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Interactions of nutrients and toxicants in the food chain of aquatic ecosystems

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97-115 auteurs
116 Bibliotheek RIVM
117 Bureau Rapportenregistratie
118-138 Reserve
138-158 Bureau Rapportenbeheer

Contents

Papers

Summary

In a workshop held at the Woudschoten Conference Centre, Zeist, the Netherlands on September 16 and 17, 1996, specialists from various countries presented papers and took part in the discussion on the state of the art for interactions between eutrophication and toxicity. They also discussed policy problems related to such interactions. On the first day of the workshop participants were presented with a series of papers on the chemical effects of combined eutrophication and toxicity, while on the second, a more-or-less integrated picture on interactions emerged, taking into account various levels in the food chain. The workshop was concluded with a discussion on future management and research.

The Woudschoten workshop was initiated by the National Institute of Public Health and the Environment in response to a request of the Netherlands Ministry of Housing, Spatial Planning and the Environment.

Conclusions forthcoming the workshop:

- As the lower the trophic states are reached in combating eutrophication, the interaction of toxicants becomes more important.
- Interactions are especially important when it comes to persistent hydrophobic substances and heavy metals.
- Although eutrophic systems act as a sink for toxic substances, it is not recommended to keep these systems eutrophied.
- It is not recommended to give priority to either contaminants or eutrophication in emission reduction; both have to be attacked simultaneously.

Samenvatting

Op 16 en 17 september 1996 werd een workshop georganiseerd over de interactie tussen toxische stoffen en nutriënten in het conferentiecentrum Woudschoten te Zeist. Wetenschappers uit verschillende landen waren uitgenodigd om de stand van zaken van het onderzoek te presenteren en daarover te discussiëren; bovendien was hun gevraagd te discussiëren over de beleidsrelevantie van de interactie. Op de eerste dag stonden de chemische effecten van de interactie centraal. Tijdens de laatste dag werden lezingen gehouden over de interactie en de effecten integraal over de voedselketen. De workshop werd besloten met een discussie over mogelijke toekomstige maatregelen en onderzoek.

De workshop was bijeengeroepen door een opdracht van het Ministerie voor Huisvesting, Ruimtelijke Ordening en Milieu aan het Rijksinstituut voor Volksgezondheid en Milieubeheer.

Enige afsluitende conclusies waren:

- Bij het terugdringen van eutrofiëring zal het belang van de interactie toenemen.
- De interactie is vooral van belang bij persistente hydrofobe verbindingen en zware metalen.
- Ondanks het feit dat eutrofe systemen als sink voor toxicanten kunnen dienen verdient het geen aanbeveling om systemen eutroof te houden.
- Het heeft geen zin prioriteiten te stellen in de emissiereductie tussen nutriënten en toxische stoffen, beide dienen voortvarend aangepakt te worden.

Preface

The workshop, "Interactions of nutrients and toxicants in the food chain of aquatic ecosystems", was held on September 16 and 17, 1996 at the Woudschoten Conference Centre in Zeist, The Netherlands. Participants attending from Canada, Norway, Sweden, the Netherlands and USA were all engaged in research on the interaction between eutrophication and contamination.

It was the concern of policy-makers for the consequences of the interaction between eutrophication and contamination that prompted the organisation of this workshop. Since toxicants and nutrients are, in general, but not without exception, studied by different experts, knowledge on the interaction of nutrients and toxicants is scarce; in fact, study on this interaction has been relatively short compared to the research on the individual compounds. It was with this information that the Netherlands Ministry of Housing, Spatial Planning and the Environment requested the National Institute of Public Health and the Environment to gather information on the actual state of knowledge on the interaction, and to draw conclusions for advising on policy related to possible further action in terms of water management measures and future research.

The first step in realising this above objective was the organisation of a workshop for international experts to present the state of the art of their research, to discuss the problem of interaction on a scientific level and to try and reach conclusions for policy- makers. The workshop was organised jointly by the National Institute of Public Health and the Environment and the Directorate General of Housing, Spatial Planning and the Environment.

This workshop was the second international workshop organised on this topic. The first one, "Interactions between eutrophication and contaminants: towards a new research concept for the European aquatic environment" was held in Utö, Sweden in Autumn 1994 (Gunnarsson *et al.*, 1995). The Utö workshop highlighted the interaction as being a major environmental problem in most coastal areas subject to high anthropogenic loadings (Gunnarsson *et al.*, 1995), which also holds for freshwater ecosystems. Obtaining a better understanding of the interactive mechanisms between eutrophication and contaminants in order to make appropriate decisions on future management of the European marine and freshwater ecosystems (Gunnarsson *et al.*, 1995) formed the essential conclusion.

The Woudschoten workshop was divided into two sessions. After Per Jonsson's introduction to the subject on the first day, the more "chemical side" was presented and discussed. This led to more insight into the solubility of persistent organic substances in the fats of organisms, and thus their ability to enter the food chain. The second day was largely devoted to effects in the food chain itself, resulting in a series of papers dealing with experimental research and modelling of the food chain in aquatic ecosystems. The workshop was concluded with a discussion on problems both in policy-making and science.

This report will provide an overview of shorter versions of the papers presented, together with the resultant final discussion.

In February 1997, at the annual winter meeting of the American Society of Limnology and Oceanography in Santa Fé, USA, a special session will be devoted to this interaction.

The organisers of the Woudschoten workshop are grateful to the National Institute of Public Health and the Environment and the Ministry of Housing, Spatial Planning and the Environment for financially supporting this initiative. Our appreciation also goes out to the participants for their contributions and enthusiastic discussion sessions, both during and outside the actual conference; an extra word of thanks for the prompt handling of the manuscripts, sparing us the trouble of sending reminders!

The cover shows an artist's impression of one "objective" of a mesotrophic Dutch aquatic ecosystem, i.e. the ecotone between a clear lake and a clear ditch system, with some of the representative species found there. One of the driving forces of our research is to recover our aquatic ecosystems in such a way as to make these species common again. We are obliged to the Amstel and Gooiland Water Authority for permission to use their "objective" illustration for water systems, which was developed by "79 Graphical Design and Production". The cover was designed by Anne Claire Alta of the RIVM Studio on the basis of this drawing.

Bilthoven and
The Hague
7 December 1996

Caroline van Maarseveen
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Douwe Jonkers
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Introduction to the interaction between nutrients and toxicants in the food chain of aquatic ecosystems

This introduction does not contend to be complete or perfect, but it does contemplate research interactions between nutrients and contaminants, and their effects on the food chain. Its aim is to briefly introduce the short papers in this report prepared by the participants before and after the international workshop on interactions between eutrophication and contaminants at the Woudschoten Conference Centre in the Netherlands.

Algal growth control

Nutrient loading leads *via* higher primary production rates to an increased biomass concentration. This higher biomass results in decreased nutrient levels, higher pH and increased self-shading. The ultimate consequence in fresh water is generally a yearly dominance of nuisance cyanobacteria, in which detritus and DOM (**D**issolved **O**rganic **M**atter) are becoming increasingly more important. Since cyanobacteria are less apt to grazing by the larger crustacean zooplankton, they are normally able to control algal biomass to a certain extent. These larger zooplankton species tend to disappear from the system and are replaced by smaller species (e.g. *Bosmina* spp.) feeding predominantly on detritus and tiny algae. However, Stansfield *et al.* (1989) brought forward the hypothesis that analogue reactions could occur when toxicant concentrations were raised so high as to affect zooplankton. They measured DDT concentrations and their breakdown products in isotope-dated sediment cores from the Norfolk Broads and back-calculated the DDT concentration in the water for the fifties. These concentrations must have been so high that *Daphnia* species could have become extinct, losing the ability to control algal biomass. Such a situation could be a common phenomenon in Dutch waters in agricultural areas, where concentrations of pesticides have been observed that exceeded the Maximum Allowable Risk Value (MTR) manifold (Geenen & van der Geest, 1995). Thus loading with nutrients alone and with contaminants affecting zooplankton can be used to explain succession phenomena in eutrophied aquatic ecosystems. If fishes are treated as toxicants (from the point of view of zooplankton not so peculiar), an analogue control mechanism will act to explain phenomena in eutrophied fresh water, which is also used in biomanipulation experiments to control algal growth (Giussani *et al.*, 1990; Gulati *et al.*, 1990).

Mechanisms of interaction

Several publications have suggested the importance of the interaction. For an overview, see Gunnarsson *et al.*, 1995; Scholten *et al.*, 1994; Jonsson, this volume; Scholten *et al.*, this volume and Taylor *et al.*, this volume.

The mechanisms that act in the interaction processes are summarised below (Taylor *et al.*, this volume):

- Biomass dilution. A higher biomass resulting from increased productivity induced by eutrophication can contribute to dilution of contaminants by uptake of the contaminant in the increased biomass.

- Growth dilution. An analogous reaction may occur if growth rates of phytoplanktonic species are enhanced. Contaminants are then taken up at a higher rate.
- Effect of dissolved organic carbon. Larger pools of DOC can compete for contaminant chemicals, inducing decreased concentrations in the water phase and biomass.
- Sedimentation. Eutrophication may enhance wash-out of contaminants by a relatively larger sedimentation rate caused by the increased biomass. An inverse relationship has been observed between plankton biomass and total concentration of organochlorines (Taylor *et al.*, 1991).
- Sediment—water interactions. Increased sedimentation may result in a higher concentration of contaminants in the sediment compartment (Pavoni *et al.,* 1990). This enhanced concentration may be partly exchanged again with the water column during mineralisation of the sedimented particles.
- Atmospheric exchange. If mechanisms, as described above, can lead to changes in concentration of hydrophobic organic chemicals, they may control the flux over the water—air interface. Oligotrophication may even lead to efflux of HOC (**H**ydrophobic **O**rganic **C**ompounds) from the water phase, while eutrophication may reverse that direction.
- Lipids and food-web structure. HOC may enter the food web faster because of the higher solubility of HOC in lipids in systems in which phytoplankton species with a higher lipid content dominate.
- Direct and indirect effects of contaminants. Contaminants may reach higher trophic levels, such as zooplankton, either by ingestion via the food chain or by direct effects (e.g. damaging the respiratory chain). The result may be the same. However, in eutrophic systems dominated by certain species of cyanobacteria, the grazing rate of these species has been found to decrease, leading to fewer effects *via* the indirect path.

To summarise, at comparable contaminant loading in eutrophic systems with high biomass, and generally higher concentrations of particles and dissolved organic carbon, lower concentrations of contaminants may occur; this mainly being due to carbon dilution and increased sedimentation. This means too that toxic effects at the same toxicant level in oligotrophic ecosystems may have a more drastic effect, since the highest concentrations of hydrophobic chemicals on an organic carbon basis are found there. It also means that in eutrophic systems higher trophic levels are better protected from toxicity. The remaining otter populations in Scandinavia were only present in productive eutrophic lakes (Olsson & Sandegren, 1991a, b). The PCB and DDT content of pike was negatively correlated with trophic state parameters (Larsson *et al.*, 1992).

EUCON project

In 1994, a new research project on the interactive processes between EUtrophication and CONtaminants (EUCON) in aquatic environments was launched by the Swedish Environmental Agency (Gunnarsson *et al.*, 1995). The overall objective of the EUCON project is to access and predict interactions between contaminants and eutrophication in aquatic ecosystems. This objective can be divided into two sub-objectives (Larsson, 1995; Jonsson, this volume):

- to provide the scientific basis for future remedial measures in ecosystems with both eutrophication and contaminant problems, and
- to provide the scientific basis for the interpretation of long-term monitoring data on contaminants, taking into account the importance of eutrophication.

Nutrient status and toxicant uptake

Numerous papers on this subject deal with the mechanisms of uptake of contaminants and their concomitant bio-accumulation in the food web of aquatic ecosystems in a chemical path *via* uptake mechanisms and solubility in lipids. Kinetics of uptake and bio-accumulation kinetics of **H**ydrophobic **O**rganic **C**hemicals (HOC) depend largely on the solubility of these compounds in phytoplankton and their passing on through the food chain (Baker *et al.*, this volume; Gilek *et al.*, this volume; Sijm, this volume; Taylor *et al.*, this volume). The biomass concentrations affect the kinetic transfer of HOC into the food chain, suggesting the importance of the trophic state of the system (Baker *et al.*, this volume). Excretion of exudates that intermediate in algal uptake of HOC accelerates the kinetic transfer (Sijm, this volume). The bio-accumulation in the food chain is dealt with by Evers & Smedes, this volume; Gilek *et al.*, this volume, Janse & Traas., this volume; Kramer *et al.*, this volume; Hendriks & van der Linde, this volume; Sijm, this volume; Swackhammer *et al.*, this volume; Taylor *et al.*, this volume and Wania, this volume. Modelling the kinetics is a valuable tool for increasing the understanding of bio-accumulation (Evers & van der Linde, this volume; Gilek *et al.*, this volume; Hendriks & van der Linde, this volume; Janse & Traas, this volume; Kramer & Aldenberg, this volume; Swackhammer *et al.*, this volume and Wania, this volume).

Monitoring, laboratory experiments and mesocosms

Interpretation of long-term monitoring data has suggested strong interaction between nutrients and contaminants (Axelman, this volume; Gilek *et* al., this volume; Gunnarsson *et al.*, 1995; Evers & Smedes, this volume). It is not simple to reveal the mechanisms behind it, since the growth of natural populations is controlled by a vast complexity of environmental factors. For this reason limnologists have also turned to experiments on a laboratory scale in eutrophication studies. This offers the advantage that the influence of a certain environmental factor on the growth and life cycle of a particular organism can be studied with minimal interference from other factors (Gons, 1977). "It is clear that many aspects of microbial behaviour reflect physiological processes which these creatures have necessarily acquired in the course of evolution to cope with the vicissitudes of life outside the laboratory" (Tempest & Neijssel, 1976). Laboratory-scale experiments in continuous cultures to explain phenomena in natural systems have proven their worth in eutrophication research (Rhee, 1980; Rhee *et al.*, 1981, van Liere & Walsby, 1983). Only a few such laboratory-scale experiments on interaction processes between nutrients and toxicants have been performed (Lederman & Rhee, 1982a, b). A system intermediate to laboratory-scale experiments and natural ecosystems are mesocosms. The complexity of the natural system has become less tangled but is still a conglomerate of interactions. Examples are found in the following: Brock & van den Brink, this volume; Currie *et al.*, this volume; Culp *et al.*, this volume and Scholten *et al.*, this volume). Laboratory experiments and monitoring in ecosystem research should be complementary.

Modelling
The inherent properties of the organisms studied form an essential element in modelling efforts (van Liere & Walsby, 1983; Janse *et al.*, 1992). The results of laboratory and mesocosm experiments are very valuable in conducting modelling (see, for example, the combined efforts of the mesocosm experiments of Brock & van den Brink (this volume) and the subsequent modelling by Janse & Traas (this volume)). Long-term monitoring data are, without a doubt, of uttermost importance for further understanding of the natural ecosystem, but also for calibration and validation of models to translate the simple experimental results into the complexity of the aquatic ecosystem (Kramer & Aldenberg, this volume). A predictive model is also a target of EUCON (Jonsson, this volume; Larsson, 1996). Modelling efforts on the interaction of nutrients and toxicants seem to be rather scarce in the literature.

Concluding remark

Monitoring, experimental research and modelling (Theo Brock's Holy Trinity) are of uttermost importance, both individually and at the integration level, for the understanding of the interaction between nutrients and toxicants.

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The Swedish EUCON project

- Priorities and some results in October 1996

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INTRODUCTION

Based on a report "Possible interactions between eutrophication and pollutant dynamics in the Baltic, the Kattegat and the Skagerrak seas. Research suggestions" the Swedish Environmental Protection Agency Research Council decided to launch the EUCON project and appointed the following project group in the beginning of 1994:

Dag Broman, Stockholm university, Stockholm
Per Jonsson, Swedish EPA, Stockholm (Project manger)
Staffan Lagergren, Swedish EPA, Stockholm
Per Larsson, Lund university, Lund
Mats Olsson, Swedish Museum of Natural History, Stockholm
Rutger Rosenberg, Gothenburg university, Fiskebäckskil
Jens Skei, NIVA, Oslo, Norway (Chairman)

In September 1994 the project group organized an international workshop at Utö in the Stockholm archipelago with the research suggestions in focus of interest. The international panel commented upon the plans and suggested a few important changes to improve the program. The final research plan for the EUCON project is presently about to be printed. The project includes both marine and limnic studies and is focused on questions leading to a better understanding of the interactive processes between eutrophication and contaminants in aquatic ecosystems. Concerning the contaminants the research focus on stable organic compounds, although other compounds/elements (e.g. trace metals, radionucleids) are also included in some of the projects.

Increased knowledge is a prerequisite for undertaking right measures for protection and managing efforts concerning the aquatic environment both locally, regionally and on a large-scale basis.

The two main marine environmental problems today, pointed out by the Swedish Environmental Protection Agency, are related to eutrophication and persistent pollutants. The Swedish government has listed a number of goalsin their work for environmental protection. Two of these are the reduction of nutrients and the reduction of disposals of harmful persistent compounds and metals, in order to improve the conditions in freshwater and in marine ecosystems and create a more healthy environment. However, the knowledge of the possible interactions between these two environmental problems is poor.

An important question is whether the downward trends of organochlorines in biota only are the results of reduced anthropogenic inputs, or if the eutrophication of the sea could exert an effect on the fate and the bioavailability of the pollutants.

There is, so far, no scientific proof of a decreased pollution burden due to an increased nutrient enrichment in the marine environment. However, these interactions are likely to be significant and represent an essential issue in future environmental management. For instance, what will happen with the populations of fish predators if measures are successful to drastically reduce the input of nutrients to the sea in order to counteract the eutrophication process, if simultaneousely taken measures to reduce the load of harmful bioaccumulative compounds are less successful?

OBJECTIVES

The overall objective with the EUCON project is:

- To assess and predict interactions between contaminants and eutrophication in aquatic ecosystems.

This objective can be divided into two sub-objectives:

- To provide the scientific basis for future remedial measures in ecosystems with both eutrophication and contaminant problems.

- To provide the scientific basis for interpretation of long-term monitoring data of contaminants, taking into account the importance of eutrophication.

A PREDICTIVE MODEL APPROACH

The project group adopted most of the recommendations from the workshop at Utö concerning modelling of the EUCON project (incl simple mass balances, focussing on specific subregions of the different sea areas, more advanced models). Within the EUCON framework projects have been initiated dealing with the following scientifically different approaches that may be useful in the overall model approach:

- Sampling of empirical field data from different types of environment
- Studies of crucial mechanisms/processes,
- Evaluation of long-term time trends.

To achieve the overall objectives we aim at establishing a predictive model that will be built on data generated from studies using the different approaches stated above. Environmental administrators are very interested in a type of model that can reasonably predict the concentration of e.g. PCBs in herring as a function of man-made changes of inputs to the ecosystem. The model approach is of great value to identify crucial processes/mechanisms that has to be investigated within the project. In certain cases, enough data is already available and has not to be further studied, while, in other cases, much scientific work has to be done to fit into the model.

The EUCON project is focussed at establishing a predictive model based on mainly the following main compartments:

- Biomass dilution
- Retention time in the water mass
- Sequestering in the sediment
- Input of contaminants to the ecosystem
- Other factors (incl. e.g. water exchange, storm frequency, resuspension frequency, food web structure)

PROJECTS

Sub-projects

At present the following EUCON sub-projects are in progress:
- Andersson, A. Eutrophication effects on distribution and sedimentation of lipids and persistent organic pollutants in the marine environment.
- Borg, H. The importance of trophic level and algal biomass for transport of persistent organic pollutants and metals in lakes.
- Broman, D. In situ characterization of processes fundamental for the interaction between persistent organic pollutants and eutrophication.
- Broman, D., Wania, F. Interaction of eutrophication and the fate of hydrophobic organic compounds in aquatic systems - A modelling approach.
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Other relevant projects

- Starting in 1993, a sediment baseline study is being performed in the Baltic Sea area (Baltic Sea and Kattegat) by HELCOM/ICES. The results of this study is expected to produce relevant information concerning the sequestering of contaminants in offshore Baltic Sea sediments.
- Time-trend analysis of existing data. This project is a joint Nordic project financed by the Nordic Council of Ministers.

SOME PRELIMINARY RESULTS

Field studies have shown that:

- transport of persistent organic pollutants seems to be more related to lipid fluxes than to carbon fluxes
- recycling of persistent organic pollutants (POPs) from sedimenting matter/sediment seem to be faster in oligotrophic than in eutrophic lakes
- sediment deposition of POPs is correlated to autochtonous algal production, whereas allochtonous factors like Fe and Al is more important for the deposition of metals
- PCB concentrations in sedimenting material in the Baltic Sea increase with water depth as a result of mineralisation of organic matter
- PCB concentrations in Baltic proper sediments are increasing during the last twenty years, whereas PCB concentrations are decreasing in pelagic biota. The increased concentrations in the sediments may to a certain extent be due to higher sequestering capacity in anoxic/hypoxic laminated sediments
- laminated sediments have been found in ca 20 investigated archipelago areas. Dating by varve counting are in good agreement with dating by radiocesium. This, together with an extensive bottom mapping of these areas, constitute a good basis for calculation of POP sediment sequestering in relation to eutrophication status

Laboratory experiment have shown that:

- sulphur bacteria mats (which periodically cover large sea bottom areas) substantially accumulate hydrophobic organic pollutants
- bioturbation result in increased fluxes of PCBs from the sediments to the water. Also without bioturbation, substantial fluxes of PCBs from the sediment to the water were found
- nitrogen starvation in relation to phosphorus may lead to increased uptake of persistent organic pollutants in some algal species, which is related to algal lipid concentrations
- blue mussels are important organisms for the fluxes of POPs in coastal areas by increasing the net deposition of POPs to the bottoms, and by accumulating substantial amounts of POPs which subsequently by predation may be substantial POP sources for fish and sea-birds
- PCB is bioaccumulated in the microheterotrophic food web
- the retention times for PCBs in water vary with nutrient trophic status
- food web transportation of PCBs may be faster than PCB sedimentation rates during certain seasons

FURTHER INFORMATION

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Gaining a Mechanistic Understanding of Bioaccumulation of Organic Contaminants by Phytoplankton

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Introduction

The accumulation of recalcitrant hydrophobic organic compounds (HOCs) in phytoplankton plays a significant role in the transport and fate of these compounds in aquatic ecosystems. The sorption of these compounds to phytoplankton can either expedite their removal from the water column or facilitate their movement into the foodweb. HOC-laden phytoplankton that settle from the water column are an important transport mechanism for the removal and eventual burial of these compounds. However, those that are ingested by higher order organisms serve as the primary source of contaminants to the foodweb. As a result, an understanding of the forces which drive and control accumulation of HOCs in phytoplankton, and an ability to predict the magnitude of accumulation under various conditions, are important. This report summarizes a number of studies that we have done to date to gain a mechanistic understanding of the bioaccumulation process, and to develop and test a model for predicting the accumulation of a class of HOCs, the polychlorinated biphenyls (PCBs), in phytoplankton.

PCBs were chosen to represent HOCs for several reasons. First, PCBs allow for the evaluation of compounds having a wide range of physical chemical properties. As a group, they range from the moderately hydrophobic (log octanol-water coefficient, K_{OW}, of 4-5) to the very hydrophobic (log K_{OW} 7-8.5). Secondly, they are a relevant contaminant and insure applicability of the model. Finally, PCBs are ubiquitous in the environment and have been demonstrated to adversely affect aquatic life, wildlife, and human health *[e.g.1]*.

The consumption of contaminated foods, particularly fish, is second only to industrial exposures as a source of PCBs to humans *[2]*. The significance of fish consumption is due primarily to the accumulation of PCBs in the aquatic foodweb. At each level of the foodweb, organisms bioconcentrate PCBs because of the hydrophobic nature of these compounds and their resistance to metabolism. In addition, as higher trophic levels consume contaminated foods, PCBs are retained more efficiently than is organic carbon and are thus biomagnified. A model for the bioaccumulation of PCBs in Lake Michigan lake trout estimated that greater than 99% of the top predator's exposure to HOCs is the result of contaminated food rather than direct exposure to water *[3]*. As the base of the foodweb, phytoplankton play a significant role in the bioaccumulation of PCBs. Phytoplankton account for the largest fractions of both the organic carbon and surface area in the foodweb. As a result, PCBs which are both absorbed in cellular carbon or adsorbed to the cell surface area are efficiently transferred into the foodweb.

Foodchain models that predict the accumulation of HOCs in fish from known water concentrations often have assumed that the primary trophic level is in equilibrium with water *[e.g., 3-5]* and have used K_{OW} to approximate the lipid-normalized bioconcentration factor *[6-7]*. One of the leading sources of uncertainty and sensitivity in the model predictions of higher order trophic levels is the phytoplankton HOC concentration. Thus accurate predictions of phytoplankton HOC accumulation are needed. However, it has been demonstrated that several factors can affect the accumulation of HOCs in phytoplankton, and that the assumption of equilibrium with water leads to biased predictions *[8-11]*.

Phytoplanton Bioaccumulation Model

Previous work has shown that the equilibrium model for predicting bioaccumulation of HOCs in phytoplankton is subject to large uncertainties *[8-11]* and is not appropriate for coupling to foodchain models. In its place, we have proposed a model based on the kinetics of the accumulation process *[12]*. This model describes accumulation as a function of multiple uptake and loss mechanisms and attempts to incorporate all of the factors that have been shown to significantly affect the process.

Empirical evaluation of the laboratory accumulation data reveal that they form an S-shaped or sigmoidal pattern *[10]*, indicating accumulation is into multiple compartments *[13]*. Thus we divided accumulation into surface and matrix components. The matrix component of accumulation was best quantified by a basic single compartment accumulation model and the surface component of accumulation was best quantified by a partitioning equation. Our model takes the form:

$$C_p = F_{lip} \cdot \left[\frac{k_u}{\frac{k_u}{K_{ow} - K_{sa}} + k_d} \cdot C_d \cdot \left(1 - exp\left(-\left(\frac{k_u}{K_{ow} - K_{sa}} + k_d \right) \cdot T \right) \right) + \left(C_d \cdot K_{sa} \right) \right.$$

where C_p is the concentration in the phytoplankton (ng/g), F_{lip} is the phytoplankton lipid fraction, C_d is the dissolved concentration of PCBs (ng/L), k_u is the uptake rate constant (days^{-1}), k_x is the depuration rate constant (days^{-1}), k_d is the growth dilution rate constant (days^{-1}), K_{sa} is the surface adsorption partitioning coefficient, and T is the time function (days). Even though complex, this equation is consistent with the fundamental hypotheses of lipid partitioning. If the system is allowed to reach equilibrium and the influence of other processes are negligible ($T \Rightarrow \infty$, $k_d \approx 0$), the equation reduces to:

$$C_p = F_{lip} \cdot C_d \cdot K_o$$

The input parameters for the kinetic equation to predict the accumulation of PCBs in phytoplankton are the congener-specific dissolved concentrations, congener K_{ow}, lipid content and growth rate of the phytoplankton, and the exposure period. It was empirically determined that constants were adequate for the uptake rate constant and the surface adsorption partitioning coefficient.

The performance capability of the new equation was tested using independent sets of laboratory and field data. In each case, the above equation was used to predict congener-specific concentrations of PCBs in the phytoplankton and these values were compared to measured values. The field data were phytoplankton samples collected from Green Bay in Lake Michigan by size fractionation (10-100 μm). Figure 1 shows the results of predicting PCBs in phytoplankton on a lipid-normalized basis, compared to the actual measured values, for both the kinetics model and the equilibrium model. A perfect fit would have a slope of one and an intercept going through the origin. It is clear that the kinetics model provides a prediction with much less uncertainty than the equilibrium model ($R^2 = 0.77$ vs. $R^2 = 0.47$) and the slope of the kinetics model is not different from 1. However, the intercept is -1.45, indicating that the model consistently underpredicts the measured values by a substantial amount. The intercept is only affected by the normalization parameter. The best absolute fit of the kinetics model occurs when predictions are made on an organic carbon basis, rather than a lipid (or dry weight) basis. The slope of this fit it 0.8, with an intercept of 0.18 and R^2 of 0.73.

The success of the carbon-based equation contradicts the hypothesis that PCBs partition only to the lipid portion of phytoplankton. There are at least three possible explanations for this observation. One is that PCBs have a greater affinity for phytoplankton lipids than they do for n-octanol. Thus, predictions based on K_{OW} would always underestimate accumulation. A second explanation is that phytoplankton components other than lipids, particularly those which are high in organic carbon, are capable of interacting with and stabilizing PCBs to an appreciable degree. A third explanation is that this observed anomaly was the result of a sampling or analytical bias. A source of analytical bias is the method used to measure the lipid content of the field samples. However, the analytical bias in the extraction and storage of lipids would be less than a factor of 2, and cannot account for the magnitude of the differences between the observed accumulation and that predicted by each of the models. Therefore, the likelihood of the other two possibilities needs to be investigated, particularly the role of non-lipid organic material.

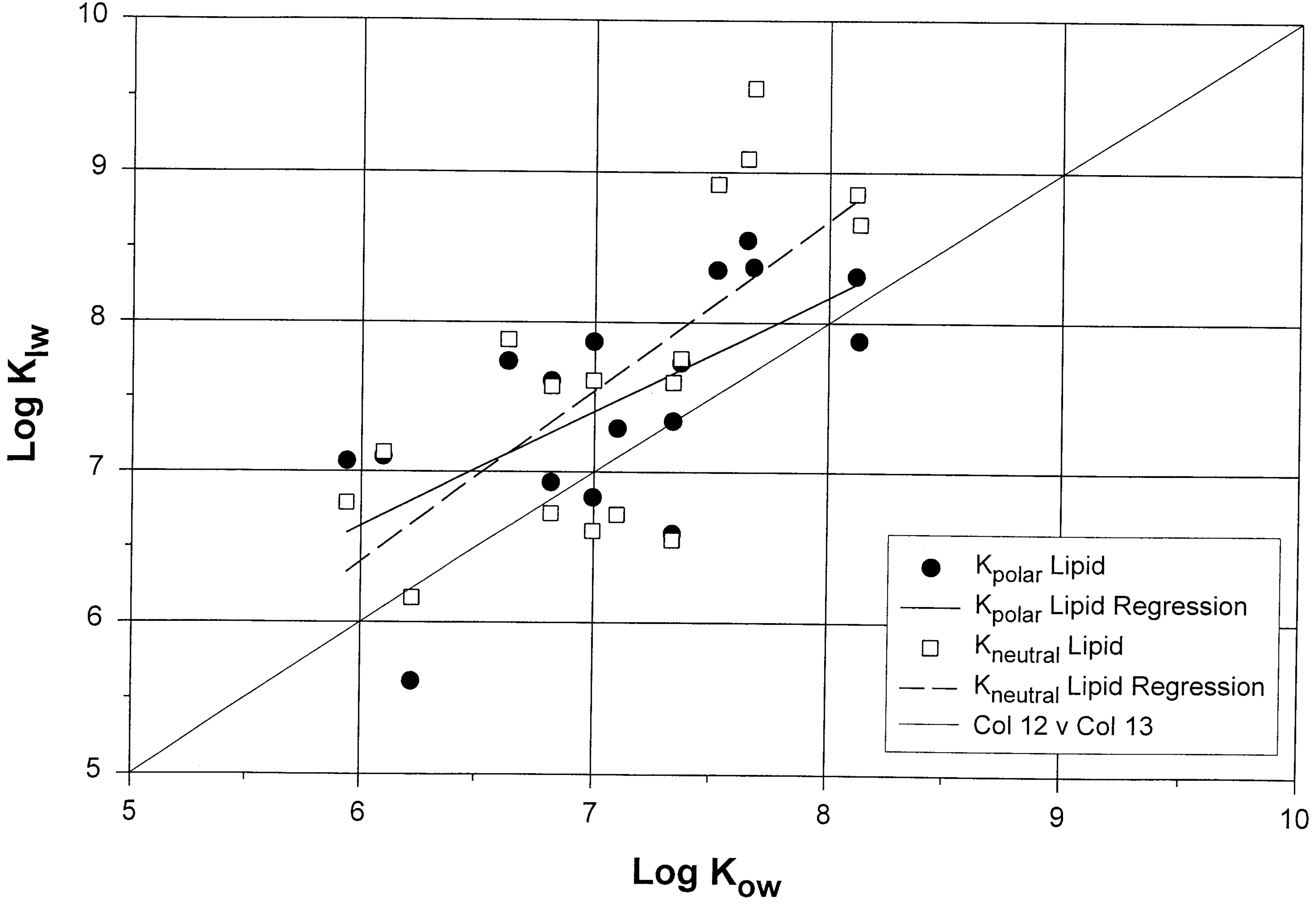
Regardless of whether the lipid or organic carbon fraction of the phytoplankton was used to define concentration, the kinetics model was a better predictor of the observed accumulation. The kinetics model always had a slope that was closer to one and a greater R^2 value.

