submitted for publication) and detritus derived from the same algae. Such studies provide insight in the fundamental mechanism of desorption from these individual types of adsorbents, and allow the modeling of HOCs for adsorbent mixtures by distinguishing between the different types of adsorbents, and taking them into account as separate phases. However, the different adsorbents in the water column of aquatic systems, do not behave independently. The accessibility of certain sorption reservoirs is probably influenced by the presence of others, and depends on the structure of the particles. Usually the different types of adsorbents and their relative contributions to the total adsorbent mass are not known. In addition, it is not clear whether, or which, relatively easily measurable adsorbent characteristics can be used as predictors of desorption characteristics.

The aim of this study is to investigate the chlorobenzene desorption characteristics of several heterogeneous suspended solids samples and sediments at short equilibration times. Short equilibration times were chosen because often nonequilibrium conditions more closely approximate conditions in aqueous environments [10]. The results are evaluated using a set of adsorbent characteristics, literature data for individual phases and data from previous investigations. Two series of experiments were performed. The first, using one single adsorbent, concerned the effect of equilibration time on gas purge induced desorption patterns for three chlorobenzenes. The second series, using ten adsorbents, concerned the effect of adsorbent characteristics on the desorption patterns after intermediate equilibration times for two chlorobenzenes.

MODELING OF DESORPTION KINETICS

Desorption rate data have been described by diffusion based models and first order multiple box models. Reviews of the two types of models were recently given by Brusseau et al [11] and Ball and Roberts [12]. For diffusion-based models, generally adsorbent homogeneity is assumed and information on the desorption mechanism and the structure and properties of the porous medium is required. Because of this mechanistic approach and physical basis, it is possible to derive the model parameters independently [7,11,13]. However, commonly the adsorbent is not spatially homogeneous. Natural sediments and complex particle mixtures as used in this study, are heterogeneous in nature, and the sorption mechanism and adsorbent properties are not known. In contrast to diffusion models, first order multiple box models do not require this type of information. They agree to the idea of adsorbent heterogeneity, since the compartments represent regions with distinct sorptive properties. An often mentioned drawback of this type of modeling is that the values for model parameters cannot be estimated independently from adsorbate and adsorbent properties, and that the number of parameters to be fitted is relatively large. However, Brusseau and co-workers showed that first order mass transfer models are applicable in situations were the exact desorption mechanisms is not known, and that they can be interpreted in terms of diffusion-based models as well [8,14]. Furthermore, first order box models are more practical because of their mathematical simplicity. For these reasons, our desorption rate data were modeled according to a two-compartment first order kinetic model in which sorption takes place in two compartments[1]. Sorption to the first compartment with size x_1 (adsorbent weight

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[1] For a detailed description of the model, see the appendix to Chapter 8.

fraction), is considered instantaneous and is quantified by the partition coefficient K_p. For the second compartment with size $(1\text{-}x_1)$, mass transfer is assumed to be characterized by forward and backward first order rate constants k_1 and k_2. In formula:

$$Cs_1 = x_1 K_p Cw \tag{1}$$

$$dCs_2/dt = k_1 Cs_1 - k_2 Cs_2 \tag{2}$$

Cw is the solution-phase adsorbate concentration, Cs_1 and Cs_2 are the sorbed-phase concentrations in the first compartment and the second compartment respectively, x_1 is the fraction of the adsorbent for which sorption is considered instantaneous, K_p is the equilibrium sorption constant and k_1 and k_2 are forward and reverse first order rate constants. Assuming that the affinity of the adsorbate for both compartments is identical [4,8,14], k_1 is related to x_1 and k_2 according to:

$$k_1 = k_2(1-x_1)/x_1 \tag{3}$$

The desorption process is described by the three constants K_p, x_1 and k_2. Because mass transfer to and from the second compartment is assumed to be diffusion through the organic matter matrix [4,14], k_2 can be expressed in terms of diffusion coefficients and adsorbent properties. In several studies [4,5,6,7,8,9] this model has been proven adequate in describing desorption rate data for sediments, soils and phytoplankton. The model describes two possible compartment configurations: a series version ($Cw \Leftrightarrow Cs_1 \leftrightarrows Cs_2$), and a parallel version ($Cs_1 \Leftrightarrow Cw \leftrightarrows Cs_2$). In the series version, the first compartment can be pictured as the exterior of the adsorbent. In the parallel configuration, the compartments resemble kinetically different sorption sites.

EXPERIMENTAL

Collection and characterization of adsorbents

The sediments, suspended solids and settling particles used in this study were representative subsamples of materials left over from an earlier study [15]. In this earlier study, for 1,2,3,4-tetrachlorobenzene (TeCB) partition coefficients were measured using a batch method. In the present study, these partition coefficients for TeCB are compared to partition coefficients obtained with a gas purge method. The methods for the determination of adsorbent characteristics and the batch method for the determination of TeCB partition coefficients are described in our previous publication [15] and are summarized here briefly. The sediment samples were taken from Lake Volkerak/Zoom in the Netherlands in May 1989, using a seabed box corer. Settling materials and suspended solids were collected in May, August and November 1989, using sediment traps and industrial centrifuges (Pennwalt AS 16) respectively. Until their use for this study, all samples were stored in polyethylene bottles at -20°C. Dry weights were determined by filtration over Schleicher & Schuell 0.45 μm membrane filters and drying at 105 °C till constant weight. Total organic carbon and inorganic carbon were measured independently with the method described by Begheijn [16]. Chlorophyll and phaeophytins were extracted with acetone and measured on a Beckman DU-64 spectrophotometer, according to standard methods [17]. Scandium was used as a measure for the clay content of the samples [18], and was measured after destruction in HNO_3/HCl by ICP-AES. Partition coefficients for TeCB were measured at room temperature, by batchwise equilibration (17 h), followed by centrifugation and GC-ECD analysis of the TeCB concentration in the aqueous phase.

Chemicals

All water used in the purge experiments was Barnstead Nanopure water. Nanograde organic solvents (acetone and 2,2,4-trimethylpentane) were obtained from Promochem (C.N. Schmidt, The Netherlands). 1,2,3,4-tetrachlorobenzene (TeCB), 1,2,4,5-tetrachlorobenzene and pentachlorobenzene (QCB) were obtained from Aldrich (98%, Aldrich Europe, Belgium). Hexachlorobenzene (HCB) was obtained from BDH Chemicals (>98%, BDH Chemicals, England). All chlorobenzenes were used without further purification. Tenax 40-60 mesh was obtained from Chrompack (The Netherlands). For the purge experiments, nitrogen or compressed air cleaned by passage through two Tenax columns in series, was used.

Gas purge desorption experiments

Details about the purge vessels, experimental procedure and control experiments were published before [9]. The method is described here briefly. The adsorbent suspensions were placed in 900 ml flasks and spiked with 50 μl of a solution of TeCB, QCB and HCB in acetone. The flasks were capped, covered with aluminum foil and thermostatted (20 $\pm$ 0.1 °C) during equilibration. Equilibration was for periods ranging from 15 h to 32 days for series one, and from four to six days for series two, both under continuous stirring. The experimental conditions during equilibration and desorption are listed in Table 1. Purge experiments were started by replacing the cap by the gas inlet tube and by using the gas flow to purge the chlorobenzenes onto Tenax column traps. Gas flows ($\approx$ 500 ml/min) were kept constant within 1% in the first eight hours, and within 3% in the remaining purge period. The total purge time was 35 days for the first series of experiments, and 5-23 days for the second series. Tenax columns were replaced at incremental intervals, determined by the mass of test compound expected in the Tenax tubes. The experiments in the first series were optimized for QCB and HCB, that is, to yield approximately the same mass of test compound in each trap. The second series was optimized for HCB. Therefore, conditions for TeCB were less ideal but still satisfactory. Immediately after finishing a desorption experiment, the adsorbents were analyzed to be able to account for possible remaining fractions of the test compounds. Chlorobenzenes were desorbed from the Tenax columns by elution with 15 ml diethyl-ether (recovery 100%). The eluates were concentrated under nitrogen after addition of an internal standard (1,2,4,5-tetrachlorobenzene in 2,2,4-trimethylpentane), to reduce the error of analysis, and were injected directly to the GC. A Hewlett-Packard 5890 double column gas chromatography system equipped with two ^{63}Ni electron capture detectors (ECD) was used in chlorobenzene quantisation. It must be noted that the gas purge method can be used for kinetic measurements as long as the chlorobenzene volatilization rate from the aqueous phase is larger than the desorption rate. For the flow rate and apparatus used in this study, a volatilization rate constant of approximately 15 - 30 day^{-1} for the chlorobenzenes was calculated. So, only desorption rate constants lower than this value, could be measured in this study.

TABLE 1:
Adsorbent characteristics and experimental conditions

Adsorbent	characteristics				experimental conditions				
	CHL mg/kg	foc	Sc mg/kg	K_pTeCB l/kg	EQ-time h	GP-time h	SW-ratio	GP-flow l/min	NR-Tenax
(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)
Series 1									
SED2	64	3.9	5.20	890	15	840	2.53	0.501	13
SED2	64	3.9	5.20	890	162	840	2.53	0.507	13
SED2	64	3.9	5.20	890	768	840	2.52	0.499	13
Series 2									
2CG5	2750	12.7	2.51	2200	96	216	0.93	0.499	10
3CT8	2470	10.7	3.07	2150	96	216	0.80	0.501	10
3S11	92	4.3	5.94	960	96	216	1.87	0.504	10
2S11	88	3.5	4.85	1110	96	216	1.92	0.506	10
2CT11	487	6.3	4.58	1190	96	216	1.53	0.504	10
2CF11	263	5.3	6.21	1290	96	216	2.03	0.498	10
2CG11	612	8.5	4.30	930	144	552	0.65	0.498	12
3CT11	387	5.8	6.04	740	144	552	0.86	0.504	12
SED1	10	1.5	3.22	320	144	552	3.33	0.505	12
SED2	64	3.9	5.20	890	96	120	1.53	0.396	10
SED2	64	3.9	5.20	890	96	120	1.50	0.399	10
SED2	64	3.9	5.20	890	96	120	1.52	0.399	10

(a) Adsorbent code. For consistency, codes are identical to those used in ref. Koelmans and Lijklema [15]. The first number refers to the sampling location, the last number to the sampling month. The letters refer to the type of adsorbent. S=settling solids. CT,CF,CG=suspended solids. SED= sediment; (b) Chlorophyll content; (c) Organic carbon fraction; (d) Scandium content; (e) TeCB partition coefficient; (f) Equilibration time; (g) Gas purge time; (h) Solid to water ratio; (i) Gas purge flow; (j) Number of Tenax columns used. (b), (c), (d) and (e) are from ref. Koelmans and Lijklema [15].

Data handling

The constants K_p, k_2 and x_1 are estimated by non linear least squares regression using the modified sequential simplex algorithm according to Nelder and Mead [19]. A relative least squares criterion was used instead of an absolute one, for reasons recently discussed by Sáez and Rittmann [20]. The sum of the amounts of test compound found in the Tenax columns and the amount of test compound found in the adsorbent after the purge experiment, was used as the value for the total amount of test compound in the system at t=0. In most studies applying the purge method, parameters are estimated from the cumulative amounts of test compound purged from suspension versus time. Then, a weighting of the cumulative amounts is needed, because of the accumulation of error.

Consequently, measurements at the end of the experiments are relatively insignificant in the estimation of the parameters. Since these measurements determine the magnitude of the slow desorption rate parameter k_2, confidence intervals for this parameter are wide. A better approach is to estimate the unknown parameters sequentially, using the amount of test compound and the purge time, as measured for each individual Tenax column. After parameter estimation, 90% confidence intervals (90% C.I.) were calculated, according to [21]:

$$SS_{90}=SS_{\min}\{1+ p/(n-p)\times F(p,n-p,90\%)\} \tag{4}$$

with SS_{90} the sum of squares at the 90% confidence contour, SS_{min} the minimum sum of squares, n the number of points in the cumulative plot of desorbed test compound versus time, p the number of parameters and $F(p,n\text{-}p,90\%)$ the F-distribution according to Fisher.

RESULTS AND DISCUSSION

Desorption experiments at different equilibration times

With three desorption experiments, the effect of equilibration time on the desorption pattern was investigated. The experiments were performed with sediment suspensions equilibrated with TeCB, QCB and HCB for 15 h, 162 h and 768 h respectively. Except the equilibration time, all conditions were identical. The desorption curves are shown in Figure 1. It appears that the desorption curves after 162 h and 768 h equilibration are almost identical. This suggests that the systems are close to equilibrium at 162 h, or that further approach to equilibrium after 162 h is very slow. The data were fitted to a two-compartment nonequilibrium model according to equations 1 - 3. The modeling results are presented in Table 2. For QCB and TeCB, the confidence intervals for K_p and k_2 are relatively large, so the discussion is limited to the kinetic parameter x_1. It appears that x_1 after 15 h equilibration, differs considerably from the x_1 values for 162 h and 768 h equilibration. The difference between 162 and 768 h is much smaller. For all chlorobenzenes, x_1 decreases with increasing equilibration time. This means that the fraction of adsorbate for which desorption is rate limited becomes larger, which can be explained from a deeper penetration in the organic matrix with time. A further observation is that at all equilibration times, x_1 decreases with decreasing hydrophobicity of the test compound. This suggests that the rate limited adsorbate fraction is larger for less hydrophobic chlorobenzenes. At nonequilibrium conditions, a larger rate limited fraction can be explained from faster diffusive transport for the less hydrophobic compounds, causing a deeper penetration in the organic matrix [4,14]. Because x_1 would *increase* with decreasing hydrophobicity at true equilibrium [4,14], we conclude that equilibrium for QCB and HCB is not reached after 768 h. Incomplete equilibrium also explains the small differences in K_p values between the chlorobenzenes. The difference between HCB and TeCB is roughly a factor two, whereas for the other adsorbents in this study (presented in the subsequent section) a factor 6 to 13 is found. Because HCB penetrates to a limited portion of the adsorbent mass, the partition coefficient is underestimated.

Desorption experiments with sediments and natural suspended solids

With ten adsorbents, the effect of adsorbent characteristics on the desorption characteristics after equilibration for 4 - 6 days was investigated. For suspended solid samples containing algae, equilibration times of four days were used. For the sediment and sediment trap samples an equilibration time of six days was used. For three adsorbents, the effect of extending the purge time from 9 to 23 days was investigated. HCB and TeCB desorption parameters are presented in Table 3. The desorption data fitted well to the model. x_1 values are estimated with the greatest accuracy, followed by K_p. Generally, confidence intervals are better for the HCB data than for the TeCB data. This is caused by the greater sensitivity of the method for HCB, and by the fact that experimental conditions were optimized for HCB. Extending the purge time from 9 to 23 days for the adsorbents 2CG11, 3CT11 and SED1, resulted in slightly different parameter estimates for both chlorobenzenes. Considering the confidence intervals, the differences are insignificant. Partition coefficients for HCB are 6 - 13 times higher than for TeCB. For most samples, the k_2 estimates for HCB are lower than for TeCB as expected because HCB is more hydrophobic than TeCB. Generally, the k_2 values for the suspended solids are higher than those for (more homogeneous) sediments reported in the literature [4,6,8], but lower than for the pure phytoplankton suspensions used in our previous investigations [9]. Except for SED2, 2CG5 and 3CT8, x_1 estimates for HCB are larger than for the less hydrophobic TeCB.

TABLE 2:
Desorption parameters and 90% confidence intervals for sediment (SED2) at different equilibration times (Series 1)

Compound	EQ-time(a) (h)	K_p ($\times 10^3$)	90% C.I.	k_2 (day^{-1})	90% C.I.	x_1	90% C.I.
HCB	15	7.7	(5.5 - 10.1)	0.079	(0.033 - 0.13)	0.87	(0.82 - 0.92)
HCB	162	12.4	(9.4 - 16.3)	0.070	(0.024 - 0.12)	0.79	(0.71 - 0.86)
HCB	768	9.4	(7.3 - 12.0)	0.079	(0.051 - 0.11)	0.72	(0.64 - 0.78)
QCB	15	3.1	(1.6 - 6.0)	0.077	(0.015 - 0.17)	0.80	(0.72 - 0.88)
QCB	162	33.6	(5.9 - 130.5)	0.014	(0.003 - 0.11)	0.51	(0.13 - 0.77)
QCB	768	6.0	(2.8 - 30.6)	0.051	(0.005 - 0.12)	0.48	(0.15 - 0.63)
TeCB	15	1.7	(0.7 - 4.1)	0.097	(0.019 - 0.27)	0.65	(0.48 - 0.79)
TeCB	162	7.3	(2.3 - 77.7)	0.083	(0.0005- 0.20)	0.27	(0.05 - 0.72)
TeCB	768	4.7	(1.4 - 29.9)	0.022	(0.007 - 0.10)	0.27	(0.12 - 0.43)

(a) Equilibration time, prior to desorption.

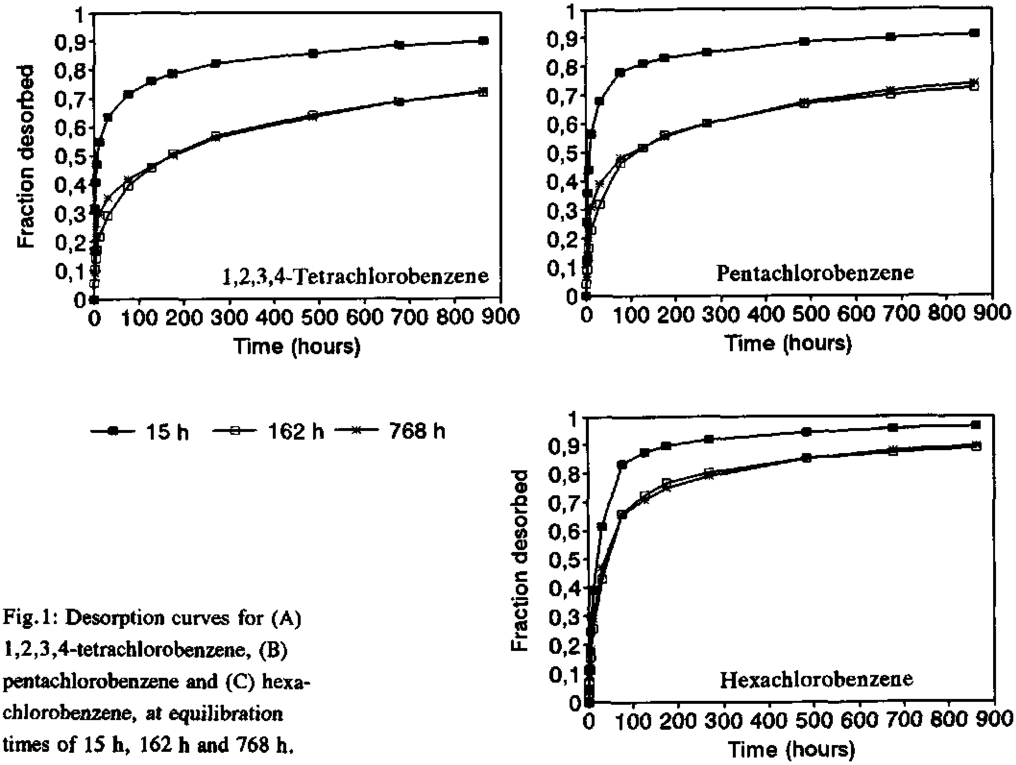

Fig. 1: Desorption curves for (A) 1,2,3,4-tetrachlorobenzene, (B) pentachlorobenzene and (C) hexachlorobenzene, at equilibration times of 15 h, 162 h and 768 h.

TABLE 3:
Desorption parameters and 90% confidence intervals

Compound	Adsorbent,(a)	K_p ($\times 10^3$)	90% C.I.	k_2 (day^{-1})	90% C.I.	x_1	90% C.I.
<u>Purge time 9 days</u>							
HCB	2CG5 (b)	19.9	(-)	0.87	(-)	0.92	(-)
HCB	3CT8	17.7	(14.0 - 22.6)	0.45	(0.12 - 0.78)	0.79	(0.64 - 0.89)
HCB	3S11	6.6	(5.3 - 8.7)	0.40	(0.09 - 0.68)	0.83	(0.72 - 0.90)
HCB	2S11	8.6	(7.1 - 10.5)	0.15	(0.05 - 0.44)	0.86	(0.77 - 0.90)
HCB	2CT11	12.5	(11.3 - 13.8)	0.13	(0.06 - 0.37)	0.90	(0.85 - 0.92)
HCB	2CF11	13.0	(11.8 - 14.2)	0.18	(0.10 - 0.40)	0.85	(0.80 - 0.90)
HCB	2CG11	12.9	(11.3 - 15.4)	0.23	(0.08 - 0.39)	0.89	(0.86 - 0.91)
HCB	3CT11	11.9	(10.0 - 14.8)	0.31	(0.08 - 0.51)	0.84	(0.78 - 0.88)
HCB	SED1	4.7	(3.0 - 6.9)	0.09	(0.03 - 0.60)	0.80	(0.65 - 0.90)
HCB	SED2	6.7	(6.1 - 7.4)	0.15	(0.10 - 0.23)	0.75	(0.69 - 0.80)
TeCB	2CG5	1.6	(1.2 - 2.1)	0.28	(0.13 - 0.48)	0.92	(0.89 - 0.94)
TeCB	3CT8	1.6	(1.1 - 2.0)	0.32	(0.17 - 0.53)	0.90	(0.87 - 0.93)
TeCB	3S11	1.3	(0.8 - 1.9)	0.32	(0.18 - 0.50)	0.65	(0.56 - 0.73)
TeCB	2S11	1.1	(0.6 - 1.7)	0.30	(0.12 - 0.55)	0.70	(0.60 - 0.79)
TeCB	2CT11	1.4	(1.0 - 1.7)	0.32	(0.20 - 0.48)	0.78	(0.73 - 0.83)
TeCB	2CF11	1.3	(0.9 - 1.6)	0.30	(0.18 - 0.45)	0.78	(0.73 - 0.83)
TeCB	2CG11	1.5	(0.7 - 2.3)	0.31	(0.13 - 0.58)	0.81	(0.68 - 0.87)
TeCB	3CT11	1.6	(0.7 - 2.6)	0.29	(0.09 - 0.58)	0.72	(0.54 - 0.81)
TeCB	SED1	0.5	(0.2 - 1.3)	0.32	(0.03 - 0.75)	0.66	(0.38 - 0.80)
TeCB	SED2	0.7	(0.5 - 1.0)	0.41	(0.06 - 0.86)	0.86	(0.75 - 0.90)
<u>Purge time 23 days</u>							
HCB	2CG11	14.4	(12.4 - 16.5)	0.09	(0.06 - 0.14)	0.86	(0.84 - 0.89)
HCB	3CT11	13.4	(11.0 - 16.0)	0.13	(0.08 - 0.19)	0.84	(0.80 - 0.88)
HCB	SED1	4.4	(3.6 - 5.3)	0.12	(0.08 - 0.17)	0.83	(0.78 - 0.87)
TeCB	2CG11	1.8	(0.4 - 3.0)	0.14	(0.03 - 0.40)	0.77	(0.48 - 0.87)
TeCB	3CT11	2.1	(0.7 - 3.5)	0.13	(0.04 - 0.34)	0.66	(0.43 - 0.79)
TeCB	SED1	0.7	(0.2 - 2.0)	0.12	(0.02 - 0.44)	0.61	(0.35 - 0.77)

(a) Adsorbent code. For explanation see Table 1; (b) Confidence intervals could not be calculated for this adsorbent.

Correlation analysis

Possible relationships between the desorption parameters (Table 3) and adsorbent characteristics (Table 1) were explored by means of correlation analysis. The results of this analysis are given in Table 4. Correlations with a significance level $p<0.10$ are underlined. It must be noted that the correlations are calculated for least squares estimates, without taking the confidence intervals into account. It follows from Table 4 that for both test compounds, the partition coefficient is determined by the organic matter fraction of the adsorbents. The correlation between K_p^{TeCB} (batch) and K_p^{TeCB} (purge) is only moderately significant. Organic matter seems highly determined by phytoplankton content as quantified by chlorophyll. The significant relationship between K_p^{HCB} and the organic carbon content of the adsorbents, is illustrated in Figure 2. Considering the correlations together, it appears that HCB desorption is fast for adsorbents containing phytoplankton, since k_2^{HCB} and x_1^{HCB} are positively correlated with chlorophyll and the partition coefficients, and to a lesser extent, with organic carbon. For TeCB, x_1 also correlates with chlorophyll and carbon content and therefore with sorption affinity.

TABLE 4:
Kendall rank correlations

	K_p^{HCB}	K_p^{TeCB} (purge)	K_p^{TeCB} (batch)	k_2^{HCB}	k_2^{TeCB}	x_1^{HCB}	x_1^{TeCB}	CHL	f_{oc}
K_p^{TeCB} (purge)	0.600	← correlation coefficient							
	0.016	← significance level (underlined for P < 0.10)							
K_p^{TeCB} (batch)	0.689	0.378							
	0.006	0.128							
k_2^{HCB}	0.422	0.644	0.378						
	0.089	0.009	0.128						
k_2^{TeCB}	-0.38	-0.42	-0.24	-0.33					
	0.128	0.089	0.325	0.180					
x_1^{HCB}	0.378	0.333	0.333	-0.02	-0.38				
	0.128	0.180	0.180	0.929	0.128				
x_1^{TeCB}	0.644	0.422	0.422	0.333	-0.02	0.200			
	0.009	0.089	0.089	0.180	0.929	0.421			
CHL	0.791	0.822	0.556	0.556	-0.33	0.422	0.600		
	0.002	0.001	0.025	0.025	0.180	0.089	0.016		
f_{oc}	0.733	0.778	0.511	0.600	-0.29	0.378	0.644	0.956	
	0.003	0.002	0.040	0.016	0.245	0.128	0.009	0.000	
Sc	-0.29	-0.24	-0.24	-0.07	-0.07	-0.11	-0.38	-0.33	-0.29
	0.245	0.325	0.325	0.788	0.788	0.655	0.128	0.180	0.245

K_p= partition coefficient, k_2= desorption rate constant, x_1= labile fraction, CHL= chlorophyll content, f_{oc}= organic carbon fraction, Sc= scandium content.

However, k_2 varies *inversely* with K_p, as was found in other studies for sediments at equilibrium [4,8,14]. A first explanation for the different K_p - k_2 relationship for HCB when compared to TeCB, is that in our experiments TeCB is at or close to equilibrium, and HCB is not. This agrees with the results for the series 1 experiments with different equilibration times (Table 2). It has been described, that equilibration for the more hydrophobic HOCs may take weeks to months [4,6,22] and that at nonequilibrium conditions, the inverse K_p-k_2 relationship may change into a positive correlation. A second explanation for the positive correlation of K_p^{HCB} with x_1 and k_2 is related to the heterogeneity of the adsorbents. They can be pictured as mixtures of phytoplankton cells and resuspended sediment-particles. For such a mixture, the parallel compartment version is more plausible than the series version. As mentioned before, the two versions are mathematically indistinguishable and the estimated model parameters can be interpreted directly in terms of the parallel model. In a previous study [9] it was found that algae have faster desorption kinetics than sediments. This means that the phytoplankton cells form a relatively readily accessible fraction of the total organic matter content. This should result in higher x_1 and k_2 values for samples containing more phytoplankton. Also the larger x_1 values for the more hydrophobic HCB point to incomplete equilibrium [4,9,14]. For 2CG5 and 3CT8 the x_1^{HCB} values are lower. Because the organic matter in these samples consists of phytoplankton cells instead of bulk organic matter, the adsorption rate is faster and both test compounds are at or near equilibrium. In that case x_1 is expected to be higher for the compound with the lowest K_p.

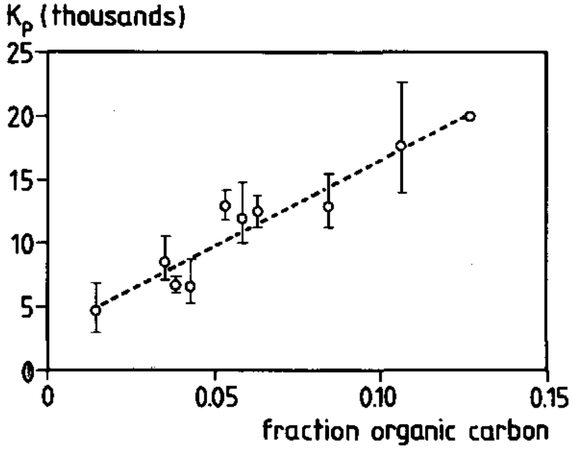

Fig. 2: Hexachlorobenzene partition coefficients as a function of organic carbon content for natural suspended particles and sediments. Error bars represent 90% confidence intervals.

From the results no influence of clay content, as quantified by the scandium content, is found. Although clay is not considered an important adsorbent for hydrophobic pollutants, it acts as a substratum for organic matter coatings. However, in the suspended solids that where sampled in spring and late summer, the organic matter consists mainly of phytoplankton causing a decrease in relative clay content by dilution.

CONCLUSIONS

The time constant for the equilibration of chlorobenzenes to sediments is in the order of months. At nonequilibrium conditions, both the hydrophobicity of the organic compound and the equilibration time determine the release pattern. At those conditions, faster desorption is found for the more hydrophobic chlorobenzenes.

Natural suspended solids obtained from Lake Volkerak/Zoom show faster desorption kinetics than sediments. The difference is explained from the fast desorption from algal cells and cell fragments, which form a major part of the organic matter in those particles. However, the desorption from natural suspended solids is still rate limited for 10 - 20% of the chlorobenzene content.

In suspended solids containing phytoplankton, both sorption kinetics and sorption affinity are determined by the phytoplankton content.

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Chapter 6

TEMPERATURE DEPENDENCY OF CHLOROBENZENE BIOACCUMULATION IN PHYTOPLANKTON

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based on:

A.A. Koelmans and C. Sánchez Jiménez. Temperature dependency of chlorobenzene bioaccumulation in phytoplankton. *(Submitted)*

TEMPERATURE DEPENDENCY OF CHLOROBENZENE BIOACCUMULATION IN PHYTOPLANKTON

Abstract- Chlorobenzene bioconcentration factors for *Scenedesmus* spp measured by batch equilibration, increased with temperature between 4.5 and 27.6 °C. A thermodynamic analysis suggests that the bioconcentration is driven by an entropy gain. Slopes of LogBCF-logK_{ow} relationships increased with temperature. These results agree with earlier reports for the analogous bioconcentration to fish.

INTRODUCTION

The behavior of micropollutants in aquatic systems is strongly influenced by sorption to algae [1,2,3]. However, data concerning the influence of environmental factors on bioconcentration factors (*BCF*) for algae are scarce compared with similar data for sediments. Measurements of *BCF* for phytoplankton at different temperatures have not been presented before. In this paper, the temperature dependency and related thermodynamic properties of chlorobenzene bioconcentration to phytoplankton are described. Because surface water temperature shows a strong seasonality, the temperature dependency of *BCF* can be relevant for the modeling of the fate of chlorobenzenes in aquatic systems and food chains. For chlorobenzene partitioning to fish lipids and to 1-octanol, a significant dependency of *BCF* with temperature was found [4]. For sediment to water partition coefficients, literature data are somewhat conflicting. Horzempa *et al.* [5] found increased sorption of 2,4,5,2',4',5' hexachlorobiphenyl at increasing temperatures. Szecsody *et al* [6] found decreased sorption of chlorobenzenes to a model soil with increasing temperatures. In a recent study, no significant variation of sorption of chlorobenzenes with temperature was found [7]. The question is whether the temperature dependency of *BCF* for phytoplankton, is similar to fish-lipids or, on the other hand similar to sediment-type organic matter.

EXPERIMENTAL METHODS

Materials

Nanograde organic solvents (acetone, diethyl-ether and 2,2,4-trimethylpentane) were obtained from Promochem (C.N. Schmidt, The Netherlands). 1,2,3-Trichlorobenzene (TCB; 99%), 1,2,3,4-tetrachlorobenzene (TeCB; 98%), 1,2,3,5-tetrachlorobenzene (98%) and pentachlorobenzene (QCB; 98%) were obtained from Aldrich Europe, Belgium. Hexachlorobenzene (HCB; 98%) was obtained from BDH Chemicals, England. For the concentration of extracts, high purity nitrogen was used. The algae were a non-axenic population of *Scenedesmus* spp, precultivated in continuous light in synthetic Z8 medium

[8], at 20 °C. The alga was chosen for its universality and its relative high resistance to decomposition compared to other algal species.

Batch equilibration procedure

Procedures for total organic carbon (TOC), dry weight, batch equilibration, dissolved organic carbon (DOC) and 400 - 750 nm absorption spectra in the filtrates after equilibration, were described before [8]. The batch procedure is summarized here briefly. A four litre, concentrated algal suspension (≈600 mg/l) was divided in eight representative subsamples. Three subsamples were used for TOC and dry weight determinations. From the measured dry weight (574 ± 1 mg/l, n=2) and TOC (209 ± 10 mg/l, n=19), an organic carbon fraction of 0.364 ± 0.018 was calculated. The remaining five batches were divided in four portions each, which were transferred to gas-tight bottles and filled with Barnstead nanopure water to minimize headspace. The resultant batches contained 45% Z8 medium and were spiked identically with 10 μl of a solution of 1,2,3-trichlorobenzene, 1,2,3,4-tetrachlorobenzene, pentachlorobenzene and hexachlorobenzene in acetone, and magnetically stirred. Each group of four batches was equilibrated for 48 h at a different temperature: 4.5 ± 0.1, 14.2 ± 0.3, 20.1 ± 1.5, 27.5 ± 0.5 or 38.6 ± 0.4 °C. Considering the required equilibration time for HCB to *Chlorella* reported by Geyer [9] of 2 to 4 h, our 48 h period was assumed to be sufficient. Equilibration was in the dark to minimize the decrease of chlorobenzene concentrations in the cells by algal growth. Prior experiments which included microscopic inspection and the testing of growth potency, showed that *Scenedesmus* survives for several weeks under these conditions. To account for possible weight losses due to algal decomposition, after equilibration one of the four batches was used for a determination of dry weight and to rinse the filtration unit prior to filtration. The three remaining batches were assumed to have the same characteristics as this batch, and were filtered (glass fibre filters, Whatmann GF/C) on all glass/metal filtration units. Filtration procedure, subsequent sample clean-up and GC-ECD analysis were as described before [8]. Because of some unexplained peaks in the chhromatogram, TCB congener quantification was problematical. Triplicate bioconcentration factors on a dry weight basis were calculated from the concentrations measured in the algae and the water. In this calculation the dry weights measured after equilibration were used. The filtrates were used for the measurement of DOC and 400-700 nm absorption spectra, to check for cell lysis and to be able to correct the observed *BCF* values for incomplete phase separation with the method described by Koelmans and Lijklema [10].

RESULTS AND DISCUSSION

BCF values are presented in Table 1. Because of the problems with the GC-analysis, *BCF* values for TCB should be interpreted with caution. Further, it must be noted that the results do not refer to algal cells under optimal growth conditions. Besides a temperature dependent change in chlorobenzene partitioning, the algae may have changed to some extent during equilibration. It appears from Table 1 that bioconcentration increases with the hydrophobicity of the compound and with temperature. The bioconcentration factors on a dry weight basis are plotted against the reciproke temperature in Figure 1 (van 't Hoff plot). From this type of plot, thermodynamic data for sorption of hydrophobic compounds can be derived, as was shown for sediments [5,7], for biosorption to micro organisms [11], for a model soil composed of porous silica coated with phenyl groups [6], and for chlorobenzene partitioning to fish [4]. Our data analysis is based upon the same calculation methods outlined in these publications.

TABLE 1:
Bioconcentration factors (×1000) on a dry weight basis at stated temperature

Compound(a)	Temperature (°C)				
	4.5	14.2	20.1	27.5	38.6
TCB	4.7 ± 1.7	1.7 ± 0.1	1.2 ± 0.3	1.6 ± 0.6	1.5 ± 0.8
TeCB	5.8 ± 0.5	6.6 ± 0.8	4.9 ± 0.2	7.9 ± 2.6	6.3 ± 2.3
QCB	14.5 ± 2.2	23.0 ± 2.8	21.7 ± 7.2	37.2 ± 11.3	26.0 ± 6.6
HCB	37.0 ± 6.2	60.9 ± 1.9	87.0 ± 46.8	144.3 ± 65.5	83.0 ± 23.2

(a) TCB=trichlorobenzene, TeCB=tetrachlorobenzene, QCB=pentachlorobenzene, HCB=hexachlorobenzene.

It is generally assumed that the bioconcentration factor of a hydrophobic chemical is a true partition coefficient, comparable to liquid-liquid partition coefficients. This assumption is dubious since algal cells do not form a homogeneous phase. Following Opperhuizen [4], several assumptions are made to be able to calculate estimates of thermodynamic parameters. (a) The bioconcentration is a partitioning process into the lipid cell fraction of the algae. (b) The lipid content and composition of the phytoplankton do not affect *BCF* significantly at the different experimental temperatures. (c) The algal lipid's mean molal volume can be represented by the molar volume of 1-octanol or another homogeneous physicochemical phase. (d) The heat of biosorption ΔH° is independent with temperature [11]. The validity of the first assumption can be deduced from the linearity of sorption isotherms, which has been found by several authors ([12] and references therein). The second assumption is the major problem in our data interpretation because lipids were not measured. However, some useful information is provided by the dry weights, DOC and absorption spectra measured after equilibration (Table 2), and by literature data. The changes in dry weight and DOC suggest that some decomposition occurred. However, except the batches equilibrated at 38.6°C, the changes are small relative to the total adsorbent mass. The spectrum (Figure 2) shows a sharp increase of absorbance in the 0.45 μm filtrate at 38.6°C. At the other temperatures, the absorption spectra are close to each other, whereby the extinction maxima show no clear trend with temperature. According to Otten and co-workers [13] the increase in absorbance connected to algal mineralization is greatest during lysis of the organisms. This suggests that possible decay processes were similar in magnitude in our experiments in the 4.5 - 27.5 °C temperature range. Consequently, we assume that in this range the effect of decomposition on *BCF* is small.

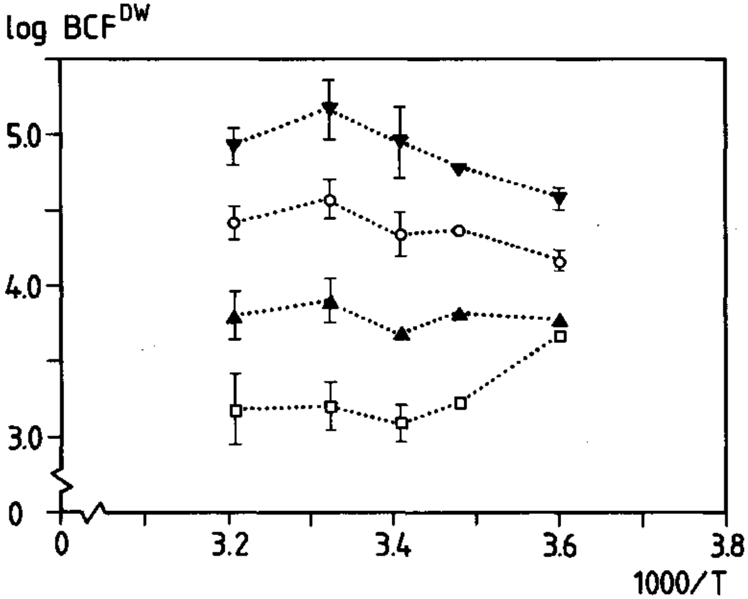

Fig. 1: Van 't Hoff plot of Scenedesmus spp bioconcentration factors for TCB (◆), TeCB (▲), QCB (○) and HCB (▼).

TABLE 2:
Dry weight and DOC before and after equilibration

	T (°C)	DW(a) (mg/l)	DOC (mg/l)
before equilibration:	20.0	245	5.0
after equilibration:	4.5	232	13.0
	14.2	234	5.6
	20.1	228	5.2
	27.5	217	8.0
	38.6	207	14.5

(a) dry weight

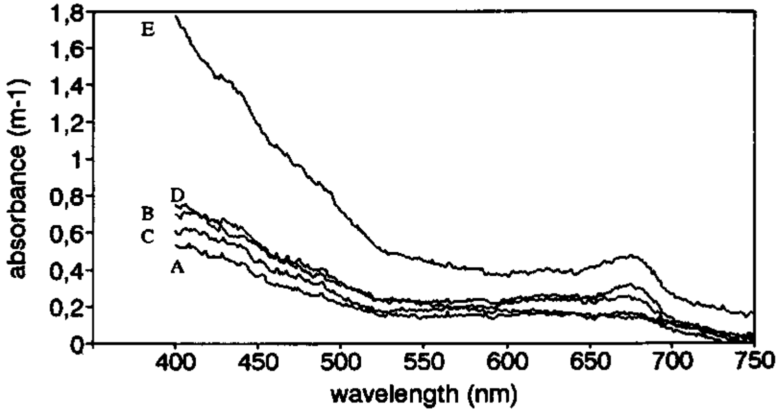

Fig. 2: 400-750 nm absorptionspectra of dissolved matter in 0.45 μm filtrates, after 48 equilibration of *Scenedesmus* spp at (A) 4.5, (B) 14.2, (C) 20.1, (D) 27.5 and (E) 38.6 °C.

Further support for this assumption was found in the literature. It has been described that the lipid content of *Scenedesmus acutus*, does not change over a wide range of temperatures [14]. Wesselius [15] found that the resistance to cellular breakdown of *Scenedesmus* ranges up to 35°C and that photosynthetic and respiratory activity decreases sharply at temperatures above 35°C because of destruction or deactivation of the enzymatic apparatus. This offers an explanation for the diverging *BCF*-values observed in Figure 1 for TeCB, QCB and HCB at 38.6 °C (1000/T= 3.21) and the relatively high dissolved organic matter production at the same temperature. Except for TCB, a negative slope is observed for the other temperatures. So the *BCF*-values decrease with decreasing temperature. According to Cobelas [16], thermophilic algae (such as *Scenedesmus*) generally tend to augment their lipids as temperature diminishes. Such a change in lipid content would result in higher *BCF*-values at low temperatures, which is the opposite of what we observed. Together, the spectra and these literature data, suggest that the fact that the observed slopes in Figure 1 are negative, is caused by other factors than changes in lipid content. Furthermore, changes in lipid *composition* are assumed to be insignificant for hydrophobic chemicals with $\log K_{ow} < 6$ ([4] and references therein).

Because of these considerations, thermodynamic calculations were performed on the results for TeCB, QCB and HCB in the temperature range 4.5 - 27.8 °C. The trends in these data form a consistent set and agree with the results described in the literature for bioaccumulation to fish [4]. TCB could not be included in the analysis because of the non-linear van 't Hoff isochore, caused by an erroneous GC-performance. The thermodynamic parameters ΔH° and ΔS° can be calculated from bioconcentration factors using:

$$logBCF^* = \frac{-\Delta H^\circ}{2.303 \times RT} + \frac{\Delta S^\circ}{2.303 \times R} \tag{1}$$

in which ΔH°(J mol^{-1}) and ΔS° (J mol^{-1} K^{-1}) are the enthalpy and the entropy changes of the transfer process, T is the absolute temperature (K), R is the gas constant (J mol^{-1} K^{-1}) and $\log BCF^*$ is the water to lipids partitioning constant based on the solutes mole fraction solubilities in the lipid and water. The latter bioconcentration factor is related to the BCF^{DW}-values as presented in Table 1, according to:

$$BCF^* = BCF^{DW} \times (\delta_{lipids}/f_{lipids}) \times 55.5/6.4 \tag{2}$$

in which f_{lipids} (g/g) is the lipid content of the algae, δ_{lipids} (g/cm^3) is the average density of the lipid fraction and the factor 55.5/6.4 is the ratio of the molar densities of water and 1-octanol. Combination of (1) and (2) yields:

$$logBCF^{DW} = \frac{-\Delta H^\circ}{2.303 \times RT} + \frac{\Delta S^\circ}{2.303 \times R} + \log[\frac{\delta_{lipids} \times 55.5}{f_{lipids} \times 6.4}] \tag{3}$$

Using equation (3), ΔH°-values were calculated from the linear regression slopes of Figure 1. ΔS°-values were calculated from the intercepts. A lipid content of 0.1 ± 0.05 was estimated from literature data (range 5 - 11%) reported for various *Scenedesmus* strains [17,18]. This estimate causes a larger but still acceptable uncertainty in our ΔS°-estimates, which we accounted for by calculating the propagation of error in the resultant $T\Delta S^\circ$-values. For the density of the natural lipids, a mean density of plant lipids of 0.92 g/cm^3 was used [19]. Finally, ΔG°-values at 292 K were calculated using the relationship: $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. Results of these calculations are listed in Table 3. The standard errors for ΔH° and ΔS° are obtained from the regression calculations. The error in ΔG° was calculated from the propagated errors in ΔH° and ΔS°. Despite of the fact that the values partially may reflect changes in lipid content, our results suggest that the free energy of transport from water to *Scenedesmus* spp is dominated by a gain in entropy. This was also found for the biosorption of malathion to the fungus *Rhizopus arrhizus* and to activated sludge [11], and for bioconcentration to fish [4]. The gain in entropy can be explained by a loss of structuring of the aqueous phase when the chlorobenzenes are transported to the algae.

TABLE 3:

Estimations of free energy, enthalpy and entropy changes of partitioning of chlorobenzenes to algal lipids at 292 K.

Compound	$\Delta G^\circ \pm$ SE (kJ/mol)	$\Delta H^\circ \pm$ SE (kJ/mol)	$T\Delta S^\circ \pm$ SE (kJ/mol)
TCB	$-^{(a)}$	$-^{1}$	$-^{1}$
TeCB	$-^{(b)}$	$-^{2}$	36.3 ± 6.1 *
QCB	-35.2 ± 10.4	24.4 ± 7.2 *	59.6 ± 7.4 *
HCB	-38.0 ± 13.0	37.3 ± 9.1 *	75.3 ± 9.3 *

* significant at $P < 0.01$

(a) ΔH° (and ΔG°) could not be calculated because nonlinear van 't Hoff isochore for TCB.

(b) slope in van 't Hoff plot is not significantly different from zero.

The slopes of linear $\log BCF^{DW}$-$\log K_{ow}$ relationships are shown in Table 4. The (298 K) $\log K_{ow}$ values were taken from [20]. The linearity of the $\log BCF^{DW}$-$\log K_{ow}$ relationships proves that bioconcentration was at equilibrium after 48 h. The slopes can be compared to similar slopes for bioconcentration to fish. The uncertainties in our data associated with the unknown lipid content of the algae do not play a role in such a comparison since the slopes are independent of lipid content. As mentioned before, the negative free energy of transfer from water to algal or fish lipids is dominated strongly by a gain in entropy ($\Delta H > 0$, $T\Delta S \gg \Delta H$). On the other hand, it has been found that the analogous transport of chlorobenzenes from water to 1-octanol is dominated by a decrease in free enthalpy ($\Delta H \ll 0$, $T\Delta S < \Delta H$) [4]. For chlorobenzenes, these thermodynamic differences play only a minor role because of a coincidental compensation of entropy and enthalpy changes, resulting in linear $\log K_{ow}$ - $\log BCF$ relationships and an increase of the slope with experimental temperature. Following Opperhuizen [4], the slopes of chlorobenzene $\log BCF$ - $\log K_{ow}$ plots can be calculated from experimental temperatures (between 13 and 33 °C) according to:

$$slope = \frac{\delta logBCF}{\delta logK_{ow}} = \frac{\Delta\Delta H^{\circ}_{lipids}}{\Delta\Delta H^{\circ}_{oct}} \times \frac{1-T_{lipids}/\beta_{lipids}}{1-T_{oct}/\beta_{oct}} \qquad (4)$$

in which $\Delta\Delta H^{\circ}_{lipids}$ and $\Delta\Delta H^{\circ}_{oct}$ are the mean contributions to the enthalpy change for substitution of one single chlorine atom in benzene for water to fish lipids and water to octanol transfer respectively, T_{lipids} and T_{oct} are the temperatures at which the respective partition coefficients are measured, and β_{lipids} and β_{oct} are the $\Delta\Delta H^{\circ}$ - $\Delta\Delta S^{\circ}$ proportionality factors (compensation temperatures) for water to fish lipids and water to octanol transfer respectively. Opperhuizen reported $\Delta\Delta H^{\circ}_{lipids}$ and $\Delta\Delta H^{\circ}_{oct}$ values of 4.55 kJ/mol and -6.92 kJ/mol, and β_{lipids} and β_{oct} values of 160 K and 714 K respectively. Using these values, slopes of the linear relationship between the log of water to fish bioconcentration factors for our experimental temperatures and $\log K_{ow}$ at 298 K were calculated, and compared with the slopes found for algae in this study, in Table 3. It appears that our findings for the temperature dependency of partitioning of chlorobenzenes to algal lipids fairly agree with the analogous dependency for fish lipids.

TABLE 4:

Comparison of measured and calculated slopes of $\log BCF^{DW}$ - $\log K_{ow}$ relationships.

Temperature (°C)	Algal lipids			Fish lipids[a]
	Measured slope ± SE	r[b]	n[c]	Calculated slope
4.5	0.61 ± 0.05 *	0.961	8	0.82
14.2	0.97 ± 0.04 *	0.985	11	0.89
20.1	1.14 ± 0.08 *	0.957	12	0.93
27.5	1.21 ± 0.10 *	0.943	11	0.98
38.6	1.11 ± 0.10 *	0.933	11	1.06

* significant at $P<5\times10^{-6}$

(a) calculated from equation (4) and thermodynamic data reported by Opperhuizen *et al* [4]

(b) the outlying data for TCB were excluded from the regression calculations

(c) number of measurements used in the regression calculations

CONCLUSIONS

Chlorobenzene bioconcentration factors for *Scenedesmus* spp measured by batchwise equilibration at non-growth conditions, varied considerably with ambient temperature. This temperature dependency is very relevant for the modeling of organic pollutant transport. The thermodynamics of chlorobenzene bioaccumulation to phytoplankton shows great similarity to the thermodynamics of bioaccumulation to fish.

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Chapter 7

BIOSORPTION OF CHLOROBENZENES TO PHYTOPLANKTON AND DETRITUS: I. *SCENEDESMUS*

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BIOSORPTION OF CHLOROBENZENES TO PHYTOPLANKTON AND DETRITUS:

I. *SCENEDESMUS*

Abstract- The influence of mineralization of phytoplankton (laboratory *Scenedesmusp* spp) on the desorption characteristics of 1,2,3,4-tetrachlorobenzene (TeCB) and hexachlorobenzene (HCB) was studied using a purge and trap method. For comparison several field samples including a sediment, algae at different growth stages, and freeze-dried algae, were used. The desorption characteristics were evaluated using multiple box models similar to those generally used for desorption from sediments. It was found for all adsorbents that the desorption could adequately be described using a two-compartment nonequilibrium biosorption model. Generally, HCB was bound stronger and released slower than TeCB. Aging and mineralization of unicell and coenobian forms of the algal species resulted in a significant 60 to 100% increase of OC normalized partition coefficients. Generally, sorption affinity as quantified by the OC normalized partition coefficient (K_{oc}) was lower, and desorption kinetics faster for algae than for soils and sediments. Evaluation of the biosorption rate parameters using a log k_2 vs. log K_p plot showed that in contrast to sediments and soils, no clear inverse relationship between K_p and k_2 exists. A bioconcentration experiment with four chlorobenzenes showed good agreement with the sorption parameters measured with the purge method, and showed a linear correlation of the bioconcentration factor with the octanol/water partition coefficient.

INTRODUCTION

In the aquatic environment, organic pollutants adsorb to the organic fraction of sediments, suspended solids (seston), zooplankton, and phytoplankton. Dependent on both equilibrium and kinetic factors, this process controls the aqueous concentrations, transport, and bioavailability of these compounds to a major extent. The settling of suspended solids, including algae or detritus, can be an important transport route of organic pollutants to the sediment [1]. Phytoplankton and zooplankton are the most abundant sources of organic material in the water column and in sediments. Therefore, seasonal variations in organic carbon content of seston, due to algal blooms, influence the distribution of organic pollutants between particles and water [2]. However, the structure and composition of the biogenic organic matter may change because of changing environmental conditions. In the case of phytoplankton, sorptive properties may change as a result of physiological changes or because of decomposition processes. In both cases the lipid content is considered an important factor [1,3,4]. Phytoplankton has lipids and proteins among its major components and typically contributes toward aquatic humic substances with high hydrogen-to-carbon (H/C) and nitrogen-to-carbon (N/C) atomic ratios. When phytoplankton decomposes, the degradation of these biopolymers results in a change in overall polarity of the material. During diagenesis, these changes usually result in a decrease in the H/C and oxygen-to-carbon (O/C) atomic ratios due to polymerization and condensation effects [5].

As a result of these processes, organic pollutants may be released from the organic matter or further accumulated because of changes in binding affinities and capacities. Several researchers have observed a variation in the sorptivity of organic pollutants for different types of organic material, including phytoplankton. It was found that sorption for dead cells is similar or higher than it is for living cells ([1] and references therein). Several other studies concern organic matter obtained from different surface waters, soils, or sediments, and having different histories. It was shown in these studies that a strong correlation exists between both aromatic content and absorptivity at 270 nm (A_{270}) of humic materials extracted from soils and sediments and the organic carbon normalized partition coefficient (K_{oc}) for hydrophobic compounds [6,7,8]. Several authors showed an empirical correlation between the H/O, H/C, or (O+N)/C atomic ratio, as an index of the polarity of the organic matter, and K_{oc} [5,8,9,10,11,12,13]. High levels of oxygen-containing functional groups (e.g., carboxyl, hydroxyl) may result in an increase in the overall polarity of organic polymers composing natural organic matter and thus in a lower affinity for hydrophobic compounds. These findings suggest limitations in the constancy and the applicability of literature K_{oc} values, which are mostly measured for sediments, and suggest that one should consider the nature or the degree of mineralization of the involved organic matter.

The objectives of this study are (a) to investigate the effect of mineralization of algal biomass *from a single source*, on the sorption equilibrium as quantified by K_{oc} for 1,2,3,4-tetrachlorobenzene (TeCB) and hexachlorobenzene (HCB); (b) to study the kinetics of the same process for the same adsorbents and test compounds; (c) to compare the sorption characteristics for algae having a different morphology and for adsorbents originating from different sources, such as detritus obtained in a laboratory system, natural detritus obtained from the field, and sediments; (d) to investigate the possibility of active uptake by comparing live and dead cells; and (e) to investigate to a limited extent the effect of the sorbate properties. The results should be applicable in integral models for the behavior of organic pollutants, models which are being developed elsewhere.

RESEARCH CONCEPTS

One method frequently used in hydrophobic sorption research is the batch equilibration method for the determination of equilibrium constants and kinetic parameters. This method, however, suffers from uncertainties associated with analytical resolution and the translatability to dynamic systems [14]. Another problem is the required phase separation. Any filtration or centrifugation of algae is fraught with complications and the possibility of artifacts, for example, loss of adsorption, contamination, changes in the partition during the separation step, lysis of algal cells [15], or incomplete phase separation [16,17,18]. The dialysis method [16], which is often used for the determination of K_{oc} values for dissolved organic matter (DOM) might be useful for equilibrium measurements but is inadequate for kinetic studies. In this study, we applied the gas-purge method as suggested by Mackay et al [19], and used by Hassett and Millicic [20] and others. This method offers the possibility to measure equilibrium and rate data from desorption experiments without phase separation. Recently, a study has been published in which a similar technique was applied to algal suspensions [21]. Besides this method, we used a batch method for comparative purposes.

During the degradation process, algal cells decompose, yielding cell fragments, smaller biomolecules, and molecular fragments. This means that the adsorbent gradually changes from a particulate "cellular" state to a colloidal and partially dissolved "humic" state. To monitor this process, several parameters were chosen to characterize the adsorbent and to determine its degree of decomposition. The total concentration of organic carbon (TOC) is needed for the calculation of K_{oc} values. Furthermore, this parameter can be used with values for the dry weight (DW) to determine the organic carbon content of the adsorbent. From TOC measurements in total and filtered samples, the percentage particulate carbon can be calculated.

Instead of the determination of H/C or O/C atomic ratios, chemical oxygen demand (COD) measurements were performed. The COD gives a direct measurement of the theoretical oxygen required to oxidize organic matter to carbon dioxide, water, and ammonia. The theoretical ratio of COD/DW varies from 1.1 for simple carbohydrates to 2.9 for saturated long-chain fatty acids, with an average for heterogeneous biological material of about 1.4 [22]. According to Stumm and Morgan [23], the complete aerobic oxidation of algal protoplasm can be described by an approximate stoichiometry:

$$\{(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)\} + 138O_2$$
$$\text{----- mineralization ---->}$$
$$106CO_2 + 16NO_3^- + HPO_4^{2-} + 122H_2O + 18H^+ + \text{trace elements} + \text{energy}$$

From this equation, a maximum COD/TOC ratio of 2.51 can be calculated. Assuming 1.42 mg COD equals 1 mg of organic algal material [22], the degree of mineralization (DM%) can be calculated from the COD measurements according to

$$DM\% = 100 \times \left(1 - \frac{COD}{1.42}\right) \tag{1}$$

Besides the degree of mineralization, the chlorophyll-a-to-phaeophytin ratio and the beam attenuation spectrum in the 0.45 μm filtrate were measured. The chlorophyll-to-phaeophytin ratio is included as a measure of the condition of the algae during the "cellular" part of the experiment and will decrease in time. From the spectra the beam attenuation factor at 270 nm (BAF_{270}) was calculated. In several studies BAF_{270} (usually called the absorbance at 270 nm, A_{270}) has been related to the aromatic content of isolated soil humic acids [6]. When light scattering plays a minor role, the BAF_{270} (in units of $1/mgC \times cm \times 10^3$) reflects absorbance of π-π^* transitions in substituted benzenes and most polyenes.

MODELING OF DESORPTION RATE DATA

Reviews of the models used in the interpretation of sorption rate data were recently given by Brusseau *et al.* [24] and Weber *et al.* [25]. For the modeling of purge data we consider the sorption rate models presented in Figure 1. In this figure, five models are presented, one without a binding agent (Model 1) and four with binding agents (Model 2 to 5).

For water containing no binding agent (Model 1), the loss of a compound by evaporation can be described as an irreversible first order reaction. The constant k_v is a first-order rate constant and is dependent on temperature, gas flow rate, Henry's law constant (HLC, $atm \times m^3 \times mole^{-1}$), and the liquid volume. If the gas phase does not equilibrate with the liquid phase, the constant is also dependent on the gas-water interfacial area and the overall liquid phase mass-transfer coefficient [19,26]. In case of equilibrium:

$$\ln\left(\frac{Cw_t}{Cw_{t=0}}\right) = -k_v t \quad \wedge \quad k_v = \frac{F \times H}{V_w} \tag{2}$$

in which t is the time (min), Cw_t is the concentration of test compound at time t (μg/L), $Cw_{t=0}$ is the concentration of test compound at time = 0 (μg/L), F is the flow rate (l/min), V_w is the liquid volume (l), and H is the dimensionless Henry's law constant. H is equal to HLC/RT, in which HLC is the Henry's law constant expressed in $atm \times m^3 \times mole^{-1}$ and R ($atm \times m^3 \times mole^{-1} \times K^{-1}$) and T (K) are the gas constant and the absolute temperature, respectively. This model has been used successfully by several researchers to determine HLC values for hydrophobic compounds. When headspace can be neglected during a purge experiment and the volatilizing compound is trapped on Tenax-columns (see "Gas purge desorption experiments"), the cumulative amount trapped in the Tenax (μg) is:

$$Q^{TENAX} = V_w(Cw_{t=0} - Cw_t) \tag{3}$$

Combination of (2) and (3) yields:

$$Q^{TENAX} = V_w Cw_{t=0}(1 - EXP(-k_v t)) \tag{4}$$

MODEL 1 (No binding agent)

$$Cw \xrightarrow{k_v} Cg$$

MODEL 2 (Binding agent, one compartment, equilibrium binding assumed)

$$Cs \overset{K_{oc}}{\leftrightarrow} Cw \xrightarrow{k_v} Cg$$

MODEL 3 (Binding agent, one compartment, general)

$$Cs \xrightleftharpoons[k_{21}]{k_{12}} Cw \xrightarrow{k_v} Cg$$

MODEL 4 (Binding agent, two compartments, equilibrium binding assumed between the liquid phase and the first compartment)

$$Cs_2 \xrightleftharpoons[k_2]{k_2} Cs_1 \overset{K_{oc}}{\leftrightarrow} Cw \xrightarrow{k_v} Cg$$

MODEL 5 (Binding agent, two compartments, general)

$$Cs_2 \xrightleftharpoons[k_2]{k_2} Cs_1 \xrightleftharpoons[k_{21}]{k_{12}} Cw \xrightarrow{k_v} Cg$$

Fig. 1: Sorption models, used in the interpretation of gas purge data.

In the presence of organic matter, the relationship between Q^{TENAX} and time is different, due to adsorption and desorption. It has been shown often that sorption of a hydrophobic chemical to organic matter at equilibrium can be described over a wide concentration range by a constant [27,28]:

$$K_b = C_b/Cw \quad \wedge \quad K_b = TOC \times K_{oc} \tag{5}$$

where C_b (μg/L) is the concentration of sorbed compound, K_{oc} is the organic carbon normalized partition coefficient, and *TOC* is the organic carbon fraction in the system. Evidence for the same type of passive equilibrium partitioning for algae can be deduced from the strong correlation found between bioconcentration and K_{ow} [29,30] or from the measured linearity of sorption isotherms [2,3,21,31]. A kinetic description of the interaction which is consistent with the equilibrium expression includes forward and backward first order reactions, as represented by Model 3[1]. The one-compartment models 2 or 3 can be used to determine the sorption constant for humic materials with purge experiments [20].

In several other kinetic studies, the one-box model failed to represent experimental data adequately [14,32,33]. For *sediments*, organic chemicals have been found to show a two-stage approach to equilibrium: a short initial phase of fast uptake or release within minutes or hours, followed by an extended period of much slower uptake or release. Wu and Gschwend [33] used a radial diffusion model to describe their data. Others used multiple-box models similar to Model 4[1] and Model 5. In these models, a readily accessible fraction of the total sorptive volume (x_1) is distinguished from a more resistant portion of the adsorbent. If chemical exchange between the aqueous phase and the labile reservoir is assumed to be sufficiently fast to maintain equilibrium between these two phases, Model 5 simplifies to Model 4, and the desorption process is characterized by K_{oc}, k_2 and x_1. The theoretical backgrounds and merits of the two-box Model 4 were discussed recently by Brusseau *et al.* [14].

For *algae*, or microorganisms in general, the bioconcentration is determined by factors such as particle size, organic content, and surface area. It may be expected that sorption to the cell surface is much faster than sorption to the cell content. Several studies point to the existence of more than one sorption reservoir [3,21,34].

Model 5 is the general two-box model. Because the two sorption reservoirs are assumed to consist of organic material (the lipid cell fraction), the forward and reversed rate constants are considered equal. Models 2, 3 and 4 are special cases of Model 5. Their applicability to describe purge rate data depends on the magnitude of k_v only.

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[1] For a detailed description of Models 3 and 4, see the appendix to Chapter 8

MATERIALS AND METHODS

Adsorbents

The original algae were a nonaxenic unicell population of *Scenedesmus* spp, in the coccal growth phase, precultivated in continuous light in a synthetic medium (Z8, Hughes et al [35]) at 20°C. The alga was chosen for its spherical form ($\phi = 11 \pm 2$ μm) and universality. Unicells occur in young, actively growing cultures and are formed in nature in early spring, when cell densities are low [36]. The algae were placed in a continuously stirred and aerated tank with a constant volume of about 140 L. At time 0, the tank was placed in a 20°C climate chamber without light. The suspension was buffered with bicarbonate to a pH of 9.0. Detritus samples at varying degrees of mineralization were obtained from this tank. Representative samples of 4 L were taken at incremental intervals and divided into eight representative subsamples of 0.5 L using a Retsch suspension divider. The subsamples were immediately used for the characterization of the adsorbents and for the determination of TeCB and HCB kinetic and equilibrium sorption parameters. At time 0, a representative subsample was placed in a 16:8-h light:dark regime at 20°C. When cell densities increased, coenobial forms of *Scenedesmus* developed in this batch. Three samples were taken from this culture at different times. One sample was taken immediately and used for characterization and a desorption experiment as described above. The second sample was freeze-dried. The resulting green powder was resuspended in Nanopure® water (Sybron-Barnstead, Dubuque, IA) and used for characterization and a desorption experiment. Microscopic inspection revealed that the cell morphology remained unchanged. Growth potency was tested in fresh medium and turned out to be zero. The third sample of coenobia was used for a batch equilibration adsorption experiment with four chlorobenzenes. The remaining portion of the coenobia was kept in the dark at 30°C for 240 days. The resultant yellow/brownish batch of detritus was also used for a triplicate gas-purge desorption experiment. Natural detritus was collected from Lake Volkerak/Zoom (The Netherlands) on May 1, 1991, using an industrial centrifuge (Pennwalt Prescription Products, Rochester, NY; AS 16). Finally, the sediment sample was left over from an earlier study and had been characterized before [2]; this sediment had been sampled from Lake Volkerak/Zoom, using a seabed box corer.

Characterization of adsorbents

Dry weights were determined by filtration over Schleicher & Schuell (Dassel, Germany) 0.45 μm membrane filters and drying at 105 °C till constant weight. COD values were determined in total and filtered samples as oxidizability by $K_2Cr_2O_7$, using a dead stop end point titrimeter, according to standard methods [37]. Total organic carbon was determined in total and filtered samples on an OIC (College Station, TX) Model 700 organic carbon analyzer. A test program revealed that an extended reaction time of 20 minutes at 90 °C was sufficient to convert all carbon. Chlorophyll and phaeophytins were extracted with acetone and measured on a Beckman (Fullerton, CA) DU-64 spectrophotometer, according to standard methods [37]. Beam attenuation spectra from 200 to 900 nm were measured on a Beckmann DU-64 spectrophotometer. All algal suspensions were microscopically examined (Nikon (Melville, NY) inverted microscope).

Gas purge desorption experiments

All water used in the purge experiments was Barnstead Nanopure water. Nanograde organic solvents (acetone and 2,2,4-trimethylpentane) were obtained from Promochem (C.N. Schmidt, The Netherlands). TeCB, 1,2,4,5-tetrachlorobenzene (98%, Aldrich Europe, Belgium), and HCB (>98%, BDH Chemicals, UK) were used without further purification. Tenax 40-to 60-mesh was obtained from Chrompack (The Netherlands). For the purge experiments, high-purity nitrogen was used.

The purge vessels were similar to those described by Mackay et al. [19] and were fitted with fritted glass outlets. The height and volume of the flasks were 40 cm and 1 liter respectively. The vessels had double walls and were connected to a Haake D1 thermostat (Proton-Wilten, The Netherlands). Prior experiments showed that chlorobenzenes can adsorb significantly to Teflon® [18]; therefore, iron stir bars were used instead of Teflon-covered stir bars. The stirring speed was 1000 rpm, resulting in a circular path of the gas bubbles through the liquid column with a total length of one and one-half to two times the height of the column. Nitrogen gas flow was regulated with flow controllers and was passed through vessels containing water to prevent evaporation from the purge vessels. Three vessels could be operated simultaneously and independently at the same temperature. A Hewlett-Packard (HP, Avondale, PA) 5890 double-column GC system equipped with two ^{63}Ni electron capture detectors (ECD) was used in chlorobenzene quantization. Congener separation was accomplished with 50-m, 0.25-mm-i.d., HP Ultra 1 (0.5-μm film thickness) and Ultra 2 (0.33-μm film thickness) columns.

The algal subsamples were placed in the gas-purge apparatus and spiked with 50 μl of a solution of TeCB and HCB in acetone. To avoid the presence of HCB microcrystals, target concentrations did not exceed 10% of the aqueous saturation value for HCB of 10 μg/L (A.A. Koelmans, unpublished results). The flasks were capped and thermostatted (20 ± 0.1 °C) during equilibration. After an equilibration period of 48 h under continuous stirring, purge experiments were conducted by replacing the cap by the gas inlet tube and using the gas flow to purge the TeCB and HCB onto Tenax column traps. Considering the required equilibration time for HCB to *Chlorella* reported by Geyer et al

[30] of 2 to 4 h, our 48-h period was assumed to be sufficient. For the experiment with the sediment, an equilibration period of 96 hours was used. Gas flows (approximately 450 ml/min) were immediately started and measured with a soap-bubble meter. All experiments were run in triplicate simultaneously, at roughly the same flow. Generally, gas flows were constant within 1%. The total purge time was > 120 h in all experiments. Tenax columns were replaced at incremental intervals, determined by the mass of test compound expected in the Tenax tubes. All experiments were optimized for HCB, that is, to yield approximately the same mass of HCB in each trap. Therefore, conditions for TeCB were less ideal but still satisfactory. The trap columns consisted of glass tubes containing glaswool and approximately 0.2 g Tenax. Preliminary experiments with Tenax columns in series showed a trap efficiency of 100%. HCB and TeCB were desorbed from the Tenax columns by elution with 15 ml diethyl ether (recovery 100%). The extracts were evaporated slowly to 4 (or 2) ml with nitrogen after addition of 4 (or 2) ml of an internal standard (45 μg/L 1,2,4,5-tetrachlorobenzene in 2,2,4-trimethylpentane), to reduce the error of analysis. The resulting 2,2,4-trimethylpentane solutions and calibration standards were injected directly to the GC. The calibration standards in the range of 10 to 140 μg/L TeCB and HCB were made in the same internal standard solution.

To test for possible anaerobic biodegradation during the 48 h equilibration period, a parallel experiment was performed in which a second aliquot from the tank was spiked. After 1, 2, 5, and 19 d a representative subsample was taken from the closed system, extracted with 2,2,4-trimethylpentane and analyzed for HCB and all lower substituted congeners and isomers. It has been described that anaerobic degradation of HCB and TeCB results in lower substituted congeners [38]. Because no such degradation products were observed in the chromatograms, we conclude that no significant degradation occurred in our experiments.

Immediately after finishing a desorption experiment, the dry weight of the algal suspensions was measured by filtration over 0.45-μm membrane filters to check for changes in adsorbent mass due to mineralization or growth. The measured changes were too small to make corrections necessary. Furthermore, the residues were analyzed to be able to account for possible remaining fractions of the test compounds. The glass frits and container walls were thoroughly rinsed with acetone to check for sorption losses. However, the resulting chromatograms showed no signs of either test compound.

For the determination of HLC values, equilibration and purge time were 1 h and 7 h respectively. Extraction and GC analysis were as described above.

Handling of purge rate data

The unknown model parameters were calculated from plots of cumulative micrograms of test compound purged from solution vs. time[2]. The advantages of this approach are described by Dunnivant et al [39]. HLC values were calculated from the purge rate data using the model developed by Mackay et al. [19] (Eqn. 4). For TeCB and HCB, HLC values of $(6.7 \pm 0.3)\times10^{-4}$ atm$\times$m$^3\times$mole^{-1} (n=9) and $(5.1 \pm 0.3)\times10^{-4}$ atm$\times$m$^3\times$mole^{-1} (n=9) were measured, respectively. The sorption parameters were calculated according to Model 3 [20] and 4 [14]. For the calculations two computer programs, based on weighted nonlinear least-squares techniques were written in BASIC (Turbo Basic, Borland International Inc.). The first program was used for the HLC determinations and incorporates explicit solutions of the normal equations to estimate the HLC and the total amount of test compound in the system. The second program was used to fit the sorption models 3 and 4, employing the modified sequential simplex method of Nelder and Mead [40]. The sum of the final cumulative Q^{TENAX} value and the amount of test compound found in the adsorbent after the purge experiment, was used as value for the total amount of test compound in the system at t=0. For Model 3, k_{12} and k_{21} were estimated. For Model 4, K_{oc}, k_2 and x_1, the latter being the readily accessible fraction of the total sorptive volume, were estimated.