The Role of Lipids in Bioaccumulation in Phytoplankton

The questions surrounding the exact role of lipids in the bioaccumulation process are two-fold. The first is (1) do HOCs have a greater affinity for phytoplankton lipids than for octanol; and (2) do lipids present a barrier to the uptake of the very hydrophobic molecules? The first question addresses the result presented above - measured HOC concentrations are substantially greater than those that are predicted on a lipid basis when K_{OW} is used to estimate lipophilicity. The second question arises from the frequent observation that the very highly hydrophobic molecules have bioaccumulation factors much less than K_{OW}, even when the system has been given a long time to reach equilibrium. A number of hypotheses have been put forward to explain this phenomenon. The kinetics hypothesis is that accumulation of the very hydrophobic compounds is very slow, and that the chemical has not yet reached equilibrium at the time that BAFs are measured *[14]*. However, given enough time, BAF would follow the predicted relationship with K_{OW}. A second explanation is that the cell membrane provides a physical barrier which the very hydrophobic materials cannot cross because of their physical size and shape *[15-16]*. We have conducted laboratory experiments to address these questions.

To test the hypothesis that PCBs have similar affinities for phytoplankton lipids as for octanol, we measured the lipid-water partition coefficients of selected PCB congeners for polar lipids (membrane lipids) using liposomes *[17]*, and for neutral lipids (internal storage lipids) using the slow-stir method *[18]*. These data are presented in Figure 2. While there is a tendency for the lipid-water partition coefficients to be greater than K_{OW}, there was much scatter in this relationship and there is no statistical difference between K_{LW} and K_{OW}. The exact relationship of

Comparison between K_{ow} and Lipid-Water Partition Coefficients



K_{OW} and lipid-water partitioning is still under investigation. It does not appear that the K_{LW} are a better predictor than K_{OW}.

We investigated the role of the membrane in a series of experiments where we applied the technique of immunogold labeling to follow the movement of a PCB molecule into a cell across the cell wall and membrane *[19]*. Electron micrographs of algal cultures incubated with congeners #52 and #153 after one day and seven days reveal a difference in the way the two congeners associate with the cell at a given time. The more hydrophobic PCB congener (#153) associates preferentially with the outer membrane, while the less hydrophobic congener (#52) quickly reaches equilibrium with the entire cell. However, there was evidence of some of the more hydrophobic congener inside the cell, indicating that the cell wall or membrane does not act as an absolute barrier. These results show that at steady state the more hydrophobic chemicals remain associated primarily with the phospholipids on the exterior of the cell and less hydrophobic chemicals associate with both the interior and exterior of the cell. In light of these results, the highly hydrophobic compounds may need to be normalized to the phospholipid fraction rather than to total lipid.

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THE INFLUENCE OF ALGAL EXUDATES ON THE BIOAVAILABILITY OF ORGANIC TOXICANTS IN THE AQUATIC ECOSYSTEM[1]

and a summary on the research within RITOX on the interaction between eutrophication and contamination of organic hydrophobic contaminants.

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Introduction

The fate of organic micropollutants in the aquatic environment is strongly influenced by bioconcentration by algae [1,2]. Algae occupy an important position in the aquatic food-chain. They are primary producers able to convert CO_2 into biomass, which is utilized by filterfeeders and other small organisms. Hydrophobic chemicals which are present in water may thus enter the food-chain by bioconcentration from water into the algae, followed by consumption of the algae by higher organisms. This is a very important phenomenon which needs to be understood and described in order to predict food-chain magnification of these compounds [3].

A significant amount of organic carbon is returned to the water column by algae through the production and excretion of exudates [4]. During a spring bloom of algae in the northern Baltic, more than 50% of the algal carbon was excreted as exudate [5]. These exudates may be associated with and also may scavenge hydrophobic organic contaminants in the water column. To date, little is known if exudate-bound contaminants exist and how they possibly affect bioavailability and lead to an interaction between eutrophication and contamination.

A number of bioconcentration studies of hydrophobic chemicals by algae have already been reported [6-11], and relationships have been developed between the bioconcentration factor (BCF) of chemicals by algae and the hydrophobicity, expressed as the octanol/water partition coefficient (K_{ow}) [12-14]. However, several observations disturbed the simple linear relationships between hydrophobicity and bioconcentration: i) differences in BCFs are found in summer and winter times [3,15], ii) the slope of the line between the log BCF and log K_{ow} is less than unity [12-15], iii) BCFs exceeded K_{ow} up to a factor 100 or more, when bioconcentration is lipid normalized [3], and iv) BCFs decrease linearly with increasing density of the algae when plotted on a logarithmic scale [16,17].

Growth, which is higher in summer than in winter, of the algae may explain both different BCFs in summer and winter and the slope of the BCF-K_{ow} line being smaller than unity, due to a lack of equilibrium [15]. It is therefore suggested that food-chain models need to use a kinetic framework rather than an equilibrium one to describe bioaccumulation of organic contaminants by algae [3,18].

A possible explanation for the relatively high lipid-normalized BCFs, which is thought to be very unlikely since it would imply that the preference of hydrophobic chemicals for algal lipids is much higher than that for octanol, is that chemicals may have different binding

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affinities towards different classes of lipids in outer membranes and internal lipid storage depots, and that not all lipids are extracted from algae resulting in apparently higher lipid-normalized BCFs [15,18,19].

Algal density dependent bioconcentration may be explained by the presence of exudate in water, which will be higher in high algal densities compared to low algal densities. High colloid concentrations will decrease sorption or bioconcentration [20]. In summer when algal density is higher, the effect of exudate on bioaccumulation will be greatest.

The aim of the present study is to examine the role algal density and exudate play in the BCFs of a series of hydrophobic chemicals in algae.

Bioconcentration model

Bioconcentration of hydrophobic chemicals can be described by a first-order one-compartment kinetic model. Growth of the algae should be included, since algae are fast-growing organisms with a doubling time in the order of days:

$$dC_{alg}/dt = k_1C_w - (k_2+\mu)C_{alg} \qquad (1)$$

C_{alg} is the concentration in the algae (μg/kg), t is time (d), k_1 is the uptake rate constant (L/kg.d), C_w is the concentration of the freely dissolved chemical in water (μg/L), k_2 is the elimination rate constant (1/d) and μ is the growth rate constant (1/d).

The organic exudate may affect the concentration of the chemicals in water. Therefore, the apparent concentration in water, C_w^* (μg/L), is the sum of the concentration of chemicals which are freely dissolved and which are exudate-bound: $C_w^* = C_w + C_wK_ps$, where s is the concentration of exudate in water (kg/L) and K_p is the exudate/water sorption coefficient of the chemical (L/kg). The assumption is that sorption of the organic chemicals to exudate is a linear partitioning process.

Combining the former two equations at steady-state results in an equation for the apparent bioconcentration factor, BCF^*:

$$BCF^* = \frac{C_{alg}}{C_w^*} = \frac{k_1}{(1+K_ps)(k_2+\mu)} \qquad (2)$$

The apparent bioconcentration factor (BCF^*) is equal to the true bioconcentration factor (BCF) only when both sorption of the chemical to exudate and growth are negligible, thus when $K_ps << 1$, and $\mu=0$. In most environmental and laboratory conditions, either growth or sorption to exudate will decrease the true BCF.

Experiments

Algae were grown until they reached the exponential phase. Then a series of bioconcentration experiments were performed.

I. Time dependent bioconcentration of anthracene was studied using three dilutions of a *Chlorella vulgaris* suspension of $11 \cdot 10^9$ cells/L (dry weight: 0.158 g/L).

II. During the growth period of a *Chlorella pyrenoidosa* culture both optical density and

COD in water were measured.

III. A *Chlorella pyrenoidosa* culture with an O.D. of 1.035 (0.476 g/L, $31.9 \cdot 10^{11}$ cells/L) was diluted and exposed to 2,2'5,5'-tetrachlorobiphenyl (PCB-52) in water. Algal and water samples were taken after 3 h. Water samples were split in two, of which one part was used to determine COD, and the other for determination of the PCB-52.

IV. A *Chlorella pyrenoidosa* culture with an O.D. of 0.820 (0.377 g/L, $25.3 \cdot 10^{11}$ cells/L) was diluted and exposed to hexachlorobenzene (HCB), 4,4'-dichlorobiphenyl (PCB-15) and PCB-52 in water. Algal and water samples were taken after 3 h. Water samples were split in two, of which one part was used to determine COD, and the other for determination of the test chemicals.

Results

Algal density (D) and apparent bioconcentration factors (BCF^*) of anthracene are shown in Figure 1. The BCF^* decreases with increasing D: $\log BCF^* = 10.44 - 0.66 \cdot \log D$ ($r^2 = 0.63$, $n = 11$).

COD-concentration in the supernatant water increased linearly with D. This means that during growth there is a continuous rate of exudate secretion by algae, where the amount of exudate is linearly related to D. COD-concentration of water after centrifugation from the undiluted algal suspension of experiments III and IV was 0.476 mmol/L oxalic acid equivalents.

The BCF^*s of HCB, PCB-15 and PCB-52 decreased with increasing D (Figure 1), and thus with increasing exudate concentration as measured by COD (Figure 2). The slope of log BCF^* vs. log COD for PCB-52 alone (experiment III) was -0.40, while the intercept (log COD = 0) was 4.64. The slope of log BCF^* vs. log COD was -0.24 for the three chemicals in combination (experiment IV), and the intercepts were 4.25 for HCB, 3.66 for PCB-15, and 4.56 for PCB-52.

Discussion

The present results show that algal density dependent bioconcentration of hydrophobic chemicals can be explained by the influence of exudate in the aqueous phase. This exudate is capable of sorption of hydrophobic organic chemicals in the aqueous phase, and thereby reduces bioavailability, which is analogously to processes occurring in sorption studies [21,22,23]. The present study shows that the centrifugation technique which is applied to separate algae and water does not separate exudate (COD) from water. Organic chemicals which are sorbed by exudate will thus also not be separated from the aqueous phase. The aqueous concentration will thus be overestimated due to the presence of exudate. The apparent bioconcentration factor is the ratio of the concentration in algae and water, therefore the presence of exudate will lead to an overestimated concentration in water and thus to an underestimation of the bioconcentration factor. Since more exudate is formed, the influence of non-separated hydrophobic chemicals bound to exudate will increase at higher algal density. A similar phenomenon has previously been observed and suggested to explain the decrease of sorption coefficients with increasing sediment density in sorption studies [20,22,23].

Although the influence of algal density on the decrease of the apparent bioconcentration factor of hydrophobic organic chemicals may be explained by the influence of exudate, there are some unexplained observations in the experimental results. Firstly, no levelling off of the apparent bioconcentration factor is observed at low algal density for neither the present experiments (Figure 1), nor those in the literature. This may indicate that exudate is always present and capable of binding chemicals in the aqueous phase or that another process causes algal density dependent bioconcentration.

A second unexplained observation is that the relationship between the apparent bioconcentration factor and the exudate concentration shows a slope of less than unity when plotted on a double logarithmic scale (Figures 1 and 2). Also a slope of less than unity is found for 2,4,5,2',5'-pentachlorobiphenyl [17] and for two phenylbenzoylurea insecticides [24] in the literature. This means that sorption of the organic chemicals is not a linear function of the algal density or exudate concentration, which may be caused by a changing constitution of exudate with concentration [4], by a Freundlich type relationship for the sorption of hydrophobic chemicals to exudate or algae [24], or when sorbate-sorption interactions are dependent on either sorbate or sorbent concentrations [25].

A third unexplained observation is that the slopes which are found in the various experiments differ, but are independent of the chemical within an experiment. Again, this can be explained when the composition of the exudate differs between experiments under different growth conditions [4], which cause different sorption properties of the organic chemicals to the exudate in the aqueous phase.

Conclusions

The decrease in apparent bioconcentration factors (BCF^*s) of anthracene, hexachlorobenzene, 4,4'-dichlorobiphenyl, and 2,2'5,5'-tetrachlorobiphenyl with increasing density of the algae *Chlorella vulgaris* and *Chlorella pyrenoidosa* is explained by an inappropriate separation of organic exudates, which bind hydrophobic organic chemicals, from water. At higher exudate concentrations the apparent higher concentrations of the chemicals in water is due to binding to exudate, which is excreted by algae in water and which increases linearly with algal density, as measured by chemical oxygen demand (COD). The expected slope of -1 between exudate concentration and BCFs on a double logarithmic scale, however, was not observed, which suggests that either sorption to exudate is not a linear process or that other processes may be involved.

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A summary on the research within RITOX on the interaction between eutrophication and contamination of organic hydrophobic contaminants.

It is essential to better understand the role which phytoplankton plays in the distribution of organic chemicals in the aqueous phase to study the interaction between eutrophication and contamination. A reduction of eutrophication may lead to a reduction in algal densities which in turn may affect the distribution of organic contaminants in the aqueous phase. Within RITOX studies are and in the coming years will be performed on the kinetics of exchange of organic chemicals from water to phytoplankton and vice versa, and on the distribution of contaminants between water, exudates and other colloidal or dissolved material and phytoplankton in lab and field situations. Cooperative studies are presently performed with the Stockholm University (Sweden) and the Technical University of Denmark (Denmark).

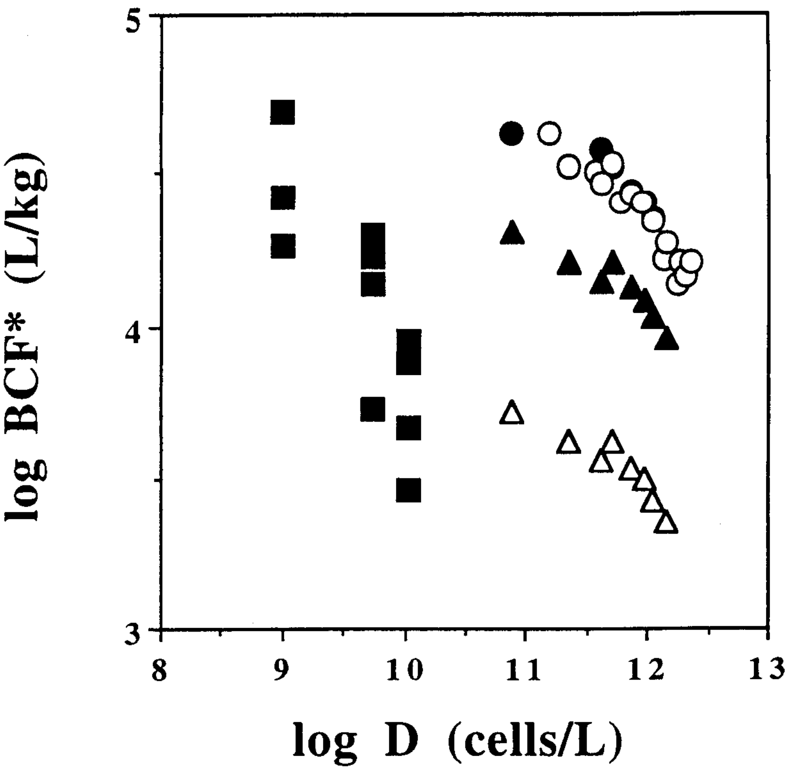

Figure 1. Relationship between algal density (D) and apparent bioconcentration factor (BCF^*) of anthracene (■) in *Chlorella vulgaris* (exp. I), of PCB-52 (O) in *Chlorella pyrenoidosa* (exp. III), and of HCB (△), PCB-15 (▲) and PCB-52 (●) in *Chlorella pyrenoidosa* (exp. IV).

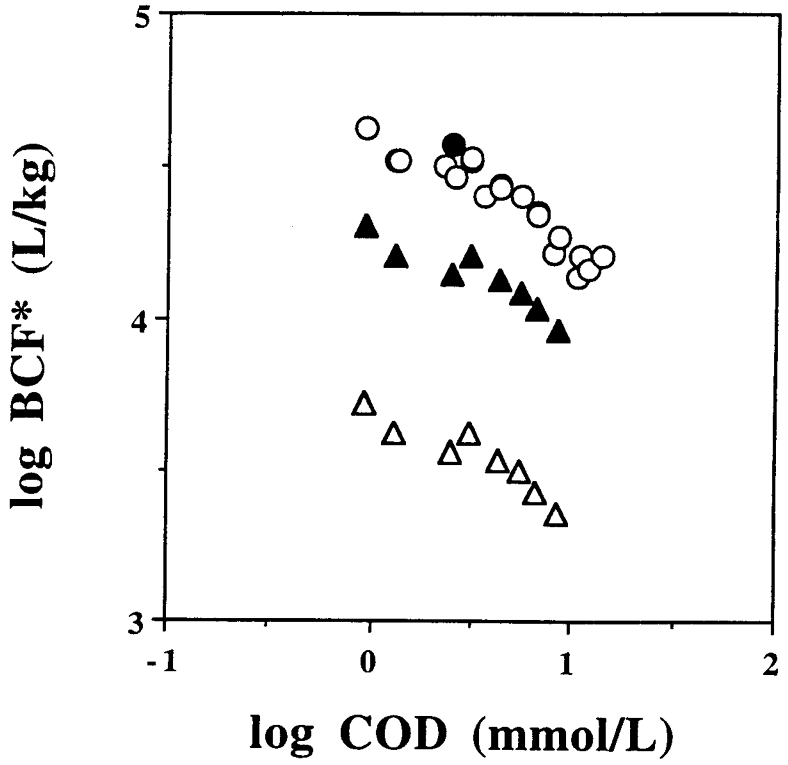

Figure 2. Relationship between exudate concentration (COD) and apparent bioconcentration factor (BCF^*) of PCB-52 (O) in *Chlorella pyrenoidosa* (exp. III), and of HCB (△), PCB-15 (▲) and PCB-52 (●) in *Chlorella pyrenoidosa* (exp. IV).

INFLUENCE OF BIOMASS CONCENTRATION ON THE KINETIC TRANSFER OF HYDROPHOBIC ORGANIC CHEMICALS IN AQUATIC FOOD WEBS

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Introduction

Uptake of dissolved hydrophobic organic chemicals (HOCs) by plankton is the important first step of bioaccumulation of these persistent contaminants in aquatic food webs. As higher organisms are exposed to HOCs primarily by ingestion of contaminated prey, HOC uptake into plankton conveys dissolved contaminants into fish. Plankton are organic-rich particles that play important roles in the geochemical cycling and aquatic residence times of hydrophobic organic contaminants. For example, efficient packaging of PCBs and PAHs by rapidly settling biogenic particles (*i.e.*, diatom aggregates, macrozooplankton fecal pellets) sweeps these contaminants from Great Lakes surface waters and delivers them to the benthos (Baker *et al.*, 1991). Thus, linkages between eutrophication and persistent, bioaccumulative chemical issues include not only the efficiency of contaminant bioaccumulation, but also the interplay between organic matter production and contaminant geochemistry.

Uptake of HOCs into phytoplankton likely results from passive transport onto and, perhaps, through the membrane at a rate dependent upon the diffusion of the compound though the stagnant water surrounding the cell and the subsequent migration through the membrane. Because phytoplankton are generally small, rich in organic carbon, and reside in turbulent surface waters, it has been generally assumed that uptake of HOCs into plankton is rapid (*i.e.*, times to equilibrium of hours, Harding and Philips, 1978; Biggs *et al.*, 1980) and can be modeled as a passive equilibrium partitioning process (*e.g.*, described by Freundlich isotherms, Harding and Philips, 1978). However, recent work has challenged this assumption, suggesting that kinetically-limited uptake of HOCs by rapidly-growing phytoplankton maintains subsaturated conditions in natural waters (Swackhamer and co-workers).

Detailed examination of the rate of HOC uptake by plankton indicates a rapid initial uptake (time scales of minutes) followed by a slower migration into the cells (time scales of hours to months). In on of the first studies of PCB uptake by phytoplankton, Harding and Phillips (1978) determined that >90% of the ultimate (48 hour) uptake of 2,2',4,5,5'-pentachlorobiphenyl occurred within the first 30 minutes of exposure, followed by a small amount of additional uptake during the next two days. Mailhot (1987) and Richer and Peters (1993) observed similar time courses, which they empirically modeled using a square hyperbola. Later, Swackhamer and colleagues (Swackhamer and Skoglund, 1991; 1993; Skoglund and Swackhamer, 1994; Stange and Swackhamer, 1994; Skoglund *et al.*, 1996) conducted a series of experiments focused primarily on the second stage of uptake, which they characterize as a very slow approach (time scales of weeks to months) to equilibrium

Although these previous studies have quantified uptake kinetics of HOCs to phytoplankton, another confounding issue is whether the concentration of biomass influences the magnitude of either the rate or the extent of HOC uptake by plankton. Harding and Phillips (1978) reported that the measured concentration of 2,2",4,5,5'-pentachlorobiphenyl adsorbed to marine plankton cells varied inversely with the cell density. Recently, Sijm *et al.* (1995) demonstrated that bioaccumulation factors (*i.e.*, the ratio of HOC associated with plankton to that dissolved in the surrounding water) varied inversely with the plankton cell density. In their studies, the magnitude of the BAF varied inversely with the measured chemical oxygen demand of the filtered media, a surrogate measure of HOC-binding ligands. They concluded, therefore, that the production of extracellular organic matter by the plankton culture results in the observed apparent dependence of algal HOC uptake on the density of biomass. This suggests a feedback between HOC accumulation at the base of aquatic food webs and overall trophic condition, with increasing eutrophication serving to dampen HOC accumulation through the production of competing ligands. While these results intriguing, extremely high biomass densities (10^{10} - 10^{12} cells/L) were used in these experiments, and whether the conclusion can be extrapolated to natural waters is an interesting question.

The question of whether biomass concentration affects HOC bioaccumulation in plankton is quite similar to the 'particle concentration effect' debate explored in the literature during the mid-1980's (O'Connor and Connolly, 1980; Voice *et al.*, 1983; Baker *et al.*, 1986; Gschewend and Wu, 1985; DiToro *et al.*, 1986). Numerous investigations of HOC sorption to artificial and natural solids found that the magnitude of the sorption constant (ratio of concentration sorbed to that dissolved) varied inversely with the concentration of solids in suspension (O'Connor and Connolly, 1980; Voice *et al.*, 1983; Baker *et al.*, 1986; Gschewend and Wu, 1985). Two schools of thought emerged. One model, consistent with the interpretation of Sijm *et al.* (1995) discussed above, is that measurements of the 'dissolved' HOC concentrations are compromised by the inadvertent inclusion of HOCs bound to very small particles ("colloids"; Baker *et al.*, 1986; Gschwend and Wu, 1985) or dissolved organic matter (*e.g.*, humic and fulvic acids; Voice *et al.*, 1983). The other model invokes either slow ("resistant") desorption kinetics (DiToro *et al.*, 1986) and/or energetic arguments (Mackay and Powers, 1987) that depend upon the concentration of particles in solution. Despite considerable discussion in the literature, the mechanisms underlying the often-observed 'particle concentration effect' on pollutant sorption distribution coefficients are unclear.

The purpose of this paper is to explore whether the uptake of hydrophobic organic contaminants by plankton depends upon the concentration of biomass in suspension, and whether such a dependence quantitatively affects contaminant bioaccumulation in aquatic food webs. Building on the previous work on HOC uptake by algae, and inspired by Sijm *et al.*'s arguments about extracellular ligand production, we conducted a series of laboratory experiments that explored the effect of biomass concentration on HOC uptake by the estuarine chrysophyte *Isochrysis galbana*. The results of these studies were incorporated into an ecosystem-process model of contaminant transfer through an estuarine food web in order to assess the quantitative importance of biomass-dependent accumulation.

Methods

Our experimental strategy was to expose algal cells growing at stationary phase under realistic light and nutrient conditions to known and constant dissolved polychlorinated biphenyl congeners. Dissolved PCB concentrations were produced and maintained by bubbling PCB-laced humidified air through a column of diluted seawater until constant levels of PCBs were measured in both the solution and in the out flowing airstream. This treatment of the experimental apparatus also preconditioned the walls with PCBs to be in equilibrium with the dissolved and gaseous phase PCB concentrations. After the apparatus and seawater was dosed with the PCB congeners, a dilute suspension of *Isochrysis galbana* cells was added to the water, resulting in final biomass concentrations of 1.4 x 10^9 and 1.1 x 10^8 cells/L in two experiments. While the dissolved PCB concentrations dropped slightly during the initial phases of the exposure (*e.g.*, first minutes), partitioning of additional gaseous PCBs into the water buffered the dissolved concentration during the five day experiments. Samples of the suspension were collected on an inverse logarithmic schedule and algal-associated (filtered-retained) and dissolved (non-filter retained) PCBs were measured. The experiments continued for at least five days, and ended when the cells began to break apart.

These experiments were conducted at very low biomass concentrations (10^8-10^9 cells/L) and correspondingly low levels of dissolved organic carbon (1-10 mg C/L). Unlike previous studies where HOCs are added as a single pulse at the beginning of the exposure, we maintained constant and low dissolved HOC exposure throughout the experiment.

Results and Discussion

Uptake of PCB congeners in our experiments followed the characteristic two step kinetics observed by Harding and Philips (1978), Mailhot (1987), and Richer and Peters (1993). Rapid (*i.e.*, time scale of minutes) initial uptake accounted for between 10 and 90% of the total PCB uptake by *I. galbana*. Additional accumulation occurred during the next several hours. Concentrations of PCB congeners associated with the algal cells did not change appreciably after 24-48 hours, suggesting that a steady-state was reached within the intact cells. Once the cells began to break apart, both DOC concentrations and measured PCB partitioning increased, suggesting that algal-derived detritus effectively binds organic contaminants.

Most interestingly, the measured 'steady-state' (*e.g.*, five day) PCB bioaccumulation factors were approximately ten-fold *higher* when biomass was 10^8 cells/L compared to when the biomass was 10^9 cells/L. In other words, the algal cells accumulated much more PCB at the lower biomass concentration, despite being exposed to the same dissolved PCB concentration for the same amount of time. In addition, by maintaining a constant dissolved PCB concentration *via* gas exchange, this observation can apparently not be explained by the production of extracellular organic ligands (the

DOC concentrations were proportionately lower in the low biomass experiment). While we do not have a satisfactory explanation for this observation, it suggests that variations in biomass concentrations in the range typically encountered in natural waters (*e.g.*, during a plankton bloom) significantly impact HOC uptake at the base of the food web.

What are the consequences of the biomass-dependent partitioning of HOCs to plankton? In addition to influencing the extent of HOC uptake, the amount of plankton biomass in the water column also influences other biogeochemical and trophic transfer processes. Specifically, the feeding behaviors of planktivorous fishes are dependent on the density of their prey, with ingestion rates increasing linearly at low algal densities and plateauing and becoming density-independent at higher algal biomass concentrations. As the HOC concentrations (mass/mass) in the algae decrease with increasing biomass (*i.e.*, BAF inversely correlated with biomass, as above), we suggest that the maximum trophic exposure of HOCs to planktivores occurs at an intermediate algal density. Using a trophic transfer model scaled to the Chesapeake Bay food web, we are exploring the interactions between biomass-dependent HOC uptake, grazing and ingestion rates, and net transfer of pollutants to higher trophic levels.

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Bioaccumulation and cycling of hydrophobic organic contaminants by Baltic Sea *Mytilus edulis*: Implications of changes in eutrophication status. A summary of an ongoing research project.

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Summary

In this paper we describe the progress of a research project concerning the influence of changes in eutrophication status on the bioaccumulation and cycling of hydrophobic organic contaminants (HOCs) in Baltic Sea blue mussels (*Mytilus edulis*). The approach of the project is to combine laboratory and field experimentation with dynamic modelling to explore the interactions between eutrophication and contamination in this biomass dominant suspension-feeding mussel. The work within the project has so far been focused on mechanistic laboratory experiments of how changes in algal enrichment influences the bioaccumulation kinetics of HOCs in blue mussels. In these experiments we show that the rate of HOC uptake is greatly influenced (up to two orders of magnitude) by changes in algal food concentrations, whereas HOC depuration mainly is unaffected by such changes in food ration. The observed differences in PCB uptake were primarily caused by the influence of food ration on the physiological activity of the mussels and only to a lesser degree by changes in PCB bioavailability due to PCB partitioning between water and algal food.

As a first step towards achieving a large-scale dynamic model of HOC cycling by Baltic blue mussels, we have established budgets of the flow of carbon as well as the flow of some important HOC groups (i.e. polycyclic aromatic hydrocarbons, polychlorinated dibenzo-*p*-dioxins and furans and PCBs) through the dense blue mussel population inhabiting the Swedish coastal zone of the Baltic proper. The established HOC budgets show that the blue mussel significantly modifies the cycling of HOCs in the coastal zone of the Baltic proper by for example: (i) increasing the net deposition of HOCs to the bottoms by 13-19% and thus also enhancing the availability of these contaminants to other benthic organisms. (ii) bioaccumulating large amounts of HOCs and thus constituting a significant contaminant source to demersal fish and waterfowl species that feed on mussels.

In the last part of this paper we also describe and discuss research requirements and outline planned modelling studies.

Background and General Objectives

Eutrophication and hydrophobic organic contaminants (HOCs) constitute major environmental problems in many marine areas (Goldberg 1993), as for example in the semi-enclosed Baltic Sea (Elmgren 1989). Recently, there has been a growing awareness that changes in eutrophication status might influence the partitioning, fate and effects of HOCs in aquatic environments (e.g. Gunnarsson et al. 1995). It has, for example, been suggested that an increase in organic matter generated by the eutrophication process will contribute to the dilution of HOCs and thereby decrease their environmental hazard (Olsson and Jensen 1975; Taylor et al. 1991). However, although several theoretical models have been proposed (review in Gunnarsson et al. 1995), very little is known of if and how changes in eutrophication will influence HOC bioaccumulation in natural populations of aquatic organisms. To increase the mechanistic understanding of these interactions a new research project area on the interactive processes between eutrophication and contaminants (EUCON) was launched by the Swedish Environmental Protection Agency in 1994.

Within the EUCON project area we have since 1994 studied the interactions between eutrophication and the bioaccumulation and cycling of HOCs by Baltic Sea blue mussels, *Mytilus edulis* (Kautsky et al. 1994-97). We argue that, since this suspension-feeding biomass dominant species is of great structural and functional importance in coastal areas of the Baltic proper (Kautsky 1981; Kautsky and Kautsky 1995) and functions as a connecting link between the pelagic and benthic ecosystems through biodeposition (Kautsky and Evans 1987), it is of great interest to assess its role in the flux of HOCs and how changes in eutrophication status may modify this role.

The general objectives of the project are:
(1) To increase the mechanistic understanding of how changes in the quantity and quality of particulate and dissolved organic carbon in the ambient water affects the bioaccumulation kinetics of HOCs in Baltic blue mussels. Within this initial phase of the project we have in manipulative laboratory experiments studied how changes in phytoplankton enrichment influences the bioavailability and bioaccumulation of selected polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) for Baltic Sea blue mussels (Björk and Gilek 1996; Gilek et al. 1996a; Björk and Gilek submitted). The results of these studies are described more in detail in the 'Influence of Algal Food Concentration' section below.

(2) To construct and refine a dynamic model of the bioaccumulation and cycling of HOCs by blue mussels in the Baltic proper. The aim is to incorporate important environmental and biological variables such as temperature, particulate organic carbon, water pumping and food consumption, and mussel growth and biomass as forcing functions in the model.

(3) To use the established dynamic model to explore implications of changes in particulate and dissolved organic carbon, and mussel biomass on important variables such as bioaccumulation, biodeposition and trophic transfer of HOCs in the Baltic proper.

The work within the project has so far been focused on mechanistic laboratory experiments, i.e. (1) above, and the modelling work has only just begun (Gilek et al. In press). Below we describe and discuss the results already generated by the project (both experimental and modelling). Thereafter, we identify research requirements and shortly describe how we plan to construct a dynamic model which is sufficiently reliable to use when exploring the influence of eutrophication.

Influence of Algal Food Concentration

Background

Per definition, hydrophobic organic contaminants (HOCs) tend to escape water and thus have a high affinity for organic matter in the aquatic environment (e.g. Karickhoff et al. 1979). Sorption of HOCs to particulate organic matter is generally thought to reduce the biological availability of these contaminants to gill breathing aquatic organisms by reducing the amount of freely dissolved compound available for accumulation across the gills and other exposed epithelia (e.g. McCarthy 1983; Schrap and Opperhuizen 1990).

However, for suspension-feeding blue mussels this partitioning towards particles also implies that a large amount the HOCs present in the water mass will be associated with the small organic particles which constitute their food source (Broman et al. 1991). Several authors have also suggested that contaminated food is an important source of HOC uptake for suspension-feeding mussels (e.g. Broman et al. 1990; Gilek et al. In press). Furthermore, blue mussels exhibit a large ability to physiologically adapt to changes in food availability by regulating water-pumping and ingestion rates as well as the efficiency with which carbon is assimilated (Winter 1978; Navarro and Winter 1982; Bayne et al. 1989). Consequently, variations in the quantity of organic particles in the water may modify contaminant bioavailability (Schrap 1990) as well as the route of contaminant exposure due to particle sorption (Schrap and Opperhuizen 1990) and/or by influencing physiological processes involved in contaminant accumulation (e.g. Boese et al. 1988; Fisher et al. 1993).

Relatively few researchers have, however, investigated the influence of changes in food concentrations on HOC bioaccumulation by suspension-feeding mussels. The results of these studies are also contradictory in the sense that both increased (Widdows et al. 1982; Brieger and Hunter 1993) and decreased (Fisher et al. 1993) bioaccumulation of HOCs have been observed in response to increases in the availability of organic food particles. Therefore, the influence of changes in algal food availability on HOC bioaccumulation by Baltic blue mussels was studied and explained in a series of three papers (Björk and Gilek 1996; Gilek et al. 1996a; Björk and Gilek submitted). In all of these studies food availability was manipulated with suspensions of the unicellular green algae *Chlamydomonas* sp. First of all (Björk and Gilek 1996; Gilek et al. 1996a) we studied whether or not HOC bioaccumulation by Baltic blue mussels is affected by changes in food availability (within natural limits). Thereafter, an attempt was made to explain the mechanisms behind the observed algal concentration effects (Björk and Gilek submitted).

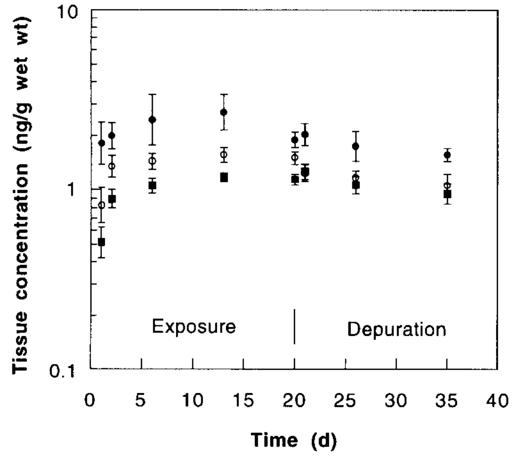

Figure 1. *Mytilus edulis.* ^{14}C-phenanthrene tissue concentration, mean (n=8) ±SE, at high (•), low (■) and brackish water background (o) POC concentration. (From Björk and Gilek 1996).

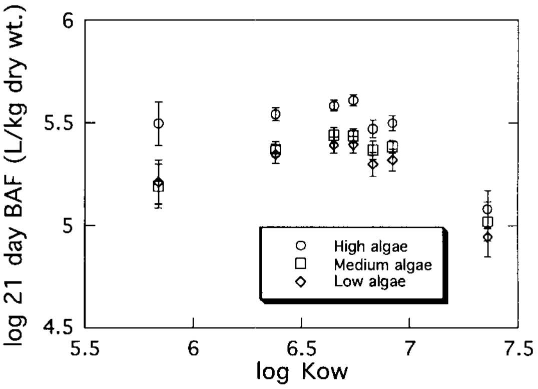

Figure 2. Bioaccumulation factors (BAFs), geometric mean±SE, n=3, of 7 PCB congeners in *Mytilus edulis* exposed to Aroclor 1248 at 3 different algae enrichments for 21 days. Values are plotted against the octanol/water partition coefficient (K_{ow}) of each PCB congener. (From Gilek et al. 1996a).

Observations

In the two first studies, algal food concentrations were manipulated in flow-through experiments lasting for several weeks. It was observed that the bioaccumulation of phenanthrene (Björk and Gilek 1996)(Fig. 1) and PCB congeners (Gilek et al. 1996a)(Fig 2) was enhanced as the algal food concentration was increased from around zero to concentrations that correspond to low-medium concentrations found in coastal Baltic waters, i.e. 0.15 and 0.32 mg particulate carbon per litre in (Björk and Gilek 1996) and (Gilek et al. 1996a), respectively. These observations are, as mentioned earlier, contrary to the findings of studies performed with other gill breathing aquatic organisms (McCarthy 1983; Schrap and Opperhuizen 1990).

It was also observed that the rate of phenanthrene depuration was unaffected by changes in algal food concentration (Björk and Gilek 1996). Therefore, we concluded that the observed increase in phenanthrene bioaccumulation must be caused by an increase in the rate of uptake. Furthermore, our calculations indicated that the observed increase in phenanthrene bioaccumulation could not be explained by an enhanced dietary uptake, but was rather caused by an increased uptake of truly dissolved phenanthrene (Table 1). We proposed that this was caused by a physiological adaptation of mussels to changes in food availability. Thus, it is expected that mussels have low filtration rates when extremely low food concentrations are present in the water (Winter 1978). As the availability of food particles increases over a threshold value, the water pumping activity of mussels is enhanced (Winter 1978) and thereby also the rate with which mussels encounter the contaminant. This 'uptake rate increase hypothesis' was also proposed as the mechanism behind the observed increase in PCB bioaccumulation with algae enrichment (Gilek et al. 1996a). The validity of this proposed mechanism was subsequently evaluated in our next study (Björk and Gilek submitted).

Table 1. *Mytilus edulis.* The relative contribution of phenanthrene (phe) from food to the total uptake day 1. Food ration is given as the amount of particulate carbon added per day and g wet mussel tissue. C_f is the concentration of phenanthrene in the POC fraction. (From Björk and Gilek 1996).

Treatment	Food ration (mg/d/g)	$\log K_{oc}$[1] (L/kg)	C_f (ng/mg)	Food uptake (ng phe/d/g)	Tissue conc. (ng phe/g)	% of total
H	0.53	4.56	0.18	0.077	2.25	3.4
L	0.26	4.76	0.29	0.060	0.58	10.4
B	0.22	4.82	0.33	0.058	0.97	6.0

[1] K_{OC} from the relationship: $\log K_{OC} = 5.74 - 0.54 \log POC$ (Björk and Gilek unpublished data).

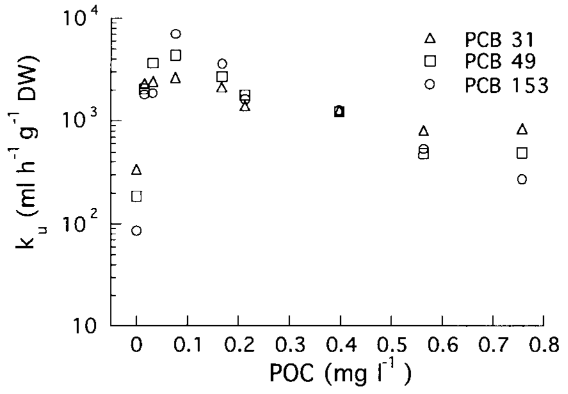

Figure 3. Relationships between the PCB uptake rate coefficients (k_u) of *Mytilus edulis* and particulate organic carbon (POC) concentration. (From Björk and Gilek submitted)

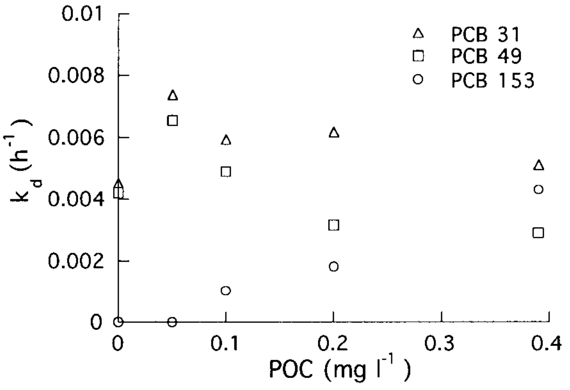

Figure 4. PCB depuration rate coefficients (k_d) of *Mytilus edulis* at 5 different particulate organic carbon (POC) concentrations. (From Björk and Gilek submitted).

Mechanisms

In Björk and Gilek (submitted) the uptake and depuration kinetics of a tri-, a tetra- and a hexa-chlorobiphenyl (PCBs 31, 49 and 153) in Baltic blue mussels were experimentally determined at different algal food rations (0-0.76 mg particulate carbon per litre). The results of these experiments indicate that the mechanism proposed in Björk and Gilek (1996) and Gilek et al. (1996a) was correct. Thus, we observed that changes in food availability significantly influenced the rate of PCB uptake (by nearly two orders of magnitude)(Fig. 3), whereas PCB depuration was mainly unaffected by differences in algal food concentration (Fig. 4). Consequently, it is predicted that PCB bioaccumulation by Baltic blue mussels is highly dependent on the availability of food particles in the water.

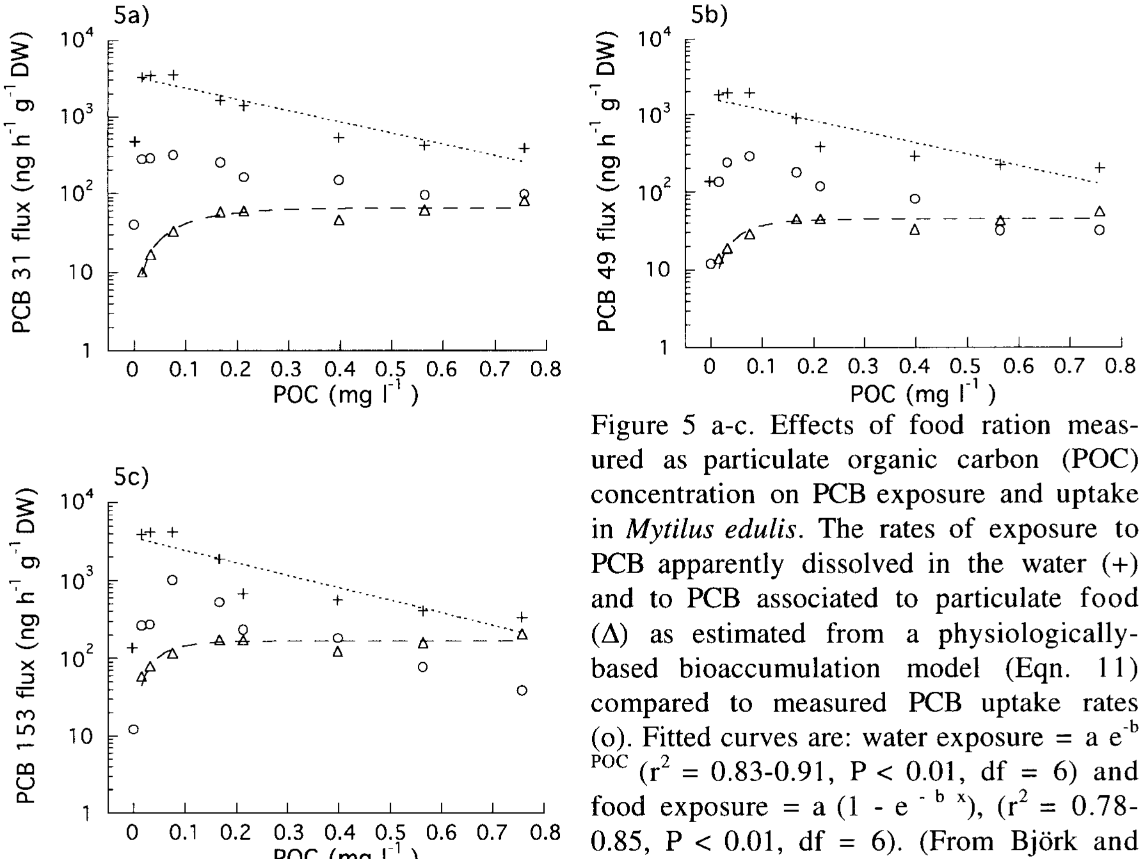

Figure 5 a-c. Effects of food ration measured as particulate organic carbon (POC) concentration on PCB exposure and uptake in *Mytilus edulis*. The rates of exposure to PCB apparently dissolved in the water (+) and to PCB associated to particulate food (Δ) as estimated from a physiologically-based bioaccumulation model (Eqn. 11) compared to measured PCB uptake rates (o). Fitted curves are: water exposure = a $e^{-b\,POC}$ (r^2 = 0.83-0.91, $P < 0.01$, df = 6) and food exposure = a (1 - e^{-bx}), (r^2 = 0.78-0.85, $P < 0.01$, df = 6). (From Björk and Gilek submitted).

A physiologically-based model (PB) was then used to describe how changes in algal food concentration influenced the rate with which mussels were exposed to the studied PCB congeners. The PB model showed (Fig. 5) that the observed changes in PCB uptake primarily were caused by the influence of food availability on the physiological activity of the mussels (i.e. water pumping and ingestion rates)(Fig. 6) and only to a lesser extent by changes in PCB bioavailability due to PCB partitioning between water and algae (Fig. 7). Thus, the observed parabolic relationship between PCB uptake and algal food concentration (Fig. 3) can be explained as follows: When no particulate food is present in the ambient water, mussels keep water pumping rates down to a minimum and consequently the exposure to PCBs truly dissolved in the water is low. When particulate food is present over a certain threshold, water pumping is increased and a maximum in water pumping is reached at low food rations as a consequence of a physiological adaptation to low food availability. This results in a much higher exposure to truly dissolved PCBs at low food concentrations compared to when no food is present. However, PCB exposure from water will decline exponentially with further increases in food ration due to a similar decrease in the rate of water pumping, whereas PCB exposure from food will increase with food ration until the maximum feeding rate is reached. This proposed physiological explanation is modified by several factors which affect the bioavailability of the contaminant. For example, the results of Björk and Gilek (submitted) indicate that the assimilation efficiencies (AEs) of truly dissolved PCBs are inversely related to the water pumping rate of mussels. Similarly, the AEs of PCBs from food particles are probably inversely related to the ingestion rate of particles, since the gut passage time decreases (and thereby also the contact time of consumed PCBs with the gut wall) with increases in ingestion rate (Bayne et al. 1989). Furthermore, at high particle concentrations the feeding capacity of mussels will become saturated and the overall assimilation efficiency will drop, since mussels will only consume a fraction of the particle associated PCBs. Food AEs are also affected by properties of the particle, e.g. the digestibility of the particle (Bruner et al. 1994). Finally, the outcome will be affected by the partitioning behaviour of the contaminant, which to a large extent is determined by the hydrophobicity of the contaminant (e.g. Karickhoff et al. 1979). To conclude, the influence of changes in food availability on HOC bioaccumulation by suspension-feeding mussels needs, to some extent, to be investigated on a case to case basis. All in all, however, it seems highly probable that homeostatic regulations of feeding behaviour in response to natural variations in food concentrations to a large extent will influence the route and rate of HOC uptake by blue mussels and probably also by other suspension-feeding mussels.

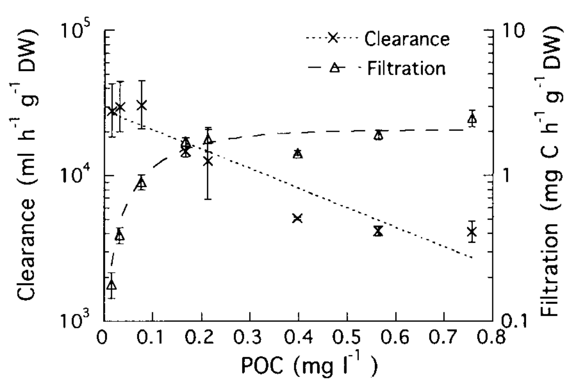

Figure 6. Algae clearance and filtration rates of *Mytilus edulis* at different particulate organic carbon (POC) concentrations. Fitted curves are: clearance = 2.8 ± 0.3 10^4 $e^{-3.1 \pm 0.2\ POC}$ ($r^2 = 0.89$, $P < 0.0001$, df = 22), and filtration = 2.1 ± 0.2 $(1 - e^{-8 \pm 3\ POC})$ ($r^2 = 0.87$, $P < 0.001$, df = 22), (mean ± SE). (From Björk and Gilek submitted).

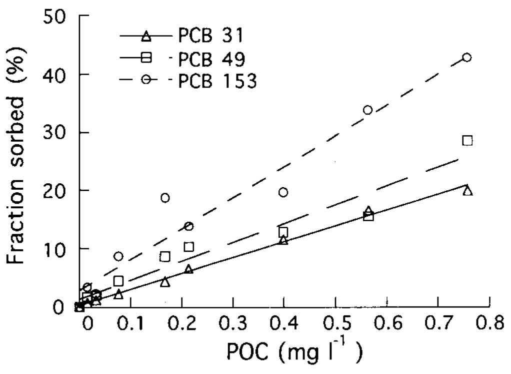

Figure 7. Fraction of PCB sorbed (Fs) to the green algae *Chlamydomonas* sp at different algae concentrations measured as particulate organic carbon (POC). Lines indicate least square regressions, Fs = a + b POC ($r^2 = 0.94$-0.99, $P < 0.0001$, df = 7) where b values (mean ± SE) are 27 ± 1, 32 ± 3 and 53 ± 5, for PCB 31, 49 and 153, respectively. (From Björk and Gilek submitted).

Implications

In the field, suspension-feeding blue mussels encounter substantial temporal (Kiørboe et al. 1981; Elmgren 1984) and spatial variations (e.g. Seed and Suchanek 1992) in suspended particulate food concentrations, and our results indicate that the route and in particular the rate of HOC uptake will be influenced by this variation in food availability, whereas no significant influence on contaminant elimination is expected.

In what way long-term changes in phytoplankton production, as e.g. observed this century in the Baltic Sea due to eutrophication (Elmgren 1989), will influence the bioaccumulation and cycling of HOCs in the dense and ecologically important blue mussel populations found in the Baltic proper (Kautsky 1981; Kautsky and Kautsky 1995) is far more complex to predict and many other factors may affect the outcome. Among many other things, shifts in mussel biomass (Kautsky et al. 1992) and changes in the transport of HOCs due to changes in phytoplankton production need to be considered. We argue that one possible means of exploring these complex interactions between eutrophication and HOC bioaccumulation in Baltic blue mussels is to, apart from further laboratory and field experimentation, adopt a large-scale dynamic modelling approach. In the remainder of this paper we describe the current progress of our modelling ambitions, discuss areas were we require further experimental data and finally outline our planned modelling studies.

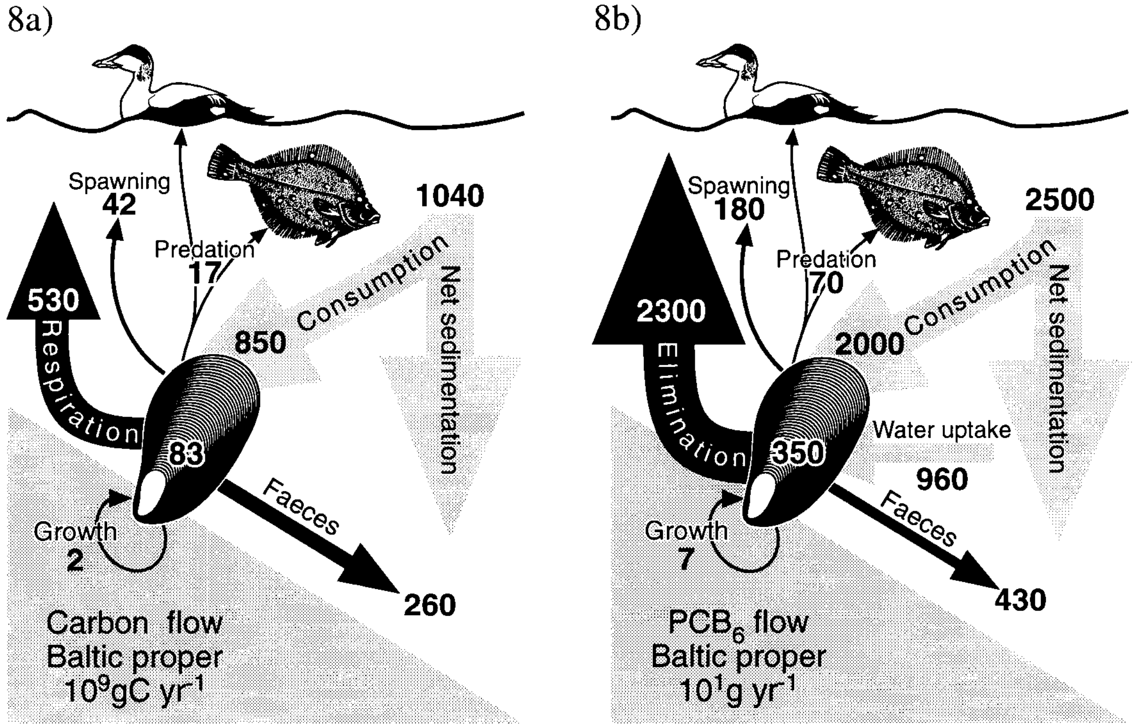

Figure 8. The annual carbon budget (a) and the established annual budget of PCB_6 (b) through blue mussels inhabiting the Swedish coastal zone of the Baltic proper. The estimated annual net sedimentation of carbon and of PCB_6 in the area are also given. Values are given as 10^9 g C yr^{-1} and 10^1 g PCB_6 yr^{-1} in figures (a) and (b), respectively. (From Gilek et al. In press, where annual budgets of PAHs and PCDD/Fs also are presented).

The Role of the Blue Mussel in HOC Cycling

As a first step towards achieving a large-scale dynamic model of HOC cycling by Baltic blue mussels, we have established budgets of the flow of carbon as well as the flow of some important HOC groups (i.e. polycyclic aromatic hydrocarbons, polychlorinated dibenzo-*p*-dioxins and furans and PCBs) through the dense blue mussel population inhabiting the Swedish coastal zone of the Baltic proper (Gilek et al. In press).

The HOC-budgets (Fig. 8b, here the PCB budget is shown as an example) were established by multiplying available HOC concentration data or assumed HOC concentrations, in the case of spawning, with the estimated carbon flows (Fig. 8a). This results in estimates of the amount of the studied HOCs accumulated in blue mussel tissues and their annual flows. Hence, to assure reliability of the established HOC budgets, it is essential that the flows of the studied HOCs are directly proportional to those of carbon. This is basically the same as assuming equilibrium partitioning of the contaminants and is a common assumption when modelling the transport and fate of HOCs in aquatic environments (e.g. Mackay et al. 1992). Furthermore, we have assumed that HOC concentrations in the mussel tissues are at steady-state. This implies that the sum of the contaminant losses are assumed to be equal to the total uptake. At present no better estimates of elimination can be achieved, because empirical determinations of the rates of elimination and metabolism of the studied HOCs by Baltic Sea blue mussels are almost completely lacking (Björk and Gilek 1996; Gilek et al. 1996b; Björk and Gilek submitted).

The established HOC budgets (Fig. 8b) show that the blue mussel significantly modifies the cycling of HOCs in the coastal zone of the Baltic proper by : (i) increasing the net deposition of HOCs to the bottoms by 13-19% and thus also enhancing the availability of these contaminants to other benthic organisms. (ii) increasing the retention time of HOCs in the water mass by recycling substantial amounts of HOCs back to the pelagic system through passive elimination. (iii) bioaccumulating large amounts of HOCs and thus constituting a significant contaminant source to demersal fish and waterfowl species that feed on mussels. (iv) liberating considerable amounts of HOCs to coastal waters of the Baltic proper via their spawning products, which significantly may contribute to the HOC exposure of herring larvae and other zooplanktivores.

Towards a Reliable Dynamic Model - Research Requirements

When establishing the HOC budgets presented above we identified several areas where we need more chemical analysis and experimental data to be able to construct a model which is sufficiently reliable to use when exploring the influence of eutrophication on bioaccumulation, biodeposition, and trophic transfer of HOCs by Baltic blue mussels.

Like all large scale extrapolations the established HOC budgets (Fig. 8b) probably have a low numerical precision, due to for example the high variability in some of the measured HOC concentrations used to establish the contaminant budgets. Thus, to increase the reliability of the HOC budgets more chemical analyses of the contaminant concentrations in blue mussels, seston, faeces and spawning products are required. At present there is also a possibility that some of the estimated HOC flows (i.e. primarily food exposure, elimination and spawning) are biased by an insufficient knowledge of these processes *in situ*. To exemplify this, the average HOC concentrations in particles that mussels feed on have in these budgets been estimated from concentrations measured in seston collected with sediment traps. This settling seston is probably quite different in composition (e.g. in particle size, carbon content, and HOC concentration) from what mussels actually ingest, since mussels actively capture and consume small particles which otherwise would stay in suspension (Kautsky and Evans 1987) and because of near-bed resuspension and sorting phenomena (Ko and Baker 1995). Thus, to increase the reliability of these HOC budgets a better understanding of the near-bed contaminant exposure situation of blue mussels in the field is required, as well as more information on HOC elimination and metabolism by Baltic blue mussels. The role of spawning in HOC elimination also needs to be investigated more in detail.

Furthermore, because the Baltic environment is characterised by such large seasonal variations in temperature and light conditions many, if not all, of the carbon and HOC flows described in the presented annual budgets will also exhibit substantial seasonality. For example, elimination of HOCs is probably highly affected by temperature (Jovanovich and Marion 1987; Gilek and Björk In prep.), and water and food uptake are presumably affected by temperature dependent pumping rates (Gilek and Björk In prep.), as well as seasonal variations in water concentrations of organic particles. Hence, incorporation of annual variations in for example pelagic primary production, mussel filtration activity, and elimination rates in a dynamic model of the HOC cycling by blue mussels will greatly increase the reliability of the presented budgets and will allow us to explore the effects of changes in important environmental variables, such as e.g. changes in primary production due to eutrophication.

Modelling

The core of the model will be a physiologically-based bioaccumulation model (Landrum et al. 1992; Björk and Gilek submitted), which describes the uptake (from both water and food), elimination and bioaccumulation of HOCs in individual blue mussels. In such a physiologically-based model HOC bioaccumulation is modelled as a function of mussel physiology, i.e. water pumping, food consumption, growth and spawning. However, the properties of the contaminant (e.g. hydrophobicity) also influence bioaccumulation in this physiological model. To this core we will incorporate environmental variables such as temperature and particulate food availability as forcing functions. In this modelling work, various PCBs will primarily be used as type substances, since this is the group of

HOCs where most information (i.e. own and literature) already is available on bioaccumulation kinetics in suspension-feeding mussels. Thus, we intend to use a combination of own experimental data (e.g. Gilek et al. 1992; Björk and Gilek 1996; Gilek et al. 1996a; Gilek et al. 1996b; Gilek and Björk In prep.; Björk and Gilek submitted), literature data as e.g. already compiled in (Björk 1995; Kautsky 1995; Gilek 1996) and new data from mechanistic experiments and field studies performed within the project (as outlined in the 'Towards a Reliable Dynamic Model' section). In the next phase, the core model will be upscaled and simplified to generate a large-scale dynamic model of the flux of HOCs in the Swedish coastal zone of the Baltic proper. This will be done by incorporating important ecological variables such as predation and mortality as well as mussel population structure and biomass (and their variation with temperature and food availability) as forcing functions. Thereafter, the established model will be used to explore different eutrophication scenarios by running the model at e.g. different availabilities of particulate organic matter and mussel biomass. Since the model is to consist of sub-models, we expect that we will be able to explore the influence of changes in eutrophication both on tissue concentration of PCBs in individual blue mussels, as well as the influence of eutrophication on large-scale HOC fluxes such as biodeposition and trophic transfer.

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Seasonal variations of PCB and PAH concentrations in SPM and blue mussels in the North Sea

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1. Introduction

Environmental problems related to eutrophication and hazardous contaminants are still most important issues of concern in management of coastal waters such as the North Sea and the Wadden Sea. Current marine pollution monitoring- and risk analysis programmes for these regions are based on the assumptions that contamination is homogeneously distributed in marine water columns, and that key environmental fate processes such as sorption and volatilization obey equilibrium partitioning concepts. These programmes, however, cannot serve their purpose if contaminants are heterogeneously distributed and do not fulfil thermodynamic equilibrium conditions with their surroundings. In (coastal) waters non-equilibrium situations occur frequently due to dynamic physical and ecological processes, such as storms and phytoplankton blooms [Reuber *et al.* 1987; Alperin *et al.*, 1991; Swackhamer and Skoglund, 1993; Skoglund and Swackhamer, 1996]. Additionally, the southwest part of North Sea is subjected to varying inputs of contaminants from The Channel, rivers like the Scheldt and the Rhine, off shore sediment disposal, and deposition from the air [Knickmeyer *et al.*, 1990; Wulffraat and Smit, 1996]. All these inputs have different pollution levels and may vary with the season. Especially in deeper waters with low amounts of suspended particulate matter (SPM), contaminants that are present in the watercolumn are usually not in true equilibrium with bottom sediments. It is hypothesised that monitoring data of contaminants in mussels and SPM in such waters reflect this variability [Hühnerfuss *et al.*, 1990, 1995; Lee *et al.*, 1996]. Therefore, data from deeper water (> 20 m.) with low SPM contents were compared with data from shallow coastal water and high SPM loads to identify possible processes occurring in the waterphase.

2. Methods

In a 5 years monitoring programme 3 times a year (February, July, and October) blue mussels (*Mytilus edulis L.*) were exposed to water for a period of six weeks. About 100 mussels from the Easter Scheldt were transplanted in baskets to 16 coastal locations at approximately 1.5 meter below the water surface. Samples were homogenised, freeze-dried and soxhlet-extracted using an acetone/hexane (1:3) mixture. After cleanup PCBs were analyzed by GC-ECD on a dual column system and PAHs were analyzed by reversed phase HPLC applying two fluorescence-detectors.

Lipid was determined gravimetrically after soxhlet extraction using the same mixture as for contaminants.

From 1988 onwards SPM was collected quarterly by a continuous-flow centrifuge (15000 rpm). The analysis was basically the same as described for mussels. After removal of carbonates using HCl vapour, elemental organic carbon was determined by combustion and subsequent GC analyses of CO_2 .

The locations in the North Sea represent rather deep areas. Estuary, such as the Ems-Dollard and Scheldt estuary, are shallow areas with a relatively high SPM load. As the programmes for both type of samples were independent, mussels from the North Sea were not exactly comparable to the SPM. However, SPM was usually sampled during the period in which mussels were exposed.

3. Water quality modelling

Validated contaminant transport models of the coastal zone of the North Sea and the continental shelf [Boon, 1996; Jaarsveld and Schutter, 1993; Evers *et al.*, 1996] were used to determine 1) the transport and dispersion of a wide variety of contaminants in water and sediments 2) to compare these concentrations with water quality objectives and 3) to gain insight into the relative contributions of pollution from different sources (such as atmospheric deposition, fluvial input, inflow from the Strait of Dover and the Atlantic, emissions from ship traffic and dredged sediments disposed of near the Dutch and Belgium coast). Specific modelling objectives are to have the correct simulation of existing pollution conditions and then conduct an impact assessment of different pollution reduction measures and strategies. The model is deterministic, dynamic, mostly linear, and theoretical. The basic formulations of the model are partial differential equations. The size of the model grid depends upon the specific application. In the Coastal Zone study the (2-D horizontal) grid has approximately 2150 computational elements, which are about 1 km x 1 km.

Model state variables are concentrations of suspended matter (organic and inorganic) in water and bottom, and total concentrations of (in)organic pollutants.

Relevant output variables are the dissolved and particulate concentrations of the state variables in water, suspended matter and bottom, the fraction adsorbed, and fluxes from water to bottom (vertical) and horizontal transport fluxes. Important inputs and forcing functions are daily wind, monthly river discharges (and river loads), monthly direct loads (sewage, dredging etc.), yearly/monthly atmospheric deposition, erosion based on yearly average values, and hydrodynamics for 11 wind conditions (as residual currents).