After parameter estimation, 95% C.I.s were calculated, according to [41]:

$$SS_{95}=SS_{\min}[1+p/(n-p)\times F(p,n-p,95\%)] \tag{6}$$

with SS_{95} the sum of squares at the 95% confidence contour, SS_{min} the minimum sum of squares, n the number of points in the cumulative plot of desorbed test compound vs. time, p the number of parameters and $F(p,n\text{-}p,95\%)$ the F distribution according to Fisher [41].

Batch adsorption experiments

A sample of *Scenedesmus* spp coenobia was divided into eight representative subsamples using a Retsch sample divider. Three of the subsamples were transferred to glass-stoppered, gas-tight oxygen bottles with a volume of 300 ml. The remaining subsamples were used for chlorophyll, phaeophytin, total TOC and TOC in a filtered sample, and dry weight determinations. In the three oxygen bottles, headspace was minimized and the batches were spiked with 10 µl of a solution of 1,2,3-trichlorobenzene (99%, Aldrich Europe), TeCB, pentachlorobenzene (98%, Aldrich Europe), and HCB in acetone. The batches were left for 48 h at 20°C on magnetic stirrers with metal stir bars.

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[2] Parameters were also estimated using the original sequential data; see Addendum to Chapter 7.

After the equilibration period, the suspensions were filtered over 1.2 μm Whatmann (Kebo, Sweden) GF/C glass fibre filters. Seventy-five-milliliter samples of the aqueous phases were stirred for 48 h with 4 ml of an internal standard solution (45 μg/L 1,2,4,5-tetrachlorobenzene in 2,2,4-trimethylpentane). The filters were thoroughly extracted with acetone (nanograde). Combined acetone extracts were shaken with diethyl ether (Merck, Darmstadt, Germany; p.a.). After addition of a saturated potassium sulfite solution, the extract was shaken with water (Nanopure). The organic fraction was separated, and the aqueous phase was extracted again with diethyl-ether. Both diethyl-ether fractions were combined and shaken again with water. The organic fraction was separated, dried with potassium sulphate (p.a.), concentrated to 5 ml on a Kuderna-Danish apparatus, and finally concentrated to 2 ml under nitrogen. The resultant concentrate was cleaned by eluting with diethyl-ether over deactivated alumina. The cleaned extract was concentrated to 2 ml, after addition of 2 ml 2,2,4-trimethylpentane with internal standard, and used for GC-analysis as described above. From the adsorbed and aqueous concentrations, bioconcentration factors on a dry weight basis (BCF^{DW}) were calculated.

RESULTS AND DISCUSSION

Adsorbent characteristics

The adsorbent characteristics are listed in Table 1. Chlorophyll concentrations and chlorophyll-to-phaeophytin ratios (CHL/PHA) are high for the fresh culture of unicells. For the aging unicell population, within two weeks the CHL/PHA ratio decreases to an almost constant level between 1 and 2 (Figure 2). Despite the lack of light for more than five months, the algae still appear green and contain a considerable amount of chlorophyll. However, COD/TOC, COD/DW and %DM (Table 1) suggest that overall degradation of the organic matter occurs during the first 52 d. This is further supported by the decrease in the percentage of particulate total organic carbon (%PTOC) and by the microscopic examinations, which show an increasing amount of debris and deformed cells. The TOC normalized beam attenuation of the DOM at 270 nm (BAF_{270}-DOM) ranges from 5.9 to 8.1 without a general trend. Finally, the organic carbon fraction of the solid particles (f_{oc}), decreases gradually from 0.35 to 0.14, which can be expected as a result of overall oxidation of organic matter. Furthermore, the disappearance of organic matter from the particulate phase, and/or precipitation of salts from the Z8 medium, might contribute to the relative enrichment of inorganic constituents.

Considering these parameters together, it can be concluded that some aerobic decomposition has occurred, but that the algal mortality and decay were not complete under the prevailing conditions. This result is consistent with those obtained from other studies [42]. According to the literature, several stages can be distinguished in the decomposition of phytoplankton [22,43]. After the death of algae, part of the biomass is released as DOM, by lysis of the cells. The larger fraction of the remaining particulate matter is also labile and decomposes within a year, whereas the rest is refractory and may resist complete degradation for many years or even decades. Furthermore, *Scenedesmus* is hard walled [44], and its degradation is slow compared to that of many other algal species.

TABLE 1:
Adsorbent Characteristics

Adsorbent[a]	CHL[b] (µg/L)	CHL/PHA[c]	COD/TOC[d]	COD/DW[e]	%DM[f]	BAF_{270}-DOM[g]	%PTOC[h]	f_{oc}[i]
Gas Purge desorption								
U-0	1290	33	2.9	1.11	22.1	5.9	85.4	0.35
U-11	910	2.2	2.9	0.99	30.2	7.3	86.6	0.32
U-38	280	0.9	2.6	0.55	61.3	8.1	75.4	0.24
U-52	510	2.0	2.3	0.53	62.7	6.3	74.3	0.21
U-81	321	1.0	-	-	-	7.5	62.7	0.22
U-171	400	0.8	3.4	0.53	62.7	7.3	82.1	0.14
C-0	1080	2.9	3.4	1.02	27.9	6.9	84.8	0.26
C-240	120	1.0	3.7	1.56[j]	-	-	89.7	0.40
C-FD	190	1.0	3.3	1.56	7.8	-	71.6	0.45
DET	0	-	1.7	0.36	75.0	22.1	47.8	0.37
SED[k]	60	0.7	-	1.69	-	14.8	-	0.021
Batch adsorption								
C-0'	2827	6.5	-	-	-	-	97.6	0.36

a. Letters refer to the type of adsorbent. Numbers refer to the age of the culture (d). U= *Scenedesmus* Unicells, C= *Scenedesmus* Coenobia, C-FD= Freeze-dried Coenobia, DET= natural detritus from Lake Volkerak/Zoom (The Netherlands), SED= sediment from Lake Volkerak/Zoom.

b. Chlorophyll content

c. Chlorophyll (µg/L) to phaeophytin (µg/L) ratio

d. Ratio of total COD (mg/L) to total TOC (mg/L)

e. Ratio of COD (mg/L) of the particles to dry weight (mg/L)

f. Degree of mineralization according to equation (1)

g. The absorptivity at 270 nm of the DOM in the filtered (0.45 µm) algal suspensions

h. Percentage particulate carbon, calculated from the TOC of the total and filtered (0.45 µm) suspension

i. The organic carbon content of the particles (>0.45 µm), calculated from total and filtered TOC and dry weight.

j. Erroneously high COD value; no derived parameters calculated.

k. For the sediment, values per unit volume were calculated from the concentrations per unit mass and the sediment-to-water ratio.

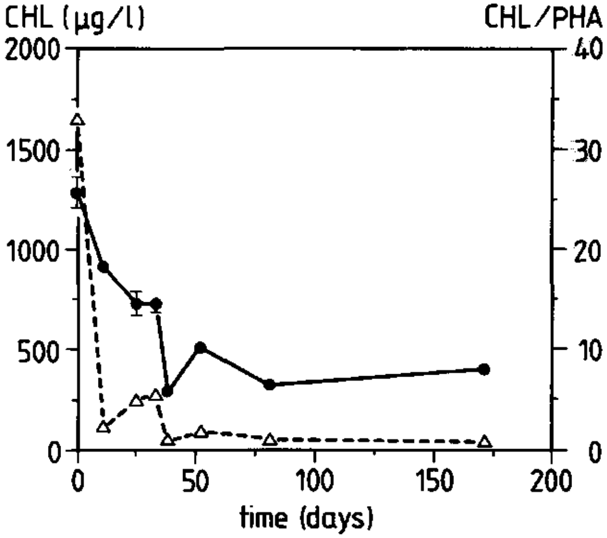

Fig. 2: Chlorophyll concentrations (—●—) and chlorophyll to phaeophytin ratios (--▵--) for mineralizing unicells under dark conditions. Error bars represent standard deviations.

The culture of coenobia showed a yellow-brown color and a decrease in chlorophyll content after 240 d decay in a light and dark regime at 30°C. In contrast to the unicellular culture, microscopic examination suggested that all cells had lysed completely. The f_{oc} of the particles increased significantly. Freeze drying the fresh coenobia resulted in a similar increase in the f_{oc} and a similar decrease in chlorophyll concentration but did not alter the microscopic appearance of the cells.

The natural detritus sample obtained from Lake Volkerak/Zoom is characterized by a high degree of mineralization and a high BAF_{270}-DOM. It can be expected that this material is heterogeneous in nature and that it contains materials with a much longer history than the other adsorbents used in this study. The high value of BAF_{270}-DOM suggests a high contribution of aromatic hydrophobic acids, as present in humic substances [8].

The sediment consists of organic matter of which a large degree of mineralization can be expected. As with the natural detritus sample, this is illustrated by the relatively high beam attenuation at 270 nm.

Modeling results of desorption experiments

An example of the cumulative amounts of HCB trapped in the Tenax columns as a function of time and model simulations is given in Figure 3. It appears that the two-compartment model (Model 4) describes the experimental data far better (smaller SS_{min}) than the one-compartment Model 3 and that the algal material consists of two distinct sorption reservoirs: a reservoir (fraction x_I) in equilibrium with the solution and a reservoir with a slow first-order decrease in HCB concentration during the time span of the experiment. This result agrees with desorption characteristics for sediments reported in the literature [14,32,33]. Because the inadequacy of the one-compartment model was observed for all adsorbents used in this study except the natural detritus sample, only the results obtained using the two-compartment model are discussed in the subsequent sections of this paper.

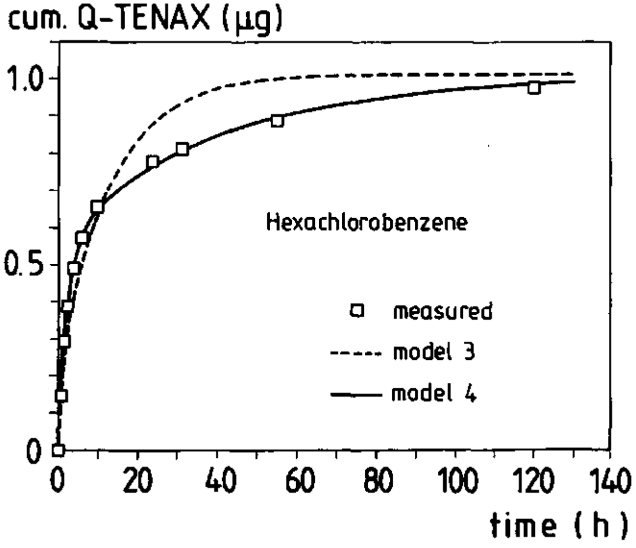

Fig. 3: Representative comparison of the least squares regressions of the one-compartment model and the two-compartment models 3 and 4, to a HCB desorption dataset (□) for *Scenedesmus* spp unicells.

The estimated parameters for each individual experiment are presented in Table 2 (HCB) and Table 3 (TeCB) with their corresponding 95% C.I.s; generally, the reproducibility between triplicate experiments is satisfactory. The confidence intervals for the least-squares estimations of K_{oc}, k_2 and x_I for HCB are in the range of ±3 to 25%, ±11 to 80% and ± 4to 60% respectively. The same ranges for TeCB are ±5 to 54%,

±18 to 1100% and ±5 to 100% respectively. This comparison shows that the K_{oc} values are estimated with the best accuracy, followed by the x_I values, and that the parameters for HCB are estimated more accurately than those for TeCB. The larger intervals for the x_I and especially the k_2 values originate from the fact that they are estimated from the end of the desorption curve, where the weights of the least-squares differences are small. The difference between HCB and TeCB can be explained by the difference in binding strength of the two chemicals, the related sensitivity of the method, and the fact that the experimental conditions were optimized for HCB.

Mineralization experiments

The HCB K_{oc} values for the mineralizing unicells show a gradual increase by a factor of two (Table 2). The average K_{oc} values and their standard deviations for HCB and TeCB are plotted against time in Figure 4. Considering the 95% C.I.s, which provide a more reliable measure of error, the differences are never significant for adjacent points in time. However, the differences are significant for the 171-d aged unicells and the unicells aged for 52 d and less. An increase in K_{oc} for a hydrophobic compound such as HCB suggests a decrease in the adsorbents' average polarity with aging. As for bioaccumulation in fish and other aquatic organisms, it has been shown that for algae, neutral biomolecules such as (neutral) lipids are the major compartments for hydrophobic partitioning. Therefore, alterations of the lipid content or composition, resulting from physiological changes and/or degradation processes induced by the stress factors, are presumably responsible for the observed K_{oc} trend. It has been described for *S. obliquus* in batch culture that the contents of proteins decrease and the contents of total lipids increase with aging [45]. In the same study, an increase of the contribution of neutral lipids was observed after 11 d. This agrees with the fact that phospholipids, being polar lipids, have a rapid turnover compared to neutral storage lipids [46]. According to Rutherford et al [13], decomposition of plant materials increases the affinity of hydrophobic compounds because of a reduction of carbohydrate content during the humification process. Particularly cellulose, an important carbohydrate component of plants with a relatively low affinity for hydrophobic compounds, is readily decomposed by microorganisms [9]. These studies show that decomposition processes can decrease the average polarity of plant materials. Although our characterization of the phytoplankton provides no evidence for such polarity changes, it is most likely that these processes occurred during our mineralization experiments.

TABLE 2:
Hexachlorobenzene desorption parameters and 95% confidence intervals

Adsorbent[a]	K_{oc} ($\times 10^3$)	95% C.I.	k_2 (d^{-1})	95% C.I.	x_1	95% C.I.
U-0	112	(83 - 145)	0.93	(0.56 - 1.40)	0.35	(0.13 - 0.54)
	116	(88 - 146)	0.97	(0.59 - 1.44)	0.37	(0.17 - 0.54)
	122	(94 - 152)	1.02	(0.57 - 1.59)	0.42	(0.20 - 0.62)
U-11	130	(118 - 141)	0.73	(0.55 - 0.94)	0.54	(0.46 - 0.61)
	116	(96 - 137)	0.76	(0.48 - 1.10)	0.46	(0.31 - 0.58)
	111	(90 - 133)	0.81	(0.48 - 1.21)	0.45	(0.28 - 0.59)
U-38	131	(124 - 138)	0.55	(0.48 - 0.62)	0.45	(0.41 - 0.48)
	130	(123 - 137)	0.63	(0.56 - 0.71)	0.42	(0.39 - 0.46)
	116	(108 - 124)	0.62	(0.54 - 0.71)	0.37	(0.33 - 0.42)
U-52	135	(121 - 149)	0.62	(0.48 - 0.76)	0.43	(0.35 - 0.50)
	154	(145 - 164)	0.60	(0.52 - 0.70)	0.46	(0.41 - 0.50)
	152	(141 - 163)	0.60	(0.50 - 0.70)	0.45	(0.40 - 0.50)
U-81	134	(120 - 145)	1.15	(0.80 - 1.61)	0.60	(0.50 - 0.68)
	178	(147 - 209)	1.07	(0.35 - 2.37)	0.69	(0.50 - 0.84)
	137	(124 - 150)	1.34	(0.94 - 1.86)	0.60	(0.50 - 0.68)
U-171	204	(171 - 231)	2.21	(0.80 - 4.27)	0.66	(0.35 - 0.86)
	221	(200 - 238)	1.57	(0.57 - 2.91)	0.78	(0.62 - 0.90)
	229	(210 - 245)	1.62	(0.30 - 4.16)	0.86	(0.65 - 0.95)
C-0	196	(159 - 232)	1.14	(0.43 - 2.07)	0.61	(0.38 - 0.81)
	214	(187 - 240)	1.15	(0.56 - 1.82)	0.64	(0.47 - 0.78)
	266	(222 - 300)	0.90	(0.18 - 2.21)	0.75	(0.48 - 0.89)
C-240	325	(271 - 382)	0.49	(0.40 - 0.59)	0.33	(0.23 - 0.42)
	345	(295 - 397)	0.55	(0.46 - 0.65)	0.34	(0.25 - 0.42)
	358	(253 - 483)	0.52	(0.40 - 0.67)	0.25	(0.11 - 0.40)
C-FD	242	(221 - 261)	1.71	(0.45 - 3.65)	0.82	(0.65 - 0.93)
	272	(263 - 280)	0.53	(0.22 - 1.14)	0.95	(0.91 - 0.97)
	236	(224 - 247)	1.31	(0.39 - 2.55)	0.88	(0.80 - 0.95)
DET[b]	212	-	0.011	-	0.98	-
	233	-	0.006	-	0.98	-
	242	-	0.005	-	0.99	-
SED	340	(323 - 358)	0.15	(0.08 - 0.24)	0.77	(0.72 - 0.81)
	305	(290 - 321)	0.13	(0.07 - 0.20)	0.75	(0.71 - 0.79)
	326	(313 - 338)	0.19	(0.13 - 0.26)	0.75	(0.72 - 0.78)

a. Letters refer to the type of adsorbent. Numbers refer to the age of the culture (d). U= *Scenedesmus* Unicells, C= *Scenedesmus* Coenobia, C-FD= Freeze-dried Coenobia, DET= natural detritus from Lake Volkerak/Zoom, SED= sediment from Lake Volkerak/Zoom.

b. Confidence intervals could not be calculated for this adsorbent.

TABLE 3:
1,2,3,4-Tetrachlorobenzene desorption parameters and 95% confidence intervals

Adsorbent[a]	K_{oc} ($\times 10^3$)	95% C.I.	k_2 (d^{-1})	95% C.I.	x_1	95% C.I.
U-0	34	(27 - 42)	0.85	(0.47 - 1.47)	0.40	(0.18 - 0.56)
	36	(26 - 46)	0.94	(0.46 - 1.77)	0.39	(0.11 - 0.58)
	34	(27 - 40)	0.78	(0.43 - 1.33)	0.45	(0.26 - 0.58)
U-11	61	(53 - 68)	1.18	(0.87 - 1.58)	0.48	(0.38 - 0.57)
	50	(44 - 57)	1.37	(1.05 - 1.77)	0.40	(0.29 - 0.50)
	50	(43 - 57)	1.20	(0.86 - 1.63)	0.45	(0.32 - 0.55)
U-38	26	(12 - 35)	1.31	(0.00 - 14.46)	0.70	(0.00 - 0.91)
	21	(17 - 24)	1.53	(0.83 - 2.80)	0.55	(0.35 - 0.67)
	-[b]		-		-	
U-52	29	(24 - 34)	0.49	(0.02 - 1.77)	0.80	(0.67 - 0.90)
	24	(21 - 27)	0.47	(0.19 - 0.92)	0.75	(0.66 - 0.81)
	29	(24 - 34)	0.51	(0.04 - 1.68)	0.80	(0.67 - 0.89)
U-81	40	(22 - 54)	1.61	(0.58 - 5.17)	0.36	(0.00 - 0.65)
	40	(34 - 46)	1.13	(0.57 - 2.11)	0.64	(0.50 - 0.75)
	25	(16 - 34)	1.80	(0.61 - 5.42)	0.45	(0.00 - 0.70)
U-171[b]	-[b]		-		-	
	-[b]		-		-	
	-[b]		-		-	
C-0	23	(15 - 29)	5.78	(0.35 - 18.32)	0.63	(0.00 - 0.91)
	21	(18 - 24)	1.43	(0.45 - 5.83)	0.79	(0.54 - 0.87)
	28	(25 - 30)	0.72	(0.15 - 1.85)	0.89	(0.83 - 0.94)
C-240	44	(36 - 53)	1.69	(1.33 - 2.13)	0.21	(0.03 - 0.36)
	41	(32 - 49)	1.71	(1.33 - 2.16)	0.17	(0.00 - 0.33)
	56	(50 - 62)	1.51	(1.24 - 1.80)	0.37	(0.28 - 0.46)
C-FD	22	(20 - 23)	0.16	(0.02 - 0.32)	0.79	(0.73 - 0.83)
	21	(20 - 23)	0.43	(0.14 - 0.87)	0.84	(0.79 - 0.88)
	20	(18 - 21)	0.39	(0.15 - 0.77)	0.83	(0.77 - 0.87)
DET	10	(7 - 13)	0.50	(0.14 - 1.19)	0.58	(0.29 - 0.75)
	17	(12 - 21)	0.49	(0.08 - 1.39)	0.68	(0.47 - 0.82)
	14	(11 - 18)	0.52	(0.16 - 1.20)	0.64	(0.45 - 0.77)
SED	22	(17 - 26)	1.92	(0.81 - 4.19)	0.55	(0.24 - 0.72)
	34	(31 - 38)	0.84	(0.58 - 1.21)	0.59	(0.50 - 0.67)
	24	(17 - 29)	1.40	(0.30 - 6.05)	0.67	(0.17 - 0.85)

a. Letters refer to the type of adsorbent. Numbers refer to the age of the culture (d). U= *Scenedesmus* Unicells, C= *Scenedesmus* Coenobia, C-FD= Freeze-dried Coenobia, DET= natural detritus from Lake Volkerak/Zoom, SED= sediment from Lake Volkerak/Zoom.

b. Erroneous results

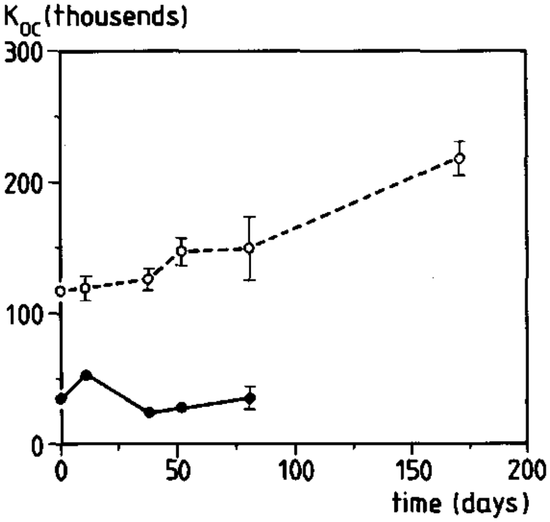

Fig. 4: Average TeCB (—●—) and HCB (--○--) K_{oc} values, as a function of time, for mineralizing unicells under dark conditions. Error bars represent n=3 standard deviations.

The TeCB K_{oc} values are a factor two to five lower than those for HCB. It was expected that TeCB would show an identical variation with time as that found for HCB, because the compounds share the same physicochemical mechanism of hydrophobic partitioning. However, a general trend with aging is not found for this compound, which may be caused by the fact that TeCB is less hydrophobic and therefore less sensitive to changes in the polarity of the adsorbent, by the lower accuracy of the results for TeCB, and by the shorter period for which data are available.

The average k_2 and x_1 values for HCB and their standard deviations are depicted in Figure 5. The graph shows a similar variation for both parameters and a gradual increase. This increase means that desorption becomes faster and is related to the changes in shape, size, and condition of the cells and cell fragments as a result of the aging process. The disruption of cellular structures eases the penetration and release of the test compounds within a given period, resulting in a larger reservoir with fast desorption x_1, whereas the slow sorption reservoir shows a similar loss of desorption resistance for the same reasons.

For TeCB, the k_2- and x_1 values are sometimes higher and sometimes lower than those for HCB. However, considering the C.I.s, these differences are never significant, except for the 52 aged unicells for which the three TeCB x_1 values are higher than those for HCB. Assuming complete equilibrium between algae and the test compounds before the desorption experiments, a larger fast sorption reservoir for TeCB could be expected because of its smaller size and partition coefficient.

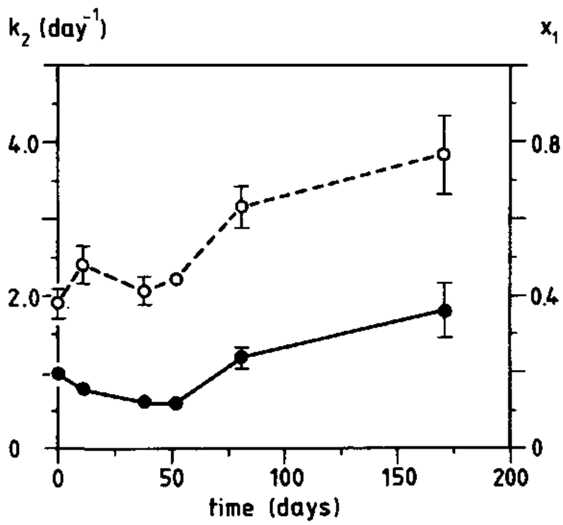

Fig. 5: First-order HCB desorption rate constant k_2 (—●—) and labile fraction x_1 (--○--) as a function of time for mineralizing unicells under dark conditions. Error bars represent n=3 standard deviations.

The 240 d aged coenobia show significantly larger K_{oc} values for both HCB and TeCB, compared to the fresh culture. Due to the long mineralization period and the fact that the aged coenobia showed far more characteristics of actually decomposed debris than the unicells, this result strongly suggests that aging and mineralization of phytoplankton as it occurred in our experiments lead to an increase in the affinity for hydrophobic compounds. For HCB and TeCB a decrease in x_1 also is observed. It is plausible that the aged material contains a relatively large portion of refractory material, in which the diffusional transport of the chlorobenzenes is slower than in the organic matrix of the live cells. The observed decrease in the labile fraction can be explained from this.

Unicells vs. coenobia

Coenobian *Scenedesmus* spp as cultured in this study shows a higher K_{oc} for HCB than the unicellular form. For the other parameters and for TeCB, no significant differences are found. As for the aging unicells, this difference must be explained from differences in protein and lipid content and cell composition. As far as we know, no similar adsorption data for HCB and *Scenedesmus* spp are described in the literature. Geyer et al [30] measured an HCB bioconcentration factor on a dry-weight basis (BCF^{DW}) of 124×10^3 for the green alga *Chlorella fusca*. *BCF*s on the same weight basis can be calculated from our K_{oc} values using the f_{oc} values listed in Table 1. This yields a BCF^{DW} of 40.5×10^3 for the fresh unicells and 57.9×10^3 for the coenobian forms of *Scenedesmus* spp.

Dead vs. live cells

The K_{oc} values for the freeze dried coenobia are essentially identical to those for the fresh coenobia for both HCB and TeCB. This suggests that the adsorptive characteristics of the organic matter remain unchanged and that the sorption process is not significantly influenced by biochemical processes unique to living cells, such as active transport. Ahlgren *et al.* [47] found that for several algal species, freeze-drying does not change the lipid content and composition. If the lipid content determines the extent of hydrophobic sorption, these results are consistent with our findings. For both test compounds x_1 is larger for the freeze dried material, although this difference is significant only for HCB. Assuming that the overall composition of the material remained unchanged after freeze-drying, this result must be explained by the breakdown of cellular structures and the increased permeability of the cell membranes.

Natural adsorbents obtained from Lake Volkerak/Zoom

The heterogeneous natural detritus sample shows a high K_{oc} for HCB, comparable to the values measured for the aged laboratory algae, and a fast release, which are expressed by the fact that x_1 is approximately one, and that the desorption curve can be described by all models mentioned in the previous sections with almost the same quality of fit. Figure 6 compares one of the triplicate desorption curves for the detritus sample to a representative curve for the 52-d aged unicells. One reason for the rapid release of HCB may be the longer history of the organic material, causing smaller particle sizes. Second, the percentage of POC was low in this sample. It may be expected that the DOM as operationally defined by the 0.45-μm filtration procedure enables a much faster desorption than the particles. In contrast to HCB, TeCB exhibits a low K_{oc} and a similar k_2 and x_1 compared to the laboratory algae. Except for the lower reliability of the TeCB data, as mentioned earlier, this observation remains unexplained.

The sediment organic matter is characterized by a high affinity for both test compounds and for HCB a much slower release pattern as compared to the algae and algal detritus. From the K_{oc} values for HCB an average $\log K_{oc}$ of 5.51 ± 0.02 can be calculated. Karickhoff and Morris [32] found values in the range 5.2 to 6.0 for soils and sediments. Deviations may originate from the differences in the type of organic material and from the chosen methods. The fresh algae in this study have significantly lower K_{oc} values. For our algal samples, k_2 values are in the range of 0.5 to 2.2 d^{-1}. Karickhoff found HCB k_2 values for soils and sediments in the range 0.03 to 1.2 d^{-1}. Our x_l values are in the range of 0.35 to 0.95. Karickhoff and Morris [32] found x_l values between 0.11 and 0.48 for HCB. This comparison of HCB data for algae or algal detritus obtained from our experiments with data for the sediment obtained from Lake Volkerak/Zoom and with sediment data published by other investigators shows that general HCB sorption affinity is lower, and HCB desorption kinetics is faster for algae, than for soils and sediments.

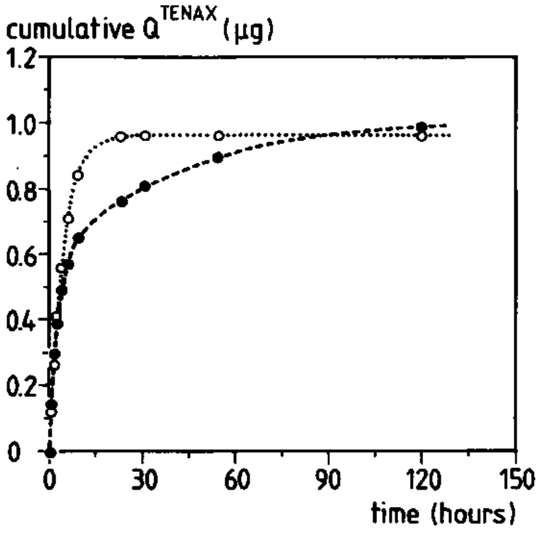

Fig. 6: Comparison of experimental desorption curves and two-compartment model simulations for detritus obtained from Lake Volkerak/Zoom (--○--) and a *Scenedesmus* spp unicell population (--●--).

For TeCB, similar data are not available in the literature, but the results for TeCB and the Lake Volkerak/Zoom sediment agree with this general conclusion. The labile fraction x_l is lower for TeCB than for HCB, which seems to conflict with the fact that TeCB is smaller, has a lower molecular weight, and is less hydrophobic. However, for sediments, Brusseau and co-workers [48] also found an increase in x_l with sorbate hydrophobicity as quantified by the octanol/water partition coefficient (K_{ow}), and interpreted this phenomenon as proof for an intraorganic matter diffusion model. The fraction x_1 represents the ratio of sorptive volume composing the instantaneous sorption reservoir to total sorptive volume, which is the sum of instantaneous and rate-limited domains. The organic matter may act as a molecular sieve, by which, within a given period, larger sorbate molecules are excluded from portions of the free volume of the adsorbent because of size constraints. Therefore, the observed size of the slow sorption reservoir ($1-x_1$) for a given adsorbent may vary with sorbate size or with the time of contact between adsorbate and adsorbent before desorption. A decrease in the volume of this reservoir would cause an increase in x_1, assuming that the volume of the instantaneous reservoir remains constant or varies more slowly with size. Besides an increase in the labile fraction with molecular size, this concept predicts a decrease in the labile fraction with the time of contact prior to desorption. Karickhoff and Morris [32] used equilibration times of 18 to 28 days, in contrast to 4 days in our study; therefore our higher x_1 values for the sediment may be caused to some extent by this mechanism.

In Figure 7, our data are compared to chlorobenzene data for various soils and sediments obtained from the literature, in a log k_2 vs. log K_p ($K_{oc} \times f_{oc} = K_p$) plot. It was found for soils and sediments that log k_2 and log K_p show a linear inverse relationship [14,32,48]. Figure 7 shows that our sediment data agree with this general rule. The linear regression equation, calculated from the sediment data of this study combined with the literature data, is shown in the figure. In contrast to the sediments, the algal samples form a cluster without a clear correlation in the right upper corner. The fast desorption for algae can be explained by the different nature of the organic matter. According to Brusseau *et al.* [48], intraorganic matter diffusion is responsible for slow desorption from sediments. Accordingly, the desorption rate constant k_2 is defined by the diffusion coefficient (which is dependent on the physicochemical properties of the adsorbent), the shape factor, tortuosity, and the diffusion path length characterizing the adsorbent. *Scenedesmus* cells sharply contrast with sediments and soils in these properties, for example, by the presence of an internal aqueous phase, by their smaller size, by their internal compartmentalization, and by their different organic matter composition.

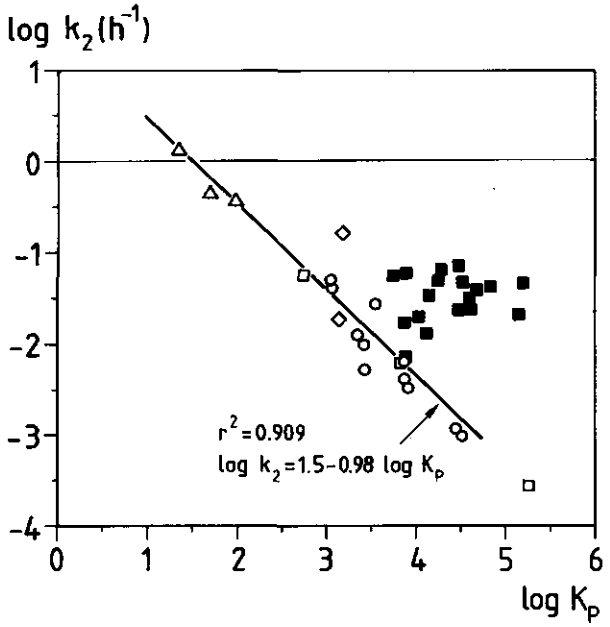

Fig.7: Chlorobenzene $\log k_2$ vs. $\log K_p$ plot for *Scenedesmus*/detritus data (■), compared to sediment data (□, sediment from Lake Volkerak/Zoom; △, from [14]; ○, from [32]); ◇, from [33]. The line is the least squares regression line, calculated using all sediment data (open symbols).

Batch adsorption of chlorobenzenes

The characteristics of the coenobia used for the adsorption experiment are given in Table 1. The *BCF*s of the four chlorobenzenes calculated on a dry-weight basis ($BCF^{DW,ads}$) are listed in Table 4. For comparison, the results obtained for coenobia with the purge method are calculated on the same basis and included in the table. Both methods yield comparable results, although it has to be kept in mind that the coenobia were taken from the stock suspension at different times, resulting in different characteristics, as shown in Table 1.

The $BCF^{DW,ads}$ is linearly correlated with K_{ow}, as measured by the slow-stirring method [49] (Table 4), and is illustrated with the calculated regression equation:

$$logBCF^{DW,ads}=(1.082\pm0.074)\times logK_{ow}-(1.419\pm0.088) \qquad r^2=0.991 \qquad (7)$$

The slope of the $\log BCF$ vs. $\log K_{ow}$ relationship is close to unity, as Opperhuizen et al [50] also found for bioconcentration of chlorobenzenes into fish at room temperature. Although our data set has a limited size, this similarity confirms the mechanism of passive partitioning and suggests that partitioning of hydrophobic chemicals to algae can be related to octanol/water partitioning with the same restrictions and advantages described in the literature for bioconcentration to fish.

TABLE 4:
Chlorobenzene octanole/water partition coefficients
and bioconcentration factors for *Scenedesmus* spp coenobia.

		Batch adsorption	Purge desorption
Compound	$\log K_{ow}$[a]	$BCF^{DW,adsorption}$ ± s.d. (n=3)	$BCF^{DW,desorption}$ ± s.d. (n=3)
1,2,3-Trichlorobenzene	4.139	975 ± 34	-
1,2,3,4-Tetrachlorobenzene	4.635	4780 ± 170	6140 ± 850
Pentachlorobenzene	5.183	16600 ± 980	-
Hexachlorobenzene	5.731	54100 ± 6500	57900 ± 9400

a. Octanol/water partition coefficient. From ref. [49].

CONCLUSIONS

The desorption of TeCB and HCB from *Scenedesmus* spp coenobia and unicells, detritus originating from the same alga, and a natural sediment can be described by a two-compartment nonequilibrium biosorption model. A one-compartment model is unsatisfactory except for a natural detritus sample containing HCB.