4. Results and discussion

Suspended matter and phytoplankton from the North Sea location exhibits short-term changes in hydrophobic chemical concentrations that are synchronized within and between areas. Offshore Noordwijk at the southern North Sea, for example, short-term deviations from long-term trends for PCBs, PAHs and hexachlorobenzene in suspended matter tend to correlate significantly with each other and with these chemicals at other offshore sites such as the Wadden Sea and the open central North Sea. This synchrony indicates that some large-scale force-probably connected to weather patterns - controls short-term patterns of hydrophobic chemical concentrations in suspended matter and various marine organisms. The hypothesis that warm spring weather and light increase conducive to phytoplankton growth produces relatively uncontaminated phytoplankton, which in turn produce lower body burdens of organisms in marine trophic food web such as mussels and vice versa for cold and darker weather.

The strong change of PCB and PAH concentrations on a lipid basis resulted from:
1) a dilution effect during seasonal lipid accumulation;
2) a concentration effect during utilisation and release of body lipids;
3) temporal fluctuations in ambient water concentrations during phytoplankton growth.

4. Conclusions

Spatial and temporal trends can be detected in concentrations of PCBs in mussels. Generally, estuarine and coastal locations showed higher concentrations than offshore locations, which challenge the importance of fluvial sources of contaminants in comparisons with atmospheric deposition.

The dramatic increase in the dissolved and particulate organic carbon during periods of intense growth has a significant influence on both contaminant concentrations in offshore-SPM as well as on body burdens in mussels and must be incorporated in water quality models.

In summary, the dynamics model reproduced the observed accumulation in SPM, including phytoplankton, better than did the traditional steady-state model.

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The role of microcontaminants and nutrients in aquatic foodchains: Putting the pieces together for plankton

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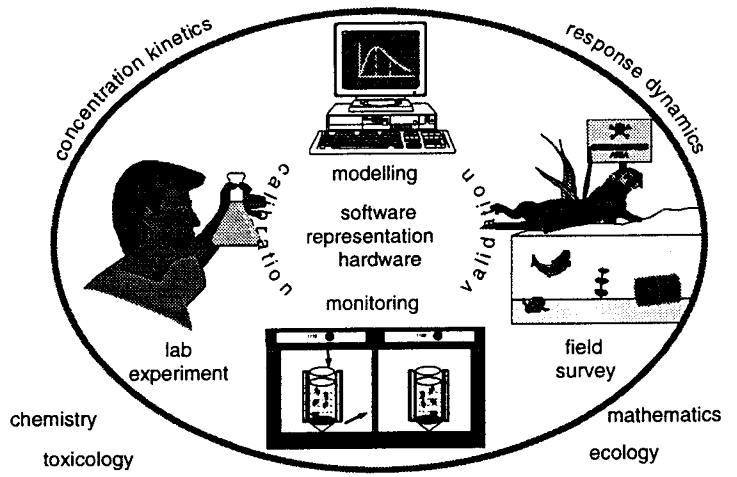
Introduction

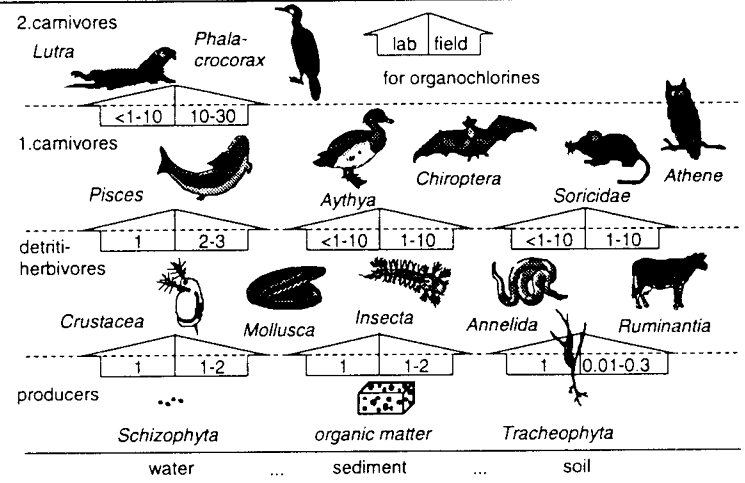
In the seventies, effects of microcontaminants in Dutch rivers and lakes were evident. Laboratory organisms died immediately when exposed to water samples and many species were not found in field surveys (Slooff 1983, Van Urk 1984). At that time, environmental quality management could rely on relatively simple tools. In the Netherlands for instance, water quality is evaluated by comparing measured concentrations to quality standards, without considering possible interaction of nutrients and toxicants.

Figure 1. Concentration kinetics and population dynamics studied in laboratory experiments and field surveys, integrated into the OMEGA-model (Hendriks and van de Guchte, 1997)



Since then, water quality has improved substantially and the question arises whether microcontaminants still affect the aquatic community. For instance, the impact of unknown compounds or indirect effects are largely missed by contemporary modeling and monitoring instruments (e.g. Hendriks et al. 1994). Furthermore, the role of priority pollutants in relation to other threats, like other microcontaminants, eutrophication, acidification, habitat destruction and diseases is hardly studied. In the past, these relationships were not important because any measure taken led to a substantial improvement. Nowadays however, improvements will be smaller and environmental managers are eager to know where to spent their funds efficiently. Unfortunately, research and management dealing with microcontaminants and nutrients also largely followed separate lines. In this paper, we will discuss our toxicants research program so far and indicate where nutrients come in.

Figure 2. Accumulation ratios of concentrations of persistent organochlorines in lab and Rhine-Meuse delta field studies for different trophic levels (Hendriks 1996b).



Methods

At our institute ecotoxicological laboratory experiments and field surveys are carried out, usually in cooperation with other organizations (Figure 1, Hendriks and Van de Guchte). These includes empirical studies of an intermediate nature, such as field assays and mesocosms (de Ruiter and Hendriks in press, Jak et al. 1996).

The results are integrated in the OMEGA-model (Optimal Modelling in EcotoxicoloGical Assessments, Hendriks 1995c). The model consists of a few well-known equations, traditionally used in chemistry, toxicology and ecology. Most parameters are set on default values, based on (cor)relations to well-known characteristics of substances and species, such as octanol-water partition constants and adult size. The parameter-sparse model can be applied for fast and generic purposes. If more information is available however, contaminant- and species-specific values can be filled in to improve the evaluation. Thus, the model can be applied to a range of various questions posed by water quality management.

In the present version of the OMEGA model, impact of nutrients is not taken into account. Here, we will discuss where incorporation of nutrients is needed and presently carried out.

Results

Concentration kinetics in organisms: not much new research needed?

As far as *equilibrium* concentrations (uptake, accumulation, elimination) of hydrophobic compounds in animals are concerned, additional information on nutrients will probably not improve the estimations. The ratio of concentrations in organic matter and in invertebrates or fish is rather similar in most situations (Figure 2). The samples were taken at locations with a different degree of eutrophication (Rhine river ... lake Markermeer). Differences in algae densities apparently do not lead to differences in accumulation at higher trophic levels, probably because other routes of intake (suspended solids, water) are more important. The general pattern may not be applicable in situations with an extreme low (sea) or high (peat) organic matter content. In addition, this conclusion may not hold for *metals* because these contaminants also adsorb to mineral particles.

Additional information on *non-equilibrium* parameters for uptake and release of in algae however, might improve our understanding of the toxicity of microcontaminants to algae themselves. For instance, desorption rates for algae measured for chlorobenzenes (Koelmans et al. 1995) are lower than extrapolated from animals (Hendriks 1995a). In addition concentration in algae under eutrophic conditions are lower than expected from equilibrium partitioning (Swackhammer and Skoglund 1993a). As more and more risk assessment model are based on internal instead of external concentrations, additional insight in this area will certainly the evaluations.

Response dynamics in populations: major improvements needed!

Unlike the variety of eutrophication models that are available for environmental quality management, modelling of effects of toxicants on populations -let alone communities- are scarce (see e.g. Dutch Health Council in prep.). Thus, if effects of nutrients and toxicants are to be integrated in models, major improvements are expected to come from ecotoxicological modelling efforts.

As a start, we have developed a single-species model of an analytical nature with logistic population growth. The rate of increase r is a function of the toxicant concentration as reflected in Figure 3.

Figure 3. Theoretical and empirical relationship between the rate of population increase of the species and the concentration of the toxicant.

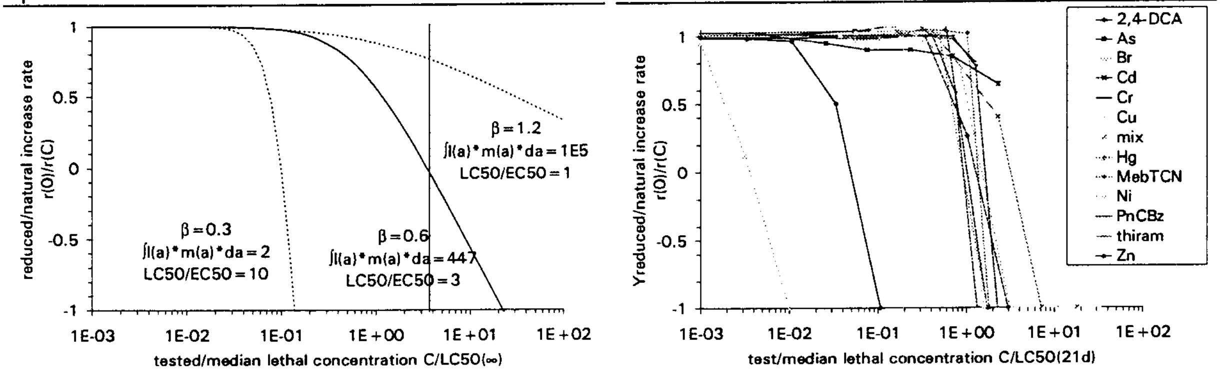


Figure 3 also shows that the theoretically derived pattern was confirmed empirically in laboratory experiments with miscellaneous compounds and invertebrates species (Hendriks and Enserink 1996). In most (zooplankton) models so far, a linear relationship was assumed (e.g. Hallam and de Luna 1984). By the way, efforts to verify carrying capacities to toxicants concentrations were less successful due to a lack of empirical data.

Currently, the model is extended to a version with a prey-predator interaction with a Lotka-Volterra type of equation. Though applicable for miscellaneous species, it will be tested to phyto-zooplankton dynamics data from mesocosm experiments (Jak et al. 1996). The analytical type of modelling is analogous to past efforts for nutrients (Scheffer 1990), that will be incorporated in the model.

Discussion

1. To extrapolate from laboratory experiments and to interpret field surveys on interaction between nutrients and toxicants, models are indispensable.
2. Since eutrophication models are abundant, most efforts should be directed towards ecotoxicological modules.
3. Next to the complex (numerical) models that are becoming available (e.g. Traas et al. 1994), there is a need for simple (analytical) models both for generic and specific purposes. Such simple models tend to indicate trends rather than exact results. For management purposes, this often suffices.
4. Nutrients are unlikely to influence toxicant accumulation in foodchains to a large extent. Research on toxicants and nutrients should therefore focus on effects.

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Toxic anorexia of daphinds: a critical factor in the development of eutrophication problems.

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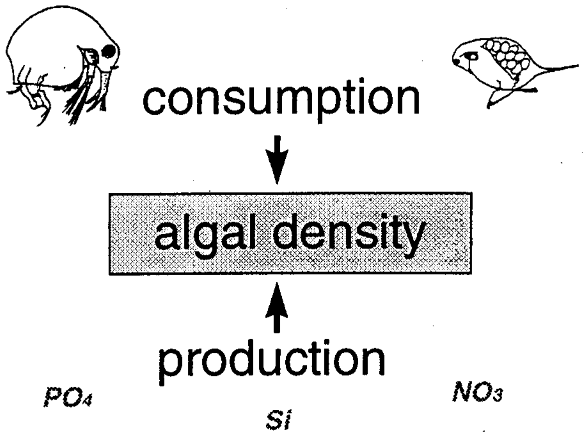
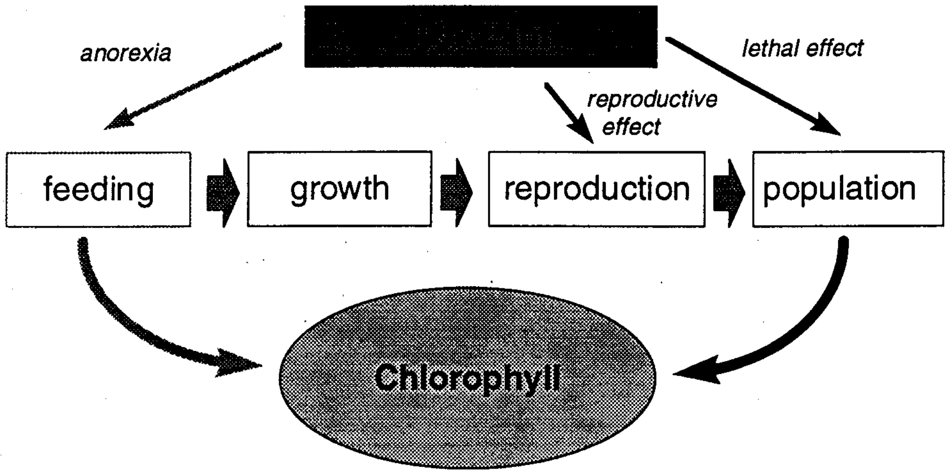
1. Introduction.

Eutrophication problems in surface waters are generally considered to be the result of progressive fertilisation, although they are actually the result of an imbalance between (progressive) algal production and algal consumption by zooplankters.



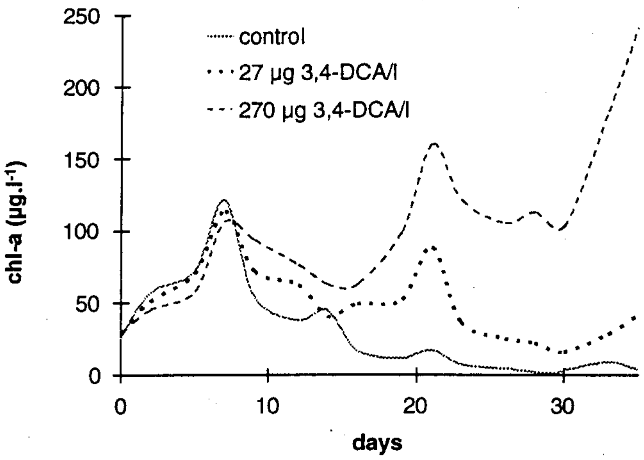
Semi-field multispecies studies at mesocosm scale reveal that grazing of phytoplankton by daphnids is often the most sensitive species interaction in an aquatic community. Almost all toxic substances (except herbicides) first reduce the grazing efficiency of daphnids: “toxic anorexia” as we name it.

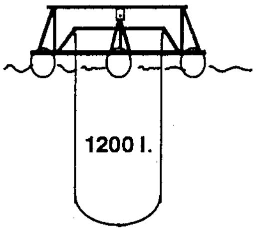


Exposure to toxicants thus result in an imbalance between algal production and algal consumption, leading to the development of enhanced algal densities and subsequent eutrophication problems (toxic or nuisance algae; turbid waters; anoxic conditions; bad smell, midge plagues etc.) under conditions of prolific algal production.

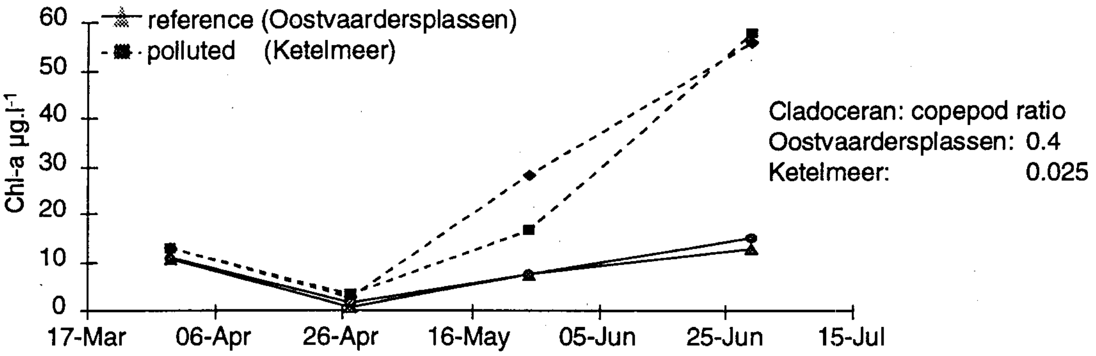
2. Mesocosm observations: Algal blooming due to toxicants.

In experiments with enclosed plankton communities it was observed that the development of the algal density is correlated with the toxic inhibition of daphnid population development. Daphnid species with the lowest algal threshold level showed the strongest reduction by toxicants (Ceriodaphnia < Daphnia < Chydorus). Less efficient grazers (viz. copepods and rotifers) benefit from reduced competition. The experiments learned that a blue-green algal bloom could be induced by the presence of toxicants, while under pristine (but eutrophic) conditions daphnids could control the algal density at low levels.

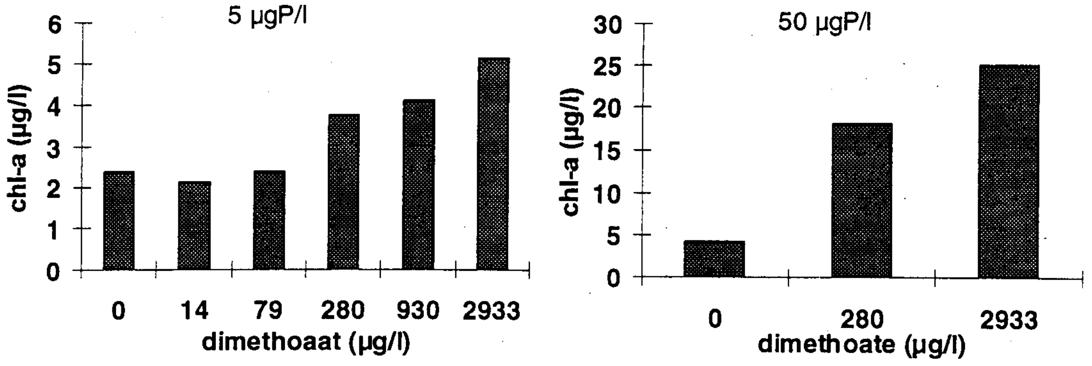




In experimental pond studies concerning the ecological effects of polluted sediments, the most sensitive response to moderately polluted sediments appeared to be the development of the algal density during spring, finally resulting in a summer bloom of blue-green algae. The algal density corresponded with the final cladoceran: copepod ratio in the early summer; high algal densities resulted from poor cladoceran functioning.



A mesocosm test with the organo P-insecticide dimethoate also indicated reduced grazing of phytoplankton by daphnids as the most sensitive species interaction, resulting in stimulated growth of filter-feeding benthic bivalves as *Sphaerium corneum*. Under the oligotrophic test condition (5 µg P.l^{-1}), this did not result in prolific algal densities. However, in additional tests with plankton samples in indoor microcosms under (fertilised) mesotrophic conditions (50 µg P.l^{-1}) it was demonstrated that the induction of algal blooming could be related to the toxic inhibition of the daphnids.

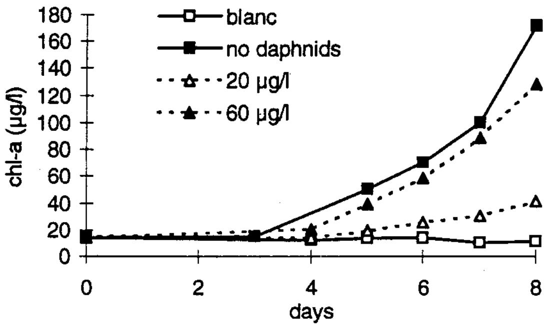


3. Plankton ecoassay: Testing toxic anorexia of daphnids.

In order to test the toxic anorexia of daphnids, a plankton ecoassay test procedure has been developed. Toxic anorexia of daphnids is established in 80 litres test containers installed in a temperature controlled room. In a hypertrophic medium stocked with cultured algae (*Chlorella*, *Scenedesmus* or others), prolific algal production rates are realised. An assemblage of daphnid-species (i.e. *Daphnia*, *Ceriodaphnia*, *Simocephalus*) at a density of 5-10 per litre are tested in these systems for their capacity to consume the algae. The balance between algal production and consumption is reflected by the development of the algal density. Under pristine reference conditions, the daphnids are capable to control algal densities at a level of 5-10 µg chlorophyll per litre. Toxic anorexia of daphnids increases the algal density over time.

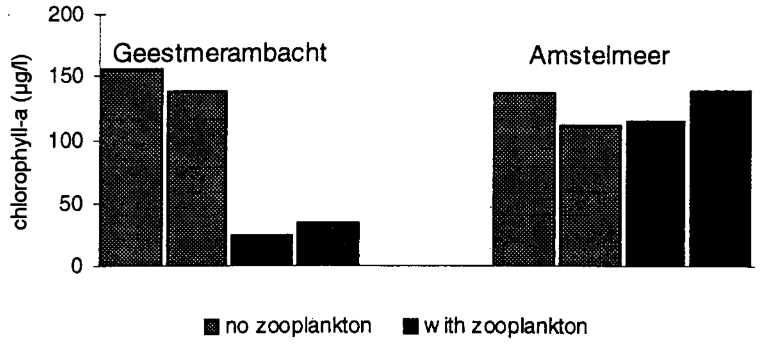
An increase of the algal density indicates toxic inhibition of grazing by daphnids. An example for dimethoate is presented below.

The algal density development is exponential in absence of daphnids, while daphnids can control the density at a low level. Even at 20µg dimethoate per litre, this grazing control fails. The NOEC for a 21 day Daphnid growth or reproduction test is 30µg dimethoate per litre.



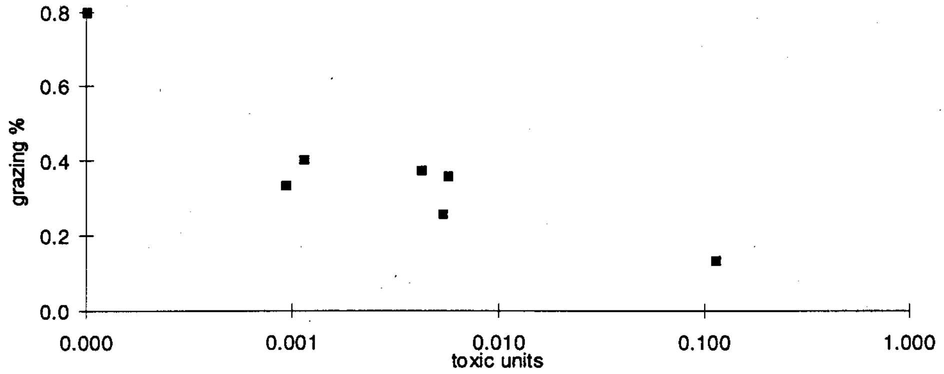
The plankton ecoassay enables the establishment of an NOEC or EC_{50} for substances or effluent dilution series for the most critical process (species interaction) in an aquatic ecosystem, representing the toxicity at the community level. The NOEC observed in a plankton ecoassay can thus be considered as a PNEC or environmental threshold level for an aquatic ecosystem. This is verified for some substances that also have been tested in mesocosms or field studies.

The plankton ecoassay has also been applied for testing toxic anorexia in field samples of surface waters (including phytoplankton, daphnids excluded). The example given below shows that daphnids added to the field samples are not capable to control algal densities in "Lake Amstelmeer", as daphnids do in the "Lake Geestmerambacht". This indicates a (as yet unresolved) water quality problem in the Amstelmeer.



The natural cladoceran: copepod ratio is 0.15 in the Geestmerambacht and 0.05 in the Amstelmeer. Without fish predation, this ratio develops within a week up to 2-5 for Geestmerambacht plankton, but remains 0.05 for Amstelmeer plankton.

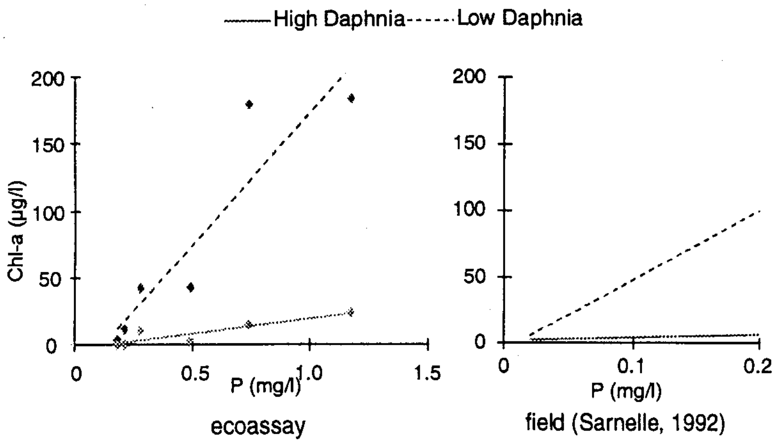
A plankton ecoassay with water samples taken from various polder waters showed an inverse relationship of daphnid grazing with sum toxic units of pesticides.



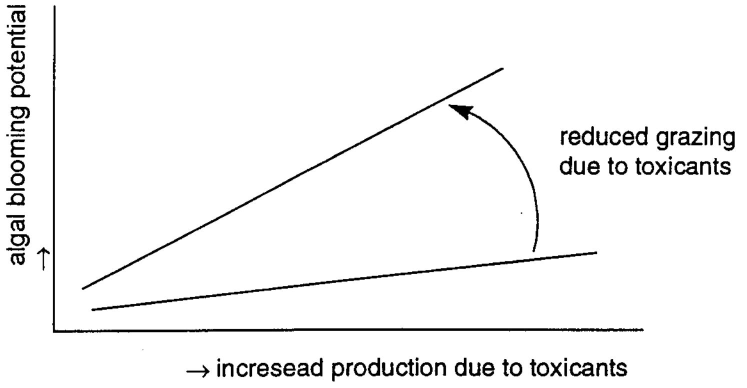
4. Plankton ecoassay: Testing P-algal responses.

The plankton ecoassay also enables us to test the response of the plankton community to various levels of nutrition. Fertilisation tests showed that the relation between phosphorus (and other nutrients) and chlorophyll strongly depends on the grazing efficiency of daphnids.

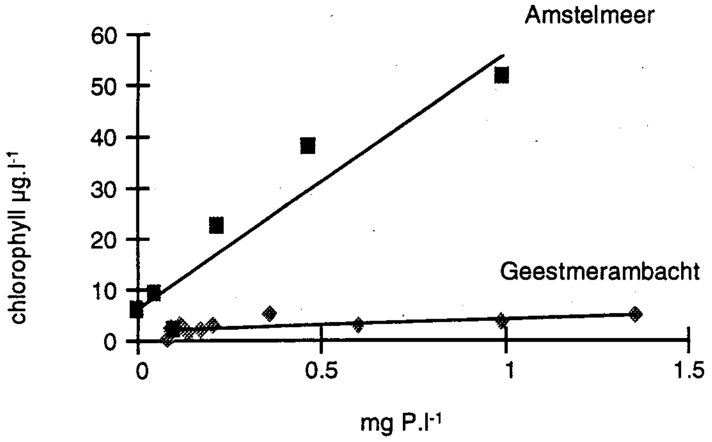
A plankton ecoassay test of a fertilisation series under presence or absence of daphnids showed a good consistency with field observations from Sarnelle (1992).



Based on this observation a model has been made to describe the interaction of nutrients and toxicants in the development of algal blooming.



This interaction between nutrients and toxicants has been confirmed in tests with field samples from Geestmerambacht and Amstelmeer.



5. Discussion

The importance of algal grazing in aquatic ecosystems is based on the fact that in a healthy, productive ecosystems the algal productions is almost completely consumed by herbivores. The production of grazers is approx. 5% of the primary production, in comparison to 1% in terrestrial ecosystems.

A small reduction of the algal grazing efficiency due to sublethal toxicity (toxic anorexia) can result in an exponential increase of the algal density under productive conditions. At high algal densities, nuisance colony forming and inedible algae become dominant: which results in a state which is experienced as "problematic, eutrophication".

Eutrophication problems have to be considered as a result of progressive fertilisation in combination with sub-optimal daphnid functioning. Toxic anorexia is an important factor to be acknowledged. Reduction of the environmental nutrient load is not in all cases effective in precluding algal blooms.

IMPACT OF COMMUNITY NUTRIENT STATUS ON FATE AND EFFECTS OF INSECTICIDES IN SHALLOW FRESHWATER ECOSYSTEMS

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Introduction

In landscapes characterized by intensive agriculture, a major environmental problem is the increased nutrient loading of freshwater ecosystems. In addition, insecticides used for crop protection may also enter these systems. Although interactions between community trophic status and organic contaminants can be expected [McCarthy and Bartell, 1988], only a limited number of experimental studies dealt with interactions of nutrients and insecticides in surface water.

In the Netherlands, various trophic states of shallow freshwater ecosystems can be distinguished. In oligotrophic freshwaters productivity is essentially limited by nutrients (inorganic N, P and/or C). Also in mesotrophic systems the availability of nutrients in the water column usually is too low for abundant algal growth. Rooted macrophytes, however, are able to exploit the nutrients in the sediment, so that shallow mesotrophic ecosystems may become macrophyte-dominated. In more eutrophic situations nutrient availability in the water column increases. This may result in better growth conditions for periphytic and planktonic algae, as well as for populations that graze these algae (e.g snails and daphnids). The periphytic and planktonic algae compete with macrophytes for nutrients and light. In very eutrophied shallow freshwaters rooted submerged macrophytes usually are absent, while algal blooms, or canopies of floating macrophytes (e.g. duckweed), dominate.

In the present paper we will compare the results of three microcosm experiments to which a similar dose (nominal 35 µg/L) of the organophosphorus insecticide chlorpyrifos was applied. The three types of community that were simulated in these microcosm experiments can be seen as three different states within the trophic gradient of shallow freshwater ecosystems, viz.;

I macrophyte-dominated microcosms (biomass c. 300 g dry weight/m^2) characterized by a nutrient-poor water column [Crum and Brock, 1994; Brock et al., 1992a, 1992b, 1993],
II microcosms with a sparser macrophyte biomass (c. 125 g dry weight/m^2) and a weekly input of extra inorganic nitrogen and phosphorus [Van Donk et al., 1995; Brock et al., 1995; Cuppen et al., 1995],
III plankton-dominated microcosms devoid of macrophytes [Crum and Brock, 1994; Brock et al., 1992a, 1992b, 1993].

In addition, we will present a general discussion on the potential impact of nutrient status on the effects of insecticides in shallow freshwater ecosystems.

Impact of community nutrient status on insecticide fate

In Figure 1 the initial dissipation of chlorpyrifos from the overlying water in the three types of microcosm is presented, as well as the partitioning of this insecticide over the water, macrophyte and sediment compartments. Particularly in the macrophyte-dominated microcosms, to which no extra nutrients were added, the initial disappearance in water was much faster than in the other types of microcosm. Macrophytes adsorbed a relatively large proportion of the dose applied. The sediment compartment was a larger sink of chlorpyrifos in plankton-dominated systems.

After the initial period of fast partitioning, the rate of disappearance of chlorpyrifos from the water column became more similar between test systems. In the period 1-8 weeks post insecticide application, a half-life of 8 days could be calculated for chlorpyrifos in water of the type II microcosms (nutrient loaded). In the macrophyte-dominated (type I) and plankton-dominated (type III) microcosms this was 10 and 11 days, respectively. When, for the same period, the dissipation of chlorpyrifos from the total microcosm (the sum of water, sediment and macrophyte compartments) is considered, the macrophyte-dominated microcosms (type I) and nutrient loaded systems with a sparser macrophyte biomass (type II) showed a more or less similar half-life (14-15 days). In contrast, chlorpyrifos in the plankton-dominated microcosms (type III) had a half-life of no less than 34 days, due to the relatively slow rate of disappearance from the sediment compartment.

Our microcosm experiments do not allow conclusions on interaction of nutrients and insecticides in plankton communities of different nutrient levels. In the plankton-dominated microcosms of Yasuno *et al* [1993], however, the dissipation of the organophosphorus insecticide pyraclofos from the overlying water was faster in the nutrient loaded systems than in microcosms without nutrient enrichment. Nutrient enrichment coincided with a larger biomass of planktonic algae and higher pH values.

Hydrophobic compounds, such as most organophosphorus and pyrethroid insecticides, have a strong tendency to partition from aqueous into organic phases. The larger the pool of organic matter present, the larger the disappearance from water due to adsorption. In shallow freshwater ecosystems, however, there is not a simple linear relationship between community trophic status and amounts and types of organic matter available. In part this can be attributed to the shift in dominance between macrophytes and algae. In general, oligotrophic freshwater ecosystems on mineral sediments are characterized by a low biomass and productivity of both algae and macrophytes. In mesotrophic to moderately eutrophic shallow fresh waters large amounts of aquatic vascular plants may be present. Most rooted submerged macrophytes are characterized by a relatively low turn-over rate. In eutrophic to hypertrophic systems predominantly planktonic algae, filamentous algae or dense canopies of duckweed are present, characterized by a relatively low biomass and a relatively high turn-over rate.

Besides partitioning, also transformation processes of insecticides may be affected by community nutrient status. In the overlying water, hydrolysis is reported to be a significant transformation process of organophosphorus insecticides such as chlorpyrifos. The rate of hydrolysis of chlorpyrifos in distilled water was found to be relatively constant up till pH 7, while above pH 7 the rate constant increased dramatically (Figure 2) [Racke, 1993]. Alkaline hydrolysis in particular may be of importance in shallow freshwater ecosystems dominated by macrophytes and/or dense algal blooms. Photosynthesis by these plants may, at least during part of the day, result in high pH values (above 9) in the ambient water, particularly when extra nutrients are supplied.

Impact of community trophic status on effects of insecticides

Exposure

As described above, factors related to community nutrient status may affect the amount of insecticide that becomes adsorbed to e.g. macrophytes, algae, detritus particles and sediment. It is suggested that chlorpyrifos adsorbed to sediments and/or organic matter is not, or at least much less, bioavailable [Racke, 1993]. Indeed it has been demonstrated experimentally that the presence of humic acids in the medium decreased the toxicity of chlorpyrifos to *Daphnia magna* [Naddy and Klaine, 1996]. It can not be excluded, however, that insecticide adsorbed to the fraction of particulate organic matter becomes available after it is ingested as food.

Information on the significance of dietary exposure of susceptible freshwater organisms (arthropods, fish) to chlorpyrifos and other organophosphorus insecticides appears to be scarce. In laboratory toxicity tests, more pronounced toxic effects are reported when *Daphnia magna* is exposed to chlorpyrifos in water in which organic matter in the form of suitable food is present, than in water with humic acids [Naddy and Klaine, 1996]. This suggests that *Daphnia* may become additionally exposed to chlorpyrifos via its food. In toxicity experiments with the isopod *Asellus aquaticus*, however, exposure via the food (decomposing leaves) hardly contributed to additional toxic effects of chlorpyrifos when also exposed via the water [Romijn, 1988]. In these experiments the chlorpyrifos concentrations in water and food were in equilibrium. That, in case of insecticides with a short half-life, additional exposure via food most probably is of minor importance is further suggested by a study with the pyrethroid fenvalerate. In this study contamination of food (algae) with fenvalerate did not contribute to an increase in bioaccumulation in *Daphnia galeata mendotae*. A reduced filtering rate of *Daphnia* as a direct sublethal effect of fenvalerate, however, may have caused a reduced intake of fenvalerate adsorbed to algae [Day and Kaushik, 1987].

Susceptibility

Besides effects on bioavailability of contaminants, community trophic status may affect the susceptibility of freshwater organisms via fitness and threshold food concentrations. At sublethal concentrations of toxicants well-fed organisms may be less susceptible than individuals that suffer food limitation [Sprague, 1985]. Also a higher food availability, e.g. in the form of algae due to nutrient loading, might compensate for a minor inhibition of the filtering rate of daphnids due to pesticide exposure [Kersting, 1983]. In addition, it is reported that food availability affects the susceptibility of organisms via effects on life-history traits. In *Daphnia* e.g., body-length and energy supply of just-born neonates are negatively correlated with the food condition of the mother *Daphnia*, and these smaller neonates may be more susceptible to toxicants than the larger ones [Enserink, 1995].

The modification of susceptibility to toxicants by community trophic status and food availability, however, most probably is of ecological relevance only in systems subject to chronic sublethal concentrations. Our microcosm-experiments do not allow a conclusion on this matter, since a relatively high dose of chlorpyrifos was applied, resulting in immediate and pronounced direct effects.

Population and community responses in the microcosms

During the first week after chlorpyrifos application, and irrespective of the type of microcosm, mortality occurred primarily among Cladocera, Copepoda, Amphipoda, Isopoda and Insecta (direct effects). Responses observed were in accordance with single species toxicity tests, indicating that results of these tests can be extrapolated to a population of the same species in ecologically more complex systems, at least when information is available on the exposure of the population in these systems. However, it also appeared that the extrapolation of toxicity data obtained for one species to populations of taxonomically related species should be done with caution. Within the Isopoda e.g., we observed that *Asellus aquaticus* and *Proasellus meridianus* were much more susceptible to chlorpyrifos than *Proasellus coxalis*. The latter even increased in the plankton-dominated microcosms after insecticide application.

The decrease in activity or reduction in population size of chlorpyrifos-susceptible species (arthropods) resulted in shifts in interactions between populations not directly affected by the insecticide (indirect effects). In all three types of microcosm, populations of nearly all trophic levels were indirectly affected via the loss of arthropod populations (Table 1). The taxa in which indirect effects were observed differed considerably between microcosm-types. It seems that the species involved, and the extend and duration of indirect effects, can only be predicted with an *a priori* knowledge of the system's structure and trophic dynamics. At higher levels of biological organisation, however, general trends in indirect effects seem to be predictable (functional groups; trophic levels). Our microcosm experiments indicate that tolerant organisms that are small, have a short generation time, and a large reproductive capacity, generally show a fast increase after the loss of arthropod populations. Furthermore, indirect effects of chlorpyrifos in the microcosms partly resemble (and may enhance) effects ascribed to eutrophication, since in all test-systems periphytic and/or planktonic algae increased after insecticide application.

Our microcosm experiments suggest that community nutrient status at least affects the types and magnitude of indirect effects of insecticides in shallow freshwater ecosystems (Table 1). The results also indicate that insecticide contamination of freshwater ecosystems may enhance the adverse effects of eutrophication by reducing the top-down (consumer) control of periphytic and planktonic algae, at least as long as non-arthropod grazers permit this to occur. In oligotrophic systems (not tested in our experiments) insecticide contamination most probably will not result in algal blooms because of nutrient limitation (bottom-up control). In mesotrophic and moderately eutrophic systems, however, the top-down control of periphytic and planktonic algae by arthropod populations (particularly daphnids) is a more important regulatory mechanism. When these arthropod populations are reduced due to insecticide contamination, algal blooms can be expected. In addition, submerged macrophytes may decline due to shading by these algae (light limitation). After decay of the submerged macrophytes, more nutrients will enter the water column, and a process comparable to eutrophication will take place. In our experiments we observed a more prolonged algal bloom when cyanobacteria increased after insecticide application. When compared with diatoms and green algae, cyanobacteria provide less suitable food for herbivorous grazers.

Conclusions and suggestions for future research

In freshwater ecosystems the interaction between nutrients and insecticides may be complex, since nutrient status has a great impact on pools of organic matter present and on ecosystem structure and functioning. After an insecticide has entered a freshwater ecosystem, partitioning and transformation processes largely determine its fate and bioavailability. Both the properties of the insecticide, as well as the prevailing environmental conditions, are important in modulating these processes. The environmental conditions of importance are often, but not necessarily, linked with community trophic status, e.g. amounts and types of organic matter (including algae and macrophytes) and pH of overlying water.

Since dietary uptake of most organophosphorus and pyrethroid insecticides probably plays a minor role, it is assumed that in freshwater ecosystems an increase in adsorption of these insecticides to sediments and organic matter, possibly caused by increased nutrient loading, generally results in a decrease in bioavailability of these compounds.

The species composition and amounts of algae and/or macrophytes in freshwater ecosystems depend, amongst other factors, on availability of inorganic nitrogen, phosphorus and carbon (bottom-up control) and on the abundance of animals that consume these plants (top-down control). By reducing arthropod populations insecticides may reduce the top-down control of primary producers such as algae [e.g. Brock et al. (1995), and literature cited therein], thereby enhancing the stimulatory effects of nutrient loading on biomass of algae. This effect, however, may be temporal since most organophosphorus and pyrethroid insecticides show a rather fast rate of dissipation. In addition, non-arthropod grazers of algae not susceptible to insecticides (e.g. gastropods, rotifers, oligochaete worms) may take over the control of algae (functional redundancy). Prolonged algal blooms, however, can be expected in nutrient loaded freshwater ecosystems in case of a frequent input of insecticides.

To gain more insight in interactions of nutrient loading and pesticide contamination in shallow freshwater ecosystems future research should focus on the impact of chronic levels (or repeated doses) of insecticides on grazers that control algal blooms and troublesome floating macrophytes (e.g. duckweed). In addition, in nutrient loaded freshwaters the impact of multiple stress caused by different types of toxicants (e.g. mixtures of insecticides and herbicides or insecticides and fungicides) needs more attention. To achieve this, the combination of laboratory experiments, microcosm/mesocosm studies and simulation models may be promising.

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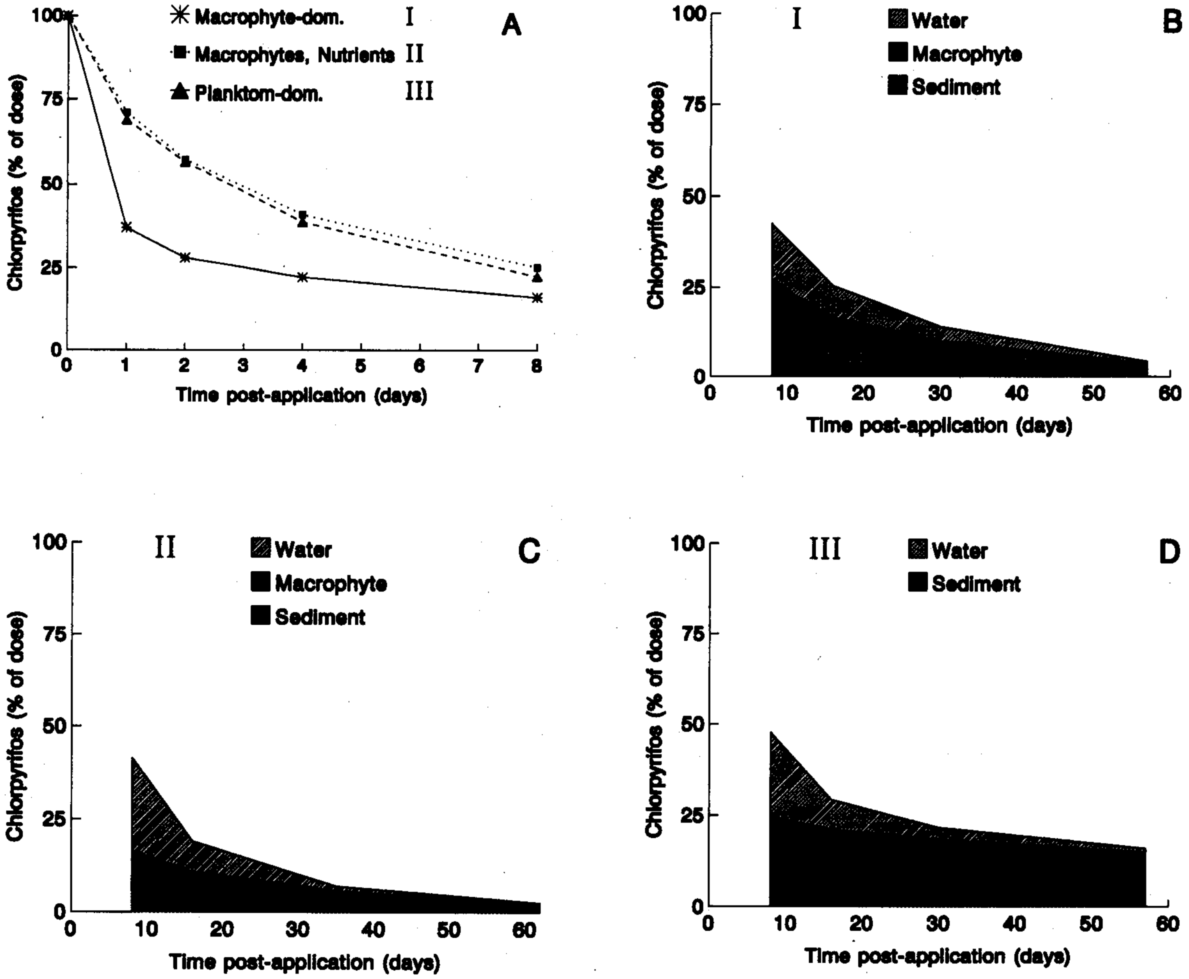

Figure 1. Chlorpyrifos, as a percentage of the dose applied, in microcosms dominated by macrophytes (I), nutrient-enriched systems with a sparse macrophyte growth (II) and plankton-dominated microcosms. A; Initial dissipation from the water column. B-D; partitioning over water, macrophyte and sediment compartments.

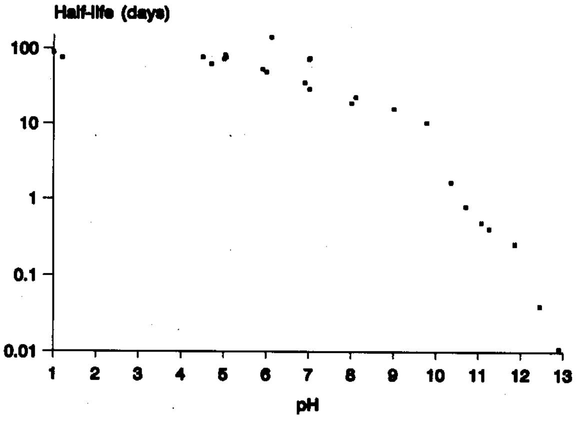

Figure 2. Relation between pH of the medium and half-life of chlorpyrifos, determined in distilled water at a temperature of 25 °C . Data modified according to [Racke, 1993].

Table 1. General overview of indirect effects of a single dose of chlorpyrifos (nominal 35 μg/L) on community structure in the three types of microcosms

I. Macrophyte-dominated
II. Nutrient-loaded with a sparser macrophyte biomass
III. Plankton-dominated

A zero (O) indicates the absence of consistent effects; a consistent decrease or increase in population density (relative to controls) is indicated by the symbols - and + respectively (n.p. = not present).

	Microcosm-experiment		
	I	II	III
Primary producers			
Phytoplankton	O	+	+
Periphytic algae	+	+	O
Macrophytes	-	O/-	n.p.
Herbivores			
Rotatoria	O	+	+
Sphaeriidae	O	O	+
Stylaria lacustris	O	+	O
Bithynia tentaculata	+	O	O
Lymnaea stagnalis	O	+	O
Potamopyrgus antipodarum	O	O	-
Detritivores			
Tubificidae	-	O	-
Dero digitata	O	-	-
Lumbriculus variegatus	O	+	O
Proasellus coxalis	n.p.	O	+
Carnivores			
Turbellaria	-	O	O
Hirudinea	O	O	-

Microcosms simulated: Modelling the combined effects of nutrients and an organophosporus insecticide

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Introduction

Increased nutrient loading and contamination with organic micropollutants are two types of stress to aquatic ecosystems that often occur together. It has been suggested that both types of pollution influence each other's effects (e.g. Gunnarsson et al., 1995). It can be expected that the bioavailability of micropollutants is affected by the system's trophic status, and that adverse effects of these pollutants depend on the ecosystem structure. On the other hand, effects of eutrophication might be enhanced by toxicants that affect herbivorous animals. Little is known about the effects of a simultaneous reduction of both types of pollutants. Therefore, a better insight in the interactions between nutrients and micropollutants is important for the further design of environmental policy. Mathematical models will be a valuable tool for this purpose.

The aim of this study is to build a mathematical model of an aquatic ecosystem in which combined effects of nutrients and micropollutants can be studied, and to calibrate it on the results of experimental studies. The model, CATS5, has been built by incorporating an existing eutrophication model (Janse & Aldenberg, 1996; Janse et al. 1992; Janse 1996) into an existing food-web model of micropollutants (Traas et al., 1995, 1996). The name CATS is an acronyme for 'Contaminants in Aquatic and Terrestrial ecoSystems'. The study is based on experimental studies on the combined effects of nutrient addition and application of chlorpyrifos, an organophosphorus insecticide, in aquatic microcosms resembling ditch ecosystems, as described by Van Donk et al. (1995), Brock et al. (1995) and Cuppen et al. (1995); see also Brock & Van den Brink, this volume).

Methodology

A food-web model of the microsms ecosystem, based on functional groups, has been combined with a description of the abiotic fate of both the insecticide and the nutrients phosphorus and nitrogen. The components of the model are depicted in Figure 1. The model comprises both the water column and the 10 cm sediment layer; both layers are assumed to be homogeneously mixed. The cycles of all three elements are considered as closed within the system. Organic matter is present in three pools: suspended in the water, as freshly settled material and as 'old' organic matter in the sediment. Settling and mineralisation are modelled as first-order processes. Inorganic nutrients were described in both the water and the pore water, in order to keep track of nutrient uptake by the vegetation. Processes involved are diffusion between sediment and water, sorption of phosphorus onto the sediment, nitrification and denitrification. The nutrient-to-dry-weight ratios of the organic matter are modelled dynamically, in order to keep the mass balances closed.

The abiotic processes of the insecticide include sorption to all organic compoments: suspended detritus, algae, macrophytes and sediment organic matter, as well as degradation (hydrolysis, photolysis and biodegradation), volatilisation and diffusion between water and sediment.

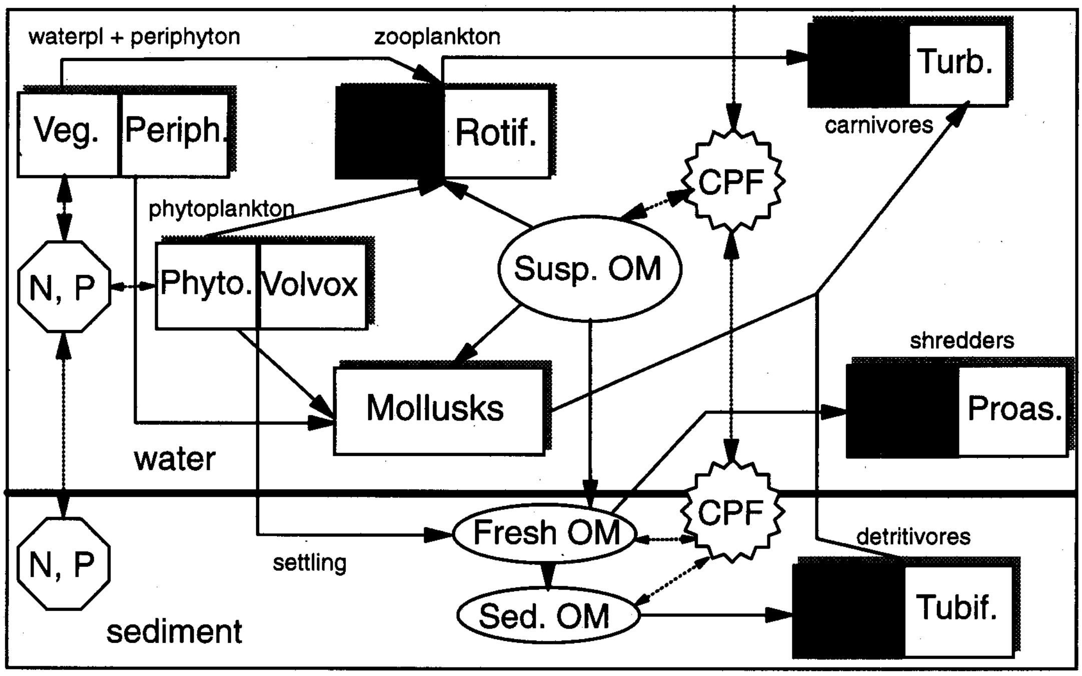

Figure 1: Diagram of food relations in CATS5, describing the effects of nutrients (N,P) and the insecticide chlorpyrifos (CPF) on aquatic microcosms, resembling ditch ecosystems. CPF-sensitive groups are shown as dark blocks, non-sensitive groups as white ones.

The primary producers in the model include macrophytes and three types of algae, *viz.* edible and non-edible phytoplankton and periphyton. All producers are assumed to be homogeneously distributed over depth. The maximum periphyton density is assumed to be dependent on the biomass of the macrophytes. The description of the primary producers and the nutrient cycles has been taken from the existing eutrophication model PCLake (Janse *et al.*, 1992; Janse & Aldenberg, 1996). Primary production is modelled by means of a depth-integrated light function, combined with Monod kinetics for nutrient uptake for the algae, and a Droop model for the aquatic plants. The macrophytes are able to extract nutrients from both the water and the pore water. All plants and algae are considered as not sensitive to the insecticide.

The food-web comprises filter-feeders, mollusks, shredders, deposit feeders and carnivores. The representatives of each group (except the mollusks) were divided in an insecticide-sensitive and a non-sensitive subgroup. This primary sensitivity has been derived from single-species toxicity tests. In general, arthropods are sensitive to the toxic compound, while non-arthropods are not. The dose-response functions from the acute (48 hrs. LC50) toxixity tests were incorporated in the model. If data was available on more than one representative of a functional group, the data for the least sensitive species were chosen. The dose-response functions were based on dissolved CPF only. Food exposure, as well as bioconcentration, were not included in the model.

Simulations were performed for three situations: control, nutrient addition and nutrient addition combined with chlorpyrifos (CPF) addition. Nutrients were added in two large doses on day 0 and day 57 and in weekly small doses between day 0 and day 120. CPF was added on day 58. The system characteristics and initial values were derived from the experimental data. The water depth was 0.5 m, the surface area 1.21 m^2. For comparison between model and data, the measured population densities were converted to dry weight. Calibration has only partly been performed as yet.

Results

First, the effects of nutrient addition are described, by comparing the control situation with the eutrophied system. The second and third topics are the fate and the primary biotic effects of the insecticide, respectively. Finally, the (secundary) effects of a combined treatment are described.

1. Effects of nutrient addition

The macrophytes show a clear response to the increased nutrient loading; simulated values are in accordance with the data (Figure 4). Nitrogen is the limiting nutrient, as may be derived from the increase of the nitrogen-to-dry-weight ratio of the macrophytes following the addition. The periphyton (Figure 5) also profits from the nutrient addition, both in the simulations and in the data; the simulated densities are clearly overestimated, however. The phytoplankton is less important in the system. The noticed effect of an increased food availability is a higher density of grazers, such as zooplankton and mollusks (Figure 6).

2. Abiotic behaviour of chlorpyrifos

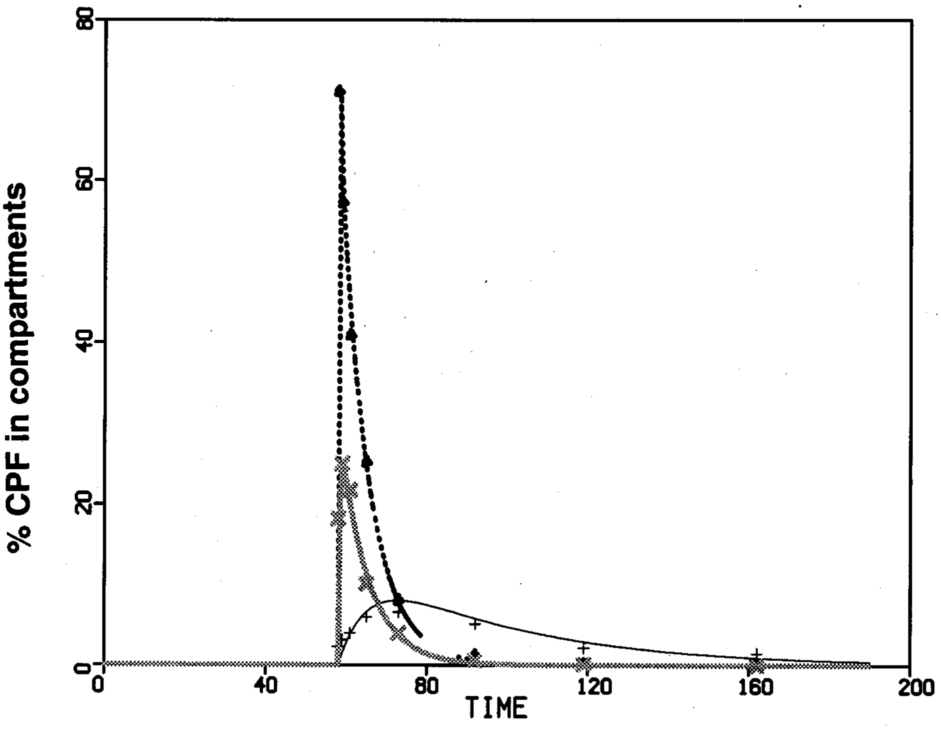

Figure 2: Simulated fate of Chlorpyrifos (CPF) in water (dotted line), vegetation (grey line) and sediment (thin line), as compared to the data (symbols). CPF was added on day 58.

CPF is modelled in several compartments: dissolved in water (bio-available), sorbed to sediment, macrophytes, algae and detritus. After the peak due to the addition on day 58, the dissolved concentration drops quite rapidly. Rapid sorption to vegetation takes place, but slower sorption to sediment (Figure 2). Compared to the results of a previous modelling study without macrophytes (Traas *et al.*, 1995), sorption to sediment is significantly less and diffusion is slower, due to the presence of macrophytes.

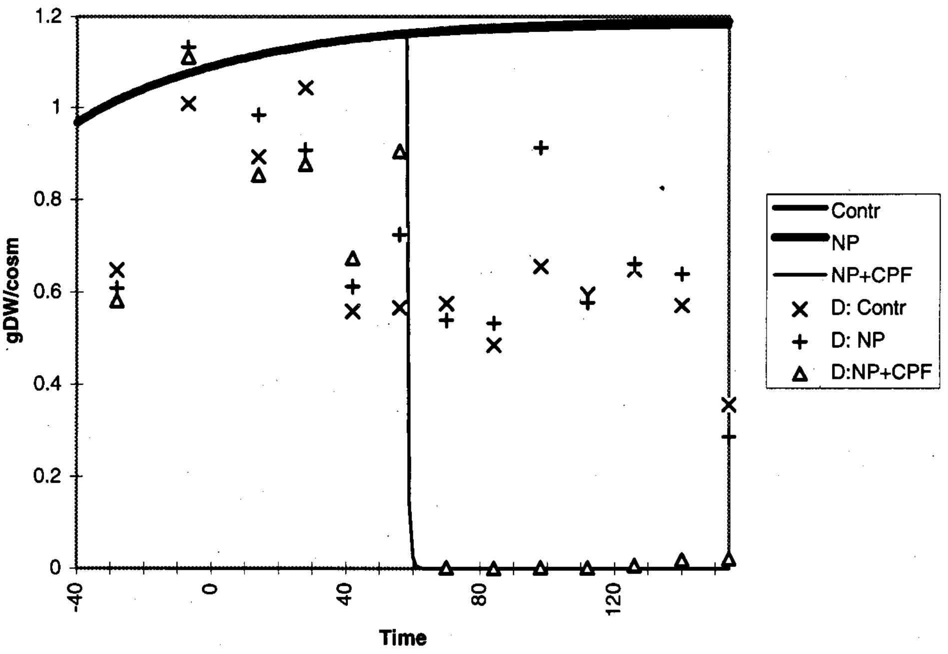

Figure 3: Simulated (lines) effects of nutrients (NP) and CPF additon on sensitive shredders, as compared to the data (symbols). Nutrients were added in two large doses on days 0 and 57 and weekly small doses between days 0 and 120, CPF was added on day 58.

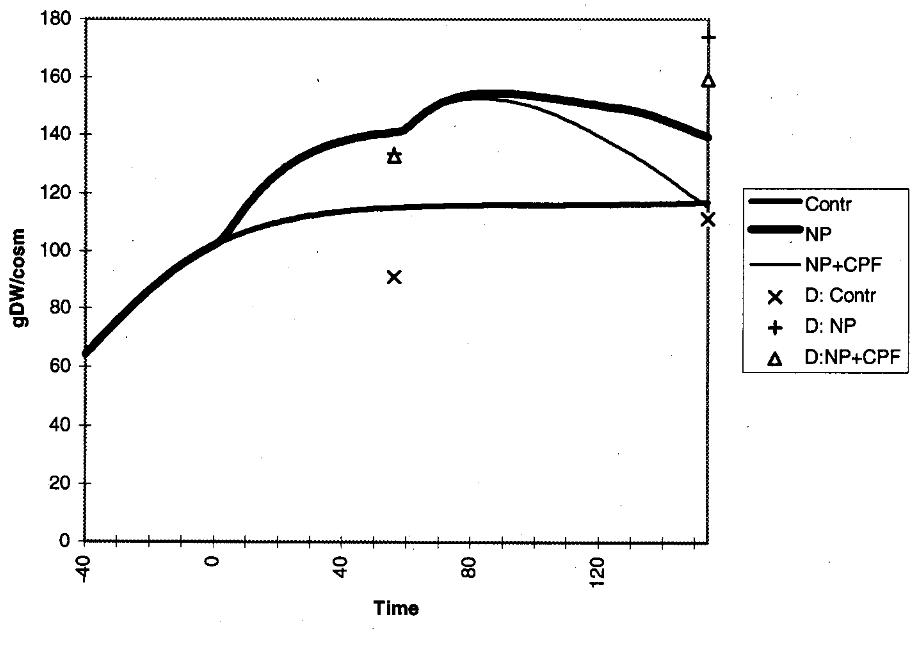

Figure 4: Simulated (lines) density of Aquatic plants in mesocosms with addition of Nutrients (NP) and Chlorpyrifos (CPF), as compared to measured densities (symbols). For treatments, see Figure 3.

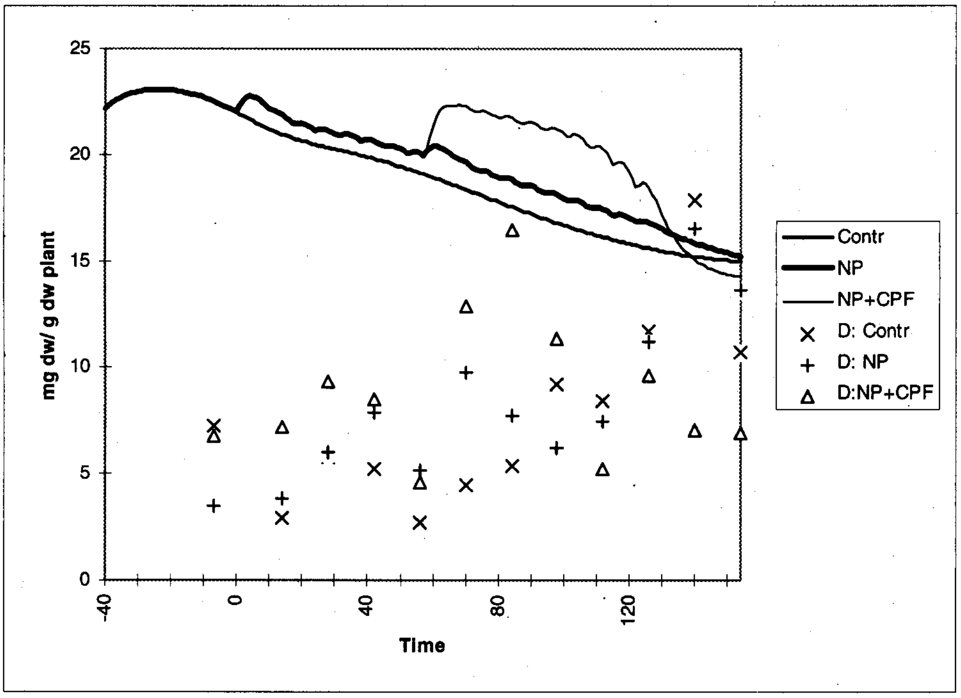

Figure 5: Simulated (lines) effects of nutrients (NP) and CPF addition on Periphyton, as compared to the data (symbols). Periphyton is expressed as mg per g macrophytes. For treatments, see Figure 3.