Aging and decomposition of unicell and coenobian cultures of *Scenedesmus* spp resulted in a 60 to 100% increase of OC normalized partition coefficients. In this study, no conclusive evidence was found explaining this increase from the polarity of the adsorbent because the polarity was not measured. However, the results are consistent with the measured changes in phytoplankton properties and with similar changes in phytoplankton and organic matter properties, that are described in the literature. Living and freeze-dried coenobia showed the same affinity for both chlorobenzenes, suggesting that the relevant adsorbent properties remained unchanged and that active transport processes did not contribute significantly to the uptake and release processes.

The desorption parameters obtained for the Lake Volkerak/Zoom sediment, which are based on the two-compartment model, agreed well with literature data. In contrast, sorption affinity on an OC basis (K_{oc}) is lower, and desorption kinetics is faster for algae than for soils and sediments. Also in contrast to sediments, for algae and detritus no linear inverse relationship between log k_2 and log K_p was found. In aquatic systems and especially in shallow eutrophic lakes, resuspended sediments and phytoplankton act as scavengers for hydrophobic compounds simultaneously. In the fate modeling of such compounds, the observed differences in sorption characteristics should be taken into account. For chlorobenzene sorption to phytoplankton, the kinetic aspects are considered relatively unimportant in most situations, because the time constants for sorption to sediments and those for other relevant processes such as algal growth or decay are much greater.

A reasonable agreement was found between TeCB and HCB *BCF*s for living algae, measured with a batch equilibration adsorption method and with a gas-purge-induced desorption method. With the batch adsorption method, a linear correlation was found between chlorobenzene *BCF*s and octanol/water partition coefficients. The relationship was very similar to those for bioaccumulation in fish. This confirms that partitioning into algal lipids and fish lipids essentially has the same features.

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Addendum to Chapter 7

In most studies applying the purge method, parameters are estimated from the cumulative amounts of test compound purged from suspension versus time. Then, a weighting of the cumulative amounts is needed, because of the accumulation of error. Consequently, measurements at the end of the experiments are relatively insignificant in the estimation of the parameters. In Chapter 7 this method is used. In later studies, (Chapter 5 and 8), we used a better method in which the unknown parameters are estimated sequentially, using the amount of test compound and the purge time, as measured for each individual Tenax column. In that case no weighting is needed. The results presented in Chapter 7 were recalculated using the sequential method, and are presented in this addendum (Table 5 and 6). Data of triplicate experiments were pooled to improve the reliability of the parameter estimates. In Chapter 7, data are presented for aging unicells up to 171 days. However, after 466 days, another purge experiment was performed using the same batch of detritus. The results of this experiment are included in table 5 and 6 (adsorbent code: U-466). The newly calculated K_{oc} values for mineralizing unicells under dark conditions, are plotted in Figure 8. The parameter estimates presented in Table 5 and 6 do not differ significantly from those reported in Table 2 and 3. The unicells after 466 days of aging have a higher K_{oc} for HCB than after 171 days. This confirms our conclusion that aging increases the K_{oc} for HCB.

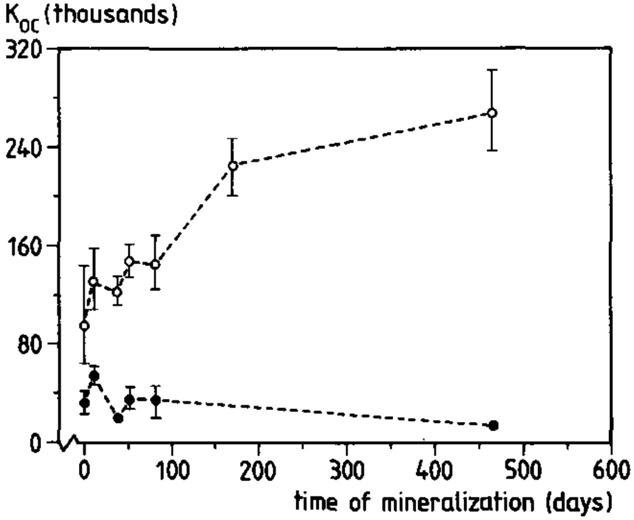

Fig. 8: Average TeCB (—●—) and HCB (--○--) K_{oc} values as a function of time, for mineralizing unicells under dark conditions. Error bars represent 90% C.I.s.

TABLE 5:
Hexachlorobenzene desorption parameters and 90% confidence intervals.

Adsorbent(a)	K_{oc} ($\times 10^3$)	90% C.I.	k_2	90% C.I. (d^{-1})	x_l	90% C.I.
U-0	95	(64 - 144)	1.43	(0.95 - 2.05)	0.28	(0.08 - 0.46)
U-11	131	(108 - 158)	0.60	(0.42 - 0.78)	0.51	(0.41 - 0.59)
U-38	123	(112 - 135)	0.61	(0.54 - 0.68)	0.42	(0.38 - 0.46)
U-52	147	(134 - 161)	0.62	(0.55 - 0.69)	0.44	(0.40 - 0.48)
U-81	145	(125 - 169)	1.31	(0.96 - 1.84)	0.60	(0.51 - 0.68)
U-171	226	(201 - 247)	1.52	(0.71 - 2.79)	0.84	(0.73 - 0.92)
U-466	267	(237 - 302)	(b)		1 (b)	
C-0	242	(189 - 293)	1.09	(0.38 - 1.89)	0.71	(0.51 - 0.83)
C-240	474	(332 - 671)	0.42	(0.33 - 0.53)	0.34	(0.25 - 0.44)
C-FD	247	(230 - 262)	1.40	(0.65 - 2.54)	0.89	(0.82 - 0.95)
DET[b]	227	-	0.015	-	0.97	-
SED	320	(290 - 352)	0.16	(0.10 - 0.26)	0.76	(0.72 - 0.79)

a. Letters refer to the type of adsorbent. Numbers refer to the age of the culture (d). U= *Scenedesmus* Unicells, C= *Scenedesmus* Coenobia, C-FD= Freeze-dried Coenobia, DET= natural detritus from Lake Volkerak/Zoom, SED= sediment from Lake Volkerak/Zoom.

b. One compartment model ($x_l \equiv 1$) has the same quality of fit as the two-compartment model.

TABLE 6:
1,2,3,4-Tetrachlorobenzene desorption parameters and 90% confidence intervals

Adsorbent[a]	K_{oc} ($\times 10^3$)	90% C.I.	k_2	90% C.I. (d^{-1})	x_l	90% C.I.
U-0	32	(23 - 42)	1.16	(0.46 - 2.58)	0.42	(0.21 - 0.56)
U-11	54	(47 - 62)	1.14	(0.91 - 1.44)	0.48	(0.39 - 0.56)
U-38	20	(17 - 23)	1.35	(0.80 - 3.86)	0.58	(0.44 - 0.68)
U-52	35	(27 - 45)	0.32	(-0.06 - 1.35)	0.85	(0.85 - 0.99)
U-81	35	(20 - 46)	1.45	(0.41 - 7.51)	0.54	(-0.08 - 0.73)
U-171[b]	(b)		(b)		(b)	
U-466	14	(10 - 17)	19	(11 - 28)	0.31	(-0.60 - 0.68)
C-0	25	(21 - 29)	0.82	(0.03 -11.20)	0.86	(0.77 - 0.94)
C-240	47	(40 - 55)	1.80	(1.51 - 2.15)	0.28	(0.17 - 0.36)
C-FD	21	(19 - 23)	0.24	(0.09 - 0.57)	0.81	(0.75 - 0.86)
DET	14	(11 - 17)	0.48	(0.13 - 1.01)	0.66	(0.50 - 0.80)
SED	22	(17 - 26)	1.92	(0.81 - 4.19)	0.55	(0.24 - 0.72)

a. Letters refer to the type of adsorbent. Numbers refer to the age of the culture (d). U= *Scenedesmus* Unicells, C= *Scenedesmus* Coenobia, C-FD= Freeze-dried Coenobia, DET= natural detritus from Lake Volkerak/Zoom, SED= sediment from Lake Volkerak/Zoom.

b. Erroneous results

Chapter 8

BIOSORPTION OF CHLOROBENZENES TO PHYTOPLANKTON AND DETRITUS:

II. *ANABAENA*

A.A. Koelmans, S.A. Anzion and L. Lijklema

based on:

A.A. Koelmans, S.A. Anzion and L. Lijklema. Dynamics of organic micropollutant biosorption to cyanobacteria and detritus. (*Submitted*)

DYNAMICS OF ORGANIC MICROPOLLUTANT BIOSORPTION TO CYANOBACTERIA AND DETRITUS

Abstract- Equilibrium and rate parameters of chlorobenzene biosorption to the cyanobacterium *Anabaena* and various types of algal detritus were measured using a gas-purge method. Organic carbon normalized sorption coefficients for detritus originating from *Anabaena* and from the green alga *Scenedesmus* were up to 3.5 times higher than the respective living species, and were positively correlated with C/N atomic ratios of the adsorbents. The desorption kinetics could be described best with a two-compartment model. The compartments were interpreted as a lipid pool near the surface of the cells and a similar pool deeper in the cell interior. The kinetic parameters measured were such, that in most aquatic systems sorption equilibrium can be assumed. A theoretical framework for predicting nonequilibrium bioconcentration caused by the combined action of slow bioaccumulation and phytoplankton growth is proposed.

INTRODUCTION

In the aquatic environment, the transport and food web accumulation of hydrophobic organic compounds (HOCs) is strongly influenced by sorption to bacteria, phytoplankton and detritus [1,2]. The significance of pollutant scavenging by biomass originating from primary production is widely accepted, but data concerning hydrophobic biosorption to algae are still scarce compared to similar data for sediments. In earlier reports, the uptake and release by phytoplankton are found to be fast, limiting the urge for kinetic data. Consequently, because kinetics is fast, in many transport models the lipid normalized bioconcentration factor *BCF* (or K_{oc} for detritus) is considered a constant under most environmental conditions, and is thought to be linearly correlated to K_{ow}, with a slope close to unity. However, this equilibrium partitioning concept is not necessarily valid for phytoplankton and its detrital products for two reasons.

First, it is unlikely that *BCF* (or, for detritus, K_p or K_{oc}) remains constant upon ageing, death and mineralization of algal biomass, or is identical for different algal species. It has been described by several investigators that K_{oc} varies for dissolved organic matter, soils and sediments of different origin [3,4,5,6,7,8]. The differences are mostly attributed to variations in the polarity of the organic matter.

Second, phytoplankton grows, which results in a 'diluting' effect on the chemical concentration in the cells. This can be described by the following equation, assuming that both biosorption and algal growth are first-order processes [1,2], and that growth does not change the sorption kinetic constants:

$$dC_A/dt=k_{12}C_W-k_{21}C_A-k_GC_A \tag{1}$$

with C_A (μg/g) the concentration in the algae, C_W (μg/l) the aqueous concentration, k_{12}

(l.g^{-1}.day^{-1}) and k_{21} (day^{-1}) first-order rate constants for adsorption and desorption, respectively. k_G (day^{-1}) is the rate constant for algal growth. This model has the following steady state solution:

$$BCF^G = C_A^e/C_W^e = \frac{k_{12}}{k_{21}+k_G} = BCF^N \times \frac{k_{21}}{k_{21}+k_G} \tag{2}$$

In which BCF^G is the bioconcentration factor for growing phytoplankton, BCF^N is the bioconcentration factor at non growth conditions, equal to k_{12}/k_{21}, and the superscripts "e" refer to equilibrium concentrations. If k_G cannot be neglected compared to k_{21}, then k_G has a significant effect on the bioconcentration factor. In recent publications of Swackhamer *et al.* [9,10], *BCF* for growing phytoplankton were invariant with K_{ow} at $K_{ow} > 10^{5.5}$. Furthermore, higher *BCF*-values were found at lower phytoplankton growth rates. These findings suggest that the biosorption rate for the more hydrophobic HOCs can be slow compared to the algal growth rate, and therefore confirm the model as condensed in equation (1). However, the evidence is indirect because no kinetic experiments allowing the estimation of distinct rate parameters (k_{12}, k_{21}), were performed.

The objective of our study is to quantify chlorobenzene biosorption rate and sorption affinity for the cyanobacterium *Anabaena* spp at non growth conditions and for detritus, and to evaluate the relevance of the factors described above. No previous studies have examined HOC sorption to cyanobacteria and the effects of mineralization in terms of multiple compartment kinetic models. The results, that is, parameters for rate and affinity, are compared to similar sorption data for *Scenedesmus* spp, which were reported by Koelmans and co-workers [11]. For delicate adsorbents such as algal cells, the gas-purge method has been proven very suitable [11,12] because phase separation is not required. In our previous study with *Scenedesmus*, we observed a 100% increase of K_{oc} with ageing. To be able to explain K_{oc} trends from polarity changes, in the current study with *Anabaena,* a more extensive adsorbent characterization, including lipids and elemental C,H,N was used.

MATERIALS AND METHODS

Origin and handling of adsorbents

Adsorbents were fresh *Anabaena* spp cells (one triplicate purge experiment), mineralizing *Anabaena*-detritus (three experiments) and mineralizing *Scenedesmus*-detritus (one experiment). Fresh *Anabaena* (originally PCC 7120) was cultured in 40 l Z-8 medium [11] under continuous light at 20°C, until a stationary phase was obtained. The medium was prepared in 0.2-μm filtered Nanopure® water (Sybron-Barnstead, Dubuque, IA) to minimize the contribution of bacteria to the total biomass. From the resultant algal suspension of 88 mg/l, a representative sample of 6.4 liters was taken. After two more days in continuous light, the light was turned off (mineralization time=0) to induce mortality and mineralization, and two liters filtered (Schleicher and Schuell, Dassel, Germany; Ref. Nr. 300412) lake water (Lake Volkerak/Zoom, The Netherlands) were added as a natural source of bacteria. Because of the dilution of the lake water in the 40 liter algal suspension, the algae related carbon still represented more than 95% of total organic carbon in the system. The 6.4 liter sample was further divided in eight subsamples of 800 mL, using a Retsch (Germany) suspension divider. Three of these subsamples were used for a triplicate purge experiment. The remaining five were used for a characterization of the adsorbent. Characterization and purge experiments were performed on the same day. This procedure of sampling and determination of adsorbent and sorption characteristics, was repeated after mineralization times of 18, 47 and 124 days. During mineralization, the suspension was aerated continuously. The resultant volume reduction of the suspension, largely compensated the loss of biomass due to the mineralization process, except a variation in adsorbent concentration of a factor two. To account for a possible influence of this variation of the adsorbent to water ratio, additional purge experiments at the two extreme concentrations were performed, using a *Scenedesmus*-detritus sample (aged for 466 days in the dark) which was left over from an earlier study [11]. This sample was diluted to the desired concentrations with Nanopure water.

Characterization of adsorbents

Determinations of adsorbent characteristics were performed at least in triplicate, on representative subsamples of the adsorbent suspensions. Shape and size of algal cells were measured using a Galai CIS-1 particle sizer (Galai Produktion Ltd, Israel). This instrument uses a video camera microscope which allows 2-D shape analysis, in combination with a rotating He-Ne laser whose time to pass over a particle is related to the particle diameter [13]. As the resolution of the video microscope is limited, also an external high-quality microscope (Nikon, Melville, NY) was used. Dry-weight and ash free dry-weight were measured after filtration over 0.45 μm membrane filters by drying at 105°C and 550°C respectively till constant weight. TOC was measured on an OIC (College Station, TX) Model 700 TOC analyzer. A test program revealed that an extended reaction time of 20 minutes at 90°C was sufficient to convert all carbon. COD was determined as oxidizability by $K_2Cr_2O_7$, according to standard methods [14]. Absorption spectra from 270-900 nm of total and filtered samples were measured on a Beckmann (Fullerton, CA) DU-64 spectrophotometer. Chlorophyll and phaeophytins were extracted with acetone and measured on a Beckmann DU-64 spectrophotometer, according to standard methods [14]. Elemental analysis (C,H,N) and total lipids were measured on adsorbent particles isolated by filtration over glass fibre filters (Whattmann, Kebo, Sweden; GF/C). Elemental content was measured with a Carlo Erba (Breda, The Netherlands) 1106 Elemental Analyzer. Some samples contained small glass fibers from the filter so weight percentages could not be calculated. However, since the blank filters showed no detectable C, H or N, the atomic ratios are not influenced by this artefact. Lipids were extracted from the adsorbents with a 10:5:4 (v:v:v) chloroform-methanol-water (1% NaCl) mixture, in a blender. This procedure was repeated twice. After centrifugation of the combined extracts, and careful drying of the chloroform layer, the lipids were redissolved in hexane. Part of this hexane fraction, was used for a spectrophotometric lipid determination using a commercial "Total Lipids" Test combination (Boehringer Mannheim, 1984 catalogue no. 124303). This method is based on the sulphophosphovanilline complexation reaction.

Gas-purge procedure

Nanograde organic solvents (acetone and 2,2,4-trimethylpentane) were obtained from Promochem (C.N. Schmidt, The Netherlands). 1,2,3,4-Tetrachlorobenzene, 1,2,4,5-tetrachlorobenzene, pentachlorobenzene (98%, Aldrich Europe, Belgium) and hexachlorobenzene (>98%, BDH Chemicals, England) were used without further purification. Tenax 40 to 60 mesh was obtained from Chrompack (The Netherlands). For the purge experiments, high-purity nitrogen was used.

The purge procedure was described before [11], and is repeated here briefly. For a triplicate experiment, three adsorbent suspensions were placed in three parallel and thermostatted (20°C) glass stoppered bottles (900 mL). Each bottle was spiked with 50-μL of a solution of 1,2,3,4-tetrachlorobenzene (TeCB), pentachlorobenzene (QCB) and hexachlorobenzene (HCB) in acetone. The total amounts present in the system were 0.95 μg TeCB, 1.25 μg QCB and 1.25 μg HCB. After an equilibration time of 24 h (*Anabaena*-detritus) or 48 h (*Scenedesmus*-detritus) under continuous stirring (metal stir bar), chlorobenzenes were purged onto 11 Tenax traps in five days, at a flow of 500 mL/min. The gas flow (constant within 1%) was regulated with flow controllers and was passed through vessels containing water, to prevent volume reduction in the algal suspensions. Tenax columns were replaced at incremental intervals. All experiments were optimized for HCB, that is, to yield approximately the same mass of test compound in each trap. Therefore, conditions for TeCB and QCB were less ideal, but still satisfactory. The trap columns consisted of glass tubes containing glass wool and approximately 0.2 g Tenax. Test compounds were desorbed from the columns by elution with 15 mL diethylether (recovery 100%). The extracts were evaporated slowly to four (or two) mL with nitrogen after addition of four (or two) mL of an internal standard (45 μg/l 1,2,4,5-tetrachlorobenzene in 2.2.4-trimethylpentane), to reduce the error of analysis. The resulting 2,2,4-trimethylpentane solutions and calibration standards were injected directly to the GC. A Hewlett-Packard (HP; Avondale, PA) 5890 double-column gas chromatography system equipped with two ^{63}Ni electron capture detectors (ECD) was used in chlorobenzene quantisation. Congener separation was accomplished with 50 m, 0.25 mm i.d., HP Ultra 1 (0.5-μm film thickness) and Ultra 2 (0.33-μm film thickness) columns. Immediately after finishing a purge experiment, the adsorbents were analyzed to be able to account for possible remaining fractions of the test compounds. For all individual purge flasks, mass balances were calculated from the amounts of test compound found in the Tenax traps and the adsorbent after purge, and the amount initially added to the systems. The mass balances of 14 purge experiments were (means ± standard deviation): 98.9% ± 1.6 for TeCB, 96.5% ± 1.8 for QCB and 97.7% ± 4.2 for HCB. Because the balances do not differ significantly from 100% we conclude that no significant losses of test compound occurred.

Data analysis

Without an adsorbent, the gas-purge induced removal of the test compounds from the aqueous phase is described as an irreversible first-order volatilization process according to:

$$dC_W/dt=-k_v\times t \quad \wedge \quad k_v=F\times H/V_w \tag{3}$$

in which t is time (day), C_W (μg/l) is the solution-phase chlorobenzene concentration referenced to aqueous-phase volume V_w (l), k_v is a first-order volatilization rate constant (day^{-1}), F is de gas flow (l.day^{-1}) and H is the dimensionless Henry constant. When headspace can be neglected during the purge experiments, and the volatilizing compound is trapped on Tenax columns, C_W can be calculated from the cumulative amounts trapped in the Tenax columns Q^{TENAX}, using:

$$C_W=\frac{Q_{t=0}-Q^{TENAX}}{V_w} \tag{4}$$

in which $Q_{t=0}$ (μg) is the amount of test compound initially present in the system.

In case of an adsorbent suspension at sorption equilibrium, the volatilization process induces desorption which can be modeled in several ways. If the rate of gas purging is sufficiently slow so that equilibrium between adsorbent and water is maintained, then the 'equilibrium binding' situation as described by Hassett and Millicic [15] may be applied:

$$dC_W\,/dt = -\frac{k_v}{1+(TOC)\times K_{oc}}\times t \tag{5}$$

in which (TOC) is de total organic carbon concentration expressed as weight fraction. As parameter to quantify sorption equilibrium, the general term K_{oc} is used instead of *BCF* throughout this paper, because the latter term is reserved for living species. Furthermore, the use of K_{oc} instead of K_p enables us to investigate organic matter properties without the influence of possible inorganic precipitation or dissolution processes. The adequacy of this one-compartment model to describe our data was compared to a first-order kinetic model in which biosorption takes place in two kinetically defined compartments. Only sorption to the first compartment with size x_1 (adsorbent weight fraction), is considered at equilibrium during the experiment and is quantified by the partition coefficient K_{oc}. For the second compartment with size $(1\text{-}x_1)$, mass transfer is assumed to be characterized by forward and backward first-order rate constants k_1 and k_2. In formula:

$$C_{A1} = x_1 K_{oc} C_W \tag{6}$$

$$dC_{A2}/dt = k_1 C_{A1} - k_2 C_{A2} \tag{7}$$

C_{A1} and C_{A2} are the sorbed-phase concentrations in the first compartment and the second compartment respectively, referenced to total sorbent mass, and k_1 and k_2 are forward and reverse first-order rate constants. Assuming that the affinity of the adsorbate for both compartments as quantified by K_{oc} is identical [16], k_1 is related to x_1 and k_2 according to:

$$k_1 = k_2(1-x_1)/x_1 \tag{8}$$

The desorption process is described by the three constants K_{oc}, x_1 and k_2. In several studies [11,16] this model has been proven adequate in describing desorption rate data for sediments, soils and phytoplankton. The model describes two possible compartment configurations: a series version ($C_W \Leftrightarrow C_{A1} \leftrightarrows C_{A2}$), and a parallel version ($C_{A1} \Leftrightarrow C_W \leftrightarrows C_{A2}$). In the series version, the first compartment can be pictured as the exterior of the adsorbent. In the parallel configuration, the compartments resemble kinetically different sorption sites. A detailed description of the model is presented in an appendix to this chapter.

Model selection was made for each triplicate experiment with pooled data on the basis of an analysis of variance (F-tests). Parameters (K_{oc} for the one-compartment model, and K_{oc}, k_2 and x_1 for the two-compartment model) were estimated by non linear least squares regression using the modified sequential simplex algorithm according to Nelder and Mead [17]. In both cases, the sum of the amounts of test compound found in the Tenax columns and the amount of test compound found in the adsorbent after the purge experiment, was used as the value for the total amount of test compound in the system at t=0 ($Q_{t=0}$). In most studies applying the purge method (including our study with *Scenedesmus* [11]), parameters are estimated from the cumulative amounts of test compound purged from suspension versus time. Then, a weighting of the cumulative amounts is needed, because of the accumulation of error. Consequently, measurements at the end of the experiments are insignificant in the estimation of the parameters. Since these measurements determine the magnitude of the slow desorption rate parameter k_2, confidence intervals for this parameter are wide. In this study we introduce a better approach in which the unknown parameters are estimated sequentially, using the amount of test compound and the purge time, as measured for each individual Tenax column. In that case no weighting is needed. A small selection of previously published results for *Scenedesmus* was recalculated using this method, to improve comparability. After parameter estimation, 90% confidence intervals (90% C.I.) were calculated, according to [18]:

$$SS_{90}=SS_{\min}\{1+ p/(n-p)\times F(p,n-p,90\%)\} \tag{9}$$

with SS_{90} the sum of squares at the 90% confidence contour, SS_{min} the minimum sum of squares, n the number of measurements in Tenax columns, p the number of parameters and $F(p,n-p,90\%)$ the F-distribution according to Fisher. All calculations described in this section were made using a computer program written in BASIC based on the analytical solutions to the models.

Besides K_{oc} as measure of sorption affinity, sorption coefficients on a lipid basis K_{lip} were calculated using $K_{lip}=K_{oc}\times f_{oc}/f_{lip}$, in which f_{lip} is the lipid content expressed as dimensionless weight fraction.

RESULTS AND DISCUSSION

Adsorbent characteristics

Mineralization of *Anabaena* was fast as can be seen from the absorbance spectra for the particles in Figure 1. The absorbance for the particles was obtained by subtracting the absorbance of 0.45-μm filtered water from the total absorbance. After six days, the absorbance decreases sharply because of mortality and lysis of the *Anabaena* cells. Until this time, absorption peaks for chlorophyll *a* (440 and 680 nm) and C-phycocyanin (around 630 nm) are pronounced. Numeric adsorbent characteristics are listed in Table 1.

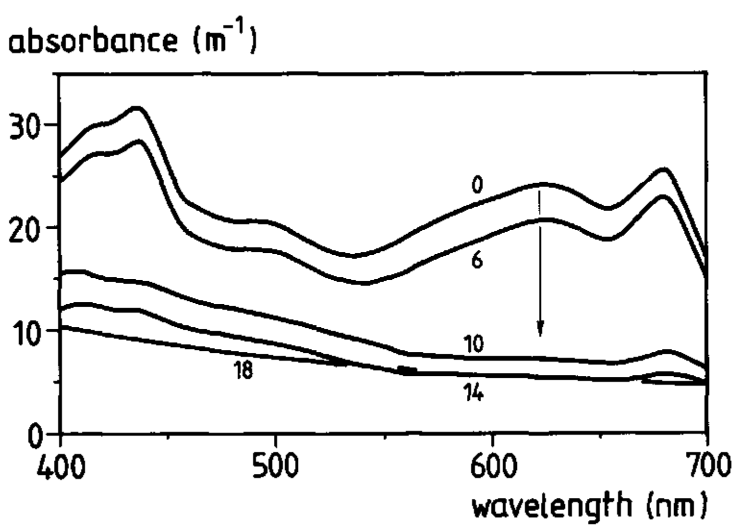

Fig. 1: Absorbance spectra of particulate matter during decay of *Anabaena* spp. Time course indicated by arrow and day numbers. After 18 days, the spectra did not change further.

Because the detritus suspension was slowly concentrated, the calculated ratios of the various parameters are the most appropriate descriptors of the mineralization process. They provide direct information on the particles. The organic carbon fraction of the particles (f_{oc}) calculated from TOC and dry-weight (DW) agrees with the organic carbon fractions measured with the elemental analysis. The organic carbon measurements are important, because they are used for the organic carbon normalization of the chlorobenzene partition coefficients. Since chlorophyll content is unique to the phytoplankton fraction of the total organic matter, the chlorophyll to dry-weight ratio (CHL/DW), and chlorophyll to phaeophytin ratio (CHL/PHA) are the best indices for algal degradation. Both show a sharp decrease with time. In contrast, the COD to TOC, and COD to DW ratios show no clear trend, while f_{oc}, lipid content, H/C and C/N atomic ratios seem to go through a maximum at 18 days. A plausible explanation for this phenomenon is that at 18 days, bacteria contribute to some extent to the total amount of biomass. However, our data do not provide direct information on bacterial growth. According to the literature [19,20], bacteria may represent up to 10% of total biomass during algal decomposition. Further, for a significant part they are attached to the detritus particles. Consequently, bacteria are considered as a part of the adsorbent whose contribution on a dry-weight basis is small, but who may have a small but measurable influence on adsorbent and sorption characteristics.

The adsorbent characteristics for the sample of *Scenedesmus* detritus of 466 days, clearly contrast with those for the *Anabaena* samples.

Selection of sorption model

The results of parameter estimations and the analysis of variance for the one and two-compartment models are given in Table 2. It appears that both models are highly significant, but the quality of fit as expressed by the mean square of residual error (MS_{error}, not shown) was better for the two-compartment model which uses three model parameters instead of one, except in two cases: QCB in combination with ANA0a, and QCB in combination with ANA18. However, the significance level for the superiority of the one-compartment model in these two cases was poor, as also can be seen from Table 2. Therefore, the two-compartment model is considered the general "best model" for biosorption to *Anabaena*. This result is similar to our previous results for *Scenedesmus* [11], although in that case the significance of the superiority of the two-compartment model was much larger. Because of these considerations, the discussion in the subsequent sections focuses on the two-compartment model results.

Effect of mineralization on sorption characteristics

The HCB K_{oc} values for *Anabaena* detritus, calculated using the two-compartment model show a gradual increase of 40% after 124 days of ageing and mineralization (Table 2). The HCB K_{oc} for *Scenedesmus* detritus is 3.5 time higher than the K_{oc} for the fresh *Anabaena* sample. This suggests a decrease in the adsorbents' average polarity with mineralization time. The measurements of elemental C and N confirm this hypothesis, as is illustrated in Figure 2, where the HCB K_{oc} for *Anabaena* and 466 days aged *Scenedesmus* detritus is plotted against the C/N atomic ratio. The C/N atomic ratio has a value of 5 for the fresh *Anabaena* sample and sharply contrasts with the value of 9.5 for the 466 days aged *Scenedesmus* detritus. Typical values for C/N-ratios are 5 - 6 for fresh phytoplankton, 7 - 9 for freshwater sediments and $\gg 10$ for pedogenic organic matter and humic materials [21]. The C/N-ratio increases with the degree of mineralization of the organic matter. This is because the nitrogenous compounds in the algae are among the most easily degradable substances, the order of degradation rate being: water-extractable carbohydrates, nitrogenous compounds, overall unfractionated natural organic matter and insoluble polysaccharides [21]. The slightly higher two-compartment model K_{oc} for ANA18 as compared to ANA47 coincidences with the slightly higher C/N ratio (Table 1) for ANA18.

TABLE 1:
Adsorbent characteristics

Adsorbent code[1]	DW[2] (mg/l)	TOC[3] (mg/l)	lipids[4] %	CHL[5] (μg/l)	COD[6] (mg/l)	LI[7] %
ANA0a	82.3	34.7	3.7	1302	91.2	-
ANA0b	106.6	50.5	3.1	1693	114.8	-
ANA18	39.8	27.9	4.1	103	55.5	-
ANA47	41.8	22.9	2.6	6	61.1	-
ANA124	98.2	30.0	1.1	11	86.3	55.9
SC466	620	72.5	0.6	276	296.7	35.7

(TABLE 1 Continued)

Adsorbent code[1]	CHL/ DW[8]	CHL/ PHA[9]	f_{oc}[10] (TOC/DW)	f_{oc}[11]	C/N[12] (± s.d., n=2)	H/C[12]
ANA0a	15.8	5.4	0.42	0.43	4.72 ± 0.02	1.69
ANA0b	15.9	5.6	0.47	-	5.07 ± 0.03	1.69
ANA18	2.6	1.3	0.70	-	6.47 ± 0.04	1.81
ANA47	0.14	0.13	0.55	-	6.28 ± 0.01	1.77
ANA124	0.11	0.21	0.31	0.28	6.87 ± 0.02	1.92
SC466	0.45	0.53	0.12	0.16	9.50 ± 0.11	1.96

(1) Capital letters refer to algal species: ANA= *Anabaena*, SC=*Scenedesmus*. Numbers refer to the age of the algae (days). The letters a,b for ANA0 refer to the culture 2 days prior to mineralization (a) and 0 days prior to mineralization (b); (2) Concentration of suspended solids (filtration over 0.45μm and drying at 105°C; (3) Total organic carbon concentration; (4) Total lipid content of particles; (5) Chlorophyll concentration; (6) Chemical oxygen demand; (7) Loss of weight after 3 h drying at 600°C; (8) Chlorophyll to dry-weight ratio; (9) Chlorophyll to phaeophytin ratio; (10) Organic carbon fraction of particles calculated as TOC/DW; (11) Organic carbon fraction measured by elemental analysis of particles; (12) Calculated from elemental analysis results

TABLE 2: Equilibrium and kinetic data for biosorption to phytoplankton and detritus, and comparison of compartment models

	One compartment model		Two compartment model							
adsorbent code[a]	K_{oc} ($\times$1000)	90%CI	K_{oc} ($\times$1000)	90%CI	k_2 (day^{-1})	90%CI	x_1	90%CI	P(2/1)[b]	$\log K_{lip}$[c]
Hexachlorobenzene										($\log K_{ow}$=5.731)
ANA0a	77.0	71.0- 83.6	73.8	65.3- 82.8	2.73	1.21-5.10	0.820	0.693-0.920	0.068 *	5.92
ANA18	87.4	84.9- 90.0	87.8	83.6- 92.4	0.87	-0.05-9.18	0.974	0.940-1.002	0.379	6.18
ANA47	92.7	87.9- 97.7	84.6	80.1- 92.1	4.78	2.27-7.66	0.805	0.779-0.901	0.004 ***	6.25
ANA124	127.2	117.3-137.4	101.4	89.1-114.9	1.38	0.81-3.44	0.825	0.743-0.891	0.012 **	6.46
SC466(35)	324.3	307.4-342.1	323.6	-	(857)[d]	-	.0093	-	0.355	6.81
SC466(70)	267.4	237.1-301.9	266.3	-	(253)[d]	-	.0011	-	0.407	6.73
Pentachlorobenzene										($\log K_{ow}$=5.183)
ANA0a	35.2	34.5- 35.9	35.1	34.0-36.2	0.22	-	0.989	-	0.518	5.60
ANA18	31.8	31.0- 32.6	31.7	30.5-32.9	0.15	-	0.991	-	0.549	5.73
ANA47	27.5	26.0- 29.0	25.4	23.8-28.0	11.4	1.50-28.5	0.834	0.569-0.951	0.094 *	5.73
ANA124	35.1	32.8- 37.4	35.1	32.0-38.3	0.64	0.01-6.69	0.959	0.915-0.994	0.258	6.00
SC466(35)	83.4	79.5- 87.5	68.3	61.9-73.8	14.0	10.5-18.5	0.530	0.281-0.714	0.020 **	6.14
SC466(70)	88.2	82.9- 93.7	62.7	24.5-76.7	9.96	6.02-14.1	0.190	-0.459-0.617	0.000 ***	6.10
1,2,3,4-Tetrachlorobenzene										($\log K_{ow}$=4.635)
ANA0a	15.7	14.4- 17.0	15.8	14.4-17.3	0.27	0.09-0.54	0.848	0.782-0.913	0.023 **	5.25
ANA18	15.1	14.4- 15.9	15.1	14.3-15.9	0.37	0.05-0.84	0.922	0.886-0.957	0.033 **	5.41
ANA47	10.6	8.8- 12.4	10.5	9.1-12.0	0.49	0.26-0.79	0.667	0.567-0.758	0.000 ***	5.35
ANA124	11.0	9.1- 12.9	10.3	8.1-12.6	5.5	2.0-12	0.734	0.510-0.908	0.099 *	5.46
SC466(35)	16.3	15.0- 17.7	14.0	12.1-15.5	14	7.0-28	0.672	0.274-0.837	0.003 ***	5.45
SC466(70)	19.1	17.0- 21.4	14.0	9.9-16.6	19	11-28	0.307	-0.595-0.675	0.006 ***	5.45

(a) For adsorbent codes, see Table 1; (b) Significance of the superiority of the two compartment model (F-test on mean squares of residual errors, *=$P<0.10$, **=$P<0.05$, ***=$P<0.01$); (c) Two-compartment model partition coefficient on lipid basis. $\log K_{ow}$ values are from [25]; (d) Estimates have no physical meaning.

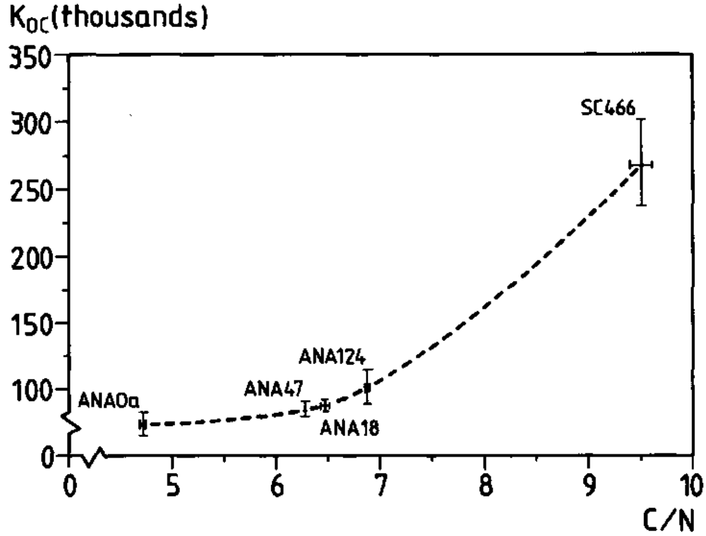

Fig. 2: Organic carbon normalized partition coefficients (K_{oc}) as a function of the C/N atomic ratio, for *Anabaena*- and *Scenedesmus* detritus.

For QCB and TeCB a similar difference in K_{oc} values is observed between the *Anabaena* samples and the *Scenedesmus* sample. This can be expected since all three chlorobenzenes share the same physico-chemical mechanism of hydrophobic partitioning. However, a clear trend within the range of *Anabaena* K_{oc} values is not observed for QCB and TeCB. Apparently, the changes in the polarity of the four *Anabaena* samples are too small to result in significant K_{oc} trends for these less hydrophobic chlorobenzenes, possibly in combination with some systematic error in the TOC-determinations. Another explanation for the diverging behavior of QCB and especially TeCB, is the fact that the gas-purge procedure generally is less sensitive for less hydrophobic compounds [3,15], and was optimized for HCB.

Besides absolute K_{oc} values as an index of sorption affinity, slopes of $\log K_{oc}$ - $\log K_{ow}$ plots can be evaluated. The slope of a $\log K_{oc}$ - $\log K_{ow}$ plot is relatively insensitive to experimental error associated with the TOC determinations, extractions and GC performance. For neutral solutes, the equilibrium partition coefficients between water and nonpolar organic solvents are empirically related to octanole-water partition coefficients according to [22]:

$$\log K_y = s_y \times \log K_{ow} + r_y \qquad (10)$$

where K_y is the partition coefficient for solvent y and water and s_y the slope (selectivity constant) of the linear relationship. The magnitude of the selectivity constant s_y was found to depend on the difference in the average polarity between solvent *y*, and the polarity of 1-octanole [23]. Schwarzenbach *et al* [24] found analogous variations in the slopes of $\log K_{oc}$ - $\log K_{ow}$ plots for natural adsorbents, for example, between sediments of different trophic state. Slopes of $\log K_{oc}$ versus $\log K_{ow}$ for our detritus samples are listed in Table 3. $\mathrm{Log}K_{ow}$ values were taken from [25]. Although the slopes were calculated for $n=3$, they are highly significant (0.0066>P>0.0580, t-test). The hypothesis that the five groups of data were sampled from populations of equal slope was tested following an analysis of variance procedure described by Sokal [26]. The difference between the slope for ANA0 and the slope for ANA124, representing a 124 day period of mineralization for the same algal species, was significant at P=0.0176. Using the data for all five adsorbents, the difference between slopes was significant at P=0.0053. We conclude that the adsorbents differ in their $\log K_{oc}$ response to $\log K_{ow}$ depending on their degree of mineralization.

TABEL 3:
Linear $\log K_{oc}$ - $\log K_{ow}$ correlations$^{(a)}$

adsorbent$^{(b)}$	slope ± SE	r^2	P$^{(c)}$ (slope)	n
ANA0a	0.610 ± 0.013	1.000	0.0135	3
ANA18	0.698 ± 0.064	0.992	0.0580	3
ANA47	0.826 ± 0.075	0.992	0.0574	3
ANA124	0.905 ± 0.037	0.998	0.0260	3
SC466(70)	1.167 ± 0.011	1.000	0.0066	3

(a) $\log K_{ow}$ values were taken from [25]; (b) See Table 1 for explanation of adsorbent codes. For SC466 the results obtained at 70 mg/l were used; (c) slope unequal to zero at stated significance level P.

The 466 days aged *Scenedesmus* detritus sample was used for experiments at two adsorbent concentrations: 35 and 70 mg/l. It follows from Table 2 that the difference in adsorbent to water ratio has no large effect on the K_{oc} estimates. For QCB and TeCB, the two-compartment model was the best model. Furthermore, K_{oc} and k_2 seem to be inversely correlated for these congeners, as was also reported for sediments and soils [16]. The value for x_1 decreases with increasing adsorbent concentration and with increasing hydrophobicity of the chlorobenzene. The first phenomenon may originate from the fact that in batch systems the period required to approach equilibrium will be shorter at a higher adsorbent to water ratio. This was shown by Banerjee [27] for the influence of fish density on equilibration time. So, after 48 h the test compounds may be closer to equilibrium at 70 mg/l, and a larger fraction of the chemicals has sorbed in the 'slow' compartment. Karickhoff [16] observed the same phenomenon for sediments and explained it from the lower diffusive transport coefficients for 'fast' desorption which he found at higher sediment to water ratios. The second trend can be explained from slower transport for more hydrophobic sorbates in the organic matrix. For HCB, both models resulted in exactly the same residual sum of squares, so the one-compartment model was finally selected. The two-compartment model results confirm that the desorption can be described using one compartment: the x_1 value is approximately zero and the k_2 estimate is physically meaningless.

The sorption coefficients on a lipid basis ($\log K_{lip}$) for HCB and QCB show an increase with mineralization time and are more or less constant for TeCB (Table 2). The uncertainty in the resultant values is relatively large due to the propagation of the errors in the determinations of lipid content and K_{oc}. However, it is clear that lipid normalisation is not very useful for this type of particles. For all adsorbents and chlorobenzenes, including the fresh *Anabaena* cells, K_{lip} values are larger than their respective K_{ow} values. This was also found by Swackhamer [10] for bioaccumulation of PCBs to *Scenedesmus* sp. Furthermore, the lipid/carbon ratio which can be calculated from the data in Table 1 decreases with a factor 2.5 during mineralization of *Anabaena*. This suggests an increase in the contribution of organic matter pools other than lipid, probably in combination with a change in lipid composition.

Desorption kinetics for living algae

The kinetics of the desorption process for living algae follows from the model selected and, for the two-compartment model, from the magnitudes of the parameters x_1 and k_2. When the 'equilibrium binding' assumption is valid for the entire adsorbent ($x_1 = 1$), desorption has to be fast compared to the rate of volatilization from the purge flasks. Since the volatilization rate constants k_v (equation 3) were approximately 30 day^{-1} for TeCB and QCB, and 20 day^{-1} for HCB, it can be argued that the respective desorption rate constants (k_{21} for the one-compartment model) are larger than these values. For such large sorption rate constants, the effects of algal growth on the steady state BCF^G as predicted by equation (2), will be small. In case of desorption from *two* compartments, as was found in this study, the overall desorption kinetics is slower, because the equilibrium binding assumption holds only for a part (x_1) of the initially sorbed mass. However, because the x_1 values are close to one (Table 2), the rate constant for slow desorption k_2 can be expected to have only limited effect on the steady state BCF under growth conditions. This can be quantified by a modification of the biosorption model for growing phytoplankton as condensed in equation (1), taking the sizes of the two sorption reservoirs into account. Combining equations (7) and (8), and assuming first-order algal growth, and constant equilibrium with adsorbent fraction x_1, access to and from the second compartment is given by:

$$dC_{A2}/dt = \frac{k_2(1-x_1)}{x_1} \times C_{A1} - k_2 C_{A2} - k_G C_{A2} \qquad (11)$$

Combination of the steady state solution of equation (11) with equation (6), yields:

$$BCF^G = C^e_A/C^e_W = \frac{C^e_{A1}+C^e_{A2}}{C^e_W} = K_{oc} \times \frac{k_2+x_1 k_G}{k_2+k_G} = BCF^N \times \frac{\alpha+x_1}{\alpha+1} \qquad (12)$$

in which $\alpha = k_2/k_G$ and K_{oc} is the general equilibrium sorption constant for live or dead biomass. For living phytoplankton, the use of BCF^N instead of K_{oc} is more common, which leads to the replacement of K_{oc} on the right hand side of (12). It follows from (12) that the influence of growth depends on the magnitudes of the k_2/k_G ratio (α) and x_1. This is illustrated in Figure 3, where the underestimation of *BCF* at steady state (the ratio BCF^G/BCF^N), is plotted as a function of x_1 and the log of the k_2/k_G ratio (α). When equilibrium binding is predominant (x_1 close to 1), growth has negligible effect on *BCF*.

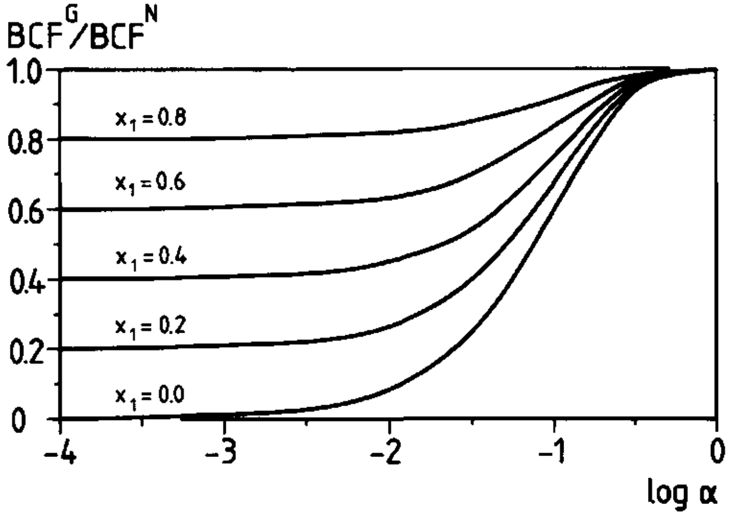

Fig. 3: The underestimation of *BCF* at steady state, as a function of log α (=log k_2/k_G), at various sizes of the 'fast' sorption reservoir x_1.

When slow sorption is predominant (x_1 close to zero), (12) reduces to an equation essentially identical to equation (2), because both k_{21} and k_2 quantify desorption rate. The relative magnitude of k_2 as compared to k_G is important in the latter case, but only when

$\log k_2/k_G < 0.1$, as can be seen from Figure 3. With x_1 values of 0.8 - 1.0, our general conclusion is that for *Anabaena* chlorobenzene bioconcentration would be at equilibrium in aquatic systems, even at conditions that promote algal growth. In our previous study, for fresh *Scenedesmus* unicells and the chlorobenzenes HCB and TeCB, much lower x_1 values of respectively 0.3 and 0.4 were found under the same experimental conditions [11]. The model parameters for these experiments were recalculated using the sequential parameter estimation technique introduced in this study, and are compared to the data for *Anabaena* in Table 4. Values for k_2 are approximately 1 day^{-1} for TeCB and HCB. However, with a literature value for the maximum growth rate for *Scenedesmus* of 2 day^{-1} [28], resulting in a minimum $\log k_2/k_G$ value of -0.3, also for *Scenedesmus* no significant effect of algal growth on the steady state *BCF* can be expected (Figure 3).

The sizes of the kinetically defined compartments are not identical for the different algal species and chlorobenzenes (Table 4). This is not caused by a different adsorbent to water ratio because the measured dry-weights are very similar. The observed differences between x_1 for different algal species may be related to the differences between the actual physical sorption reservoirs. There is experimental evidence that accumulation of nonpolar HOCs in living algal cells is a partitioning proces into the lipid fraction [11,29]. In addition, accumulation at or near the cell surface may be important. This surface accumulation may be Langmuir-type surface adsorption as was described recently by Wang and co-workers [30]. However, they showed that for HOCs with $K_{ow} > 1000$, the contribution of surface adsorption as compared to partitioning is negligible. Consequently, the kinetically defined compartments for our chlorobenzenes should be interpreted as lipid pools of different accessability. Formally, these pools may be parallel or in series because our model cannot distinghuis between those two configurations. For algal cells a series version with fast partitioning to cell wall lipids versus a slower partitioning deeper in the cell matrix seems plausible. However, it cannot be assumed a priori that the fast sorption is restricted to the cell wall lipids. Depending on the thickness of the cell wall, the distribution of the various organelles in the cell and the sorbate properties, lipid pools close to the cell wall and cell membrane might contribute to the fast sorption compartment. This interpretation of the two-compartment model suggests a positive correlation between x_1 values and surface areas of the algal cells. The basic assumption herein is that the surface area is positively correlated with the relative amount of lipids in or close to the cell wall. In our experiments the approximate cell geometries were spheres (*Scenedesmus* unicells), bars (*Scenedesmus* coenobia) and cylinders (*Anabaena* strains). From the approximate dimensions of the cells the surface-to-volume ratio (S/V-ratio) was estimated. The results are listed in Table 4 and show a positive correlation between x_1 and S/V-ratio as expected, for both TeCB and HCB.

TABLE 4: Surface-to-volume ratios and two-compartment model parameters for living phytoplankton

Adsorbent[(a)]	DW[(b)] (mg/l)	A/V[(c)] (μm^{-1})	K_{oc} ($\times$1000)	90% C.I.	k_2	90% C.I. (day^{-1})	x_1	90% C.I.
Hexachlorobenzene								
U-0[(d)]	68	0.54	95	(64 - 144)	1.43	(0.95 - 2.05)	0.28	(0.08 - 0.46)
C-0[(d)]	67	0.73	242	(189 - 293)	1.09	(0.38 - 1.89)	0.71	(0.51 - 0.83)
ANA0a	88	1.35	74	(65 - 83)	2.73	(1.21 - 5.10)	0.82	(0.69 - 0.92)
1,2,3,4-Tetrachlorobenzene								
U-0[(d)]	68	0.54	32	(23 - 42)	1.16	(0.46 - 2.58)	0.42	(0.21 - 0.56)
C-0[(d)]	67	0.73	25	(21 - 29)	0.82	(0.03 - 11.2)	0.86	(0.77 - 0.94)
ANA0a	88	1.35	16	(14 - 17)	0.27	(0.09 - 0.54)	0.85	(0.78 - 0.91)

(a) Letters refer to the type of adsorbent. U= *Scenedesmus* Unicells, C= *Scenedesmus* Coenobia., ANA= *Anabaena*; (b) Dry-weight of algal suspension during purge experiment; (c) Surface area-to-volume ratio. Calculated from the approximate surface and volume of the algal cells as estimated from particle size measurements and shape analysis; (d) The parameters for fresh *Scenedesmus* were recalculated from experimental results reported in [11], using a sequential parameter estimation technique.

Besides differences in desorption kinetics between different algal species, the purge experiments with unicell and coenobium forms of living *Scenedesmus* showed a larger 'fast' compartment for TeCB than for HCB (Table 4). In the present study the differences for fresh *Anabaena* (Table 2, ANA0a) are smaller and there is no clear trend in the magnitude of x_1 with sorbate hydrophobicity. However, the results show that the kinetic compartment sizes for a given adsorbent depend on sorbate properties. This observation confirms that 'fast' sorption is not restricted to the cell wall lipids, because then a constant x_1 for all chlorobenzenes would be expected for a given species. Although lipids may still be the most important accumulation reservoir for HOCs, the location and distribution of physical lipid compartments in the cells, do not automatically determine the kinetic compartments. The fraction of total lipids which acts as 'fast' sorption compartment may vary with sorbate hydrophobicity because of differences in the effective diffusional transport rate in the cell matrix. As is described for sediments [16], the less hydrophobic compounds are assumed to have larger diffusive transport rates, resulting in a larger x_1. Although algae have an internal aqueous phase containing organelles which makes the diffusion processes more complex, our data suggest that the relationship between sorbate hydrophobicity and x_1 is similar to that for sediments.

CONCLUDING REMARKS

In this study a maximum variation of a factor three for the K_{oc} of hexachlorobenzene was observed for phytoplankton and detritus at various degrees of mineralization. This variation is of the same order of magnitude as described in the literature for sediments and soils of different origins. Such differences emphasize the importance of the nature of the organic matter involved, and illustrate the limitations of the concept of constant partitioning which is widely used in contaminant transport models. For surface water systems, it may be appropriate to use different K_{oc} values for dissolved organic matter, (resuspended) sediments, phytoplankton and detritus. For sediment systems, a lower K_{oc} value might be used for the top layer which contains large fractions of undegraded plankton.

Regarding the high desorption rate constants found in this study, it seems unlikely that chlorobenzene accumulation in *Anabaena* and *Scenedesmus* and similar species would be at nonequilibrium in aquatic systems, even under favourable growth conditions. However, the fact that the rate of biphasic desorption decreases with increasing sorbate hydrophobicity and with decreasing surface-to-volume ratio, suggests that much slower kinetics may be expected for hydrophobic compounds with $\log K_{ow} > 6$, (for example PCBs) and algal species or clusters of larger size.

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Appendix

ANALYTICAL SOLUTIONS TO THE ONE- AND TWO-COMPARTMENT MODELS

In this appendix derivations of the one-compartment model (Chapters 7,8) and the two-compartment model (Chapters 5, 7, 8) are given.

The one compartment model

This section describes the derivation of a general solution to Model 3 page 141. The total concentration of the test compound in the adsorbent suspension (C_T) at any time is:

$$C_T = C_b + C_w \tag{1}$$

in which C_w (μg/l) is the aqueous concentration, and C_b (μg/l) is de bound concentration. The rate expressions according to Model 3 are:

$$dC_b\ /dt = k_{21}C_w - k_{12}C_b \tag{2}$$

$$dC_w\ /dt = k_{12}C_b - (k_{21} + k_v)C_w \tag{3}$$

$$dC_T\ /dt = -k_vC_w \tag{4}$$

$$dC_g\ /dt = k_vC_w \tag{5}$$

At equilibrium, the rate of adsorption equals the rate of desorption, so $dC_b/dt=0$ and:

$$K_b = k_{21}/k_{12} \tag{6}$$

The differential equations (2) - (5) were solved using the matrix method outlined by Lewis and Johnson [1], to give explicit expressions for C_b and C_w as a function of time. From these expressions, expression (1) and (2), initial values C_b^0, C_w^0 and C_T^0 and the volume of the liquid phase *Vw*, the expression relating Q^{TENAX} to time was calculated:

$$Q^{Tenax} = Vw(C_T^{t=0} - C_T) \tag{7}$$

and

$$
\begin{aligned}
C_T= & \\
& \frac{C_T^0}{(B_{22}-B_{23})(1+K_b)} * [(K_b B_{22} B_{23}-B_{12} B_{13})(e^{-\lambda_2 t}-e^{-\lambda_3 t}) \\
& \qquad +K_b(B_{12} B_{23} e^{-\lambda_2 t}-B_{13} B_{22} e^{-\lambda_3 t}) \\
& \qquad +B_{12} B_{23} e^{-\lambda_3 t}-B_{13} B_{22} e^{-\lambda_2 t}]
\end{aligned}
\tag{8}
$$

In which:

$$B_{12}=\frac{\lambda_2-k_{21}+k_v}{k_{12}+k_{21}+k_v-\lambda_2} \tag{9}$$

$$B_{13}=\frac{\lambda_3-k_{21}+k_v}{k_{12}+k_{21}+k_v-\lambda_3} \tag{10}$$

$$B_{22}=\frac{\lambda_2-k_{12}}{k_{12}+k_{21}-\lambda_2} \tag{11}$$

$$B_{23}=\frac{\lambda_3-k_{12}}{k_{12}+k_{21}-\lambda_3} \tag{12}$$

$$
\begin{aligned}
\lambda_2 &= 0.5[(k_{12}+k_{21}+k_v)+\sqrt{(k_{12}+k_{21}+k_v)^2-4k_{12}k_v}] \\
\lambda_3 &= 0.5[(k_{12}+k_{21}+k_v)-\sqrt{(k_{12}+k_{21}+k_v)^2-4k_{12}k_v}]
\end{aligned}
\tag{13a,b}
$$

In our solution the parenthesis (Eqn. 8) and the B_{13} constant (Eqn. 10) differ from the equation published by Hassett and Millicic [2].

The two compartment model

This part describes the derivation of a general solution to Model 4 page 141. Initial assumptions are that the adsorbent consists of two kinetic compartments. The compartments differ in their *accessability* for the adsorbate, but not in their *affinity* for the adsorbate.

The chemical concentrations of the adsorbate in the compartments are defined as:

S1 = mole adsorbate per gram organic matter of compartment 1
S2 = mole adsorbate per gram organic matter of compartment 2

It is assumed that the sorption to the first compartment is so fast that the aqueous phase is in continuous equilibrium with this first compartment. In formula:

$$S1=K_pC_w \tag{14}$$

Furthermore, it is assumed that transport *between* the two compartments is rate limiting and takes place through first-order processes according to:

$$dS2/dt=k_{12}S1-k_{21}S2 \tag{15}$$

At equilibrium:

$$S1^e/S2^e=k_{21}/k_{12} \tag{16}$$

where the superscripts "e" refer to equilibrium concentrations. Because the two compartments are both composed of organic matter, it is assumed that the affinity of the adsorbate for both organic matter reservoirs is equal. In that case (16) simplifies to:

$$S1^e/S2^e=k_{21}/k_{12}=1\ ,\ thus\quad k_{21}=k_{12}\equiv k_2 \tag{17}$$

So both rate constants are assumed equal and are indicated by k_2. In a next step the adsorbed concentrations in compartment 1 and 2 (*S1* and *S2*) are referenced to *total* organic matter mass (C_{S1} and C_{S2}):

$$C_{S1}=x_1S1 \Rightarrow S1=C_{S1}/x_1 \tag{18}$$

$$C_{S2}=(1-x_1)S2 \Rightarrow S2=C_{S2}/(1-x_1) \tag{19}$$

in which x_1 is the fraction of the adsorbate bound in the first compartment at equilibrium. Because at equilibrium the adsorbate is distributed uniformly in the total organic matter mass, x_1 also equals the size of the 'fast' organic matter reservoir.

For the first compartment, substitution of (18) in (14) yields:

$$C_{S1}=x_1K_pC_w \tag{20}$$

When the aqueous concentration decreases because of gas purging which is modeled as a first order volatilization process (Eqn. 4 and 5), the desorption from the first compartment is given by:

$$dC_{S1}/dt=x_1K_pC_w\ /dt=-x_1K_pk_vt \tag{21}$$

Substitution of (18) and (19) in (15) and rearrangement yields the expression for the desorption from the second compartment:

$$\frac{dC_{s2}}{dt}=\frac{k_2(1-x_1)}{x_1}\times C_{s1}-k_2C_{s2} \tag{22}$$

So at a given k_v, the desorption process is fully described by the three parameters K_p, x_1 and k_2. The constant k_2 describes the transport between the first and the second compartment in both directions. The models derived by Karickhoff [3] and Brusseau [4] are essentially identical. However, for brevity Brusseau [4] uses the composite parameter "k_1" instead of the term "$k_2(1-x_1)/x_1$".

From the purge experiments, no direct information on the concentrations in either the aqueous phase or the adsorbent compartments is obtained, because only the total amount removed from the total suspension (Q^{TENAX}) is trapped in the Tenax columns. However, when the differential equations (8) and (9) are solved simultaneously the following expression can be derived:

$$\frac{Q^{Tenax}}{Q^{Tenax^{t=0}}}=1-\frac{A}{\epsilon}(1+\epsilon+B_+)e^{B_+\Gamma}-\left(\frac{y_2^0-A}{\epsilon}\right)(1+\epsilon+B_-)e^{B_-\Gamma} \tag{23}$$

in which:

$$A=\frac{\epsilon y_1^0-(1+B_-)y_2^0}{B_+-B_-} \tag{24}$$

$$B_\pm=0.5\times[-(1+\alpha+\epsilon)\pm\sqrt{(1+\alpha+\epsilon)^2-4\alpha}\,] \tag{25}$$

$$y_1^0=R_1/R_T \tag{26}$$

$$y_2^0=\frac{R_T-R_1}{R_T} \tag{27}$$

$$R_T = V_g + \frac{V_w}{H} + \frac{mK_{oc}}{H} \tag{28}$$

$$R_1 = V_g + \frac{V_w}{H} + \frac{mx_1K_{oc}}{H} \tag{29}$$

$$\Gamma = k_2 t \tag{30}$$

$$\alpha = \frac{F}{k_2 R_1} \tag{31}$$

$$\epsilon = \frac{m(1-x_1)K_{oc}}{R_1 H} \tag{32}$$

and: F=flow (l/min), K_{oc}= partition coefficient, H= Henry's Law constant, m= adsorbent mass (kg), x_1= adsorbent fraction for fast sorption, Vg= headspace volume (l), Vw= liquid volume (l), k_2= first order desorption rate constant (min^{-1}), t= time (min). The total amount removed from the system (Q^{TENAX}) depends uniquely on the parameters K_p, x_1 and k_2 which can be estimated using curve fitting techniques.

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Chapter 9

TRACE METAL SORPTION TO PHYTOPLANKTON: THE INFLUENCE OF CHLORINITY AND DECOMPOSITION

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TRACE METAL SORPTION TO PHYTOPLANKTON: THE INFLUENCE OF CHLORINITY AND DECOMPOSITION

Abstract- The uptake of Cd, Cu and Pb by the cyanobacterium *Anabaena* spp in surface waters with different chlorinity, and at various degrees of algal decomposition, was studied using batch experiments. The isotherms for Cd and Cu could be described with the Freundlich equation. For Pb a linear isotherm was satisfactory. In general, the Freundlich affinity constant K_f decreases with increasing chloride concentration. For Cd this decrease was explained with a speciation model based on complexation with chloride. The Freundlich exponent for Cd and Cu was relatively constant among surface waters with different chlorinities. The distribution coefficient (K_d) for *Anabaena* spp was largest for Pb, followed by Cd and Cu. Mineralization of *Anabaena* spp for 42 days resulted in a decrease of the solid to water ratio of a factor twelve, and an increase in K_d for Cd (factor four), Cu (factor eight) and Pb (factor 10 - 20). The increase in K_d is attributed partially to a decrease in solid to water ratio, and partially to a higher affinity of the metals for the adsorbent. These results indicate that assuming constant K_d values for mineralizing phytoplankton and detritus in water quality models may result in significant underestimations of bound fractions. The extent to which this fraction is underestimated, depends on the time course of the distribution coefficient and the solid to water ratio during the mineralization process.

INTRODUCTION

In the aquatic environment, settling particles have been recognized as important scavengers for organic and inorganic contaminants [1,2]. As such, they have strong influence on the residence times and geochemical cycling of these substances. Several sediment trap and suspended solid studies have demonstrated that the vertical flux of particulate matter is one of the most important natural removal mechanisms for organic and inorganic contaminants [1,2,3,4,5]. These studies also show that among the constituents of settling materials in lakes, planktonic particles and detritus are the dominant vectors for trace metals and hydrophobic organic compounds. Besides the effect on transport processes, accumulation in planktonic particles and detritus also affects the bioavailability of heavy metals. The extent to which a contaminant is accumulated determines the concentration of metal in solution and, consequently the potential for transport in the water column or uptake by organisms. Accordingly, an important variable in models describing contaminant transport or accumulation in aquatic food webs and food chains is the sorbed fraction of the total contaminant concentration, α_p

$$\alpha_p = \frac{S_p \times K_d}{(S_p \times K_d) + 1} \tag{1}$$

with S_p = the concentration of suspended solids (phytoplankton, detritus and or resuspended sediments), expressed in mg dry weight/l, or mg C /l

K_d= the distribution coefficient (for living phytoplankton and under equilibrium conditions, the K_d is usually called the bioconcentrationfactor *BCF*).

It follows from equation 1 that the bound fraction is determined by the product $S_p \times K_d$. Many studies concern the processes that influence the magnitude of S_p, such as photosynthesis, mineralization, horizontal transport, sedimentation and resuspension. Also many studies concern the sorption of contaminants to natural particles, especially the significance of particle and aqueous phase composition and the differences among chemically different contaminants. However, very few studies have measured the redistribution of trace metals from decomposing plankton. Fisher and Wente [6], studied the accumulation and subsequent release under dark conditions of Ag, Am, Au, Se and Sn from three species of marine phytoplankton. They found significant differences in the time course of metal:dry weight ratios for the different metals and species, and also found significant temperature effects. Lee and Fisher [7] studied the degradation and release rates of C, Cd, Co, Ag, Am, Ce, Se and Zn from phytoplankton debris. They also found that release rates were very different for different metals. For some metals, the release was much slower than the release of C (the mineralization rate), so that for these metals settling of detritus will be an important transport process, while for other metals rapid recycling can be expected. However, in both studies only bound fractions were considered. When fractions are considered, it is not possible to discriminate quantitavely between the effect of disappearing organic mass (ΔS_p) and the effect of a possible change in the distribution coefficient (ΔK_d), as can be seen from equation 1. As far as we know, no experimental studies have determined distribution coefficients simultaneously with the aging and decomposition of phytoplankton.

In this study, the metal sorption characteristics and the effect of mineralization of phytoplankton on the distribution of heavy metals between solid and aqueous phase were investigated. Three metals of environmental concern (Cd, Cu and Pb) were chosen as test elements. The cyanobacterium *Anabaena* spp was chosen as test species because of its rapid mineralization [8] and its natural occurrence in many fresh water lakes, for example Lake Volkerak/Zoom (The Netherlands). Two series of experiments were performed. In the first series, the general metal sorption characteristics of living *Anabaena* cells in a wide metal concentration range were investigated by measuring adsorption isotherms in surface waters of different chlorinity. In the second series, distribution coefficients were measured for decomposing *Anabaena* cells as a function of mineralization time. The experimental conditions were attuned to environmental conditions typical for some Dutch surface waters, especially those in Lake Volkerak/Zoom.

EXPERIMENTAL METHODS

Adsorption isotherms

The original algae used, a PCC 7120 strain of *Anabaena* spp, were a kind gift from Pim de Nobel, MSc, Department of Microbiology, University of Amsterdam. A schematic representation of the subsequent manipulations on behalf of the experiments in this study, is given in Figure 1. The algae were cultured in a 100% Z8 mineral medium [9]. Three l of this culture were used to prepare a 40 l 80 mg/l suspension of the same alga. For this 40 l culture, an adapted Z8 medium without trace metals was used to minimize interference with the subsequent metal accumulation experiments. From the 40 l suspension 20 liter was taken and concentrated to one liter by settling overnight and removal of the overlying water with a siphon. The concentrated suspension was diluted with one liter of surface water sampled from Lake Volkerak/Zoom (sampled on June 5th 1992 at location VZ3). Sampling locations are indicated in Chapter 2, Figure 1. This suspension was concentrated to 0.6 liter by settling and subsequent siphoning of the supernatant. The resultant volume was divided in four representative subsamples of 150 ml using a Retsch (Germany) suspension divider. The four subsamples were each filled up to 2 l with surface water samples of different chlorinity: (a) Hollandsch Diep water (sampled on May 14th 1992 at location HD16/17, $Cl^- \approx 100$ mg/l, abbreviation HD), (b) water from Lake Volkerak (sampled on June 5th at location VZ3, $Cl^- \approx 270$ mg/l, abbreviation VZ3), (c) water from Lake Zoom (sampled on June 6th 1992 at location VZ7, $Cl^- \approx 600$ mg/l, abbreviation VZ7) and (d) North Sea water (sampled on June 26th 1992 at the beach near Noordwijk, $Cl^- \approx 16000$ mg/l, abbreviation NS). Particles were removed from these samples prior to their use in this study by filtration over Schleicher and Schuell (Dassel, Germany) Ref Nr. 300412 ø=15 cm filters. The additions of the seawater sample to the concentrated algal suspensions were made carefully in small aliquots in a five h period, to minimize osmotic shock. After the additions no lysis was observed (microscopic inspection, Nikon (Melville, NY) inverted microscope).

Each of the four two liter suspensions was divided in eight representative subsamples of 250 ml using a Retsch suspension divider. From one of these subsamples, a small aliquot was used to measure chloride concentrations with a Marius (Utrecht, The Netherlands; Chlor-o-counter II) coulometric chloride titrator, and electric conductivity using a conductance cell. Thus, four series of eight samples were prepared, each series having a known chloride concentration. From the eight bottles, two were left as blanks, three were spiked with 1, 2 and 4 ml of spike solution 1 and three were spiked with 1, 2 and 4 ml spike solution 2. The spike solutions were solutions of the metal salts ($Cd(NO_3)_2.4H_2O$, $Cu(NO_3)_2.3H_2O$ and $Pb(NO_3)_2$ all Merck, p.a.) in Nanopure water (Sybron-Barnstead, Dubuque, IA) and had heavy metal concentrations of

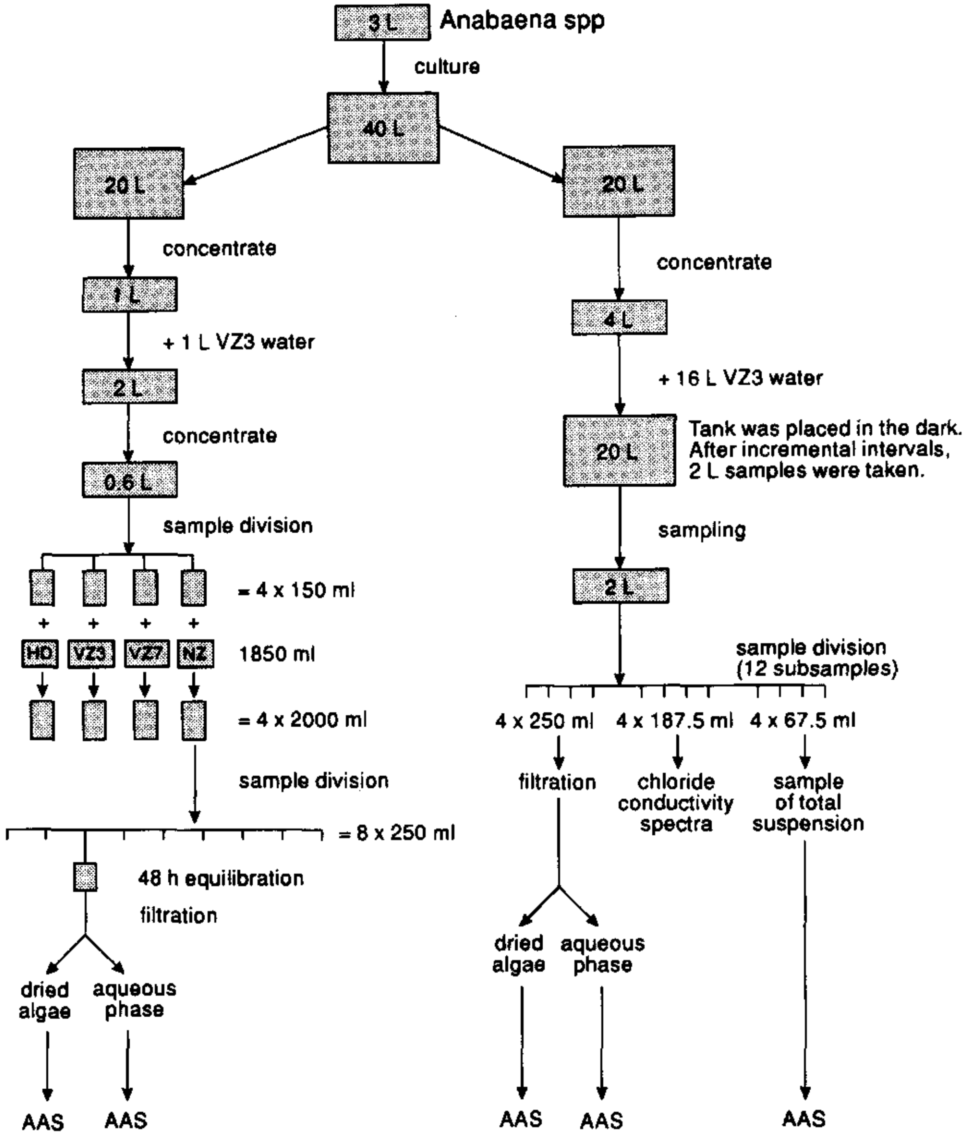

Fig. 1: Schematical representation of the experimental procedures used to measure adsorption isotherms at different chloride levels (left hand side) and distribution coefficients at different degrees of algal decomposition (right hand side).