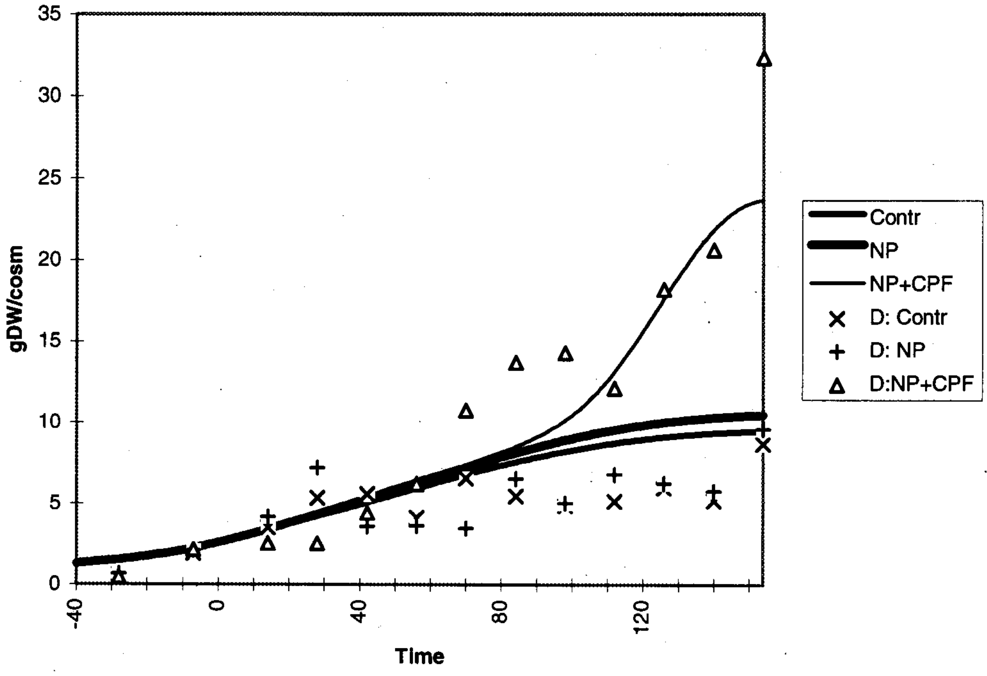

Figure 6: Simulated (lines) effects of nutrients and CPF addition on Mollusca, as compared to the data (symbols). For treatments, see Figure 3.

3. Direct biotic effects of chlorpyrifos

Direct effects were comparable in all cosms. In general, arthropods are sensitive to CPF. As an example, the sensitive shredders, mainly consisting of *Gammarus pulex* and *Asellus aquaticus*, are shown (Figure 3). The 'spontaneous' gradual decline in the controls could not be explained by the model. Nutrient addition only did not stimulate the growth of this functional group.
For some groups, the effects were less pronounced than observed in plankton-dominated cosms in an earlier study (Traas *et al.,* 1995), probably due to a lower bio-availability of the insecticide as a result of a higher sorption to the aquatic plants.

4. Combined effects of nutrients and chlorpyrifos

Being released from grazing pressure because Cladocerans are wiped out by the insekticide, the algae and especially the periphyton show a striking extra increase in biomass following the CPF addition on day 58 (Figure 5). This has an adverse effect on the vegetation, probably due to increased shading (Figure 6). Some 30 days after the CPF addition, the non-arthropod grazers (mollusks) increase, probably due to release from competition (Figure 6). The less-sensitive shredders (*Proasellus*) show a rapid come-back after a temporary decline. Initially, the overall shredder function, *viz.* the processing of fresh organic material into 'old' organic material, is lowered compared to the control (results not shown).

Discussion

In general, the observed effects of nutrients, chlorpyrifos and a combination of both could be reproduced reasonably well by the CATS5 model. A formal calibration, however, remains to be done. The main conclusions from the microcosm experiments, as described by Van Donk et al. (1995), Brock et al. (1995) and Cuppen et al. (1995) (see also Brock & Van den Brink, this volume) were: (1) Of the primary producers, the macrophytes and, temporarily, the periphyton took benefit of a nutrient addition, in contrast to the planktonic algae. (2) Due to an increased food availability, also arthropod grazers increased following nutrient addition. (3) The decline of arthropod grazers after chlorpyrifos treatment caused an increase in algae, especially periphyton, which had a negative impact on the macrophytes' growth. (4) Later, non-susceptible, non-arthropod grazers took over the role of periphyton controller. (5) These shifts were accompanied by changes in the carnivores group. (6) Arthropoda play important roles in freshwater ecosystems, since their reduction by an insecticide affects nearly all trophic levels, as well as important ecosystem processes like decomposition.

Most of these conclusions could be confirmed, at least in a qualitative way, in this model study. Several other authors (*e.g.* Stansfield *et al.*, 1989) have provided evidence for the hypothesis that the effects of nutrients and insecticides on algal biomass are additive, *i.e.* that insecticides may enhance the effects of eutrophication by reducing the top-down control of algae. The preliminary results presented here are consistent with this hypothesis. Although there are also indications for the alternative hypothesis that the adverse effects of toxicants might be less pronounced in more eutrophic systems because of a lower bio-availability of the compound, this phenomenon seems to play a minor role for chlorpyrifos, and possibly for other insecticides as well.

From the reasonable correspondence between model and data we may conclude that the assumptions on which the model is based together can predict the main combinatory effects in this system. These assumptions comprise the definition of the food-web, the incorporated primary dose-effect functions of CPF and the description of uptake and cycling of nutrients. This correspondence indicates that the basic assumptions seem sound, although this does not necessarily provide a proof of the correctness of all model formulations. A sensitivity analysis will provide insight in the relative importance of the different processes and pathways. The results are still preliminary, as an extensive calibration has not yet been performed. In particular, the modelling of the periphyton and its interaction with grazers should be improved. It should be noted that also the conversion of population sizes to dry-weight introduces some uncertainty. The model will be tested and improved further to become a useful tool for risk assessment of substances and for evaluating environmental policy measures.

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EFFECT OF NUTRIENT ADDITIONS ON CADMIUM BIOAVAILABILITY TO AQUATIC INVERTEBRATES IN LITTORAL ENCLOSURES

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INTRODUCTION

Cadmium was added to the epilimnion of Lake 382 at the Experimental Lakes Area (ELA) in northwestern Ontario from 1987 to 1993 in an effort to test the efficacy of the Canadian water quality guideline for Cd, for the protection of aquatic life in softwater lakes (Malley et al. 1989). As part of the ELA agreement with the Ontario Ministry of Environment and Department of Natural Resources, all ecosystems at the ELA must be returned to pre-experimental state after completion of a study. Nutrient additions were considered as a potential remediation technique for Lake 382 because they may: 1) decrease dissolved Cd in the water column (Hart 1982), 2) dilute Cd in the sediment and pore water by increasing the organic content of the sediment (Thomas 1987), and 3) reduce the redox potential of the sediment/water interface (Gambrell et al. 1991). These factors may decrease bioavailability of Cd to aquatic invertebrates. However, increased organic matter in water and sediment will affect Cd bioavailability to organisms differently, depending on the niche of an aquatic organism, the route of accumulation and time. High organic matter in the sediment may increase contaminant exposure for infaunal organisms (Knezovich et al. 1987, Harvey and Luoma 1985), but over the long term may dilute sediment contaminant concentrations, thus decrease exposure (Thomas 1987). Therefore, the objective of this study was to compare the bioavailability of Cd to aquatic invertebrates in nutrient-enriched and control littoral enclosures. This would provide information on the importance of organic matter on the fate and bioavailability of Cd to aquatic invertebrates that inhabit different niches of an aquatic system.

MATERIALS AND METHODS

Lake 382

Beginning on June 23, 1987 and continuing every ice-free season until 1993, Cd, as $CdCl_2 \cdot 2\frac{1}{2}H_2O$, and its radioactive tracer ^{109}Cd, was added to the epilimnion of Lake 382 at the ELA (Malley et al. 1989, Lawrence et al. 1996). Lake 382 is a very soft water, oligotrophic lake located within the Canadian Shield; it has a surface area of 36.9 ha, a maximum depth of 13.1 m and a mean depth of 5.8 m.

Enclosure experiment

In 1991 four enclosures, 5 m diameter x 2 m deep, with polyethylene walls, were placed in the littoral zone (1.75 m depth) of the south bay of Lake 382. The enclosures were of the same design as described in Fairchild et al. (1992). The water and sediments within the enclosures were consequently isolated from the multi-year, ongoing, Cd additions to the whole lake which took place simultaneously with this study. The enclosures remained in place for the two year duration of the study.

Solubilized nutrients at a molar ratio of approximately 10:1 nitrogen:phosphorus, were added to two randomly chosen enclosures, two enclosures were used as controls. The nitrogen source was $NaNO_3$ fertilizer (NPK ratio 13:0:0) and the phosphorus source was reagent grade phosphoric acid (H_3PO_4). The nutrient solution was added to the two enclosures weekly from June 5, 1991 until September 15, 1991, and from May 14, 1992 to October 15, 1992. Approximately 56 g of $NaNO_3$ and 1 mL of H_3PO_4 were added in 1991 and 89.6 g and 1.6 mL in 1992 in each of the enriched enclosures.

Concentrations of dissolved and particulate carbon, nitrogen and phosphorus, and chlorophyll *a* and pH levels were determined every two weeks in each enclosure using methods described in Stainton et al. (1977).

In 1991, Cd concentrations were determined from water filtered through a three µm Nucleopore® polycarbonate filter. In 1992, Cd concentrations were determined by taking duplicate, unfiltered water samples using acid-washed 60 mL Nalgene® bottles. Cadmium in water and in the $NaNO_3$ fertilizer was measured on a Varian 975 atomic absorption spectrophotometer (AAS) equipped with a GTA-95 graphite furnace, 24 h after acidification to 0.5% with nitric acid.

Sediment cores (0 to 2 cm layer) were obtained with a Kajak-Brinkhurst (KB) corer in the same manner as described in Fairchild et al. (1992). The sediment was freeze dried and weighed dry prior to analysis. Duplicate subsamples were digested in Teflon® beakers for 15 min at 100°C in an aqua regia mixture and Cd analysed by AAS.

Concentrations of Cd in pore water were determined by centrifuging the top two cm of duplicate sediment cores in acid-washed 250 mL Nalgene® centrifuge tubes at 4000 RPM for 30 min. The supernatant was siphoned off, and Cd analysed by AAS, 24 h after acidification to 0.5% with nitric acid.

Biota in enclosures

Floater mussels, *Anodonta grandis grandis* (Say), were collected from ELA Lake 104, transported to Lake 382, and placed into the enclosures in two, closed-bottom, plastic-mesh cages constructed with a wooden frame. Six mussels were sampled from each enclosure (day 0, 53, 88, 119 and 339, in 1991 and day 0, 14, 33, 61, 90 and 126, in 1992), and stored at -40°C until analysis. The soft tissues were removed, weighed after blotting dry and then freeze dried, homogenized, and Cd analysed using air-acetylene flame AAS with background correction (Currie 1993).

Male freshwater crayfish, *Orconectes virilis* (Hagen) were collected from ELA Lake 468, transported to Lake 382 and placed into a plastic-mesh cage with three rocks obtained from the shoreline of Lake 382 (three crayfish per cage, six cages per enclosure). Crayfish were removed from the cages on each sample day of one uptake experiment in 1991 (days: 0, 48, 83 and 114) and two uptake experiments in 1992 (days: 0, 8, 15, 27, 64 and days: 0, 8, and 36), and stored at -40°C until analysis. The whole organism was weighed after blotting dry; Cd analysis was performed as described for the floater mussels.

Duplicate zooplankton samples were obtained using a 30-cm diameter Wisconsin net (mesh size 200 µm) pulled vertically through the top 1 to 1.5 m of each enclosure and stored at -40°C until analysis. Samples were thawed, filtered through Nitex® screening, allowed to dry overnight, weighed and analyzed by AAS.

Immature benthic invertebrates, including Chironomidae and *Hexagenia limbata* (Serville) were obtained on each sample day using a 15 x 15 cm Ekman grab. Organisms and sediment were sieved through a 400-µm mesh, hand sorted into acid-washed glass scintillation vials and stored at -40°C until analysis. The organisms were blotted dry and approximately 10 to 15 mg of wet tissue analysed by AAS.

Statistical analysis

The concentrations of Cd in the abiotic and biotic samples were compared ($p<0.05$) using Procedure GLM of SAS (SAS Institute 1989) and Tukey's mean test. Where necessary the data were log transformed because of non-homogeneity of variance, prior to statistical analysis.

RESULTS

Mean concentrations (± 1SD) of chlorophyll *a* in the enriched and control enclosures were 2.04 ± 0.85 and 1.75 ± 0.77 µg/L in 1991 and 9.99 ± 1.52 and 1.52 ± 0.53 µg/L in 1992, respectively. Chlorophyll *a* concentrations were significantly different (t-test, $p<0.05$) between the two treatments in 1992 but not in 1991.

The enriched enclosures had greater concentrations of Cd in the filtered water than the control enclosures in 1991 (73 to 99 ng/L vs. 15 to 22 ng/L, respectively, Figure 1). In 1992, the enriched enclosures usually had higher concentrations of Cd in whole water samples compared to the control enclosures. Cd concentrations in the enriched enclosures ranged from 46.0 to 103 ng/L compared to 23 to 84.0 ng/L in the control enclosures in 1992 (Figure 1). However, the differences were not as pronounced as in 1991, and a statistically significant difference was only found on the Sept. 8 sample day. The $NaNO_3$ fertilizer contributed approximately 2.09 and 3.34 µg of Cd to the enriched enclosures in 1991 and 1992, respectively.

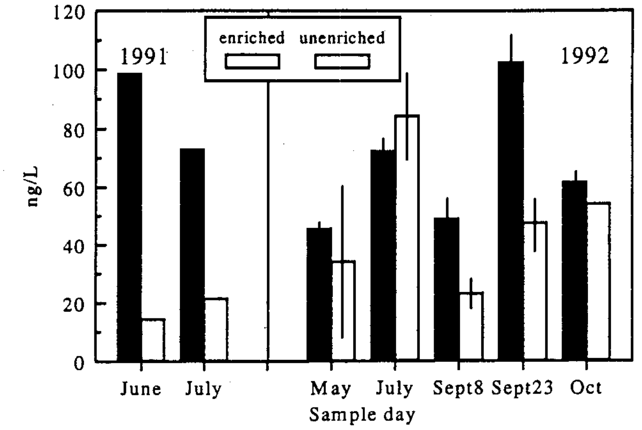

Figure 1. Mean concentrations of cadmium in the water column of nutrient enriched and control littoral enclosures, ELA, 1991 and 1992. Error bars equal ± 1SD.

There were no significant differences between Cd concentrations in the sediment of the enriched and control enclosures in any year. Concentrations ranged from 0.30 to 0.59 µg/g dry wt. in 1991 and 0.27 to 0.57 µg/g dry wt. in 1992.

Concentrations of Cd in the pore water from the enriched and control enclosures were not affected by the nutrient additions at any sampling date. Concentrations ranged from 0.19 µg/L to 1.53 µg/L from all enclosures in 1991 and 1992.

Nutrient additions did not have a consistent effect on Cd concentrations in floater mussels in 1991 (Figure 2). In 1992, mean concentrations of Cd in mussels from the enriched enclosures were slightly lower than those from the controls over most sample days. However, statistically significant differences were only observed on day 14 in 1992. Concentrations in the mussels in 1992 were very similar to concentrations detected on comparable sampling days in 1991 (Figure 2), even though the enclosures had been isolated from the lake for 12 months.

Nutrient additions had no consistent effect on Cd accumulation by the crayfish *O. virilis* in 1991 (Figure 3). In 1992, there appeared to be lower Cd accumulation by crayfish in the enriched enclosures compared to the controls (Figure 3), however, these differences were not statistically significant. Cd concentrations in crayfish were approximately 10 to 30% of concentrations in mussels.

The zooplankton sampled were mostly Copepods and they accumulated approximately the same Cd concentrations as the mussels (3.0 to 59.9 µg/g dry wt., Figure 4). Zooplankton in the enriched enclosures appeared to accumulate more Cd than those in the controls during the early part of the accumulation studies in both years, but the differences were not statistically significant at any date.

In 1991 and 1992, mean Cd concentrations in chironomid larvae from the enriched enclosures were consistently higher relative to the control enclosures, however, mean concentrations were not significantly different at any sampling time. Concentrations of Cd ranged from 0.59 to 1.78 µg/g wet wt. in 1991 and from 1.2 to 2.6 µg/g wet wt. in 1992 (Figure 5). Nutrient additions had no consistent effect on the bioaccumulation of Cd by the mayfly nymph, *H. limbata*. Cadmium concentrations in mayfly nymphs ranged from 0.1 to 0.7 µg/g wet wt. in 1991. No *H. limbata* samples could be obtained in 1992.

DISCUSSION

There were slight increases in Cd concentrations in the water column of the enriched enclosures compared to the controls at most sample days. This may have been a result of the increase in the amount of dissolved and particulate organic matter (DOM and POM, respectively) in the water column. Dissolved organic matter and POM were in the form of chlorophyll *a*, phytoplankton and bacteria (Malley et al. 1996) and likely increased the available binding sites for Cd in the water column. Particulate and DOM in water will enhance the apparent solubilities of contaminants in water (Hart 1982, Servos 1988), thus, concentrations will appear to increase in unfiltered water with high DOM and POM. At the rate nutrients were supplied in this study production of chlorophyll *a* and POM did not result in statistically significant effects on the Cd water concentrations. Increased nutrient additions either for a longer period of time or at greater concentrations may have increased production of DOM and POM and subsequently resulted in greater sedimentation rates that would clear the water column of particulate-bound Cd.

Cd added to the enclosures via the $NaNO_3$ fertilizer used for the nutrient additions was likely not the cause of the slight increase in Cd water concentrations observed. The nutrient additions would have contributed <1% (approximately 98 pg/L, enclosure volume = 34000 L) of the prevailing concentrations in the nutrient enriched enclosures.

Concentrations of Cd in the sediment were not significantly affected by the rate of nutrient additions used. Increased sedimentation of seston in more eutrophic systems may decrease concentrations of Cd in the sediment by dilution, increase organic matter content of the sediment (Thomas 1987), and increase acid volatile sulfide content (DiToro et al. 1990). A combination of these factors may result in decreased Cd concentrations or decreased bioavailability in sediment (Hart 1982, Allan 1986).

Concentrations of Cd in the pore water were also not affected by the nutrient additions. Over time, increased particulate matter or seston in the enriched enclosures would be expected to cause changes in the partitioning of Cd from the water column and sediments to the pore water. Increased organic matter associated with the sediments could complex Cd and prevent diffusion of Cd into pore water. Alternatively, increased POM and DOM could increase pore water concentrations because of entrainment of Cd-associated particles into the pore water (Hart 1982).

At the rate of nutrient additions used in this study there were few statistically significant differences in the accumulation of Cd by biota in the nutrient enriched enclosures compared to the control enclosures. There did appear to be increased accumulation of Cd in zooplankton and chironomids (Figure 4 and 5, respectively). Copepods, the predominant zooplankton, typically filter feed on particles ranging from 1.5 to 22 µm (Barnes 1980). Because there were increases in these particle sizes in the enriched enclosures, specifically <3 µm in diameter, and these particles contained a high percentage of Cd (Malley et al. 1996), the copepods in the enriched enclosures may have obtained a significant portion of their Cd from this source.

Slight reductions in Cd accumulation were observed in mussels and crayfish from the enriched enclosures at some sampling dates in 1992 (Figure 2 and 3, respectively). However, the results were neither statistically significant or consistent over all sample days. It has been shown that more eutrophic conditions result in lower concentrations of contaminants in some biota (Taylor et al. 1991, Larsson et al. 1992, Athalye and Gokhale 1991). Decreased accumulation could be a result of increased sorptive sites for freely dissolved contaminants, consequently decreasing contaminant bioavailability from water (Taylor et al. 1991, Larsson et al. 1992). Decreased accumulation may also be observed as a result of biomass dilution, either by increased body weight under more eutrophic conditions (Athalye and Gokhale 1991) or increased population biomass, resulting in less contaminant per unit biomass (Taylor et al. 1991). There were no increases in body weight in crayfish and mussels from the nutrient enriched enclosures relative to the control enclosures, therefore, biomass dilution was not a factor affecting accumulation in these organisms in this study.

CONCLUSIONS

Nutrient additions to the enclosures appeared to increase Cd concentrations in the water column of the enriched enclosures, likely because of increased particulate matter in the water column in the form of bacteria and algae. At the rate nutrients were supplied to the enriched enclosures in this study, major effects on Cd bioavailability were not observed. While increases in POC and DOC may have reduced freely dissolved Cd concentrations, this was offset by increased concentrations on fine particles ingested by filter feeders. Nutrient additions at higher rates or for longer periods of time may have resulted in greater differences in the abiotic and biotic compartments that were sampled.

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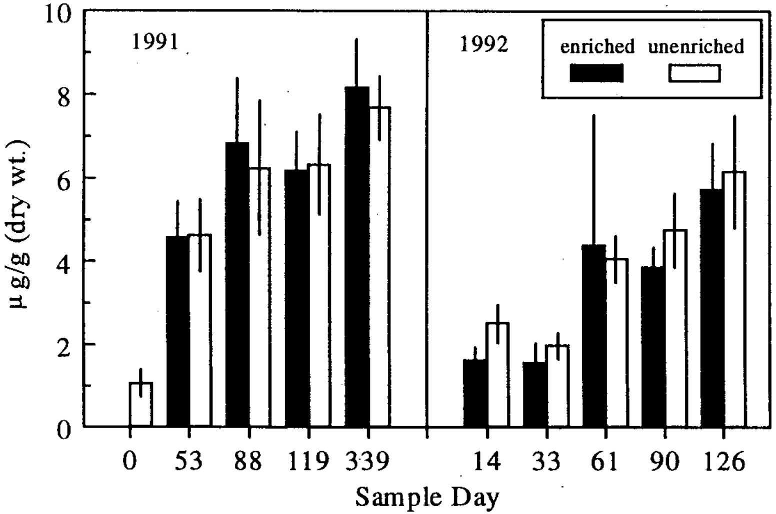

Figure 2. Mean concentrations of cadmium in the floater mussel *Anodonta grandis grandis* (Say), in nutrient enriched and control enclosures in 1991 and 1992. Error bars equal ±1 SD.

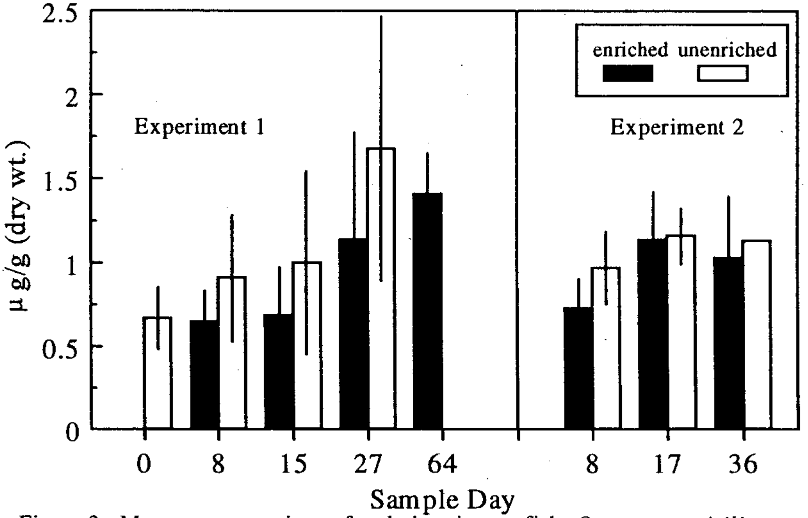

Figure 3. Mean concentrations of cadmium in crayfish, *Orconectes virilis* (Hagen), in nutrient enriched and control enclosures in two separate uptake experiments in 1992. Error bars equal ±1 SD.

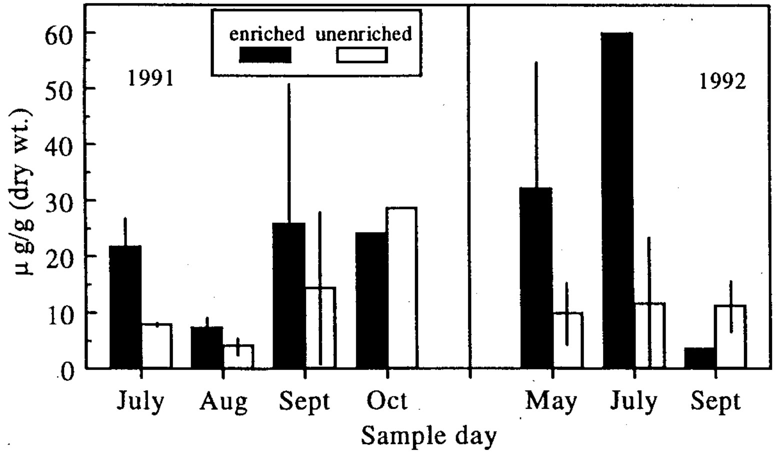

Figure 4. Mean concentrations of cadmium in zooplankton in nutrient enriched and control enclosures in 1991 and 1992. Error bars equal ±1 SD.

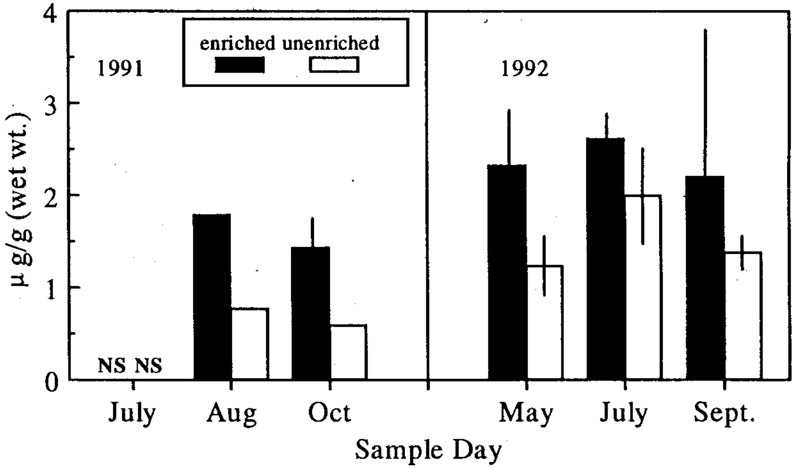

Figure 5. Mean concentrations of cadmium in larval Chironomidae from sediment in nutrient enriched and control enclosures in 1991 and 1992. Error bars equal ±1 SD. NS indicates that no sample could be obtained.

Ecological risk assessment: a need for integrating fate and effects of nutrients and toxicants

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Introduction

Within water quality modelling emphasis has been on either ecological risk assessment of toxic substances or eutrophication. Ecological risk assessment consists of an effects (dose-response) assessment and an exposure assessment [1-3]. Combined these should lead to risk characterization, a quantitative comparison using PEC and PNEC resulting in a risk quotient. This can be used as an estimate for the probability of occurrence of adverse ecosystem effects. The distinction between effects and exposure can also be found in the two model categories used in risk assessment: effects models and fate models. Only in recent years integration of these two types of models has been attempted [3-5]. Eutrophication research on the other hand mainly focuses on the relationship between nutrients and water quality parameters [6-9]. The Dutch governement has defined objectives to decrease eutrophication as well as reduce the emission and effects of toxic substances [10]. The question arises if and how managerial actions will interfere with each other. Therefore, fundamental knowledge of the interaction of nutrients and contaminants is demanded. Recently more attention has been given to this subject [overview in 11], also in the Netherlands [12,13]. We propose an integrated modelling approach linking fate and effects of toxic substances as well as nutrients in order to incorporate several feedback mechanisms, indirect effects and other complex interactions at the ecosystem level.

Model

The model describes a branch of the river Rhine, the river IJssel, with its sedimentation areas, lake Ketelmeer and lake IJsselmeer, which have suffered severely from high inputs of both nutrients and toxic substances in the past. Only from the seventies onward international sanitation programmes have significantly improved the situation. Despite the improvements further actions are required because the problems of high chlorophyll levels as well as high loading of certain heavy metals and organic micropollutants remain.

The system is subdivided into 8 segments with closed mass balances. Each segment has a water and a sediment phase. Included are the nutrients NO_3, NH_4, PO_4 and SiO_2 as well as suspended solids subdivided into inorganic and organic matter. Cd was chosen as toxicant, because of the data available. Phytoplankton consists of three groups: diatoms, green algae and cyanobacteria. Filterfeeding cladocerans were assumed to be the main zooplankton group.

Forcing functions are temperature, light and wind as well as input concentrations of nutrients. Processes concerning nutrients, suspended matter and phytoplankton are described in De Nijs et al. [14]. The CATS model [15,16] was used to incorporate toxicant speciation and accumulation processes. The main feature of the used model is that there are separate but coupled cycles for biomass, nutrients and contaminant with varying ratios. The model is calibrated on the years 1970-1985 and validated on the period 1985-1990 and it describes reasonably well the dynamics of the system.

Method

Two different scenarios have been calculated through with the model over the year 1991 and compared to the normal 1991 calculation: a P-reduction scenario and a scenario in which effects of Cd are imposed on the zooplankton. A scenario with phosphorus was chosen because it is the limiting nutrient in this system. The P-reduction scenario contains a reduction of total-P at the boundary Lobith of 50 %. The Cd-effects scenario comprises a theoretical effect of Cd on the zooplankton of a 10 % decrease of maximum filtering rate and a 10 % increase of respiration and mortality rate.

Specific points of interest are the reaction of phytoplankton and zooplankton biomass, Cd dissolved versus adsorbed and the accumulation of Cd by the algae and zooplankton. Difference quotients have been calculated as the relative change of an outputvariable per relative change of an inputvariable or parameter. These quotients are a measure for the sensitivity of the outputvariable for the inputvariable or parameter. They are also a measure for indirect effects in a complex ecosystem. The seasonal variation is included in the difference quotients. These quotients are denoted as Δvar/ΔP and Δvar/ΔCd eff. in figures 2 & 3.

Phosphorus reduction

Reduction of phosphorus shows little or no effect on chlorophyll-a (fig. 1a). Zooplankton in contrast shows a decrease in biomass (fig. 1b). This indirect effect can be explained by looking at the difference quotients. The decrease in P causes a decrease in diatom biomass which in its turn causes a decrease of zooplankton biomass (fig2a). Due to less zooplankton grazing, the egestion of particles is decreased, resulting in less detritus. This improves the light climate from which the algae, but especially the greenalgae, show less negative effects from P reduction (fig.2b). This again causes a small response in zooplankton. These responses to less light limitation are only temporarily, because then the cyanobacteria start to bloom. They show a positive response to the reduction of P due to the improved light climate and the fact that they are less limited by P than the other phytoplankton groups. There is also a decreased grazing pressure not only through the decreased zooplankton, but also because zooplankton prefers other algae over cyanobacteria. The result as a whole is that the level of chlorophyll-a remains almost the same.

As a result of the drop in detritus concentration the Cd adsorbed onto detritus decreases as well (fig.2c). This leads to an increase of the other fractions of cadmium: adsorbed onto inorganic matter but also cadmium dissolved. This higher concentration of dissolved Cd in its turn causes an increase in Cd accumulation in phytoplankton as well as zooplankton. The small bump in Cd content occurs when light climate is improved and phytoplankton and zooplankton biomass are less negatively influenced by P reduction, pointing at biomass dilution.

Cadmium effects on zooplankton

When zooplankton is stressed by Cd grazing pressure on algae is decreased and detritus from egestion decreases as well. This causes a higher biomass of phytoplankton (fig. 3b) and less cadmium adsorbed onto detritus (fig. 3a). As a result a higher total concentration of Cd adsorbed onto or accumulated by phytoplankton is found as well as a higher content. The total concentration of Cd in algae is the inverse of Cd adsorbed onto detritus, whereas the content is trailing due to an increased phytoplankton biomass.

All phytoplankton groups favour from effects on zooplankton but diatoms and green algae more (fig.3b). PO_4 concentration drops rapidly and the algae are P limited. Cyanobacteria have less profit from decreased grazing pressure and improved light climate but are also less limited by P. Overall there is an increase in chlorophyll-a where zooplankton biomass is even lower than with the phosphorus reduction scenario (fig 1a,b).

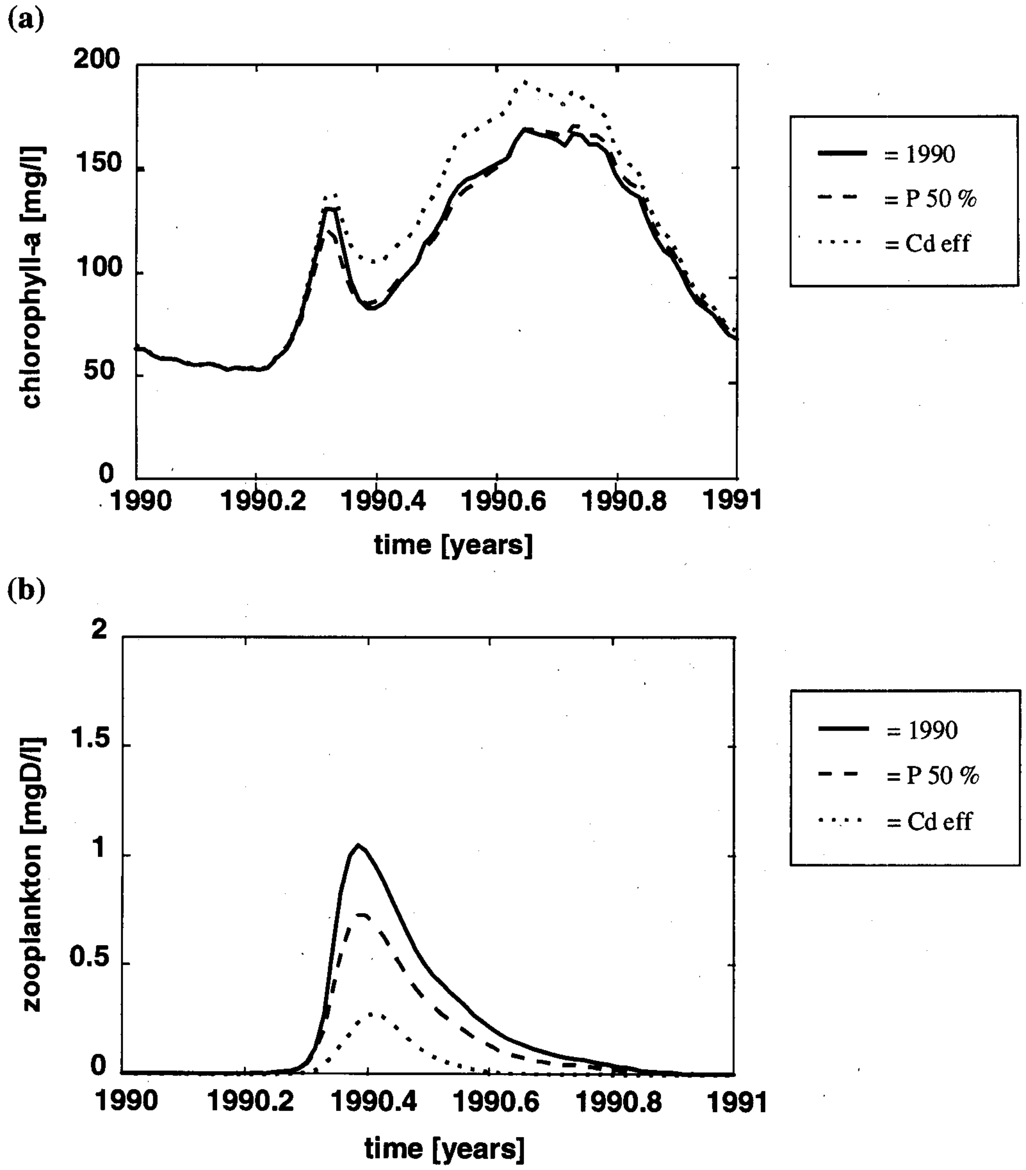

Figure 1. (a) chlorophyll-a and (b) zooplankton biomass at the different scenarios compared to the standard 1991 run

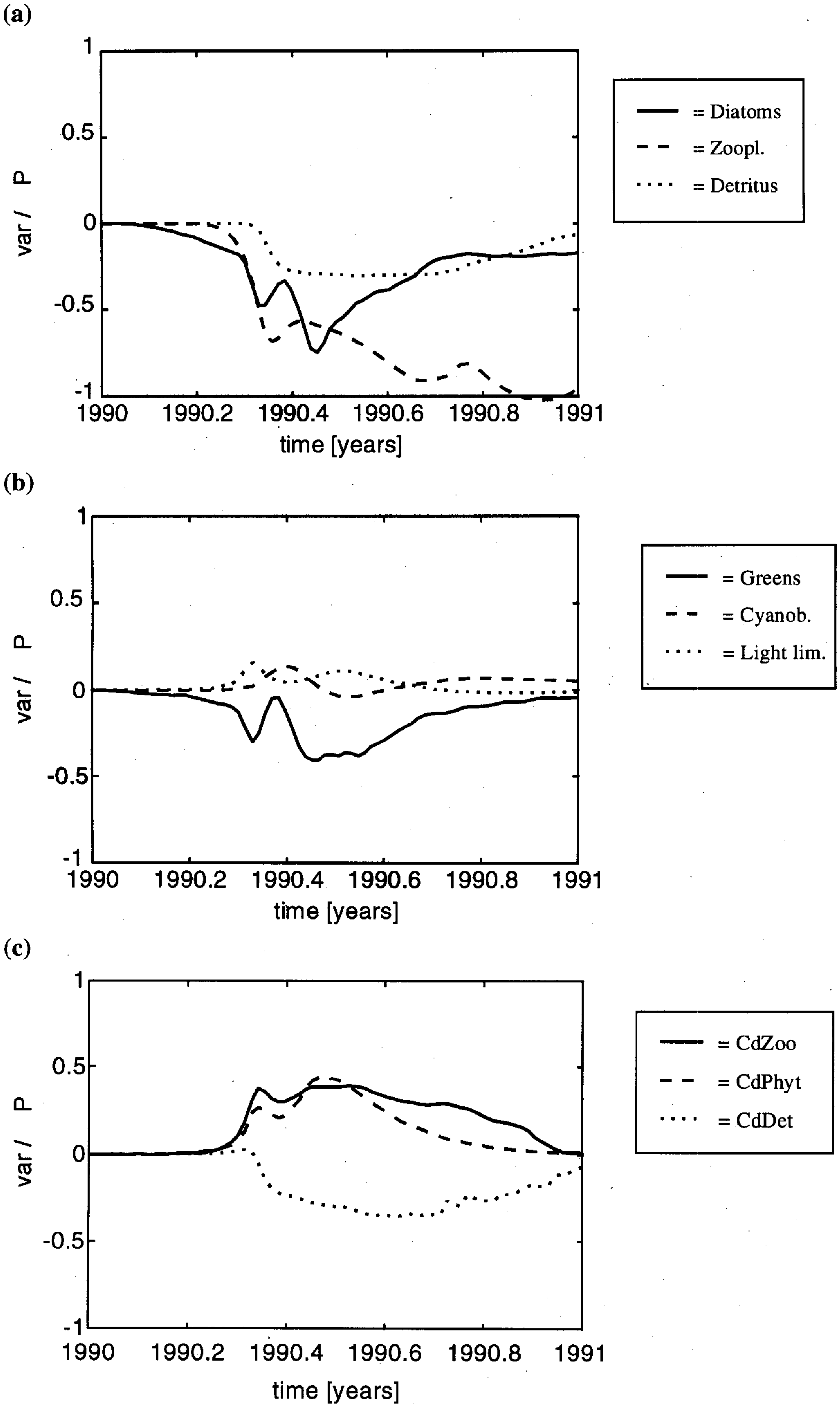

Figure 2. difference quotients related to P-reduction

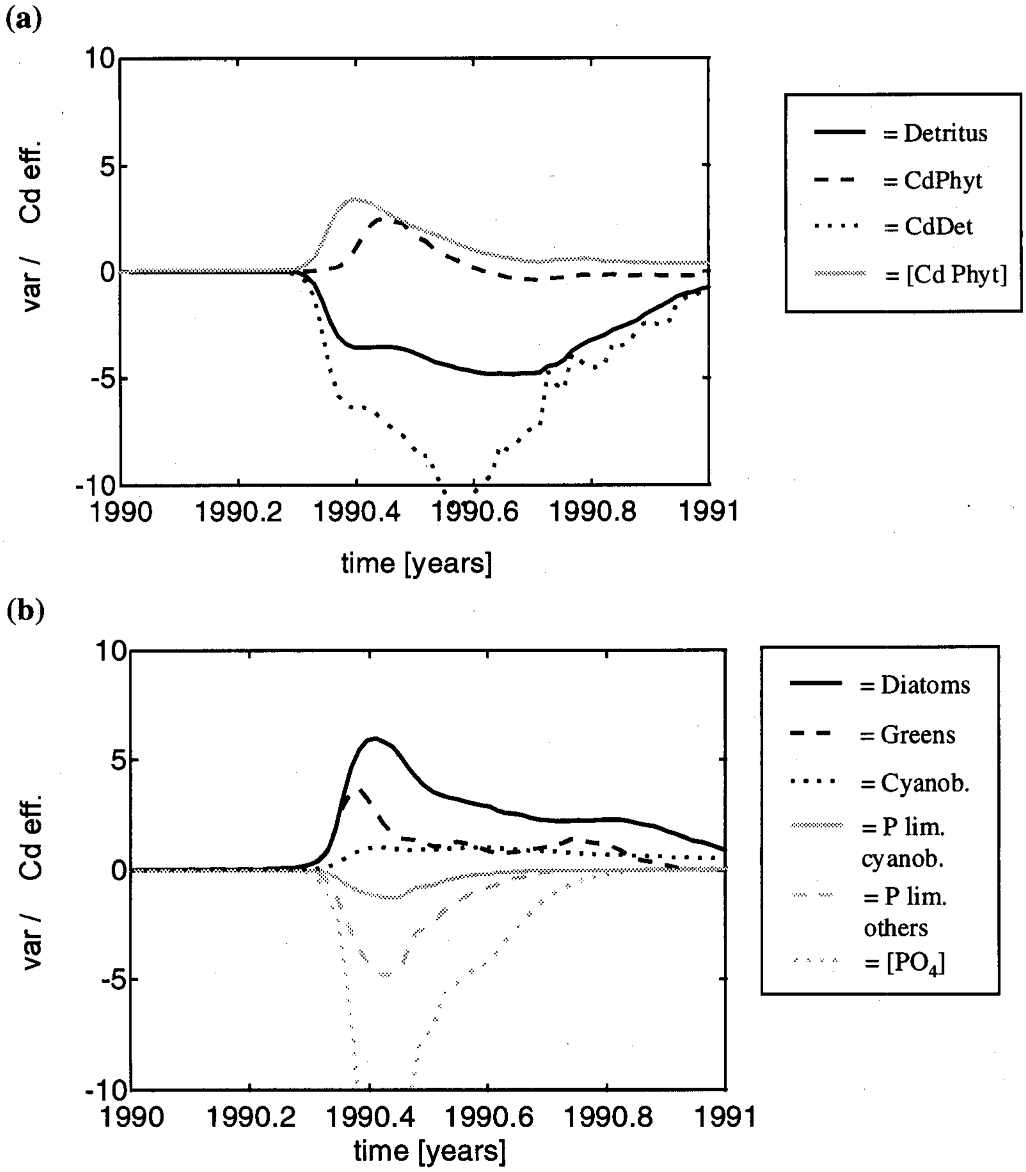

Figure 3. difference quotients with respect to Cd effects imposed on zooplankton

Discussion and conclusions

Results show that a change in trophic state will change the PEC due to a change in partitioning [17]. This changes the accumulation of toxic substances (biomass dilution [18]) which possibly leads to a change in toxic effects. Results also show that when effects can be expected (PEC > PNEC) this will lead to a change in ecosystem structure which in its turn changes the PEC again. The occurring effects will alter the trophic state of the ecosystem with its own implications. Therefore, interactions between PEC, nutrients, effects and biotic components verify the necessity for integrated modelling in risk assessment. Errors might arise using fate models or effects models standalone. When a change in trophic state is to be expected also nutrients should be incorporated

It is shown that nutrient reducing measures may not suffice to prevent algal blooms. Toxicant stress in combination with high concentrations of nutrients may induce an increase in phytoplankton biomass due to less efficient zooplankton grazing. Model results show that in order to change the present state of eutrophication it might be necessary to also decrease the input of contaminants affecting the zooplankton.

Although the model has been calibrated and validated, this has been done particularly for nutrients, suspended matter and chlorophyll-a. Further validation with respect to the different algal groups, zooplankton as well as toxic substances remains necessary. A check of the difference quotients on data and other systems is required. The model has to be improved on the dynamics of toxicants in phytoplankton and zooplankton and by incorporation of dose-effect relationships. Furthermore a validation of the effects on zooplankton is important. An extension of the model with other functional ecosystems groups like zoobenthos, molluscs, fish and waterfowl as in the CATS model is planned for the future. Despite these considerations the model offers a greater insight into the complex mechanisms within ecosystems.

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Teasing Apart Nutrient-Contaminant Impacts in River Ecosystems: Strategies for Artificial Stream Research

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Introduction and Objectives

In natural environments, such as large rivers, the high degree of spatial heterogeneity and the challenge of obtaining true replicates makes it difficult for biomonitoring studies to predict quantitatively the impacts of complex effluents on biota (Buikema and Voshell 1993, Forbes and Forbes 1994). Although biomonitoring provides important observations and insights into patterns of effluent effects on benthic biota, inferential hypothesis testing through field assessments is often impossible (Cooper and Barmuta 1993). To alleviate these problems, we developed an artificial stream system that simulates flowing water environments for the purpose of assessing the effects of effluent discharges on riverine food webs (Culp and Podemski 1995). Experimentation using artificial streams provides a promising, complimentary approach to biomonitoring assessments because artificial streams provide control over relevant environmental variables and true replication of treatments. Thus, causality (i.e., cause and effect) can be assigned definitively and the contrasting effects of nutrient and contaminant effects of BKME on benthic food webs can be isolated and measured.

In the Athabasca River we isolated the effects of nutrients from those of complex BKME, and tested their separate impacts on a food web comprised of primary producers (attached algae) and secondary producers (benthic insects) during spring and autumn. To accomplish this, we compared the effect of adding 1% BKME dilutions to the benthic community, to the effect of only adding the nutrients (nitrogen and phosphorus) contained in BKME. The response variables measured included the ash-free dry biomass (AFDM) and chlorophyll *a* of periphyton, the abundance and composition of benthic insects, and the biomass of abundant insect taxa (caddisflies, mayflies and stoneflies). Our experiments were carried out in spring and autumn because these seasons are times when nutrient enhancement is likely to increase autochthonous primary production as a result of low discharge, high effluent concentration and low turbidity.

The approach applied in the Fraser River was to examine biomass and community responses of periphyton exposed to different BKME concentrations (0, 1 and 3%), while simultaneously quantifying concentrations of common BKME contaminants in the periphyton tissue. Periphytic communities can be an important resource base in riverine food webs and often represent a major pathway by which energy and, perhaps, contaminants are transferred to higher trophic levels. To date, there is a lack of information on the concentration of specific contaminants in periphyton tissue exposed to BKME and the effects of these contaminants on the survival, composition and growth of periphyton communities.

Multiple Species Approach Using Artificial Streams

Studies employing artificial streams and measuring community-level endpoints are relatively rare, and usually involve large (i.e. > 50m long) outdoor, artificial streams (Swift *et al.* 1993). While community level studies of this type generally involve greater ecological complexity and a higher level of environmental realism, their use represents considerable logistic and financial problems that often limit the number of treatments and the level of replication. To circumvent these difficulties, we developed a transportable artificial stream facility (Culp and Podemski 1995, Podemski and Culp 1995) that can be used to assess the effects of potential stressors on a variety of community-level endpoints including community structure, community processes, and the growth and fecundity of selected community members. The system consists of 16 circular streams with a natural stream flora and fauna, to which water from the study stream is delivered and test substances (BKME or nutrient solutions) are added continuously to individual streams via peristaltic pumps and a network of insulated delivery lines. This system allows for the application of several replicated treatment levels, and the measurement of community-level endpoints under ambient physico-chemicals conditions.

The chief advantage of the multiple species approach using river-side artificial streams is the environmental realism achieved by incorporating study river water, natural substrata, and ambient light, temperature and water velocity. This approach improves accuracy, thereby producing results that can be more directly applied to field situations. The test community includes multiple trophic levels constructed from random samples from the study river, rather than an artificially constructed gnotobiota. As a consequence, measurements of community-level endpoints, such as taxonomic composition, respiration, production and decomposition, are possible. These community level measures integrate both the direct effects of stressors, and importantly, indirect effects that cannot be simulated in single species or simple food chain systems (e.g., competition-mediated shifts in community structure, biomagnification). As a result, the approach is ideally suited for the identification of potential indicator taxa.

Nutrient-Contaminant Effects on the Athabasca River

Our experiments and in-river observations provide strong evidence that the dominant effect of the fully-mixed BKME discharge (i.e., 1% dilution) to the upper Athabasca River was that of nutrient enrichment and stimulation of food web productivity. In autumn both the nutrient and BKME treatments stimulated primary production of the largely diatom algal community relative to the control treatment, which was representative of conditions upstream of the effluent discharge (Table 1). Experimental findings corresponded to in-river trends where periphyton biomass increased at sites downstream of the effluent relative to upstream reference sites.

The effluent-induced nutrient enrichment, and subsequent increase in periphyton biomass during autumn, elevated food availability for secondary producers inhabiting the upper Athabasca River. Abundances of total insects and several dominant taxa (stoneflies, mayflies and midges) increased in the nutrient and BKME treatments (Table 1), a trend that corresponds to the autumn in-river samples, when abundance increased downstream of the effluent discharge. Communities downstream of the BKME discharge exhibited a similar shift and were likewise dominated by mayflies, stoneflies and midges. Although these community shifts are clearly effluent-induced, the BKME-exposed communities included many taxa (mayflies and stoneflies) that are considered to be sensitive to pollution (Rosenberg and Resh 1993), suggesting that composition shifts were a response to enrichment rather than toxicity. Because the Athabasca River upstream of the BKME discharge is phosphorus-limited and oligotrophic, the present effluent-loads to the upper river provide levels of nutrient enrichment that increase benthic riverine productivity without the biotic changes associated with severe eutrophication.

If the BKME treatments had deleterious effects on the benthic biota, these would be expected to be manifested through reductions in insect growth and biodiversity, and through distinct changes in community composition where pollution-tolerant taxa become dominant. The fact that growth was similarly increased in the nutrient and BKME treatments indicates that nutrient enrichment effects where not masked by deleterious contaminant effects. BKME exposure also produced no measurable effect of contaminants at the community level. Biodiversity, as measured by family richness, was similar among all treatments and seasons. Shifts in community composition in the nutrient and BKME treatments were similar and largely reflected the abundance of taxa responding to increased periphytic resources. Lowell et al. (1995) and Dubé and Culp (1996) hypothesized that metabolic changes caused by the effluent could negatively affect successful reproduction through decreased fecundity or less viable eggs, but our studies produced no measurable sublethal toxicity effects at the population or community level. We caution that our experiments did not examine the bioaccumulation of lipophilic contaminants that may not affect insects, but could be concentrated by higher consumers including fish and birds.

Nutrient-Contaminant Effects on the Fraser River

Results of artificial stream experiments indicate that the most pronounced impact of BKME on the periphyton community was that of nutrient enrichment and the subsequent increase in primary production. There was little evidence of any direct contaminant effect on the periphyton community. Such an experiment was possible through the use of an artificial stream system in which exposure to BKME could be accurately and precisely controlled.

Total periphyton biomass as chlorophyll *a* and periphyton AFDM increased over the course of the experiment in all treatments (Table 2). Mean biomass levels at the experiment's end were 4-6 fold higher in the 1% and 3% streams than in 0% streams. Diatoms dominated all periphyton communities and differences among treatments were largely due to changes in relative abundances of different types of diatoms. Concentrations of BKME contaminants were generally low in periphyton tissue (Table 2). Dioxin and furan levels in periphyton were below detection levels and varied between 0.1 to 0.3 pg/g in all samples. Tissue concentrations of fatty acids (with the possible exception of myristic acid) did not vary significantly with BKME addition. Concentrations of total resin acids and total chlorinated phenolics did vary with treatment level but the differences were only apparent in a minority of individual compounds within each contaminant group and were largely restricted to mean differences between the 0% and 3% treatments. Concentrations of total PAHs also varied significantly across treatment levels but mean concentrations differed only between the 1% and 3% treatment levels. Despite a lack of regulatory guidelines regarding the direct toxic effects of BKME contaminants on periphyton, the results of this experiment indicate that contaminant concentrations are generally low and their toxic effects on periphyton probably minimal at the BKME dilutions tested. Nevertheless, the responses of periphytic algae in the Fraser River are similar to the Athabasca River experiments were nutrient enrichment appeared to be the major effect of BKME.

Strategy for Artificial Stream Application

The development of a unique, field-based artificial stream system provided the means by which a mechanistic understanding of the effects of BKME-related nutrient and contaminant stressors on the benthic biota of the upper Athabasca and Fraser Rivers could be obtained. Because artificial streams provided the ability to conduct a properly replicated experimental design with a high degree of environmental realism, we could quantitatively address questions that could not be examined using field observations alone. Causality could be assigned definitively in a field application where inferential hypothesis testing was very limited, such that, the nutrient enrichment and contaminant effects of BKME on the riverine biota could be unequivocally determined. Essentially, the use of artificial streams allowed the ecological effects of BKME on riverine benthos to be investigated at a more manageable scale than that of whole ecosystem manipulation (Kimball and Levin 1985). By applying a strategy that combined artificial stream results with quantitative field observation, we were also able to link this mechanistic understanding of stressor effects directly to *in situ* situations in large river ecosystems. Future applications of artificial streams to northern rivers could include the linkage of artificial stream experiments with water quality models in order to contribute directly to the development, parameterization, and testing of models for predicting ecosystem-level responses to nutrient and contaminant addition. They would also be valuable tools for assessing the potential for additional effluents to raise overall contaminant and nutrient concentrations to levels that could degrade the ecosystem. Artificial stream research is a promising technique for consideration in aquatic environmental effects monitoring programs for industrial effluents because cause and effect scenarios can be investigated, and ecological indicators for riverine biota developed under experimentally controlled dose-response regimes.

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Table 1. Mean (±SE) value of chlorophyll a (μg/cm^2), periphyton ash free dry mass (AFDM mg/cm^2), capnid stoneflies, chironomids, and total insects in the control, nutrient and 1% effluent treatments during the autumn 1993 experiment in the Athabasca River, Alberta, Canada.

	Treatments		
Response Variables	**Control**	**Nutrients**	**1% Effluent**
Periphyton Chlorophyll *a*	0.23 ±0.04	7.54±0.78	7.72±0.57
Periphyton AFDM	0.27±0.07	0.67±0.15	0.78±0.07
Capnid Stoneflies	35±14	81±13	75±7
Chironomids	66±14	572±287	325±79
Total Insects	446±74	1065±322	918±151

Table 2. Mean (±SE) value of chlorophyll a (μg/cm^2), periphyton ash free dry mass (AFDM mg/cm^2), total resin acids (ng/g), total fatty acids (ng/g), total chlorinated phenolics (ng/g), and total polycyclic aromatic hydrocarbons (PAHs ng/g) in the 0%, 1% and 3% effluent treatments during the autumn 1994 experiment in the Fraser River, British Columbia, Canada.

	Effluent Concentration		
Response Variable	**0%**	**1%**	**3%**
Chlorophyll *a*	4.40±0.63	16.69±3.77	14.89±3.76
Periphyton AFDM	2.17±0.15	6.23±0.40	5.19±0.76
Total Resin Acids	92.5±27.2	1229.4±91.7	5045.8±622.9
Total Fatty Acids	92348±12508	123370±6873	126841±13960
Total Chlorinated Phenolics	1.79±0.16	5.25±0.26	7.23±0.44
Total PAHs	20.13±1.90	17.08±0.70	26.59±1.54

Modelling the Interaction of Eutrophication and Hydrophobic Organic Contaminant Behaviour in Aquatic Systems

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Introduction

A variety of interactions may occur between the behaviour of hydrophobic organic contaminants (HOCs) in an aquatic systems and the latter's trophic status (e.g. Gunnarsson et al. 1995). The mass balance of organic carbon constitutes the link between these two environmental issues. The eutrophication status determines concentrations in water and sediment as well as the transport fluxes and mineralisation rates of organic carbon in the aquatic system. The dynamics of organic carbon in turn determine to a large extent the aquatic fate of HOCs and their uptake into the food chain. While several modes of interaction have been proposed, there is an incentive to get a more comprehensive and quantitative picture of the processes involved.

The approach described here is to take a well established model of HOC behaviour in aquatic systems and parameterise it for several typical HOCs in a generic lake. The input parameters of the model which are related to the dynamics of organic carbon are adjusted to reflect different trophic conditions of the lake. Namely, scenarios of eutrophic and oligotrophic conditions are defined, and the differences in simulated HOC behaviour evaluated. This approach, when refined and extended, could (i) initially provide insight into which processes are most likely to matter in the interaction of contaminant behaviour and eutrophication, (ii) eventually identify the direction and quantify the magnitude of changes in HOC behaviour induced by changes in trophic conditions, and (iii) ultimately predict the likely response of HOC behaviour upon changes of the eutrophic status of a specific aquatic system.

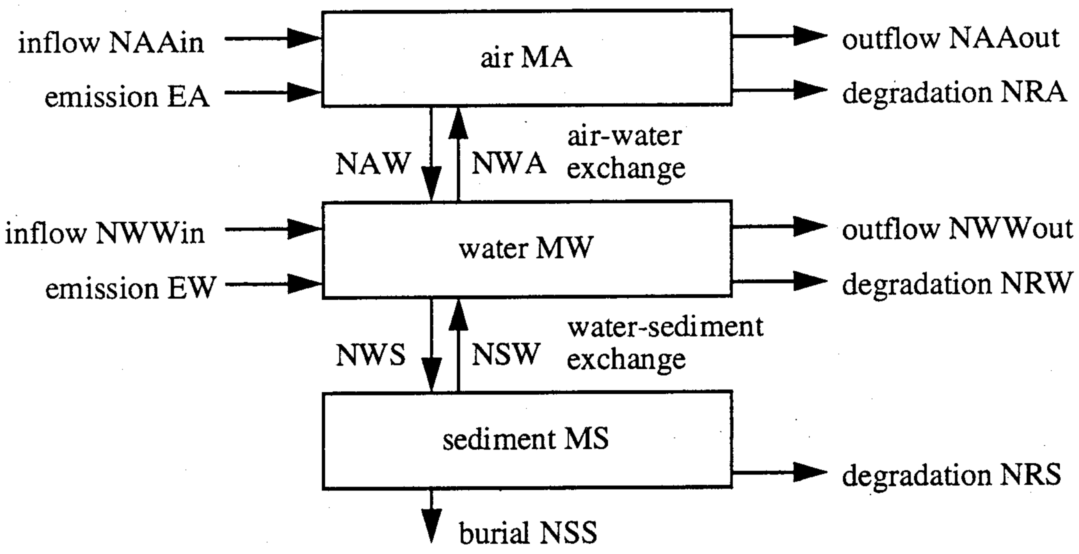
Model Description

The model used in the illustrative calculations is a substantially modified version of the QWASI model by Mackay et al. (1983). This fugacity-based compartmental mass balance model has been used repeatedly for describing the behaviour of various HOCs in lakes and other aquatic systems (e.g. Wania et al. 1996) and is believed to capture reasonably well the most relevant fate processes. The most important modifications from the original model are the:

- inclusion of the atmosphere above the lake as a compartment, the concentration of which is calculated rather than being a model input. This allows for the lake to have an influence on the concentration in the air above the lake, which may be of importance for large lakes and chemicals with large air-water exchange fluxes. The user has to input the background concentration in the air flowing into the lake area.
- description of the particle-associated transport of HOC on the basis of particulate organic carbon (POC) rather than total solids, and the derivation of the transport parameters for POC settling, resuspension and burial within the model.
- calculation of some of the transport parameters describing the atmosphere-water exchange from meteorological and chemical specific data instead of using generic values.

- programming the model in Stella II-format to facilitate the modelling of non-steady state scenarios with time-variant input parameters (a feature which is not used in the present calculations).

Very briefly, the model structure includes three well-mixed compartments, eleven transport and three transformation processes:



A mass balance is formulated over each of the three compartments:

$$\begin{aligned}
dMA/dt &= EA + NAAin + NWA - NAAout - NRA - NAW \\
dMW/dt &= EW + NWWin + NAW + NSW - NWWout - NRW - NWA - NWS \\
dMS/dt &= NWS - NSS - NRS - NSW
\end{aligned}$$

and each of these transport and degradation processes is described with mathematical expressions, which take into account environmental and chemical properties. For more detail on how these expressions look like and how they are derived see Mackay et al. (1983) and Wania et al. (1996).

Mass Balance of Particulate Organic Carbon

No effort has so far been undertaken to describe in detail the changes in the dynamic behaviour of POC that go along with eutrophication. These changes will be very dependent on the particular situation in a specific lake. Instead, it is assumed that in a eutrophic lake a general intensification of the turnover of POC occurs, with a respective increase in POC concentrations, production, transport and loss by burial and decomposition. Two scenarios for a eutrophic and a oligotrophic lake are defined which correspond to a doubling of both the POC cycling intensity and POC concentrations. The intensity of resuspension and mineralisation is the same in both scenarios.

Model parameters describing the dynamics of particulate organic carbon (POC)

carbon related input parameters	**high OC**	**low OC**	**ratio**
POC concentration in lake water g/m^3	0.5	0.25	**2.00**
POC concentration in inflowing water in g/m^3	1	0.5	**2.00**
POC mass fraction in surface sediment in g/g	0.08	0.04	**2.00**
intensity of POC degradation in water$^{(1)}$	0.8	0.8	**1.00**
resuspension intensity$^{(2)}$	0.7	0.7	**1.00**
intensity of POC degradation in sediment$^{(3)}$	0.7	0.7	**1.00**
biological productivity in gC/(m^2·a)	150	75	**2.00**

calculated POC fluxes in gC/(m²·a)	**high OC**	**low OC**	**ratio**
riverine inflow	10	5	**2.00**
outflow	5	2.5	**2.00**
water column mineralisation	128	64	**2.00**
sedimentation	90	45	**2.00**
resuspension	63	31.5	**2.00**
sediment mineralisation	18.9	9.4	**2.00**
sediment burial	8.1	4.1	**2.00**

(1)fraction of POC input to the water column mineralised in the water, (2)fraction of gross-deposited POC which is resuspended, (3)fraction of net-deposited POC mineralised in the surface sediment

A major limitation of the present model is that the partitioning of HOC to non-particulate organic carbon, often referred to as dissolved organic carbon (DOC) or colloidal material, is not taken into account.

Illustrative Model Calculations

Model calculation are performed for four HOCs with different physical-chemical characteristics. They are assumed to have similar degradation half-lifes.

Physical-chemical properties at 10 °C	**γ-HCH**	**HCB**	**DDT**	**PCBs**
molecular mass in g/mol	290.9	284.8	354.5	360.9
vapour pressure in Pa	0.0305	0.0226	$2.85 \cdot 10^{-6}$	$5.92 \cdot 10^{-5}$
Henry's law constant in Pa·m³/mol	0.134	17.6	0.633	16.2
log K_{OW}	3.8	5.5	6.2	7.0
degradation half-life in air in days	30	30	30	30
degradation half-life in water in years	1	1	1	1
degradation half-life in sediment in years	10	10	10	10

For all four chemicals the following input scenario is assumed to apply.

direct emission in g/day		*inflow concentrations*	
into air	100	in inflowing air in pg/m³	50
into water	10	in inflowing water in pg/L	100

Generic values are used for several additional environmental input parameters.

meteorological and atmospheric information		*lake properties*	
temperature	10 °C	lake area	10^{10} m²
wind speed	5 m/s	lake depth	20 m
precipitation rate	750 mm/a	water residence time	2 years
height of the atmosphere	2000 m	surface sediment depth	0.01 m
aerosol content	$2 \cdot 10^{-11}$ m³/m³	water content in surface sediment	0.85 m³/m³
dry particle deposition velocity	7.2 m/h	*transport parameters*	
scavenging ratio	200000	diffusive MTC water-sediment	0.0004 m/h

Steady-state is assumed to be established, i.e. dMA/dt = dMW/dt = dMS/dt = 0.