Cd: 2.098 mg/l, Cu: 0.389 mg/l, Pb: 0.5230 mg/l (spike solution 1)

Cd: 20.98 mg/l, Cu: 3.89 mg/l, Pb: 5.230 mg/l (spike solution 2).

The amounts of metal added were such that after equilibration, aqueous concentrations of approximately 0.1 - 10 μg/l were expected. The metal dosages were based on the known dry weight of the algal suspensions and literature values for the K_d for the metals [10,11]. After addition of the spike solution the bottles were adjusted to pH=8.5 with 1 M NaOH (Merck, p.a.).

The bottles were agitated using short (one h) magnetic stirring periods (with Teflon® coated stir bars) alternating with 23 h periods under continuous light on a shaking platform at a temperature of 20°C. After 24 h pH was adjusted to 8.5 with NaOH. One hour before phase separation the algae were kept in suspension and pH was adjusted once again. Phase separation was after a total equilibration period of 48 h, by filtration in an all Teflon filtration unit, over preweighed Schleicher and Schuell 0.8 μm cellulosenitratre membrane filters. Although commonly 0.45 μm is used as an operational boundary for dissolved species, the use of 0.8 μm filters was necessary to shorten the filtration times, and accordingly to minimize contamination and risks of damage to the cells. At the moment of phase separation, pH values were measured and tabulated. It was found in prior experiments with *Scenedesmus* spp that 48 h was sufficient to approach a steady state distribution (Koelmans, unpublished results). Because the cell wall thickness is less, and surface area is larger for *Anabaena* strains (100-200 μm length and 2-3 μm diameter) than for *Scenedesmus* cells, we assume that our suspensions were at sorption equilibrium. This is supported by several other studies. Romeo and Gnassia-Barelli [12] report equilibration times of 48-72 h for Cd and <48 h for Cu uptake by *Prasinocladus marinus*, *Amphidinium carterae*, *Chaetoceros curvisetum* and *Chaetoceros protuberans*. Uptake was faster at lower metal concentrations. Xue et al [13] report equilibration times of several hours for Cu uptake to *Chlamydomonas rheinhardii*. The first 50 ml of the filtrates were rejected. The remaining filtrates were acidified with concentrated HNO_3 (Merck, p.a.; 65%) in the filtrate:acid ratio of 84:16 (v:v). The filters with residu were placed in specially designed glass containers which minimized contamination by dust but allowed drying in an incubator (2 h, 105°C). After drying, filters were weighed and destructed (2 h, 100°C) in a 84:16 mixture of Nanopure water and concentrated HNO_3 (v:v). Cd, Cu and Pb concentrations in aqueous phase, and destructed algal phase samples were measured with a Varian Spectraa-300 (graphite furnace) atomic absorption spectrometer using external standards and background correction.

For all batches, mass balances were checked by expressing the recovered amounts after phase separation as fractions of the added amount before phase separation. The added amount is the amount added in the laboratory, plus the average amount of metal found in the blank batches. The metals in the blank batches originate from the surface waters used, and from the originally used algal growth medium. The measured concentrations were plotted as adsorption isotherms. The isotherms were fitted to:

(a) a linear sorption model according to:

$$C_s = K_d \times C_w + b \tag{2}$$

with C_s and C_w the concentrations in the algae (μg/g) and the concentrations in the aqueous phase (μg/l), respectively

(b) the Freundlich equation (egn. 3) by non-linear regression according to Marquardt [14], or

(c) the Freundlich equation (eqn. 3) by linear regression of log - log transformed adsorbed and dissolved concentrations (logC_s versus logC_w).

$$C_s = K_f \times C_w^n \tag{3}$$

To select the best model, an analysis of variance was performed for all regressions. Models were tested for significance using the F-test. The difference among the slopes of the linear regression lines obtained by method (c) for the different surface waters was tested using a procedure described by Sokal [15].

Mineralization of *Anabaena*

20 l of the same *Anabaena* suspension described in the previous section was concentrated to four l by allowing the particles to settle and by siphoning of the supernatant (see also the right hand side of Figure 1). Approximately 16 l surface water sampled from Lake Volkerak (sampled on June 5th 1992 at location VZ3) were filtrated (Schleicher and Schuell filter ref Nr. 300412 ø=15 cm), and were transferred to a clean, acid rinsed polyethylene tank. Subsequently, the concentrated algal suspension was added carefully. The resultant algal suspension in 80% Lake Volkerak water, was spiked with 10 ml 16 mg/l Cu, 33 mg/l Cd and 27 mg/l Pb (as in the previous section metals were weighed as nitrate salt, Merck p.a.). The tank was placed in a 20°C climate room under continuous light and magnetic stirring for a 48 h period, during which further adaptation, some algal growth and distribution of metals between dissolved and sorbed states was accomplished. Subsequently, decomposition was induced by turning off the light and representative 2 l samples ware taken at time=0, 6, 18, 28 and 42 d. A representative 0.5 liter portion of this sample was divided in twelve representative subsamples, using a Retsch suspension divider and acid rinsed polyethylene bottles. Four of these subsamples (volume 67.5 ml) were destructed and prepared for AAS analysis, as described in the

previous section. With these samples total metal concentrations (algae plus aqueous phase) were measured. Four other bottles with 250 ml algal suspension were filtrated and used for the determinations of sorbed and aqueous phase concentrations. The last four bottles with 187.5 ml each were used for the measurements of chloride concentration, electric conductivity and absorption spectra, the latter in total and filtrated samples. Filtration procedure and metal analysis were as described in the previous section. With this procedure, quadruplicate data on total, aqueous phase and algal bound metal concentrations were obtained.

During the decomposition process, pH in the tank was measured daily and adjusted to pH=8.5 with small aliquots of NaOH. The suspension was continuously aerated (MB-12 Metal Bellows pump). To minimize volatilization from the tank, the air was saturated with water. When necessary, volatilization was compensated for by adding Nanopure water.

After the first mineralization experiment, a second experiment was started. Conditions and methods were identical to the first experiment except the spiked amounts, the sampling intervals and the time period in which the suspension was kept at a constant volume. The spike amounts were ten times lower than in the first experiment. Samples were taken at time= 0, 7, 14, 30 and 71 days and the volume corrections were made only till day 14.

RESULTS AND DISCUSSION

Adsorption isotherms

Mass balances for all batches are presented in Figure 2. For Cd, the balances are systematicly below 100% (range 50-98%). The mass balances for Cu and Pb are approximately 100% on the average, but show considerable ranges (Cu: 71-130%, Pb: 44-155%). Deviations from 100% are caused by random errors in the chemical analysis, by contamination and by sorption to container walls, filters and filterunits. The large range for Pb is determined by two outliers. When these are excluded, the range is 71-116%. For the interpretation of balances, it should be noted that in the majority of all sorption studies with environmental samples, balances are not checked at all and that a balance of 100% is assumed (e.g., [6,7,16,17,18,19,20]). In the studies where balances are reported, the quality of the balances is similar to ours or worse [21,22,23].

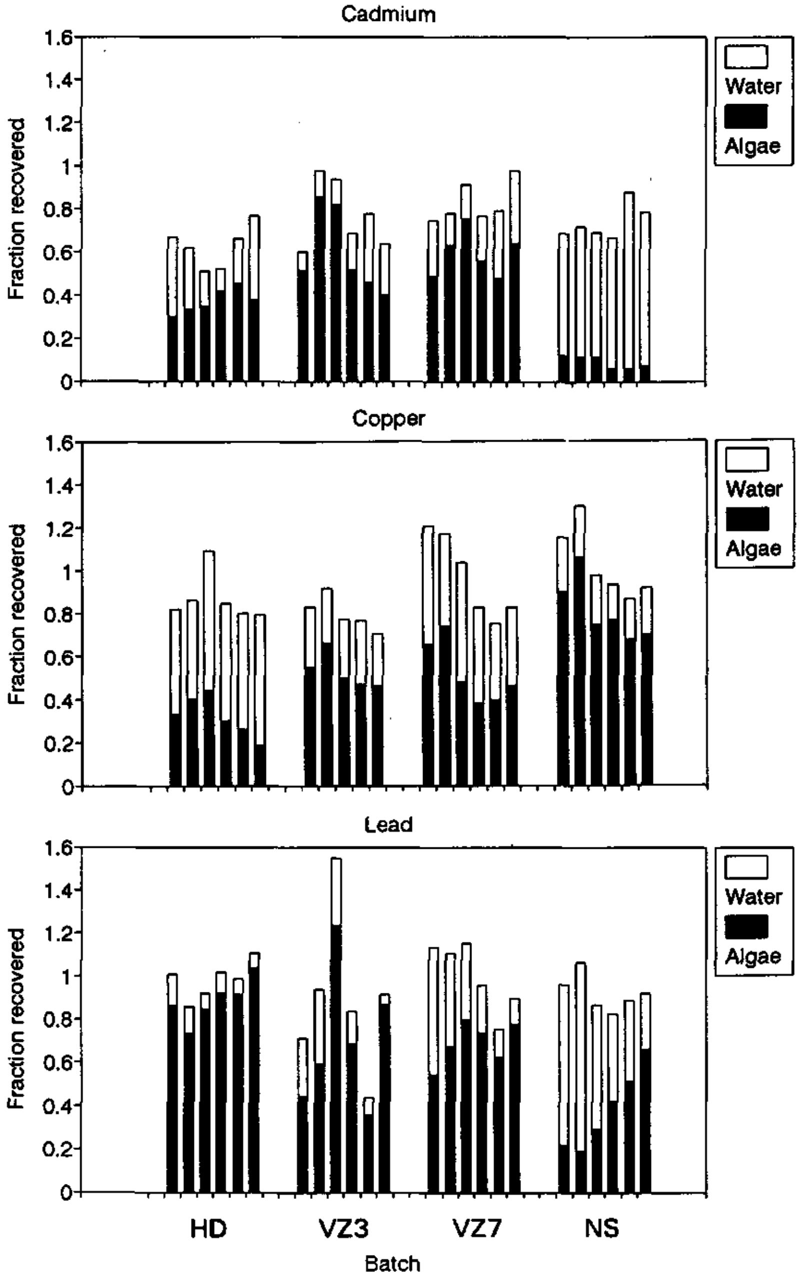

Fig. 2: Mass balances for individual batches used for the measurement of adsorption isotherms, for (A) Cadmium, (B) Copper and (C) Lead. The mass balances are calculated as the recovered amount after phase separation as fraction of the added amount.

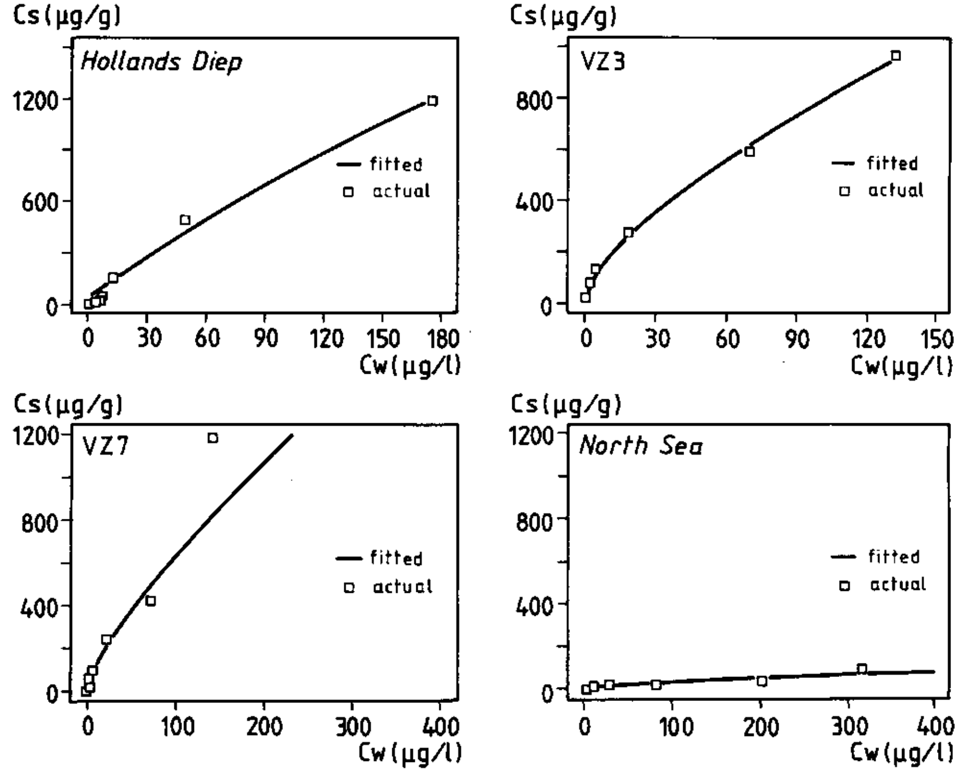

Fig. 3: Adsorption isotherms for cadmium to *Anabaena* spp in water sampled at (A) Hollandsch Diep, (B) VZ3, (C) VZ7 and (D) the North Sea. Curves represent non-linear least squares estimate to the Freundlich equation.

Adsorption isotherms are presented in the figures 3, 4 and 5. Generally, the isotherms fitted well to the Freundlich equation. The fit is worst for Pb, followed by Cu. This is caused by the lower sensitivity of the analytical methods for these metals, as compared to Cd, and the corresponding larger interference of matrix effects. The shape of the isotherms for Cd and Cu indicates that no precipitation reactions occurred. In that case, an increase in *Cs* at constant *Cw* would be observed. The isotherms have such total aqueous metal concentration ranges that in fresh waters ($Cl^- \approx 8$ mg/l, no dissolved organic matter), carbonate and hydroxide precipitates with Cu and Pb might be formed [24]. However, in our 0.8 μm filtrates Cl^- and organic ligand concentrations are so high that no saturation with regard to hydroxide or carbonate precipitates is reached. Complexation with Cl^- is especially important for Cd. Long and Angino [25] showed that at $Cl^- >$ 8 mg/l and pH=8.5, more than 90% of total Cd is present as the free ion Cd^{2+} or as the chloride complexes $CdCl^+$ and $CdCl_2$. Pb and Cu also form complexes

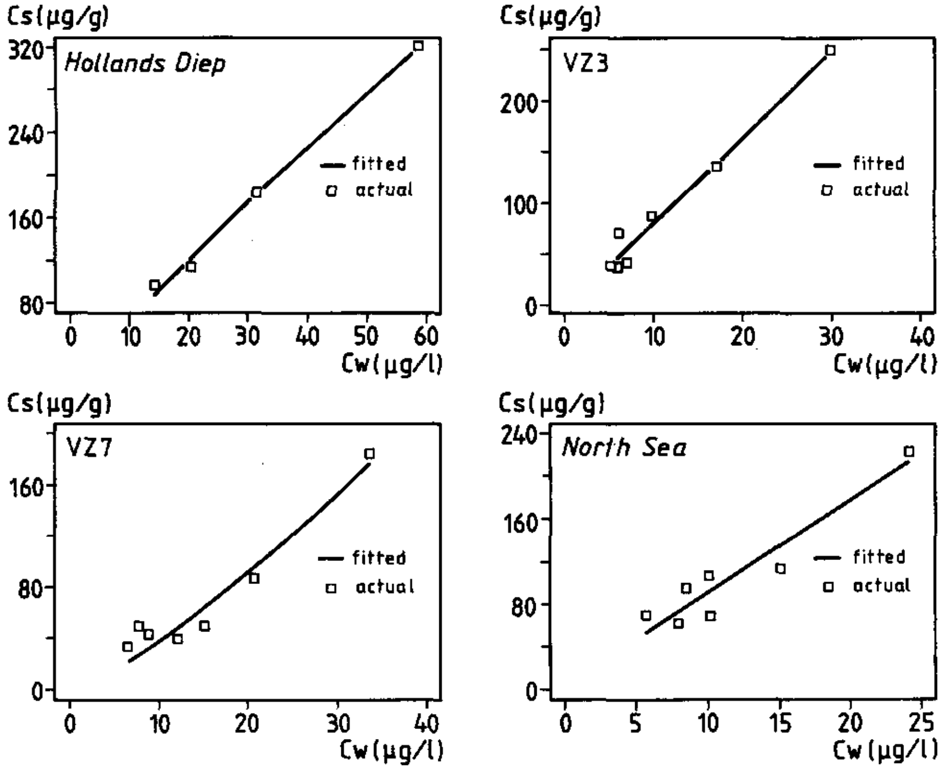

Fig. 4: Adsorption isotherms for copper to *Anabaena* spp in water sampled at (A) Hollandsch Diep, (B) VZ3, (C) VZ7 and (D) the North Sea. Curves represent non-linear least squares estimate to the Freundlich equation.

with Cl^-. Further they have been found to form extremely stable complexes with natural organic ligands [24,26] which increases the aqueous solubility for these metals. Verweij [26], who studied Cu speciation in Lake Tjeukemeer, reported >90% of Cu bound with organic ligands (DOC=20-40 mg/l) at pH values between 8 and 9.

The isotherms are based on eight data points: six resulting from the batches spiked in the laboratory, and two resulting from the "blank" batches. The values for these (identical) blank batches relate to the background metal concentrations caused by the presence of trace metals in the original culture medium and by the possible presence of heavy metals in the surface waters used. For Cd aqueous concentrations were sometimes below the detection limit for the blank batches. Consequently, some Cd isotherms contain only six or seven data points. Especially for Pb and Cu no clear trend exists in the three or four points at lower concentrations. Apparently, background concentrations for these metals were too high compared to the added amounts.

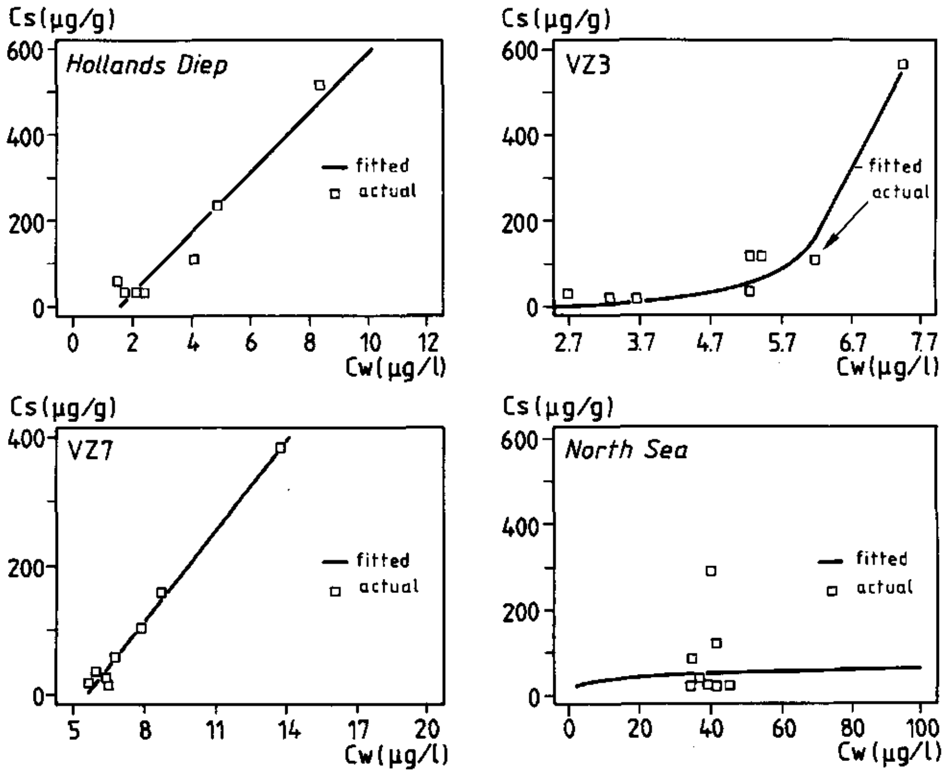

Fig. 5: Adsorption isotherms for lead to *Anabaena* spp in water sampled at (A) Hollandsch Diep, (B) VZ3, (C) VZ7 and (D) the North Sea. Curves represent non-linear least squares estimate to the Freundlich equation.

The isotherms were meant to describe the metal distribution under the environmental conditions and concentration ranges found in Lake Volkerak/Zoom. An overview of the lowest aqueous concentrations of the isotherms and recent aqueous metal concentrations in the lake is given in Table 1. It appears from the Table that the Cd concentrations at VZ7 and HD16/17 are covered by the isotherms. The aqueous Cd concentration at VZ3 is a factor 45 lower than the lowest concentration in the isotherm. However, considering the good fit to the Freundlich equation, extrapolation of the isotherm to lower concentrations seems justified. For Cu, aqueous concentrations are only a factor two below the lowest isotherm concentration, so extrapolation is also allowed in this case. For Pb, the isotherms do not fit well to the Freundlich equation and the actual concentrations in the lake are 10 - 60 times lower than the isotherm concentrations. Although our judgement may contain some arbitrary elements, we conclude that for Pb no extrapolations should be made.

TABLE 1:
Aqueous phase metal concentrations in four surface waters

location[a]	Cadmium		Copper		Lead	
	is.[b] (μg/l)	natural[c] (μg/l)	is.[b] (μg/l)	natural[c] (μg/l)	is.[b] (μg/l)	natural[c] (μg/l)
HD16/17	0.09	0.17	6.2	3.5	0.09	0.0
VZ3	0.9	0.02	5.4	2.5	2.7	0.3
VZ7	0.01	0.03	3.2	2.6	5.7	0.1
NS	4.8	[d]	5.7	[d]	34.3	[d]

(a) HD= Hollandsch Diep, VZ3= Lake Volkerak, VZ7= Lake Zoom; (b) Lowest aqueous metal concentration of the isotherm; (c) Concentration in actual natural water (data from the Institute of Fresh Water Management and Waste Water Treatment, The Netherlands); (d) Data not available.

The (empirical) sorption model parameters are listed in Table 2. In the table also the range in pH values measured at the moment of phase separation is listed. The ranges show that despite the pH adjustments made, the isotherms are measured at a pH a little higher than the planned value of 8.5. For each isotherm only the parameters for the most significant sorption model are reported. In most cases, these are the Freundlich parameters calculated with Marquards' algorithm for non-linear regression [14]. In some cases for Pb a linear model with negative non-zero intercept was selected. A negative non-zero intercept suggests some systematic error in the measured concentrations, probably due to contamination of the aqueous phase samples, or the presence of a constant aqueous metal fraction which does not participate in the distribution process. It is plausible that certain aqueous Pb species do not participate in the distribution process. However, it is unlikely that aqueous Pb species can make up 100% of all Pb species at $Cs=0$. Several authors report a high affinity of Pb for algal cells [27]. Therefore, we assume that some systematic error occurred, in which case the best estimate of the distribution coefficient will be the slope of the line. Linear isotherms result in constant K_d at varying metal concentration. A Freundlich isotherm with $n<1$ results in a decrease in K_d with increasing metal concentration. To enable comparison of distribution coefficients, a 'standard' distribution coefficient $K_d^{0.05}$ was defined as the Cs/Cw ratio at an aqueous concentration (Cw) of 0.05 μg/l. These standard K_d values are included in Table 2 and can be calculated from Freundlich parameters according to:

$$K_d^{0.05}=\frac{K_f\times 0.05^n}{0.05} \qquad (4)$$

TABLE 2:
Freundlich parameters for metal sorption in surface waters of different chlorinity.

isoth. (a)	K_f^1 ± SE (b)	n ± SE^2 (c)	r^2 (d)	F-ratio (e)	N^3 (f)	pH-range (g)	K_d (h)
Cadmium							
HD mf	16.9 ± 5.3	0.83 ± 0.06	0.991	382.0	7	8.5-9.0	1.4
VZ3 mf	38.0 ± 5.5	0.66 ± 0.03	0.997	1307.5	6	8.6-9.1	5.3
VZ7 mf	29.3 ± 6.9	0.63 ± 0.06	0.974	162.1	8	8.5-9.5	4.4
NS lf	0.73 ±	0.77 ± 0.08	0.956	86.4	6	8.3-8.4	0.07
Copper							
HD mf	7.9 ± 1.4	0.91 ± 0.05	0.995	1078.1	4	8.5-9.0	0.52
VZ3 mf	7.5 ± 1.0	1.03 ± 0.08	0.973	260.0	7	8.6-9.1	0.34
VZ7 mf	2.2 ± 1.1	1.25 ± 0.16	0.934	110.6	7	8.5-9.5	0.05
NS mf	9.9 ± 4.0	0.96 ± 0.14	0.889	116.7	7	8.3-8.4	0.56
Lead							
HD lin	70.1 ± 7.8	n≡1	0.941	80.2	7	8.5-9.0	$70^{(i)}$
VZ3 mf	$(2\pm3)\times10^{-3}$	6.36 ± 0.83	0.953	96.3	8	8.6-9.1	-
VZ3 lin	88.8 ± 30	n≡1	0.600	9.0	8	8.5-9.5	$89^{(i)}$
VZ7 lin	46.9 ± 2.4	n≡1	0.985	387.8	8	8.3-8.4	$47^{(i)}$
NS	(no correlation between *Cs* and *Cw*)		0.05				

(a) Isotherm and model code. For explanation of isotherm (surface water) code, see table 1. Model code: mf=Freundlich estimated using non-linear Marquard algorithm, lf=Freundlich estimated using linear regression on log - log transformed data, lin= linear isotherm estimated using linear regression; (b) Freundlich constant (for linear model K_d); (c) Freundlich exponent (for linear model equal to 1); (d) correlation coefficient; (e) SS-regression/SS-residuals; (f) Number of data points in the isotherm; (g) pH range of the batches, at the moment of phase separation; (h) Hypothetical K_d value (l/g) calculated from the model parameters by extrapolating *Cw* to 0.05 µg/l; (i) Slope of linear isotherm with non-zero intercept.

The calculation of $K_d^{0.05}$ values is an extrapolation to low aqueous concentration. Therefore, the $K_d^{0.05}$ values in general, but especially those derived from isotherms with non-zero intercept should be interpreted with caution.

For Cd and the surface waters sampled at VZ3, VZ7 and NS, an inverse correlation is found between K_f^{Cd} and log[Cl^-], or between $K_d^{0.05}$ and log[Cl^-]. This observation is based on three chloride concentrations only, but agrees with literature data [28]. A simple speciation model which accounts for the effect of complexation by chloride on the K_d is given in the next section. The K_f values for VZ3 and VZ7 of 38 and 29 l/g are close to literature values of 22-31 l/g for Cd sorption to *Cryptomonas* [11] and of 22 l/g for Cd sorption to *Asterionella formosa* [29]. The reason for the diverging behavior of the algae in water sampled from the Hollandsch Diep (HD) remains unknown. A key factor may be the difference between the algae in waters of different chlorinity, which develops in time. As a result of the different chlorinities and the different, possibly toxic, metal concentrations, the sorption and uptake characteristics of the algae in the individual batches will probably change during equilibration. The differences among the values for the exponent 'n' for the surface waters sampled at the four locations, are difficult to interpret. The significance of the influence of chlorinity on the isotherms for Cd was established by an analysis of variance of the log - log transformed Freundlich isotherms, following a procedure described by Sokal [15]. It appears that the transformed isotherms for Cd in the set HD/VZ3/VZ7 and the set HD/VZ3/VZ7/NS are different at a significance level of 0.0012 and 0.0006 respectively.

Also the data for Cu suggest some influence of chlorinity. Except in water sampled at the North Sea, the K_f and K_d values decrease with increasing chlorinity. However, the differences are not significant ($p > 0.1$). In water sampled from the North Sea, the K_d for Cu is larger than the K_d for Cd. In VZ3, VZ7 and HD water, the order is reversed. Compared to Cd, the Freundlich exponents for Cu are closer to one. HD differs by a high affinity constant K_f. Besides the influence of water composition, such differences in K_d among surface waters may relate to the toxicity of the metals to phytoplankton. At low concentrations, the metals are taken up and have no toxic effects or are used as essential trace elements. However, at different toxic concentrations, different physiological responses may occur. Therefore, the mechanism of bioaccumulation may be depending on metal concentration. Further, at a certain total metal concentration, the toxic concentration is influenced by the metal speciation and thus by chloride and the other components in the water [26,30,31].

For Pb no significant correlation between *Cs* and *Cw* is found in water sampled from the North Sea. The most plausible explanation is the higher detection limit for Pb, the high contribution of matrix effects in the AAS determination, and the high background concentration of Pb in the seawater. Because of these reasons, the amounts added in the laboratory were too small to cause significant differences among the batches. Another explanation may be some precipitation of carbonate species [24]. For the set surface waters HD, VZ3 and VZ7 no significant influence of chloride on sorption characteristics was proven (different at $p=0.386$). Including NS increases the significance level to $p=0.087$. However, because the Pb/NS isotherm shows no correlation between *Cs* and *Cw*, this evidence is not conclusive.

A speciation model for the influence of chloride on the K_d for Cd

In this section a simplified model for the influence of complexation by chloride on the K_d is described. Because the contribution of $CdCl_n$ complexes with $n > 2$ is negligible in surface waters [24], the model only considers $CdCl^+$ and $CdCl_2$ complexes. Accordingly, the complexation of Cd by chloride can be described by the following reaction equations and equilibrium expressions:

$$Cd^{2+}+Cl^{-} \rightleftarrows CdCl^{+} \qquad K_1=\frac{[CdCl^{+}]}{[Cd^{2+}][Cl^{-}]} \tag{5}$$

$$Cd^{2+}+2Cl^{-} \rightleftarrows CdCl_2 \qquad K_2=\frac{[CdCl_2]}{[Cd^{2+}][Cl^{-}]^2} \tag{6}$$

If it is assumed that only the free aqueous Cd^{2+} ion adsorbs [26,30] by formation of a surface complex with the phytoplankton cells [13,27,32], that competition among metals at trace levels for surface sites can be neglected, and when charges are omitted for convenience, bioaccumulation at constant pH is described by:

$$Cd^{2+}+Alga \rightleftarrows Alga\text{-}Cd \qquad K_3^c=\frac{[Alga\text{-}Cd]}{[Cd^{2+}][Alga]} \tag{7}$$

in which K^c_3 is a conditional complexation constant, valid under the prevailing experimental conditions. In equation (7), 'Alga' represents a binding site at the algal surface, available for Cd. The formation of the surface complex 'Alga-Cd' causes a saturation of the surface, which is consistent with the measured convexity of the sorption isotherms at higher Cd concentrations.

The distribution coefficient K_d is defined as the ratio of the adsorbed concentration, and the total aqueous concentration, the latter being operationally defined by the 0.8 μm pore diameter of the filters used. Therefore, all complexes with chloride and other ligands L_i contribute to the aqueous concentration. In formula:

$$K_d=\frac{[Alga\text{-}Cd]}{[Cd^{2+}]+[CdCl^{+}]+[CdCl_2]+\sum[Cd(L_i)_j]} \tag{8}$$

By taking the reciprocal of (8), and elimination of the free aqueous Cd ion and the Cd complexes using (5), (6) and (7), (8) can be written as:

$$\frac{1}{K_d}=\frac{K_1[Cl^{-}]}{K_3^c[Alga]}+\frac{K_2[Cl^{-}]^2}{K_3^c[Alga]}+\frac{1}{K_3^c[Alga]}+\sum\frac{K_i[L_i]^j}{K_3^c[Alga]} \tag{9}$$

At low Cd concentrations, the adsorbed amount of Cd is small compared to the number of binding sites on the algal surface and the concentration of unoccupied binding sites '[Alga]' can be considered constant. If it is further assumed that other ligands than chloride play a negligible role, then the last term in (9) can be neglected, which reduces

(9) to:

$$\frac{1}{K_d} \approx C \times (1 + K_1[Cl^-] + K_2[Cl^-]^2) \tag{10}$$

with

$$C = \frac{1}{K_3^c[Alga]} = constant \tag{11}$$

Exclusion of other ligands than Cl^- in (9), is allowed when the different K_i and the concentrations of complexing ligands are such that $K_1[Cl^-]+K_2[Cl^-]^2+1$ is (much) larger than $\Sigma K_i L_i$. The testing of this condition can be established with speciation calculations for which many computer programs are available. Instead we refer to reports by Long and Angino [25], and Bodek and co-workers [24] who show that in surface waters with $Cl^- >$ 8 mg/l, Cd chloride complexes compete successfully with the other ligands and with sparingly soluble precipitates, such as $Cd(OH)_2$, CdO, $CdCO_3$, CdS and $Cd_3(PO_4)_2$. Because in our batches chloride concentrations are much higher than 8 mg/l (Table 3), the use of (10) is allowed. With equation (10) no absolute K_d values can be calculated because the magnitude of the C-term is unknown. However, since this value does not change with chloride concentration under the assumptions made, *relative* K_d values can be calculated for the chloride concentrations in our experiments. For the complexation constants literature values are used: $K_1=100$, en $K_2=400$ ([24], at zero ionic strength). These complexation constants were corrected for the different ionic strengths of the four surface waters in this study using the Davies approximation for calculation of ion activity coefficients [24]. Because the water composition was not known completely, ionic strength values (I) were estimated from electric conductivity (EC, see Table 3) using the empirical relation [24]:

$$I = 1.6 \times 10^{-5} \times EC \tag{12}$$

The results of these calculations are presented in Table 3. In the table the K_d for VZ3 is scaled arbitrarily to 1. By similar normalization of the standard $K_d^{0.05}$ values (Table 2) which were estimated from the measured isotherms, the measured differences can be compared with the differences predicted by the model. It appears that the normalized measured coefficients for VZ7 and NS agree well with the normalized predicted coefficients. For water sampled from the Hollandsch Diep a lower K_d is measured than predicted. One explanation for the lower K_d may be a diverging physiology of the algae. Second, because the Cl^- concentration was not very high, ligands other than Cl^- may have had a significant effect, in which case simplification of (9) is not allowed. Our results show that the phytoplankton/water distribution of Cd in waters of different salinity is regulated by the free Cd^{2+} activity in solution, which is determined by the combined effect of complexation by (mainly) Cl^- and increasing ionic strength. This agrees with results reported by Comans and Van Dijk [33] who studied Cd uptake by suspended particles from the River Rhine at different salinity.

TABLE 3:

Comparison of measured and predicted relative distribution coefficients for Cd and *Anabaena* spp.

						relative to K_d^{VZ3}	
Location[(a)]	Cl^- (mg/l)	EC[(b)] (mS/cm)	I[(c)] (mM)	K_1[(d)]	K_2[(d)]	model K_d	measured K_d
HD	100.2 ± 1.8	0.75	12	65	289	1.2	0.3
VZ3	266.7 ± 4.3	1.43	23	56	259	1.0	1.0
VZ7	544.1 ± 10.9	2.43	39	49	235	0.8	0.8
NS	15735 ± 360	45.1	722	33	172	0.03	0.014

(a) For explanation of location codes, see Table 1; (b) Electric conductivity; (c) Ionic strength, calculated from EC using eqn. (12); (d) Equilibrium constants for complexation with chloride according to eqn. (5) and (6), corrected for ionic strength using the Davies approximation for ion activity coefficients [24].

The influence of mineralization on the adsorption of heavy metals to *Anabaena* spp

The effect of mineralization on the distribution of Cd, Cu and Pb was investigated in two experiments. The two experiments differed only in the amount of metals added and the sampling inervals. For each experiment, a large batch of *Anabaena* was equilibrated with the metals and was allowed to age and mineralize under dark conditions. The redistribution of the metals between solid and aqueous phase was measured as a function of time.

The time course of the mineralization process for experiment 1 is pictured in Figure 6. It appears that dry weight decreased from approximately 180 mg/l to 16 mg/l in 42 days in the first experiment. In this period the volume was corrected for volatilization so that the dry weights can be used to estimate the mineralization rate constant. The dry weight data for the first experiment fitted well to the first order model for algal mineralization kinetics described by Jewell and McCarty [34]:

$$\ln\frac{(M-fM_0)}{(M_0-fM_0)}=-k't \qquad (13)$$

in which M is total mass at time t, f is the refractory fraction of the total algal-related material at time zero (M_0), and k' is a first order rate constant. This model was fitted to the data for the first mineralization experiment, using Marquardts' algorithm for non-linear regression. Regression estimates (± standard error, 20 observations fitted) for the refractory fraction f and the rate constant k' were 0.115 ± 0.008 and 0.30 ± 0.018 day^{-1} respectively. These values are a little higher but agree well with data reported by Otten and co-workers [35], who measured a refractory fraction of 0.07 and a rate constants of 0.06 to 0.19 d^{-1} for the cyanobacterium *Oscillatoria limnetica*. Dry weights, chloride concentrations and electric conductivity, the latter as a measure of total ionic strength, are presented in Table 4. In the second experiment algal decay was very similar as was concluded from the absorption spectra (not shown). The second experiment was carried out in a constant volume till 14 days. After the periods in which volumes were corrected, some concentration took place as can be seen from the dry weights (Table 4). Chloride concentrations were approximately 20% higher than in the first experiment.

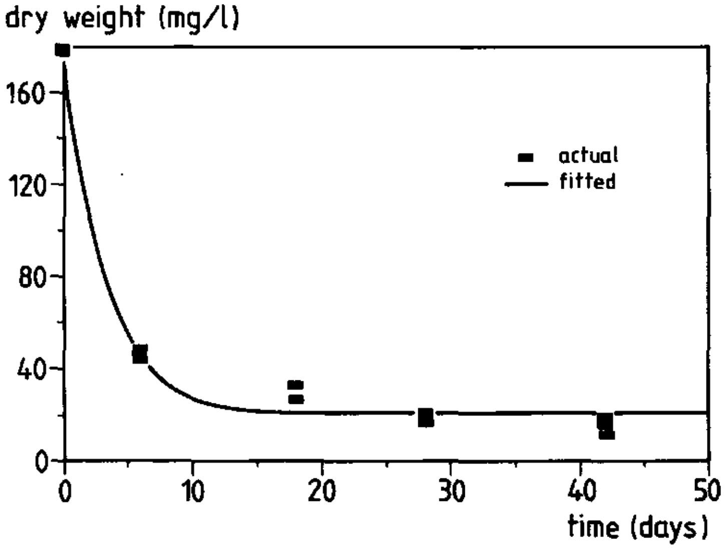

Fig. 6: Dry weight as a function of time, during mineralization of *Anabaena* spp in the presence of Cd, Cu and Pb. The continuous line represents the model fit to the data for experiment 1.

TABLE 4:
Dry weight, chlorinity and electric conductivity during mineralization
Experiment 1

day:	0	6	18	28	42
	constant volume				
Dry weight (mg/l):	178.3	45.6	28.6	18.1	16.3
(± s.d., n=4)	± 1.1	± 2.5	± 3.3	± 2.0	± 3.5
Chlorinity (mg/l):	245.6	257.9	288.1	274.6	256.7
(± s.d., n=5)	± 2.2	± 7.5	± 1.0	± 9.0	± 2.2
Conductivity (mS/cm)	1.49	1.70	1.98	2.03	1.92

Experiment 2

day:	0	7	14	30	71
	constant volume				
Dry weight (mg/l):	182.6	58.4	15.4	32.2	85.4
(± s.d., n=4)	± 2.9	± 2.2	± 3.7	± 1.8	± 3.9
Chlorinity (mg/l):	297.8	335.1	392.5	290.0	334.1
(± s.d., n=5)	± 2.2	± 2.2	± 2.0	± 5.3	± 4.1
Conductivity (mS/cm)	1.53	1.86	2.18	1.65	1.84

Distribution of Cd, Cu and Pb

In the experimental procedure used, a certain contamination by metals cannot be avoided. Besides the known amounts added in the laboratory and contamination, other metal sources were the background metal levels in the surface water and the trace levels present in the algal cells because of the original growth media. These inputs were considered as an extra but unknown spike of metals, which participate in the distribution process. Consequently, mass balances based on the known spike concentrations are meaningless and provide no information on experimental quality. Instead, mass balances were calculated as the amount recovered after phase separation, relative to the amount measured in the total suspension. The latter amounts vary to some extent because of possible contamination, volatilization of water and sorption of metals to other than algal surfaces. The mass balances are presented as the total heights of the bars in the figures 7

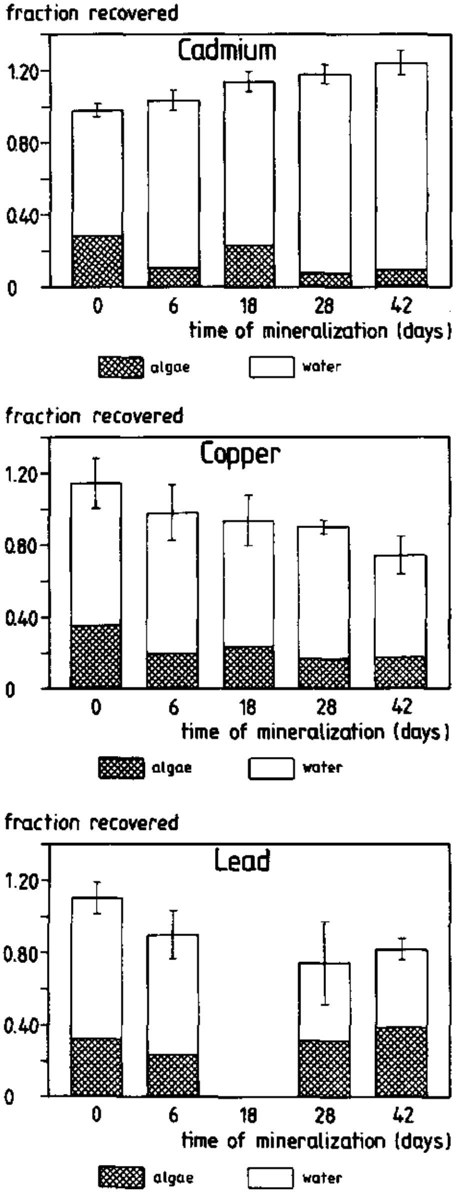

Fig. 7: Mass balances for (A) Cd, (B) Cu and (C) Pb as a function of decomposition time for experiment 1. Bound and aqueous fractions are calculated relative to the amount measured in the total algal suspension. Error bars refer to n=4 standard deviations.

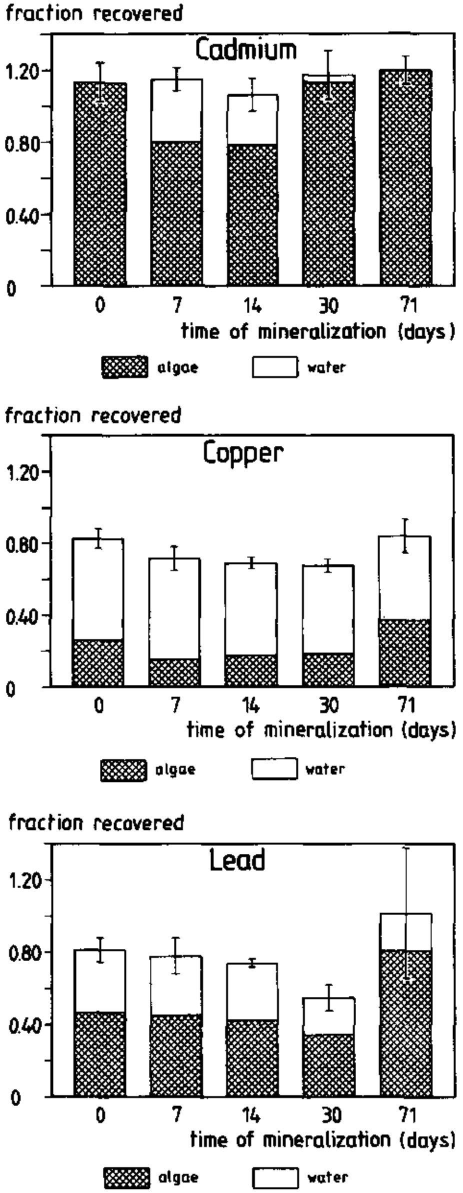

Fig. 8: Mass balances for (A) Cd, (B) Cu and (C) Pb as a function of decomposition time for experiment 2. Bound and aqueous fractions are calculated relative to the amount measured in the total algal suspension. Error bars refer to n=4 standard deviations.

and 8. The error bars refer to the propagated standard deviations in the mass balances which were calculated from the quadruplicate determinations of the fractions recovered from water and algae, and the concentration in the total suspension. The balances do not differ significantly from 100%. In the first experiment (Figure 7) the ranges are Cd: 98-124%, Cu: 74-114% and Pb 74-110%. In the second experiment these ranges are Cd: 106-120%, Cu: 67-84% and Pb: 55-102%. The difference from 100% is caused by the same factors as mentioned in the previous section. Whether the metals are mobilized as a result of decomposition can be seen directly from the figures 7 and 8 by comparing the shaded areas, which represent the bound fractions, with the total heights of the columns. In the first experiment, some Cd (Figure 7 A) seems to be transferred to the aqueous phase. For Cu (Figure 7 B), the bound fraction remains approximately constant till day 42. For Pb (Figure 7 C) the bound fraction increases in time. In the second experiment, aqueous Cd could be detected in two cases only (Figure 8 A). However, the results for the first 14 days suggest some mobilization of this metal. As in the first experiment, the bound fraction for Cu (Figure 8 B), is approximately constant and increases for Pb (Figure 8 C). As indicated in equation (1), when temperature and water composition are constant, mobilization of a metal as a result of decomposition, depends on the combined effect of the decrease in biomass and possible changes in the distribution coefficient K_d. When K_d remains constant, the metal can be expected to be transferred to the aqueous phase. However, when K_d increases, for instance because of a change in sorption affinity and capacity or aqueous phase composition, the bound fraction may remain constant or even may increase. Because the concentration of detritus decreases a factor ten in experiment 1 while the bound fractions do not change much (Cd, Cu) or increase (Pb), an increase of K_d follows from the observations.

The numerical values of total, aqueous and bound concentrations, and distribution coefficients are presented in Table 5 (experiment 1) and Table 6 (experiment 2). All standard deviations relate to quadruplicate determinations, unless indicated otherwise. The small relative error in Cw and C_{total} illustrates the quality of the experimental and analytical procedures used. The errors in C_{algae} and C_{bound} are larger because of the large error in the algal dry weight determination and the larger number of sample manipulations. Distribution coefficients are plotted as a function of mineralization time in Figures 9. In experiment 1 (Figure 9 A) the coefficients increase in time and are highest for Pb, followed by Cu. This order agrees to those reported in the literature for bioaccumulation of metals to algae [36,37]. It must be noted that in case of a non linear sorption isotherm, the K_d is dependent on the total metal concentration. Whether the K_d increases or decreases with changing total metal concentration, depends on the shape of the isotherm for the mineralizing material. For the fresh cells, most isotherms are practically linear since the Freundlich exponents are close to one (Table 2). However, the differences in aqueous phase concentrations during mineralization are so small, especially for Pb and Cd, that no significant influence is expected. For experiment 2 (Figure 9 B), K_d values increase in the period in which was corrected for volatilization. After 14 days, the K_d values decrease which is attributed to some precipitation of calcite. As a result, the data after 14 days do not relate to sorption to detritus only. For experiment 2, Cd is the metal with the highest K_d values. Also this difference in the affinity series between the experiments can be explained by non-linear isotherms and the different aqueous metal concentrations as compared to the first experiment.

TABLE 5:
Distribution of Cd, Cu and Pb over *Anabaena* spp and water as a function of mineralization time for experiment 1. All standard deviations relate to quadruplicate determinations.

time (day)	C_{total}[(a)] (μg/l)	C_w[(b)] (μg/l)	C^{bound}[(c)] (μg/l)	C_{algae}[(d)] (μg/g)	K_d (l/g)
Cadmium					
0	14.8 ± 0.2	10.4 ± 0.5	4.15 ± 0.23	23.3 ± 1.2	2.24 ± 0.06
6	14.8 ± 0.6	13.8 ± 0.5	1.49 ± 0.04	32.7 ± 1.1	2.37 ± 0.12
18	15.9 ± 0.3	14.5 ± 0.6	3.60 ± 0.57	126 ± 10	8.71 ± 0.86
28	15.4 ± 0.6	16.9 ± 0.2	1.16 ± 0.01	60 ± 11	3.52 ± 0.63
42	14.3 ± 0.7	16.4 ± 0.5	1.31 ± 0.05	84 ± 19	5.10 ± 1.19
Copper					
0	24.4 ± 2.7	19.3 ± 1.3	8.63 ± 0.66	48.4 ± 3.7	2.51 ± 0.20
6	37.3 ± 5.7	29.2 ± 1.1	7.31 ± 0.18	152 ± 20	4.86 ± 0.86
18	53.0 ± 3.4[(e)]	37.4 ± 5.4	12.2 ± 4.07	429 ± 152	11.8 ± 4.5
28	43.7 ± 1.1	32.0 ± 1.3	7.23 ± 0.29[(e)]	403 ± 38	12.7 ± 0.80[(e)]
42	42.6 ± 5.9	24.3 ± 0.5[(e)]	7.27 ± 0.14	489 ± 111	21.4 ± 4.6[(e)]
Lead					
0	16.8 ± 0.9	13.2 ± 0.4	5.35 ± 1.00	30.0 ± 5.5	2.27 ± 0.35
6	23.8 ± 3.5[(e)]	15.8 ± 0.3	5.56 ± 0.42	122 ± 13	7.76 ± 0.83
18	- -	2.11 ± 0.26	74.4 ± 9.8	-	
28	32.7 ± 8.6[(e)]	14.1 ± 1.0	10.26 ± 3.71	565 ± 181	39.8 ± 12.0
42	30.1 ± 1.4	13.1 ± 0.7	11.63 ± 1.25	623 ± 30	47.5 ± 0.60

(a) Concentration measured in total suspension; (b) Concentration measured in filtrate (0.8 μm poresize) of algal suspension; (c) Concentration measured in algae isolated by filtration, referenced to suspension volume; (d) Concentration measured in algae isolated by filtration, on algal dry weight basis; (e) Outliers removed (Dixon, Q-test, $\alpha=0.05$)

TABLE 6:

Distribution of Cd, Cu and Pb over *Anabaena* spp and water as a function of mineralization time for experiment 2. All standard deviations relate to quadruplicate determinations.

time (day)	$C_{total}^{(a)}$ (μg/l)	$C_w^{(b)}$ (μg/l)	$C^{bound(c)}$ (μg/l)	$C_{algae}^{(d)}$ (μg/g)	K_d (l/g)
Cadmium					
0	2.14 ± 0.04	n.d.	2.42 ± 0.23	13.3 ± 1.4	-
7	2.19 ± 0.04	0.77 ± 0.01$^{(e)}$	1.75 ± 0.13	30.1 ± 3.1	37.2 ± 6.7
14	2.61 ± 0.07	0.73 ± 0.02$^{(e)}$	2.05 ± 0.03$^{(e)}$	125 ± 17$^{(e)}$	172 ± 18$^{(e)}$
30	1.29 ± 0.10	n.d.	1.46 ± 0.12	45.2 ± 2.7	-
71	1.62 ± 0.05	n.d.	1.94 ± 0.11	22.8 ± 2.0	-
Copper					
0	20.3 ± 0.2	11.5 ± 1.0	5.29 ± 0.28$^{(e)}$	28.9 ± 1.2$^{(e)}$	2.9 ± 0.6
7	45.9 ± 3.4	25.8 ± 1.7	7.03 ± 0.65	121 ± 13	4.7 ± 0.5
14	53.8 ± 2.2	27.8 ± 0.5	9.25 ± 0.46$^{(e)}$	626 ± 140$^{(e)}$	22.5 ± 5.1$^{(e)}$
30	21.0 ± 0.8	10.3 ± 0.5	3.83 ± 0.26	119 ± 13	11.6 ± 1.3
71	12.3 ± 1.3	5.8 ± 0.3	4.52 ± 0.12$^{(e)}$	52.2 ± 1.9	10.5 ± 2.4
Lead					
0	6.09 ± 0.27	2.11 ± 0.34	2.84 ± 0.10$^{(e)}$	15.6 ± 0.33$^{(e)}$	6.8 ± 1.1$^{(e)}$
7	7.58 ± 0.61	2.50 ± 0.57	3.41 ± 0.09$^{(e)}$	58.2 ± 3.1$^{(e)}$	29.0 ± 5.9
14	8.71 ± 0.16$^{(e)}$	2.75 ± 0.14$^{(e)}$	3.70 ± 0.04$^{(e)}$	249 ± 47$^{(e)}$	80.2 ± 8.2$^{(e)}$
30	10.1 ± 1.1$^{(e)}$	2.07 ± 0.19	3.46 ± 0.35$^{(e)}$	107 ± 15$^{(e)}$	68.9 ± 28.8
71	11.1 ± 1.8	2.31 ± 0.37	8.93 ± 3.51	103 ± 37	47.0 ± 19.2

(a) Concentration measured in total suspension; (b) Concentration measured in filtrate (0.8 μm poresize) of algal suspension; (c) Concentration measured in algae isolated by filtration, referenced to suspension volume; (d) Concentration measured in algae isolated by filtration, on algal dry weight basis; (e) Outliers removed (Dixon, Q-test, $\alpha=0.05$).

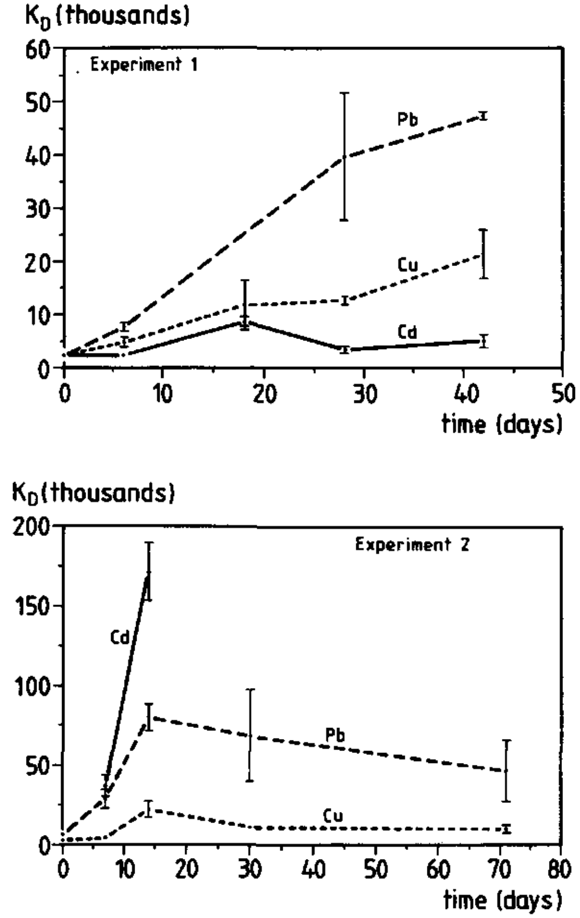

Fig. 9: Distribution coefficients for Cd, Cu and Pb as a function of time, in a mineralizing suspension of *Anabaena* spp. A=experiment 1. B=experiment 2.

For an increase of K_d with the degree of mineralization at constant pH, chloride concentration and temperature, several explanations can be given. First, sorption may be (partially) irreversible so that redistribution after mineralisation is impossible, or is strongly retarded. However, because the time intervals between sampling were large (more than six days) we assume that kinetics do not play a role, at least not after the first week. Second, mineralization may increase the surface available for sorption, for example by the breakdown of algal cells. Several studies provide strong evidence that sorption to the surface of microbial cells should be distinguished from (active) uptake/release processes through the cell membrane [6,7,13,27,32,38]. Another contribution to the surface available for sorption may be from growth of bacteria responsible for the mineralization of the algae. However, according to several authors (e.g. [34,39]), the decomposers usually represent only a small fraction of the total biomass. Further, our measurements of TOC and absorption spectra in the 0.8 μm filtrates do not support the hypothesis of abundant bacterial growth. Therefore, the effect of bacteria is considered small. Third, analogous to the effect of sediment concentration on sorption equilibrium constants for hydrophobic chemicals ([40] and references therein) the increase in K_d may be caused by the decrease in the solid to water ratio. Several authors report the same effect for heavy metal sorption (e.g., [17,20,41]). One explanation is that the solid to water ratio influences the clustering of algal cells, which effects the accessability of the algal surfaces for sorption. Another explanation is the incomplete phase separation during the filtration. In the filtrates particles <0.8 μm may remain. The binding of metals to these particles may cause the dependency on the solid to water ratio. For a full description of this effect, which is beyond the scope of the present discussion, the reader is referred to reference [40]. Besides changes in particulate matter concentration and composition, during the mineralization process also the aqueous phase changes. Due to mineralization, the concentration of complexing agents in the form of dissolved organic matter (DOM) may be larger which increases the operationally defined aqueous metal concentrations. Further, mineralization results in a downward shift in the size spectrum of the particulate material over time, as was also noted by Fisher and Wente [6]. Consequently, in time an increasing fraction of the particulate material is considered 'aqueous'. Our analysis does not provide further information on this aspect. However, when other factors would be constant, the increase in DOM and non-filterable particulate material would increase Cw and lower the K_d. Shephard et al [42] reported that in a freshwater lake 53% of the total Cd was complexed by organic ligands produced by aquatic macrophytes and phytoplankton. We conclude that with the available data it is not possible to discriminate quantitatively among the possible processes. Although the different processes may have counteracting effects, the nett effect measured in this study is an increase in K_d.

In Figure 10, a comparison is made between the actual course of the bound fraction as measured in the first experiment (with variable K_d), and the hypothetical time course which would have been measured if the K_d would have remained constant at the value of the first day. Because the actual K_d values increase, the bound fraction remains quite high, despite the disappearance of 90% of the initial biomass (upper curve). When the K_d would have remained constant, the amount of mobilized metals would have been much larger at the actual mineralization rate (lower curve). The difference between the curves clearly illustrates that variation in the distribution coefficient as a result of changing sorption characteristics, strongly influences the mobilization of heavy metals.

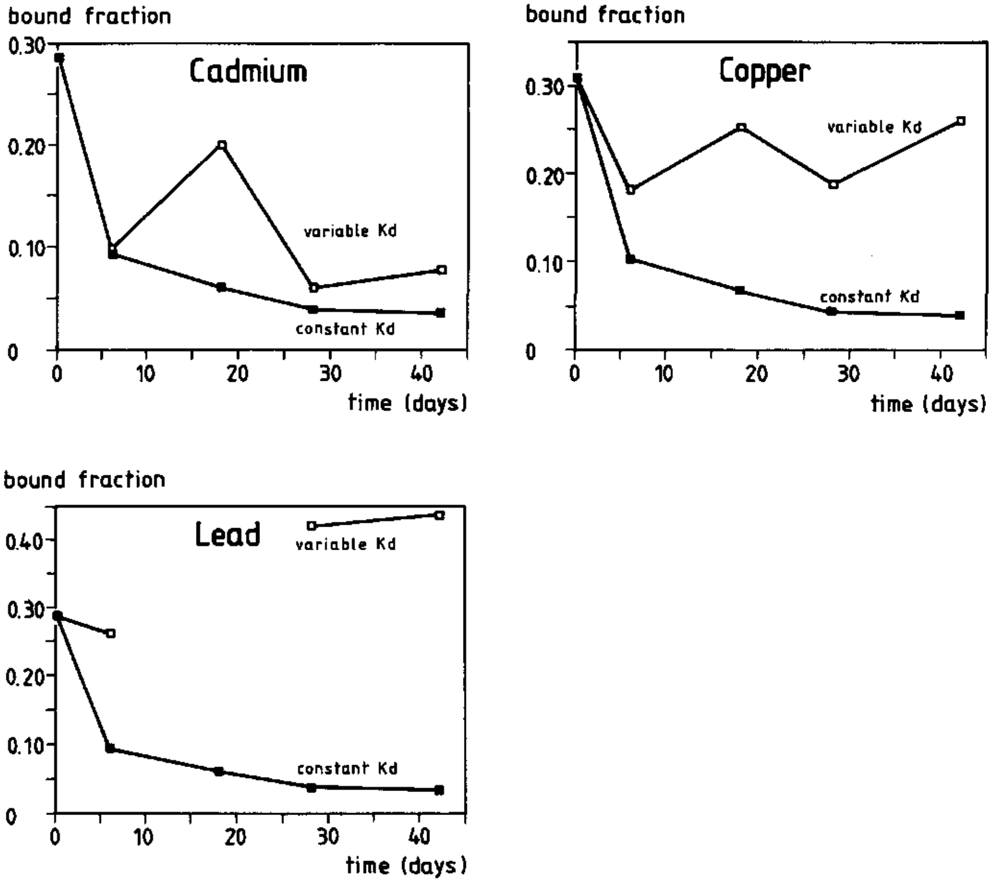

Fig. 10: Time course of the fraction bound metal for experiment 1. (—□— = actual course with variable K_d, —■— = hypothetical course if K_d would have remained constant at the value of day 0).

CONCLUDING REMARKS

Several conclusions can be drawn which are valid under the experimental conditions used in this study. The equilibrium distribution of Cd and Cu to *Anabaena* spp in surface waters with varying chloride concentrations can be described with the Freundlich equation. For Pb a linear isotherm is satisfactory. In general, the Freundlich affinity constant K_f decreases with increasing chloride concentration. It is demonstrated with the help of a simplified speciation model, that this decrease for Cd can be explained by complexation by chloride. The Freundlich exponent, which is a measure of the curvature of the isotherm, is relatively constant for Cd: range 0.63 - 0.77 for a range in chloride concentrations of 300 - 16.000 mg/l, and Cu: range 0.91 - 1.25 for a range in chloride concentrations of 100 - 16.000 mg/l. The K_d for *Anabaena* spp is largest for Pb, followed by Cd and finally Cu. Mineralization of *Anabaena* spp in a laboratory system with a chloride concentration range of 250-300 mg/l results in an increase in K_d for Cd (factor four), Cu (factor eight) and Pb (factor 10 - 20). The increase is attributed partially to a decrease in solid to water ratio, and partially to a higher affinity of the metals for the adsorbent. Because the increase in K_d is coupled to a decrease in the solid concentration because of mineralization, mobilization of the heavy metals is limited.

The experiments simulated processes that may occur in the environment. Phytoplankton species, temperature, pH and aqueous composition were close imitations of an actual fresh water lake (Lake Volkerak/Zoom). However, translation of the results to natural environmental systems is not straightforward. Retention of metals by phytoplankton is very variable among metals and species. In our experiments no mixed algal populations or grazers were present. Further, in natural systems fecal pellets contribute to the settling flux, a process not considered in our experiments. Although they were taken from a natural system, the bacterial populations may have developed quite different in our experiments. Aqueous metal speciation was not considered exhaustively and metal concentrations were still quite high as compared to many natural systems. Finally, also differences in light climate and turbulence which were not characterised may alter the results. Despite of this, an important generalisation can be made: The supposition that K_d values for mineralizing phytoplankton are constant, as in many water quality models, may result in a wrong estimate of the bound fraction. The extent to which this fraction is erroneous, depends on the course of the distribution coefficient and the solid to water ratio during the mineralization process.

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Chapter 10

SUMMARIZING DISCUSSION

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Summary

In the past decades, the worldwide increase in industrial activity has resulted in the contamination of air, water and soil. In water systems, the fate and bioavailability of contaminants is strongly influenced by sorption to aquatic particles, such as sediments, suspended solids, phytoplankton and detritus. To increase the understanding of this process, the equilibrium and kinetics of sorption of some chlorobenzenes and heavy metals to a wide variety of natural particles was investigated and described in this thesis (Chapter 2 - 5). Special attention was paid to sorption of micropollutants to phytoplankton and detritus (Chapter 6 - 9).

In aquatic systems, the sorption of heavy metals and hydrophobic organic compounds (HOCs), is strongly influenced by suspended solids composition. This composition may vary in space and time. In Chapter 2, the variation in particle composition and contaminant concentration was described and interpreted for Lake Volkerak/Zoom (The Netherlands). Heavy metals appeared to be correlated with clays and organic matter. For HOCs only organic matter content was significant, which in turn was mainly controlled by primary produktion. The seasonality in phytoplankton caused a strong seasonality in metal and HOC content of the suspended solids. Normalisation of metal concentrations to scandium removed most seasonality, and removed differences between sediment trap and continuous flow centrifuge samples. In contrast, organic carbon normalisation of HOC concentrations did not remove such differences. Particles with higher C/N ratios also had higher organic carbon normalised HOC concentrations. This suggests an influence of organic matter type on HOC sorption equilibrium, possibly in combination with nonequilibrium for sorption to phytoplankton.

To quantify the sorption equilibrium, usually the distribution or partition coefficient (K_p), being the ratio of the sorbed and dissolved pollutant concentration is used. Such coefficients can be calculated from field data or measured in the laboratory. To be able to measure HOC sediment/water partition coefficients, first the effect of incomplete phase separation has to be quantified. In Chapter 3, the frequently used Gschwend and Wu model [1] was criticized and adapted accordingly. The adapted model was tested on the partition coefficients for 1,2,3,4,-tetrachlorobenzene (TeCB) to three sediments which were measured at different sediment to water ratios with a batch equilibration method. Besides, the model was tested with a literature dataset for sorption of hexachlorobenzene (HCB). The measured dependency of K_p with the sediment to water ratio was described with the adapted model which included adsorption to container walls and partitioning to three 'phases': water, a sediment fraction which was separable by centrifugation and a sediment fraction which was not separable by centrifugation. It was shown that the nature of this fraction varied significantly with sediment concentration. Despite this variation, the model used one organic carbon normalised partition coefficient for the separable sediment fraction and one for the non-separable sediment fraction. It was concluded that corrections for incomplete phases separation can be made on the basis of the adapted model and dissolved organic carbon measurements.

A selection of 26 suspended solids and sediments sampled from Lake Volkerak/Zoom was used for sorption studies with 1,2,3,4-tetrachlorobenzene and cadmium in the laboratory (Chapter 4). The adsorbents varied widely in phytoplankton, organic carbon and clay content. Cadmium sorption coefficients were also determined for an isolated suspension of *Cryptomonas* spp. Sorption isotherms for TeCB were linear, regardless the contribution of phytoplankton to the organic matter fraction, which was almost 100% for some samples. Partition coefficients for TeCB also were proportional to the organic carbon content. These observations suggest that HOC (bio)sorption to phytoplankton is a partitioning process. Sorption of cadmium was not at equilibrium in the laboratory, and was mainly to iron-, manganese-(hydr)oxides and organic matter, the first being exclusively associated with the clay fraction. Due to a decrease in relative clay content during algal blooms, a proportional decrease in the cadmium distribution coefficient was found. Laboratory and field data distribution coefficients for cadmium sorption to the iron, manganese and organic matter phases were estimated according to the model of Oakley et al [2] and were both in agreement with literature data for isolated model phases. This suggests that this model can be used to predict cadmium distribution coefficients from adsorbent characteristics (Fe-, Mn- and organic matter content), under the environmental conditions of Lake Volkerak/Zoom.

Suspended and settling solids often are complex mixtures of resuspended sediments, planktonic particles, detritus and inorganic precipitates. The sorption kinetics for such mixtures may be different than for the separate particle types. In Chapter 5, for ten sediments, suspended and settling solid samples, the relationship between chlorobenzene desorption kinetics and particle characteristics was investigated using a gas-purge [3] method. The desorption patterns could be described with a first-order two-compartment model. The results show that when the equilibration time for adsorbent suspensions contaminated in the laboratory is longer, desorption is slower. At nonequilibrium conditions, the more hydrophobic chlorobenzenes are released faster than the less hydrophobic ones. The two-compartment model parameters were related to adsorbent characteristics, such as organic matter-, phytoplankton- and clay content. The partition coefficient was proportional to the content of organic matter, which in turn was mainly determined by the concentration of phytoplankton in the samples. This confirms the results described in Chapter 4, which were obtained with a batch equilibration technique. The desorption rate was positively correlated with the phytoplankton content. This suggests that phytoplankton cells form an easily accessible fraction of the total adsorbent. Because sediments contain less phytoplankton, suspended solids sampled in Lake Volkerak/Zoom showed faster desorption kinetics than sediments. However, the desorption from natural suspended solids was still rate limited for 10 - 20% of the chlorobenzene content.

The sorption to phytoplankton was further investigated using algal cultures. In Chapter 6, the temperature dependency of chlorobenzene bioaccumulation to *Scenedesmus* spp was studied. The *BCF*s were measured by 48 h batch equilibration and were found to increase with temperature between 4.5 and 27.6°C. A thermodynamic analysis suggests that the bioconcentration is driven by an entropy gain. LogBCF - logK_{ow} plots were linear, and slopes increased with temperature. These results agree with earlier reports on the analogous bioconcentration to fish.

In aquatic systems, settling of planktonic particles is an important route of contaminants to the sediment. During settling and also in the sediment, decomposition and mineralization of the cells takes place, which may change the sorptive properties for HOCs and heavy metals. In Chapter 7, the influence of mineralization of phytoplankton (laboratory *Scenedesmus* spp) on the desorption characteristics of two chlorobenzenes was studied using a purge and trap method. For comparison several field samples including a sediment, algae at different growth stages, and freeze dried algae were included. The desorption characteristics were evaluated using multiple box models similar to those generally used for desorption from sediments. It was found for all adsorbents that the desorption could adequately be described using a two-compartment nonequilibrium biosorption model. Generally, HCB was bound stronger and released slower than TeCB. Ageing and mineralization of unicell (171 days) and coenobian forms (240 days) of the algal species resulted in a significant twofold increase of the K_{oc} for HCB. In an addendum to this chapter, the results of an additional experiment with the same batch of unicells after 466 days are reported. This experiment shows that after 466 days of mineralization, the increase in K_{oc} for HCB is a factor three. The gas-purge method was not sensitive and accurate enough to measure significant K_{oc} differences for the less hydrophobic TeCB. Generally, sorption affinity as quantified by the K_{oc} was lower, and desorption kinetics faster for algae than for soils and sediments. Evaluation of the biosorption rate parameters using a log k_2 versus log K_p plot showed that in contrast to sediments and soils, no clear inverse relationship between K_p and k_2 exists for algae. A bioconcentration experiment with four chlorobenzenes showed good agreement with the sorption parameters measured with the purge method, and a linear correlation of the bioconcentration factor with the octanol/water partition coefficient. The linearity of the logBCF - logK_{ow} plot and the fact that the slope was close to unity, proves that chlorobenzene bioaccumulation was at equilibrium after 48 h.

The chlorobenzene biosorption to phytoplankton and detritus may be different among algal species. In Chapter 8, equilibrium and rate parameters of chlorobenzene biosorption to the cyanobacterium *Anabaena* and various types of algal detritus were measured using a gas-purge method. Organic carbon normalized sorption coefficients for detritus originating from *Anabaena* and from the green alga *Scenedesmus* were up to 3.5 times higher than for the respective living species, and were positively correlated with C/N atomic ratios of the adsorbents. This result supports the higher organic carbon normalised HOC concentrations observed for settling solids in Lake Volkerak/Zoom (Chapter 2), which also had higher C/N elemental ratios compared to the suspended solids in the same lake. The chlorobenzene desorption kinetics could be described best with a two-compartment model. The compartments were interpreted as a lipid pool near the surface of the cells and a similar pool deeper in the cell interior. The kinetic parameters measured were such, that in most aquatic systems sorption equilibrium can be assumed. The rate of biphasic desorption decreased with increasing chlorobenzene hydrophobicity and with decreasing surface-to-volume ratio. This suggests that much slower kinetics may be expected for hydrophobic compounds with $K_{ow} > 10^6$, for example, PCBs, and algal species or clusters of larger size. A theoretical framework for predicting nonequilibrium bioconcentration caused by the combined action of biphasic bioaccumulation and phytoplankton growth is proposed. In an appendix to this chapter, a full mathematical description of the compartment models is given.

Mineralization of phytoplankton might also result in a redistribution of sorbed heavy metals. Further, sorption of metals is strongly influenced by changes in salinity. In Chapter 9, the solid/water distribution of cadmium, copper and lead for the cyanobacterium *Anabaena* spp in surface waters with different chlorinity, and at various degrees of algal decomposition, was studied using batch experiments. Adsorption isotherms for cadmium and copper could be described with the Freundlich equation. For lead a linear isotherm was satisfactory. In general, the Freundlich affinity constant K_f decreased with increasing chloride concentration. For cadmium this decrease could be explained with a speciation model based on complexation with chloride. The Freundlich exponent for cadmium and copper was relatively constant among surface waters with different chlorinities. The distribution coefficient (K_d) for *Anabaena* spp was largest for lead, followed by cadmium and copper. Mineralization of *Anabaena* spp resulted in a decrease of the solid to water ratio and an increase in K_d for cadmium (factor four), copper (factor eight) and lead (factor ten - twenty). The increase in K_d is attributed partially to a decrease in solid to water ratio, and partially to a higher affinity of the metals for the adsorbent. These results indicate that assuming constant K_d values for mineralizing phytoplankton and detritus in water quality models may result in significant underestimations of bound fractions. The extent to which this fraction is underestimated, depends on the time course of the distribution coefficient and the solid to water ratio during the mineralization process.

Implications for water quality management

One of the major questions in water quality management with regard to micropollutants is how the quality of the water system changes under different management alternatives. In the Netherlands, the management alternatives are often evaluated with regard to the required general environmental quality standard AMK (Algemene Milieu Kwaliteit), which are set to safeguard against the ecotoxicological risks of environmental pollution. Predictions of the pollution level are made using water quality models. The quality of these predictions depends on the quality of the description of the chemical and physical processes that occur in the aquatic system in consideration, and on the quality of the parameter values which are entered in the model. For the transport and bioavailability of pollutants, sorption is an important process. Sorption determines the distribution over sorbed and aqueous states of a pollutant. Sorbed pollutants are not, or less bioavailable and are not subject to volatilization and photolysis. Processes like biodegradation and hydrolysis are different for sorbed and aqueous states of a pollutant. Therefore, in many models a distinction is made between the dissolved and sorbed states of a pollutant. The dissolved fraction of total pollutant α_d, can be calculated according to [1,4,5,6]:

$$\alpha_d = \frac{1}{1 + S_c \times K_d^c + S_p \times K_d^p} \tag{1}$$

in which S_p and S_c are the suspended particle and the non-settling colloidal particles (macromolecule) concentration respectively, and K_d^p is the distribution coefficient for suspended particles, and K_d^c is the partition coeficient for colloidal particles. Similarly, expressions can be given for the bound fractions as a function of the same parameters. It can be seen from equation (1) that the distribution of a contaminant over dissolved and sorbed states depends on the particle and non-settling particles concentration and the distribution coefficients K_d. Equations such as (1) are used in many models, for example in the widely used US EPA model TOXIWASP [7] (for HOCs), and in the Netherlands in the Delft Hydraulics model DELWAQ-IMPAQT [8,9] (both HOCs and heavy metals). In these models, HOC sorption is considered instantaneous, and distribution coefficients are entered as constants. In TOXIWASP a distinction is made between sorption to sediments and biota. In DELWAQ-IMPACT HOCs can sorb to dissolved organic carbon, particulate organic carbon and phytoplankton. Although in a recent IMPAQT version different K_{oc} values can be entered, to date the same partition coefficient is used for algae as for particulate organic carbon and dissolved organic carbon [10]. Further, no distinction is made between fresh phytoplankton and detritus with respect to sorption affinity. To describe sorption of metals, this model uses constant partition coefficients, or cation echange capacities which are calculated from the contributions of the organic matter and silt fraction. However, it was shown in this study that distribution- and partition coefficients in a waterbody like lake Volkerak/Zoom are highly variable in space and time because:

1. At more or less constant environmental conditions K_d values for trace metals depend on the content of iron(hydr)oxides, manganese(hydr)oxides and organic matter in the natural aquatic particles. It was shown for Lake Volkerak/Zoom that this content varies considerably in time and space (Chapter 2), and that K_d values for cadmium differ up to factor 30 (field data) or a factor 300 (laboratory) (Chapter 4).
   For mineralizing planktonic particles in the laboratory, K_d increases up to a factor 10 - 20 (lead) were observed under conditions similar to those in Lake Volkerak/Zoom (Chapter 9).
2. When K_p values for HOCs are calculated with respect to an aqueous phase which contains organic matter, the K_p depends on the organic carbon fraction in the aqueous phase and the particle to water ratio (Chapter 3). Further, K_p depends on organic matter content and composition. It was shown for 1,2,3,4-tetrachlorobenzene that laboratory K_p values varied a factor 30 for particles from lake Volkerak/Zoom (Chapter 4). Organic matter content of suspended solids showed a strong seasonal variation (Chapter 2, Chapter 4). Normalization to organic carbon removes only a part of the variation. Comparison of carbon normalised HOC concentrations (field data) in settling solids with those in simultaneously sampled suspended solids, showed a difference of a factor 2 - 6. Under controlled laboratory conditions, significant K_{oc} differences between fresh phytoplankton cells, detritus and sediments were found (Chapter 7, Chapter 8). The ranges in K_{oc} for the different particle types for HCB, (which were measured with the highest accuracy) are summarized in Table 1.
3. Hydrophobic sorption to suspended solids may not be at equilibrium in many aquatic systems. This is caused by retarded adsorption or desorption (Chapter 5), or for phytoplankton by the combined action of retarded bioaccumulation and algal growth (Chapter 8). Although not described in this thesis, similar phenomena might occur

for heavy metals.

TABLE 1:
Summary of hexachlorobenzene K_{oc}-ranges
found for various types of aquatic particles

group	particles included in group 1, 2 or 3	K_{oc} range[a] ($\times 10^3$)
1[b]	living fytoplankton only	77 - 242
2[c]	living fytoplankton plus detritus	77 - 474
3[d]	living phytoplankton plus sediments	77 - 320

(a) measured with a gas-purge method, (b) group 1 includes *Anabaena* spp, *Scenedesmus* unicells and *Scenedesmus* coenobia, (c) group 2 includes al species in group 1 plus all detritus particles, (d) group 3 includes group 1 plus one sediment.

Generalisations on the relevance of the variations found in this study for environmental fate modeling are not straightforward. Depending on the purpose of the modeling and the system in consideration, simplifications may be tolerable. Further, the uncertainties in other parameter values may be so large that K_d differences of one order of magnitude are irrelevant. The consequence of these findings is that in some cases it might be appropriate to use a (seasonally) time dependent K_d for metals, or to use different K_{oc} values to quantify HOC sorption to dissolved organic matter, (resuspended) sediments, phytoplankton and detritus. For sediment systems, a lower K_{oc} value might be used for the top layer which contains large fractions of undegraded plankton. It can be expected that for non-reactive hydrophobic organic micropollutants more or less constant K_{oc} ratios are found for different adsorbents [11,12]. This means that these K_{oc} differences also can be expected for more hydrophobic HOCs than chlorobenzenes, such as PCBs or PAHs. Depending on colloid and suspended particle concentration, variations in K_d (or K_{oc}) of roughly one order of magnitude as found in this study, can have large consequences on pollutant speciation. This is illustrated in Table 2 (modified from [6]) were the pollutant speciation is tabulated as a function of K_{oc} for four types of aquatic systems with their typical f_{oc} values, S_c and S_p ranges: river headwaters (S_p=5-50 mg/l), rivers downstream of agricultural field runoff (S_p=15-150 mg/l), field runoff drain channels (S_p=30-600 mg/l), and lakes (S_p=0.5-5 mg/l). The symbols α_d, α_p and α_c refer to the dissolved pollutant fraction, the fraction sorbed to particles and the fraction which is associated with colloids. For each aquatic system and for four K_{oc} values, the α_d-, α_p- and α_c-ranges are presented for their respective $K_p \times S_p$-ranges. Under constant solution phase conditions (for example constant pH etc.) an analogous discussion can be given for heavy metals. In that case only the K_p, which refers to hydrophobic partitioning, should be replaced by K_d. Table 2 shows that a difference in $\log K_{oc}$ of one unit, causes considerable shifts in pollutant speciation. Because bioavailability is highly influenced by speciation, it is concluded that when such differences are not taken into account, the ecotoxicological risks of environmental contamination may be assessed erroneously.

TABLE 2:(a)

Values of α_d, α_p and α_c for ranges of $\log K_d S_p/\alpha$ that might occur for organic compounds of varying K_{oc} in River Headwaters, Lake Waters, Downstream of Agriculture, and in an Actual Agricultural Field drain.

log K_{oc}	log $K_d^p S_p/\alpha_w$	log $K_d^c S_c/\alpha_w$	α_d	α_p	α_c
River, Headwaters(b)					
4	3.40-4.40	2.70-3.70	0.997-0.971	0.003-0.024	0.001-0.005
5	4.40-5.40	3.70-4.70	0.971-0.769	0.024-0.193	0.005-0.039
6	5.40-6.40	4.70-5.70	0.769-0.249	0.193-0.626	0.039-0.125
7	6.40-7.40	5.70-6.70	0.249-0.032	0.626-0.807	0.125-0.161
Lake Water(c)					
4	2.40-3.40	2.70-3.70	0.999-0.993	0.000-0.003	0.001-0.005
5	3.40-4.40	3.70-4.70	0.993-0.930	0.003-0.023	0.005-0.047
6	4.40-5.40	4.70-5.70	0.930-0.571	0.023-0.143	0.047-0.286
7	5.40-6.40	5.70-6.70	0.571-0.118	0.143-0.294	0.286-0.589
River, Downstream of Agriculture(d)					
4	3.65-4.65	2.88-3.88	0.995-0.950	0.004-0.043	0.001-0.007
5	4.65-5.65	3.88-4.88	0.950-0.657	0.043-0.293	0.007-0.050
6	5.65-6.65	4.88-5.88	0.657-0.161	0.293-0.718	0.050-0.122
7	6.65-7.65	5.88-6.88	0.161-0.019	0.718-0.839	0.122-0.142
Agricultural Field Drain(e)					
4	3.78-5.08	3.08-4.38	0.993-0.874	0.006-0.105	0.001-0.021
5	4.78-6.08	4.08-5.38	0.933-0.410	0.056-0.492	0.011-0.098
6	5.78-7.08	5.08-6.38	0.581-0.065	0.350-0.780	0.070-0.156
7	6.78-8.08	6.08-7.38	0.122-0.007	0.732-0.828	0.146-0.165

(a) Data were taken from [6].

(b) S_p=5-50 mg/L with $(f_{oc})_p=0.05$; S_c=0.5-5 mg/L with $(f_{oc})_c=0.10$; $K_d=f_{oc}\times K_{oc}$

(c) S_p=0.5-5 mg/L with $(f_{oc})_p=0.05$; S_c=0.5-5 mg/L with $(f_{oc})_c=0.10$; $K_d=f_{oc}\times K_{oc}$

(d) S_p=15-150 mg/L with $(f_{oc})_p=0.03$; S_c=1.5-15 mg/L with $(f_{oc})_c=0.05$; $K_d=f_{oc}\times K_{oc}$

(e) S_p=30-600 mg/L with $(f_{oc})_p=0.02$; S_c=3-60 mg/L with $(f_{oc})_c=0.04$; $K_d=f_{oc}\times K_{oc}$

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Samenvatting

Met de groei van de chemische industriële bedrijvigheid in de laatste decennia is de vervuiling van lucht, water en bodem sterk toegenomen. Vervuilende stoffen die in lage concentraties al betrekkelijk toxisch zijn, worden vaak aangeduid met de term *microverontreinigingen.* De lotgevallen en de biologische beschikbaarheid van microverontreinigingen in oppervlaktewateren, worden sterk beïnvloed door adsorptie aan deeltjes zoals sediment-, zwevend stof-, fytoplankton- en detritusdeeltjes. Om het adsorptieproces beter te begrijpen en te kwantificeren werd een studie gemaakt van de evenwichtsligging en de kinetiek van de adsorptie van enkele microverontreinigingen (chloorbenzenen en zware metalen) aan een groot aantal typen deeltjes (Hoofdstuk 2 - 5). Speciale aandacht werd besteed aan de adsorptie aan fytoplankton en detritus (Hoofdstuk 6 - 9).

De adsorptie van microverontreinigingen aan deeltjes in aquatische systemen wordt sterk beïnvloed door de samenstelling van die deeltjes. De samenstelling varieert in de tijd en tussen verschillende lokaties. In Hoofdstuk 2 worden de variatie in de samenstelling en de variatie in de gehaltes aan microverontreinigingen, beschreven en geïnterpreteerd voor zwevend en bezinkend slib uit het Volkerak/Zoommeer. Het bleek dat de gehaltes aan zware metalen in het slib sterk gecorreleerd zijn met de gehaltes aan klei en organische stof. Voor de onderzochte organische microverontreinigingen (chloorbenzenen, pesticiden en PCBs) daarentegen bleek alleen organische stof van belang te zijn. Het gehalte aan organische stof werd sterk beïnvloed door algengroei. De seizoensvariatie in de groei van algen veroorzaakte een significante variatie in de gehaltes aan zware metalen en organische microverontreinigingen. Door normeren van de metaalgehaltes op het scandiumgehalte, verdween de seizoensafhankelijkheid. Ook werden verschillen in gehaltes tussen deeltjes die met een doorstroomcentrifuge waren bemonsterd, en deeltjes die in dezelfde maand met sedimentvallen waren gemonsterd, door normering opgeheven. Organische microverontreinigingen werden genormeerd op organisch koolstof. In de genormeerde gehaltes bleef echter een zekere seizoensvariatie aanwezig. Genormeerde gehaltes van deeltjes die met sedimentvallen waren gemonsterd waren hoger dan genormeerde gehaltes van deeltjes die in dezelfde maand met centrifuges waren gemonsterd. De sedimentval-deeltjes hadden ook een lager algen-gehalte en een hogere C/N ratio. Dit suggereert een invloed van het *type* organische stof op de ligging van het adsorptie-evenwicht, eventueel in combinatie met verschillen in adsorptiekinetiek tussen de typen deeltjes.

De ligging van het adsorptie-evenwicht wordt meestal uitgedrukt met een distributie- of partitiecoëfficiënt (K_p), die gedefinieerd is als de ratio tussen de concentratie geadsorbeerde stof, en de concentratie opgeloste stof. Partitiecoëfficiënten kunnen worden berekend uit veldgegevens of kunnen worden gemeten in het laboratorium. In beide gevallen moet worden gecorrigeerd voor het feit dat de scheiding tussen vaste fase (sediment) en water niet volledig is. In Hoofdstuk 3 wordt kritiek gegeven op het model van Gschwend en Wu dat vaak voor die correcties gebruikt wordt. Een aangepaste versie van het model werd getest met partitiecoëfficiënten voor 1,2,3,4-tetrachloorbenzeen (TeCB) die bij verschillende sediment/water ratio's waren gemeten. Daarnaast werd het model getest met literatuur gegevens voor de adsorptie van hexachloorbenzeen. De gemeten afhankelijkheid van K_p met de sediment/water ratio werd beschreven met het aangepaste model. Het model bevat de mogelijkheid te corrigeren voor adsorptie aan glaswanden. Daarnaast gaat het model uit van adsorptie aan een sedimentfractie die isoleerbaar is door centrifugeren, en aan een fractie die niet isoleerbaar is. De aard van deze laatste fractie bleek te variëren met de sediment/water ratio. Ondanks deze variatie, kon de afhankelijkheid van K_p met de sediment/water ratio worden beschreven met één op organisch koolstof genormeerde partitiecoëfficiënt (K_{oc}) voor de bulk organische stof, en één K_{oc} voor opgelost/colloidaal organische stof (DOC).

De relaties tussen adsorptie- en deeltjeskarakteristieken werden verder onderzocht voor cadmium en TeCB met behulp van 26 sediment en zwevend slib monsters uit het Volkerak/Zoommeer (Hoofdstuk 4). De monsters waren in verschillende seizoenen genomen en varieerden sterk in de gehaltes aan algen, organisch koolstof en klei. Cadmium distributiecoëfficiënten werden ook gemeten voor een suspensie van *Cryptomonas* spp. De adsorptie isothermen voor TeCB waren lineair, ongeacht de soms hoge bijdrage van fytoplankton aan de fractie organische stof. TeCB partitie coëfficiënten waren evenredig met het organische koolstof gehalte van de monsters. Deze bevindingen suggereren dat (bio)sorptie van organische microverontreinigingen aan algen een partitie proces is. Sorptie van cadmium bereikte geen evenwicht in het laboratorium, en was voornamelijk gerelateerd aan ijzer- en mangaan(hydr)oxiden en organische stof. De ijzer- en mangaan(hydr)oxide gehaltes waren sterk gecorreleerd met de kleifractie. Als gevolg van afname van het kleigehalte door "verdunning" met algen nam ook de K_d voor cadmium af in periodes met sterke algenbloei. Cadmium distributie coëfficiënten voor de ijzer-, mangaan- en organische stof fase werden geschat op basis van een model ontwikkeld door Oakley et al. De resultaten kwamen goed overeen met coëfficiënten uit de literatuur voor geïsoleerde modelfasen. Dit suggereert dat het model van Oakley, voor de condities in het Volkerak/Zoommeer, gebruikt kan worden om distributiecoëfficiënten te voorspellen uit deeltjeskarakteristieken.

Zwevend slib is vaak een complex mengsel van geresuspendeerd sediment, fytoplankton deeltjes, detritus en anorganische precipitaten. De adsorptiekinetiek voor zulke mengsels kan sterk verschillen van de kinetiek voor elk afzonderlijk type deeltjes. In Hoofdstuk 5 wordt voor tien zwevend slib en sediment monsters, de relatie tussen de desorptiekinetiek van chloorbenzenen en deeltjeskarakteristieken onderzocht met behulp van een doorblaas (gas-purge) methode. De desorptiekinetiek kon worden beschreven met een eerste orde twee-compartimenten model. Desorptie vanuit in het laboratorium gecontamineerde sedimenten was langzamer naarmate de incubatietijd langer was. Het bleek dat de hydrofobere chloorbenzenen bij het ontbreken van sorptie-evenwicht sneller desorberen dan de minder hydrofobe. De parameters van het twee-componenten model werden gerelateerd aan de deeltjeskarakteristieken zoals organische stof-, fytoplankton- en kleigehalte. De partitiecoëfficiënt was evenredig met de fractie organisch koolstof, welke voornamelijk werd bepaald door de fytoplankton fractie. Dit bevestigd de resultaten beschreven in Hoofdstuk 4, die met een batch methode waren verkregen. Ook de desorptiesnelheidsconstante was positief gecorreleerd met de fractie fytoplankton. Dit suggereert dat de fytoplankton cellen een betrekkelijk makkelijk toegankelijke fractie van het totale adsorbens vormen. Omdat de sediment monsters minder fytoplankton bevatten dan zwevend slib monsters, was de desorptie voor zwevend slib sneller dan voor sediment. Toch was ook de desorptie voor zwevend slib nog snelheids-beperkend voor 10-20% van het gehalte aan chloorbenzenen.

De (bio)sorptie van microverontreinigingen aan fytoplankton werd verder onderzocht met behulp van algen culturen. In Hoofdstuk 6 wordt een onderzoek naar de temperatuurafhankelijkheid van bioaccumulatie (*BCF*) van chloorbenzenen aan *Scenedesmus* spp beschreven. De *BCFs* werden gemeten na een evenwichtsinstelling van 48 uur, en namen toe in het temperatuurgebied van 4.5 tot 27.6°C. Een thermodynamische analyse suggereert dat de bioaccumulatie wordt gedreven door een toename in entropie. LogBCF - logK_{ow} relaties waren lineair. De hellingen namen toe met de temperatuur. Deze resultaten komen overeen met eerdere publikaties over de analoge bioconcentratie in vissen.

In aquatische systemen worden veel microverontreinigingen getransporteerd door bezinkende fytoplankton deeltjes. Tijdens de bezinking in de waterkolom en afzetting in het sediment, mineraliseren de cellen waardoor de sorptieaffiniteit en -capaciteit voor zware metalen en organische microverontreinigingen zou kunnen veranderen. In Hoofdstuk 7 wordt een onderzoek naar de invloed van veroudering en mineralisatie van *Scenedesmus* spp op de sorptiekarakteristieken gepresenteerd. Ter vergelijking werden algen in verschillende groeistadia, sediment en detritus uit het Volkerak/Zoommeer en gevriesdroogde algen onderzocht. De sorptiekarakteristieken werden gemeten met behulp van een doorblaas (gas-purge) methode en geïnterpreteerd met behulp van dezelfde soort compartiment modellen als gebruikt wordt voor de beschrijving van desorptie vanuit sediment. Het bleek dat biosorptie kon worden beschreven met behulp van een twee-compartiment model. Over het algemeen werd hexachloorbenzeen (HCB) sterker gebonden en langzamer gedesorbeerd dan TeCB. Veroudering en mineralisatie van unicellen (171 dagen) en coenobia (240 dagen) resulteerde in een twee keer hogere K_{oc} voor HCB. De resultaten van een extra experiment met de unicellen na 466 dagen worden beschreven in een addendum bij Hoofdstuk 7. Dit experiment liet zien dat de K_{oc} toename na 466 dagen, een factor drie bedraagt. De doorblaasmethode was niet gevoelig en nauwkeurig genoeg om significante K_{oc} verschillen aan te tonen voor het minder hydrofobe TeCB. Over het algemeen waren de K_{oc} waarden lager, en de desorptie sneller voor algen dan voor sediment. Uit een evaluatie van de desorptiesnelheidsconstante k_2 met behulp van een log k_2 versus log K_p plot, bleek dat in tegenstelling tot sedimenten en bodems, voor algen en detritus deeltjes geen inverse relatie tussen k_2 en K_p bestaat. Met behulp van een batch methode werden *Scenedesmus* *BCF*s gemeten voor vier chloorbenzenen. De *BCF*s kwamen goed overeen met de resultaten die met de doorblaasmethode werden verkregen, en waren lineair gecorreleerd met de octanol/water partitiecoëfficiënt. De lineariteit van log*BCF* - logK_{ow} relaties, en het feit dat de helling ongeveer gelijk was aan één, bewijst dat evenwicht was bereikt na 48 h.

De biosorptie van organische microverontreinigingen hoeft niet gelijk te zijn voor verschillende algensoorten. In Hoofdstuk 8 worden de evenwichts- en snelheidsconstanten beschreven voor biosorptie van chloorbenzenen aan *Anabaena* spp en verschillende soorten detritus. Partitiecoëfficiënten (K_{oc}) waren maximaal 3.5 keer hoger voor detritus dan voor levend *Anabaena* en waren positief gecorreleerd met de C/N ratio van het organisch materiaal. Dit resultaat is in overeenstemming met resultaten uit Hoofdstuk 2 waar ook hogere op organisch koolstof genormeerde gehaltes aan organische microverontreinigingen werden gevonden voor deeltjes met een hogere C/N ratio. De sorptiekinetiek kon het best worden beschreven met een twee-compartimenten model. In een appendix bij Hoofdstuk 8 wordt een volledige afleiding van het twee-compartimenten model gegeven. De compartimenten werden geïnterpreteerd als een lipide reservoir vlakbij het oppervlak van de cellen, en een soortgelijk reservoir dieper in de cel matrix. De kinetische parameters waren zodanig dat in de meeste aquatische systemen biosorptie-evenwicht zou bestaan. De desorptiesnelheid nam af met toenemende hydrofobiciteit en met afnemende oppervlakte/volume verhouding van de cellen. Dit suggereert dat nog veel langzamere sorptie kan worden verwacht voor verbindingen met logK_{ow}>6, en voor algensoorten of -clusters van grotere omvang. In hoofdstuk 8 wordt een model voorgesteld om de invloed van een dergelijke trage ad- en desorptie op de steady state evenwichtsconstante voor groeiende algen te beschrijven.

Net zoals voor organische microverontreinigingen kan mineralisatie van fytoplankton ook leiden tot een herverdeling van *zware metalen* over de vaste fase en waterfase. Ook wordt de adsorptie van zware metalen sterk door het chloridegehalte van het oppervlaktewater beïnvloed. In Hoofdstuk 9 worden deze aspecten bestudeerd voor de blauwalg *Anabaena* spp en de metalen cadmium, koper en lood. Adsorptie isothermen voor cadmium en koper konden het beste worden beschreven met de Freundlich vergelijking. De isotherm voor lood was lineair. Over het algemeen nam de affiniteitsconstante K_f af met toenemende chloride concentratie van het gebruikte oppervlaktewater. Voor cadmium werd de invloed van het chloridegehalte verklaard uit een afname van de vrije ionconcentratie door complexering met chloride en een toename van de ionsterkte. De Freundlich exponent voor cadmium en koper was betrekkelijk constant voor de oppervlaktewateren met verschillend chloridegehalte. De distributiecoëfficiënt (K_d) voor *Anabaena* spp was het grootst voor lood, gevolgd door koper en cadmium. Mineralisatie van *Anabaena* spp veroorzaakte een afname in de concentratie algen, en een toename van de K_d voor cadmium, koper en lood. De toename in K_d wordt toegeschreven aan de afname van de concentratie algen, en aan een hogere affiniteit van de metalen voor detritus. Deze resultaten geven aan dat het gebruik van een constante K_d voor verouderende, mineraliserende algen en detritus in waterkwaliteitsmodellen kan resulteren in een significante onderschatting van de gebonden fractie. De mate van onderschatting wordt bepaald door het verloop van de K_d en de concentratie aan vaste stof tijdens het mineralisatieproces.

Implicaties voor het waterkwaliteitsbeheer

Een van de belangrijkste vraagstukken in het waterkwaliteitsbeheer met betrekking tot microverontreinigingen, is hoe de waterkwaliteit veranderd bij verschillende management alternatieven. In Nederland worden deze alternatieven vaak geëvalueerd aan de hand van de Algemene Milieu Kwaliteits-norm (AMK), die vastgesteld is om de ecotoxicologische risico's van milieuvervuiling te beperken. Voorspellingen van de toekomstige vervuilingsgraad worden gemaakt met behulp van waterkwaliteitsmodellen. De kwaliteit van deze modellen hangt af van de kwaliteit van de beschrijving van de chemische en fysische processen die optreden in het te beschouwen watersysteem, en van de kwaliteit van de parameter waarden die in het model worden ingevoerd. Voor het transport en de biologische beschikbaarheid van microverontreinigingen, is sorptie een belangrijk proces. Sorptie bepaald de distributie van een verontreiniging over vaste en vloeistoffase. Geadsorbeerde verontreinigingen zijn niet, of minder biologisch beschikbaar en zijn niet onderhevig aan verdamping of fotolyse. Voor verontreinigingen in geadsorbeerde toestand zijn processen als biodegradatie en hydrolyse anders, dan voor opgeloste verontreinigingen. Daarom wordt in veel modellen onderscheid gemaakt tussen de geadsorbeerde en opgeloste vorm van een te modelleren verontreiniging. De fractie van de totale concentratie die opgelost is, wordt bepaald door de concentratie aan deeltjes en de distributiecoëfficiënt K_d. In veel modellen is de K_d dan ook een belangrijke parameter. Veel-gebruikte modellen voor het transport van microverontreinigingen zijn het US EPA model TOXIWASP (voor organische microverontreinigingen) en het Nederlandse model DELWAQ-IMPACT (voor organische microverontreinigingen en zware metalen), dat ontwikkeld is door het Waterloopkundig Laboratorium. In deze modellen wordt sorptie als een instantaan proces beschouwd, en worden distributiecoëfficiënten beschouwd als constanten. In TOXIWASP wordt onderscheid gemaakt tussen (bio)sorptie aan sedimenten en biota. In DELWAQ-IMPACT kan onderscheid worden gemaakt tussen sorptie aan opgeloste organische stof, aan sediment en aan fytoplankton. Tot op heden wordt echter dezelfde distributiecoëfficiënt gebruikt voor al deze typen adsorbentia. Verder wordt geen onderscheid gemaakt tussen sorptie aan fytoplankton en detritus. Voor zware metalen worden ook constante distributiecoëfficiënten toegepast, of wordt gebruik gemaakt van de CEC (Cation

Exchange Capacity) die wordt berekend uit de fracties organische stof en silt.

Uit de in dit proefschrift beschreven studie echter, bleek dat distributie- en partitiecoëfficiënten sterk kunnen variëren in ruimte en tijd vanwege:

1. Bij min of meer constante milieucondities worden K_d waarden voor zware metalen in het Volkerak/Zoommeer bepaald door het gehalte aan ijzer(hydr)oxiden, mangaan(hydr)oxiden en organische stof in de sediment of zwevend slib-deeltjes. Het bleek dat de samenstelling van de deeltjes in het Volkerak/Zoommeer sterk variëert in plaats en tijd (Hoofdstuk 2), en dat K_d waarden voor cadmium een factor 30 (veldgegevens) of een factor 300 (laboratorium) kunnen verschillen.

   Voor mineraliserende algen werden in het laboratorium K_d toenames tot een factor 10 - 20 (lood) gemeten onder condities gelijk aan die in het Volkerak/Zoommeer (Hoofdstuk 9).
2. Als K_p waarden voor organische microverontreinigingen worden berekend voor water dat behalve de verontreiniging ook opgeloste of colloïdale organische stof bevat, dan is de K_p afhankelijk van de organisch koolstof concentratie in de waterfase en de concentratie van de deeltjes (Hoofdstuk 3). Daarnaast blijkt de K_p afhankelijk te zijn van de fractie organisch koolstof, en het *type* organische stof. K_p waarden voor TeCB varieerden een factor 30 voor sediment en zwevend slib monsters uit het Volkerak/Zoommeer (Hoofdstuk 4). Het organisch koolstof gehalte van zwevend slib varieert sterk (Hoofdstuk 2, Hoofdstuk 4). Normalisatie op organisch koolstof verwijdert de variatie in geadsorbeerde concentraties slechts ten dele. Bezinkend slib (sedimentval) had 2 - 6 keer hogere genormeerde concentraties dan zwevend slib (centrifuge). Onder gecontroleerde laboratorium condities werden met steeds dezelfde methode, significant verschillende K_{oc} waarden gevonden voor verschillende algen soorten, voor detritus ten opzichte van levende algen, en voor levende algen ten opzichte van sediment (Hoofdstuk 7, Hoofdstuk 8).
3. Waarschijnlijk is er voor organische microverontreinigingen vaak geen sprake van sorptie- of bioaccumulatie-evenwicht. Dit wordt veroorzaakt doordat ad- en desorptie erg traag kunnen verlopen (Hoofdstuk 5), of voor fytoplankton omdat algengroei de steady state *BCF* kan beïnvloeden. Alhoewel niet beschreven in dit proefschrift, kan dit ook gelden voor zware metalen.

Generalisaties met betrekking tot de relevantie van de in deze studie gevonden variaties in distributiecoëfficiënten voor het modelleren van microverontreinigingen, zijn niet zonder meer te geven. Afhankelijk van het doel van de modellering en het te modelleren watersysteem, kunnen vereenvoudigingen gerechtvaardigd zijn. Daarnaast kunnen onzekerheden in andere parameters zo groot zijn dat verschillen in K_d of K_p van één orde van grootte irrelevant zijn. Echter, in andere gevallen kan het noodzakelijk zijn een K_d voor metalen te gebruiken die afhankelijk is van de slibsamenstelling, en die dus varieert in de tijd. Ook kan het nuttig zijn aparte K_{oc} waarden te gebruiken voor opgeloste organische stof, sediment, fytoplankton en detritus. Voor sedimenten kan een lagere K_{oc} gebruikt worden voor de toplaag, die een relatief grote fractie niet-gedegradeerd plankton bevat. Omdat K_{oc} verschillen bestaan voor adsorptie van HCB aan algen en detritus, is het waarschijnlijk dat dergelijke verschillen ook bestaan voor veel andere organische microverontreinigingen.

Variaties in K_{oc} of K_d zoals gemeten in deze studie kunnen grote effecten hebben op de verdeling van microverontreinigingen over de vaste fase (sediment, zwevend slib) en waterfase. Omdat de biologische beschikbaarheid sterk door deze verdeling wordt beïnvloedt, kan het gebruik van constante verdelingscoëfficiënten leiden tot een foutieve inschatting van de ecotoxicologische risico's van milieuverontreiniging.

Abstract

Sorption to natural aquatic particles plays an important role in the bioavailability and fate of micropollutants. The characteristics of sorption were investigated for hydrophobic organic compounds (HOCs) and heavy metals using a wide variety of natural aquatic particles. Special attention was paid to (bio)sorption to phytoplankton and detritus. The extent of sorption can be quantified by a distribution- (K_d) or partitioncoefficient (K_p). It was shown in this study that such coefficients in aquatic systems are variable in space and time because:

1. At more or less constant environmental conditions K_d values for trace metals depend on the content of iron(hydr)oxides, manganese(hydr)oxides and organic matter in the natural aquatic particles. It was shown for Lake Volkerak/Zoom that this content varies considerably in time and space, and that K_d values for cadmium differ up to factor 30 (field data) or a factor 300 (laboratory). For mineralizing planktonic particles in the laboratory, K_d increases up to a factor 10 - 20 (lead) were observed under conditions similar to those in Lake Volkerak/Zoom.
2. When K_p values for HOCs are calculated with respect to an aqueous phase which contains organic matter, the apparent K_p depends on the organic carbon fraction in the aqueous phase and the particle to water ratio. Further, K_p depends on organic matter content and composition. It was shown for 1,2,3,4-tetrachlorobenzene that laboratory K_p values varied a factor 30 for particles from lake Volkerak/Zoom. Organic matter content of suspended solids showed a strong seasonal variation. Normalization to organic carbon removes only a part of the variation. Comparison of carbon normalised HOC concentrations (field data) in settling solids with those in simultaneously sampled suspended solids showed a difference of a factor 2 - 6. Under controlled laboratory conditions, significant K_{oc} differences between fresh phytoplankton cells, detritus and sediments were found.
3. Hydrophobic sorption to suspended solids may not be at equilibrium in many aquatic systems. This is caused by retarded adsorption or desorption, or for phytoplankton by the combined action of retarded bioaccumulation and algal growth.

key words - algae, bioaccumulation, chlorobenzenes, hydrophobic compounds, sediment, sorption, heavy metals

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Curriculum Vitae

De schrijver van dit proefschrift werd geboren op 21 juli 1962 te Den Helder. Na het behalen van het Atheneum-B diploma aan het Katholiek Gelders Lyceum te Arnhem in 1980, begon hij zijn studie Scheikunde aan de Rijksuniversiteit Utrecht. In 1984 werd het Kandidaatsexamen afgelegd, met specialisatie Biologie (S2). Tijdens de daaropvolgende doctoraalfase was hij gedurende anderhalf jaar werkzaam als assistent bij het propaedeuse practicum voor chemiestudenten, met een 0.5 aanstelling. Het Doctoraalexamen vond plaats in augustus 1987, met de specialisatie Anorganische Chemie (Prof.ir. J.W. Geus), en de bijvakken Milieugeochemie (Prof.dr. C.H. van der Weijden) en Milieutoxicologie (Prof.dr. W. Seinen). In januari 1988 volgde een aanstelling als projectmedewerker bij de Landbouwuniversiteit Wageningen, (Sectie Waterkwaliteitsbeheer, Vakgroep Waterzuivering). Het project betrof een onderzoek naar het gedrag van microverontreinigingen in het Volkerak/Zoommeer en werd uitgevoerd in opdracht van Rijkswaterstaat. In mei 1988 volgde een aanstelling als Universitair Docent bij dezelfde Sectie. Door een reorganisatie was de Sectie Waterkwaliteitsbeheer van 1989 tot 1994 onderdeel van de Vakgroep Natuurbeheer, en is dezelfde sectie sedert 1 januari 1994 onderdeel van de nieuwe Vakgroep Waterkwaliteitsbeheer en Aquatische Ecologie.