The four chemicals show a different chemical fate in the lake (for high OC conditions):

	γ-HCH	**HCB**	**DDT**	**PCBs**
relative media distribution in % under high OC conditions				
air	1.6	13.0	0.3	0.3
water	94.9	32.0	12.8	5.0
surface sediment	3.5	55.0	86.9	94.7
relative importance of loss processes from water in %				
outflow	27.4	4.2	10.4	4.8
degradation	38.0	5.9	14.4	6.6
volatilisation	24.3	83.9	27.4	30.5
sedimentation (including W-S diffusion)	10.2	6.0	47.8	58.1

relative importance of loss processes from sediment in %				
burial	0.6	6.9	8.4	8.8
degradation	1.4	16.7	20.5	21.5
resuspension (including S-W diffusion)	98.1	76.4	71.1	69.6

The relatively water soluble γ-HCH partitions mostly into the water column, is lost from the lake predominantly by outflow and degradation, and its transfer to the sediment is relatively minor. HCB is hydrophobic but fairly volatile, and thus tends to volatilise quickly from the lake. DDT and PCBs, highly hydrophobic and rather involatile, are efficiently transferred to the sediments while volatilisation is still a significant process. The general nature of this chemical behaviour is not changed by a two-fold reduction in the POC rates and concentrations.

	γ-HCH	**HCB**	**DDT**	**PCBs**
relative media distribution in % under low OC conditions				
air	1.6	17.8	0.5	0.5
water	96.5	42.7	19.8	6.3
surface sediment	1.9	39.5	79.7	93.2

The media distribution experiences a small shift from the sediments to the water column for all four chemicals, but the overall partitioning behaviour is not altered. However, this does not mean that there is no influence of the POC dynamics on the calculated chemical fate in the lake. A closer inspection reveals the changes that occur.

Z-values are chemical capacity value expressing the capability of a phase to hold or retain a chemical (see Mackay 1991 for detail). Z-values for water are slightly higher under eutrophic conditions, especially for very hydrophobic chemicals. Sediment Z-values increase markedly for all compounds as a result of higher POC levels in sediments. Correspondingly, fugacity, a measure for the escaping tendency of a chemical from a phase, is lower in both water and sediment under high OC conditions. However there seems to be no significant impact on the deviation from equilibrium between water and sediment, expressed by the fugacity ratio.

	Bulk Z-values in mol/(Pa·m^3)					
	water			***sediment***		
	high OC	**low OC**	**ratio**	**high OC**	**low OC**	**ratio**
γ-HCH	7.47	7.46	**1.00**	555	294	**1.89**
HCB	0.0605	0.0587	**1.03**	210	110	**1.91**
DDT	2.08	1.83	**1.14**	28600	15000	**1.91**
PCBs	0.188	0.125	**1.50**	7210	3780	**1.91**

	Fugacities in 10^{-10} Pa					
	water			***sediment***		
	high OC	**low OC**	**ratio**	**high OC**	**low OC**	**ratio**
γ-HCH	1.34	1.34	**1.00**	1.34	1.34	**1.00**
HCB	7.47	7.55	**0.99**	7.41	7.45	**0.99**
DDT	2.47	2.92	**0.85**	2.45	2.87	**0.85**
PCBs	10.5	13.5	**0.78**	10.4	13.2	**0.79**

	equilibrium status between water and sediment (FW/FS)		
	high OC	**low OC**	**ratio**
γ-HCH	1.00	1.00	**1.00**
HCB	1.01	1.01	**1.00**
DDT	1.01	1.02	**0.99**
PCBs	1.01	1.02	**0.99**

For the very hydrophobic HOCs truly dissolved concentrations in water as well as concentrations on suspended solids expressed on a carbon basis are higher under low POC conditions. Although levels in bulk sediment are lower under low POC conditions, sediment concentrations are higher when expressed on a carbon basis. The model thus affirms the "biomass dilution" hypothesis, which suggests that increased primary production may result in a dilution of contaminants (Gunnarsson et al. 1995).

	Bulk media concentration					
	water concentration in pg/L			*sediment concentration in µg/m³*		
	high OC	**low OC**	**ratio**	**high OC**	**low OC**	**ratio**
γ-HCH	290	291	**1.00**	21.6	11.4	**1.89**
HCB	12.9	12.6	**1.02**	44.3	23.3	**1.90**
DDT	182	190	**0.96**	2480	1520	**1.63**
PCBs	71.6	60.9	**1.18**	2720	1800	**1.51**

	Truly dissolved compound in the water column					
	truly dissolved fraction			*truly dissolved concentration in pg/L*		
	high OC	**low OC**	**ratio**	**high OC**	**low OC**	**ratio**
γ-HCH	1.00	1.00	**1.00**	290	291	**1.00**
HCB	0.94	0.97	**0.97**	12.1	12.2	**0.99**
DDT	0.76	0.86	**0.88**	138	163	**0.85**
PCBs	0.33	0.49	**0.67**	23.6	29.8	**0.79**

	Concentration on solids in ng/g POC					
	suspended solids			*sediment solids*		
	high OC	**low OC**	**ratio**	**high OC**	**low OC**	**ratio**
γ-HCH	n.a.	n.a.	**n.a.**	0.76	0.76	**1.00**
HCB	1.55	1.51	**1.03**	1.55	1.55	**1.00**
DDT	87.4	106.4	**0.82**	87.0	101.3	**0.86**
PCBs	95.9	124.2	**0.77**	95.4	120.0	**0.80**

As a result of the general shift from the suspended solids to the truly dissolved phase under low POC conditions, HOC volatilisation becomes more, sedimentation and sediment burial less important, i.e. there is a shift from downward to upward directed transport. The extent of HOC loss by outflow and degradation is relatively unaffected.

	Fluxes in mmol/day					
	volatilisation			*water to sediment transfer*		
	high OC	**low OC**	**ratio**	**high OC**	**low OC**	**ratio**
γ-HCH	242	243	**1.00**	102	99.1	**1.03**
HCB	245	248	**0.99**	17.6	11.0	**1.60**
DDT	372	440	**0.85**	648	406	**1.59**
PCBs	348	446	**0.78**	664	429	**1.55**
	outflow with water			*sediment burial*		
	high OC	**low OC**	**ratio**	**high OC**	**low OC**	**ratio**
γ-HCH	274	274	**1.00**	0.572	0.286	**2.00**
HCB	12.4	12.1	**1.02**	1.21	0.609	**1.99**
DDT	141	147	**0.96**	54.5	32.0	**1.70**
PCBs	54.4	46.2	**1.18**	58.7	37.2	**1.58**

These model results are in accordance with the "wash out" hypothesis which postulates that eutrophication intensifies the settling of particle bound HOCs, thus decreasing the amount in the water column, while accelerating the burial to deeper sediment layers (Gunnarsson et al. 1995). The increase in volatilisation is balanced by the decrease in sedimentation, the effective residence time in the water column thus remaining virtually unchanged. The chemical residence time in the overall lake environment is shorter under low OC conditions because loss from the atmosphere is more efficient than loss from the surface sediment.

	Average chemical residence times in days					
	in total system air-water-sediment			*in water column*		
	high OC	**low OC**	**ratio**	**high OC**	**low OC**	**ratio**
γ-HCH	26.6	26.2	**1.02**	200	201	**1.00**
HCB	3.5	2.6	**1.35**	30.8	30.9	**1.00**
DDT	124.1	83.2	**1.49**	75.8	89.5	**0.85**
PCBs	124.8	84.1	**1.48**	34.8	34.2	**1.02**

Non unexpectedly, the effect of changes in organic carbon dynamics on HOC behaviour is most pronounced for the most hydrophobic contaminants (log $K_{OW} > 6$).

Discussion and Conclusions

Lower POC conditions lead to higher concentrations both in the dissolved phase and in the solid phases, when the latter are expressed on a carbon basis. Biotic uptake of HOCs is thus likely to be enhanced, independent whether the uptake route is diffusion from the water or ingestion of organic matter in suspension and sediment. This is also indicated by the higher fugacity values in water and sediment at low POC conditions, assuming that lower trophic level organisms approach equilibrium conditions with their environment.

The presented approach seems capable of capturing some of the hypothesised interactions of eutrophication and HOC behaviour in aquatic systems, namely the "biomass dilution" and the "wash out" hypotheses. Other suggested elements of this interaction, namely the effects on food chain structure, growth rates, and benthic re-mobilisation, could potentially be included. This opens the prospect of describing quantitatively the impact of eutrophication on HOCs behaviour in lakes and other aquatic systems. Aspects requiring further attention in this undertaking are:

- the role of dissolved organic carbon on the partitioning and transport of HOCs,
- the extension of the model to include the uptake of HOCs into organisms and their transfer within the food chain, and
- kinetic aspects such as rapid biological growth rates or the seasonal nature of the carbon cycle, which necessitate the use of non-steady state modelling approaches.

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Eutrophication and persistent pollutants - effects on plankton and fish in lakes

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Introduction

Several fundamental lake processes may affect the turn-over and bioavailability of persistent pollutants when turning from a oligotrophic to a eutrophic state. The processes have their origin in the change of the ecology of the lake, but the effects can be expressed both as biotic and abiotic mechanisms. An example of an ecological change resulting in an influence on an abiotic process is volatilization of PCB. As a lake evolves from a nutrient-poor to a nutrient rich state, due of discharge of e.g. phosphorus in sewage, the amount of suspended organic matter in the water column increases. The increase is mainly a result of increased phytoplankton abundance, as phosphorus is the limiting nutrient in lakes. As phytoplankton abundance increase, a higher proportion of PCB in the dissolved state is partitioned to the particulate state. Since only PCB in the dissolved state is subjected to volatilization (Achman et al. 1993, Hornbuckle et al. 1994), the flow of PCB from water to air will decrease . However, an antagonistic process works on PCB transport directed from air to water, in which volatilized pollutants in the air are transferred across the surface microlayer and dissolve in the lake water. This process is probably affected by the abundance of phytoplankton in the water; as PCB is partitioned from the dissolved to the particulate phase a new equilibrium of PCB from air to water is established. The PCB transport from air will then increase. Both processes have been indicated in laboratory experiments (Larsson 1983), as well as the first one in indicative field experiments (Achman et al. 1993, Hornbuckle et al. 1994). However, they have never been quantified in the field and it is not known which one of the processes that dominate in a eutrophic lake. The reasoning will also be valid when comparing a gradient of lakes of differing trophic status.

Phytoplankton

The phytoplankton community is different in eutrophic and oligotrophic lakes. As an example, the community structure of lakes in southern Sweden can be described. The phytoplankton biomass of a eutrophic lakes during a year is dominated by blue-green algae such as *Planktothrix*, *Anabaena* and *Apanizomenon*. The blooms of these algal species are accentuated in the autumn but may continue during winter depending on species and ice formation. These species contain low amounts of lipids and, consequently, should contain low amounts of lipophilic, persistent pollutants on a fresh- or dry weight basis (Amotz-Ben et al. 1985, Shitrin and Chisholm 1981, Larsson et al., submitted). They are not subjected to a high grazing pressure from zooplankton, as zooplankton are selective feeders and reject blue-green algae. Consequently, a transfer of pollutants in a pelagic food chain from phytoplankton - zooplankton - fish does not include a link composed of blue-greens. On the other hand, cyprinid fishes like roach (*Rutilus rutilus*) forage directly on sedimented colonies of blue-green algae, when other food resources are scarse (Lessmark 1983). The phytoplankton community of oligotrophic lakes is more diverse, and is dominated by such algal groups as diatoms and green algae. These groups contain more lipids than blue-greens (Amotz-Ben et al. 1985, Shitrin and Chisholm 1981), and should thus contain higher concentrations of lipophilic pollutants on a fresh- or dry weight basis. They are readily consumed by zooplankton, and constitute a first link in the pollutant transfer in the food web. The dissimilarities in phytoplankton communities between eutrophic and oligotrophic lakes may lead to the observered effect of higher pollutant concentration in biota of nutrient-poor aquatic ecosystems.

Another variable of importance for the uptake of pollutants in phytoplankton is lipid quality. The composition of lipids differ for various phytoplankton species, and the quality of lipids is of importance for the uptake of lipophilic pollutants (Ewald and Larsson 1994). Triacylglycerols seem to be more efficient and have a higher bioconcentration factor for PCB than phospholipids. It is known that phytoplankton species as diatoms and green algae contain higher amounts of triacylglycerols than do blue-green algae(Amotz-Ben et al. 1985, Shitrin and Chisholm 1981), and this may lead to differences in pollutant uptake between the phytoplankton communities of nutrient-poor and nutrient-rich lakes.

Zooplankton

The dominating groups of zooplankton in lakes of northern Europe are cladocerans and copepods. These two groups differ in both in physiological and ecological character. Cladocerans, like *Daphnia magna*, are subjected to high predation pressure from planktivorus fish. It has been concluded that the "top-down" effects in lakes, i.e. the effect of fish on the trophic state of lakes, to a large extent is depending on the grazing by large cladocerans. The filtering effect of *D. magna* may lead to decreased abundance of phytoplankton in the lake, with higher secci-depth and a clearer water as a result. The effect is especially pronounced in the summer, as cladocerans have a short generation time and is short-lived at temperatures above 20 °C (a few weeks, Larsson 1989 and references therein), and respond fast to increased phytoplankton abundance compared to copepods. However, large cladocerans are susceptible to predation from plantivorus fish, such as cyprinids (roach and juvenile bream, *Abramis brahma*), that generally are abundant in eutrophic lakes and maintain a low abundance of these large cladocerans. Small cladocerans and copepods are not subjected to such high predation pressure and dominate eutrophic lakes where cyprinids are abundant. In oligotrophic lakes, the zooplankton community is more diverse, and the predation pressure not as high as in eutrophic lakes, and large cladocerans are more abundant.

The different zooplankton composition in eutrophic and oligotrophic lakes probably affect concentration of persistent pollutants. The shorter life-span of cladocerans compared to copepods (life-span of months up to a year) indicate that, if uptake of persistent pollutants is age-dependent as shown for fish, this will result in higher pollutant levels of the copepods. Additionally, the fat content of copepods is higher (Larsson et al., submitted) than in cladocerans which will add to this effect.

Copepods generally dominate the zooplankton community in winter at low water temperatures in both eutrophic and oligotrophic lakes, a phenomenon indicating that differences in zooplankton community structure and, possibly, pollutant levels will increase during this time.

Fish

We recently showed that the uptake of persistent pollutants in fish decreased in an increasing trophic gradient of lakes, as shown by the trophic stutus indicators total-phosphorus, chlorophyll a and secci-depth (Larsson et al. 1992). The fish species investigated was northern pike (*Esox lucius*), a mainly piscivorus predator. The reasons for decreasing concentrations of PCB or DDTs in pike as lakes turn more eutrophic may depend on several factors, including the limnology of the lakes and physiological and/or ecological variables of the fish affected by the trophic gradient.

The growth-rate of fish may influence on concentration of persistent pollutants. Assuming that the growth of a fish is directly related to food consumtion, and that concentration of pollutants in food is constant (or rather that the assimilation of pollutants is constant), no "growth dilution" of pollutants in the fish will occur. However, if the food conversion factor principally differ from the pollutant assimilation factor over the life-time of a fish, growth dilution can be a significant factor governing concentration of pollutants in fish. If the food-conversion factor not is related to the pollutant assimilation factor, both concentration of pollutants over a fish lifetime as well as concentration of pollutants between fishes of different habitat richness (food availability) will be affected. The food conversion factor is highest in the juvenile stages , as biomass may double in a time-scale of weeks or months. As the fish grow older, food conversion decreases and result in an instantaneous yearly growth rate of a few percent (Larsson et al. 1991). Consequently, if food conversion and pollutant assimilation is not coupled, concentration of pollutants increase fast when food conversion decrease. Comparing growth rate of fish in habitats of different food availability will lead to the same conclusion, fast growing fish will biodilute the pollutants. If then comparing eutrophic and oligotrophic aquatic ecosystems, it is by no means obvious that predatory fish have a higher growth rate in nutrient-rich lakes. Some species , as pike and *pikeperch (Stizostedion lucioperca*) generally have a higher growth rate in eutrophic lakes, while perch (*Perca fluviatilis*) do not.

Lake turn-over - internal processes

The degradation rate of organic matter produced in the phototrophic zone may affect the turn-over rate of persistent pollutants in the pelagial of lakes. Especially the production of lipids in phytoplankton, the further sedimentation and degradation of seston containing lipids and the final incorporation into the sediment seems to affect turn-over of the persistent pollutants. When the particles settle in the water column, the most mobile and energy-rich compounds are degraded first. Accordingly, the lipids degrade fast, probably as a result of microbial attacks. In an oligotrophic south-Swedish lake, lipid content decreased from the seston to the material found in sediment traps situated 5 m above the bottom , the same trend being evident in the eutrophic lake (Larsson et al. submitted). However, the persistent pollutants were not released in the same proportions during this loss of lipids from the particles, but instead were concentrated in the remaining fat. We suggest that the pollutants are released according to exponential kinetics, as lipids mineralize from the remains of the particle. This occurs either at or just above the sediment surface, where abundance of microbes increases (Wetzel 1983). The major part of the persistent pollutants then recycles back to the water column. Our results suggest recycling of persistent pollutants to be faster in oligotrophic than in eutrophic lakes, as shown by the more effective degradation of lipids in the settling particles and the higher turnover time. Also the morphometry of a lake should affect the process, since a longer settling time as present in deeper lakes, results in more effective degradation of settling particles (Wetzel 1983). Although it has been suggested that the transport of persistent pollutants in aquatic ecosystem is coupled with the organic carbon cycle (Mackay 1989), we found the coupling of lipids to be more significant.

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Empirical evidence for the importance of lake trophic status and food web in bioaccumulation in southern Ontario lakes.

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Introduction

In southern Ontario, the contamination of fish by hydrophobic organochlorines (OCs) and metals is a significant concern, and has resulted in a monitoring plan to advise the public on consumption. Even a cursory examination of these data illustrates that the pattern of contamination of fish in lakes by OCs does not match the distribution of industrial and agricultural activity that one might associate with sources. On a global scale, the distribution of limnetic contamination by OCs is driven by proximity to sources, atmospheric circulation patterns and physical chemistry.

The observed pattern in southern Ontario is of high contaminant levels in large piscivorous fish, especially salmonids, in the Great Lakes and in smaller oligotrophic to mesotrophic lakes. Contaminant levels in eutrophic lakes, and in more eutrophic areas of the Great Lakes, are generally lower.

The major source of OCs for most lakes in Ontario is believed to be the atmosphere. Additional sources probably account for the high levels in some of the Great Lakes, for example, Lake Ontario, and a few smaller lakes. However, in many lakes the relative abundance of diverse OC species is very similar, and this "fingerprint" reflects that the atmosphere is the common source (MacDonald and Metcalfe 1991; Taylor et al. 1991). DDT and its metabolites are the most abundant OCs, despite that their local use of these has been virtually eliminated for about 15 years. PCBs are also abundant, despite many years of restricted use. Minor differences in the relative abundance of OCs among lakes may reflect differences in physical chemistry and in bioaccumulation as determined by lake morphology, chemistry and biology.

The focus of this paper will be to review the empirical data on the pattern of OC contamination in these lakes with a view to evaluating the various possibilities as to how lake trophic status affects bioaccumulation.

How do eutrophication and bioaccumulation interact?

1) Biomass dilution

Eutrophic lakes may be protected from the high concentrations of OCs in biota because the hydrophobic contaminants they receive are diluted to a greater degree in a larger POC pool (Fig. 1). They do not have lower OC concentrations on a volumetric basis, but, if biomass is sampled rather than whole water, the observed concentrations are lower. Hence the observed pattern of low OC levels in eutrophic lakes.

Empirical evidence for this phenomenon exists at the zooplankton level (Taylor et al., 1991; Fig. 2) and has been recently confirmed independently (Patterson, 1996). The effect is strongest for the most hydrophobic compounds (Fig. 2).

The empirical relationship with total phosphorus is weaker ($r^2 = 0.13$), and it is not unlikely that the strong relationship with zooplankton biomass overestimates the importance of trophic status because zooplankton biomass among these lakes is strongly determined by presence and abundance of planktivores, especially fish but also *Mysis*

(Almond et al. 1996). In contrast, nutrient concentration in these lakes plays a relatively minor role in determining zooplankton biomass. The total phosphorus concentrations are low, about 4 to 15 $\mu g\ P \cdot L^{-1}$ in summer.

2) Effect of Dissolved Organic Carbon

Dissolved organic carbon (DOC) also binds with OCs, reducing their availability to organisms. As DOC is a large pool relative to POC in lakes, changes in DOC that might accompany changes in trophic status could profoundly influence bioaccumulation. Recent work by DeLucca et al. (1996) indicates PCB levels in zooplankton are negatively (although weakly) related to DOC. The negative effect of DOC is evident at values >5 $mg \cdot L^{-1}$.

3) Growth Dilution

Fast-growing autotrophic organisms such as phytoplankton gain contaminants by absorbtion from the water, but absorbed contaminants are diluted by the growth of the phytoplankton such that equilibrium concentrations may never be attained. The importance of this growth dilution should be related to the relative magnitudes of the uptake constant for contaminants and their exponential rate of population increase. The latter is relatively well known, so the rate constant for uptake of contaminants is of critical importance. It is not unlikely that surface properties and hence tendency for bioaccumulation varies among species.

The form of the relationship between algal growth rates and trophic status has undergone considerable debate in the oceanographic literature, but a dominant view has been of high mass-specific productivity in oligotrophic oceans. In southern Ontario, our data based on P-turnover has been quite opposite; growth rate, measured as turnover, increases with nutrient concentration (Hudson and Taylor, in preparation). Pending consensus of the magnitude of uptake constants for OCs, it appears that this could be a mechanism leading to reduced bioaccumulation of OCs at the base of the food chain in eutrophic lakes. However, measurements of OC partitioning in lakewater suggest that uptake by plankton sufficiently rapid (Richer and Peters 1993) that growth dilution may not be important.

A new angle on this idea comes from Patterson et al. (1996) who reported that among our lakes, lipid normalized PCB content of mysids is correlated with PO_4 turnover time; less nutrient limited systems have greater PCB/lipid.

For fish, bioenergetic models have indicated that growth dilution may be an important factor in bioaccumulation. However, our empirical data on lake trout indicate that fast-growing fish are more contaminated, possibly because growth and size is related to lipid content and attributes of the food chain.

4) Sedimentation and sediment-water interactions

Phosphorus loss rates in from the epilimnia of our lakes are on the order of 0.2 to 1.3% per day (Guy et al. 1995) and are correlated with particle-size distribution. A preliminary, casual look at our data support that the lakes with high mass-specific sedimentation have large zooplankton, efficient food webs, and lightly contaminated fish. Enclosure studies suggest that sedimentation rates should increase with nutrient loading, but are also very sensitive to food web structure.

To the extent that OCs in the sediment are exchangeable with the water column, nutrient loading (via increased particle particle concentration) should enhance return of contaminants, whereas decreased nutrient loading should decrease the mobility of sediment-bound OCs.

The net result is that lowest volumetric concentrations of OCs should occur in eutrophic lakes with low planktivory lakes and the highest volumetric concentrations should occur in oligotrophic lakes with high planktivory.

5) Atmospheric Exchange

OCs enter lakes via direct gas-liquid exchange with the atmosphere, and an emerging view is that this process is relatively important compared to precipitation and dry fallout. If this is the case, nutrient loading (via increased mass and surface area of particles, and increased DOC) should increase contaminant movement into the lakes. As for sediment exchange, increased nutrient loading may lead to increased volumetric concentrations (even if biomass-based concentrations are lower). We have recently collected data that will allow us to test this hypothesis, but the analysis is yet to be done.

4) Lipids and Food Web structure

As I indicated above, interpretation of the negative relationship between zooplankton biomass and OC contamination is complicated by the importance of planktivory in our lakes in determining zooplankton biomass. Similarly, food web effects on contamination of fish are obscured by a strong correlation between food web type and lipid content of fish (Rasmussen et al. 1990).

Bentzen et al. (accepted) have disentangled these factors using analysis of covariance. On accounting for the strong correlation between the PCB content of lake trout and lipid, it remains that presence of planktivores in the system increases the PCB content of lake trout (Fig. 4). Our explanation of this effect is that the presence of planktivores increases the length of the food chain and decreases its ecological efficiency, leading to greater biomagnification. The positive effect of lipids on bioaccumulation is thought to result from the decrease in OC depuration with increased lipids (Borgmann and Whittle 1991). They make the fish a better sink. These lipid and food web effects appear to be strong relative effect of growth dilution, which would predict the opposite effect.

Our group has examined also whether lipid content of lake trout reflects lipid content of lower trophic levels. Phytoplankton and zooplankton lipids are not correlated with each other, nor are either correlated with lipid content of lake trout. Apparently, the increased lipid content of lake trout in lakes with planktivores is because of more dependence on fish in their diet, and/or more food.

Summary and Management Implications

1) There are a number of mechanisms whereby changes in nutrient loading may change contaminant levels in lake biota, including biomass dilution, growth dilution, changes in atmospheric and/or sediment exchange, changes in storage lipid content of organisms, and changes in food web structure. The net effect of nutrient loading alone should be to increase contaminant concentrations in the water (mass · volume^{-1}), but decrease contaminant concentrations is biota (mass · mass $^{-1}$).

2) Empirical evidence from oligotrophic to mesotrophic lakes in southern Ontario supports these expectations, but also indicates that food web structure has a strong impact as does lipid content, at least in fish. Food web structure is not independent of trophic status.

3) Decreases in trophic status through biomanipulation will have an opposite impact on bioaccumulation compared to decreases in trophic status through nutrient reductions.

Where bioaccumulation of OCs is an issue as well as eutrophication, both approaches to eutrophication management should be considered.

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The Biomass Dilution Effect

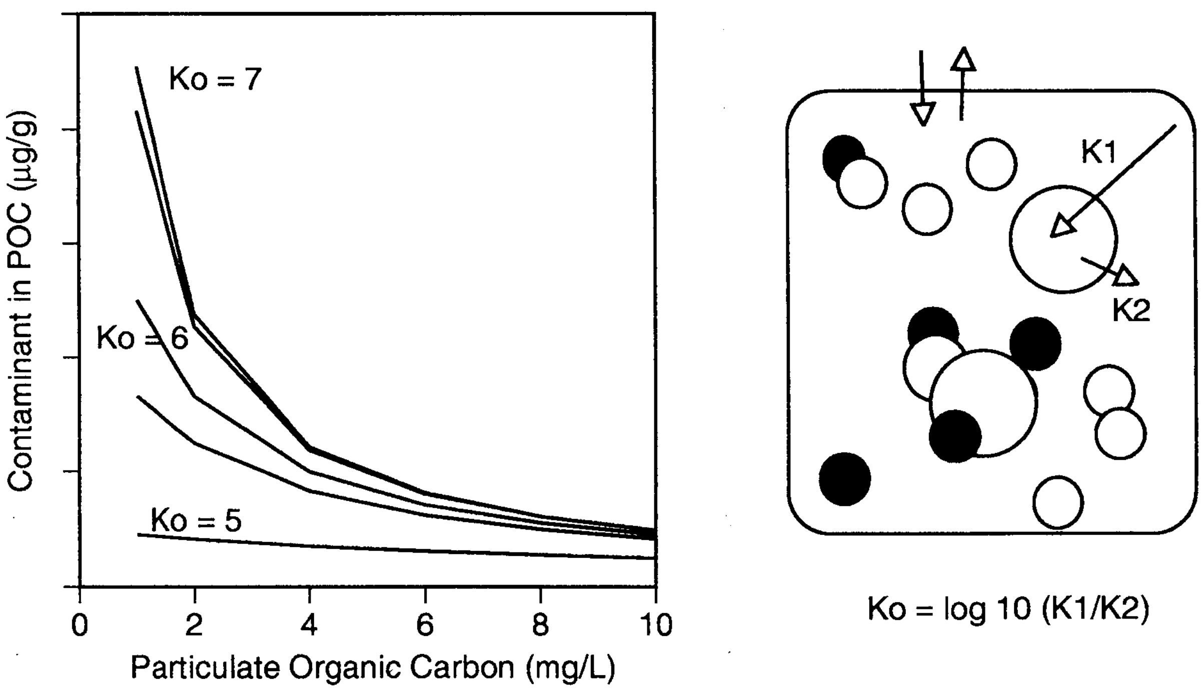

Fig. 1. A simple 1-CFOK model of biomass dilution predicts that organochlorine contamination of particulate organic carbon (POC) will decrease with POC concentration for sufficiently hydrophobic compounds. Exchange with other compartments, such as the atmosphere or the sediment, might weaken these predictions.

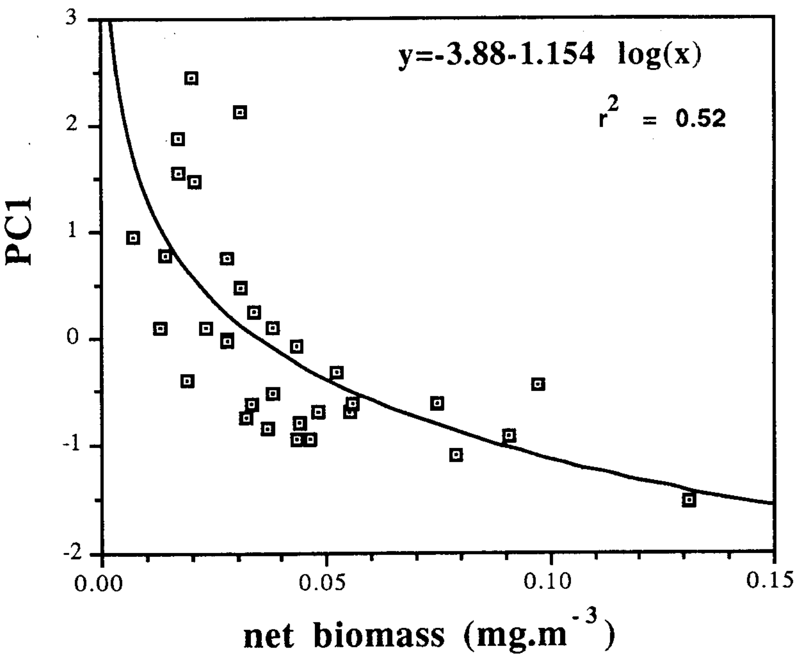

Fig. 2. Organochlorine contamination of zooplankton and zooplankton biomass are negatively correlated amnong lakes.

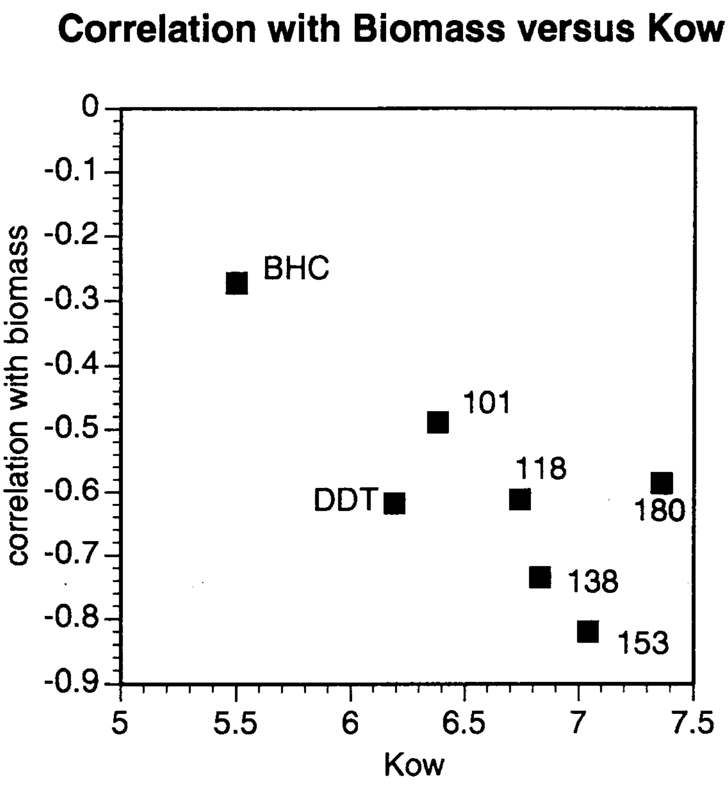

Fig. 3. The negative correlation between organochlorine contamination of zooplankton and zooplankton biomass is strongest for the most hydrophobic organochlorines.

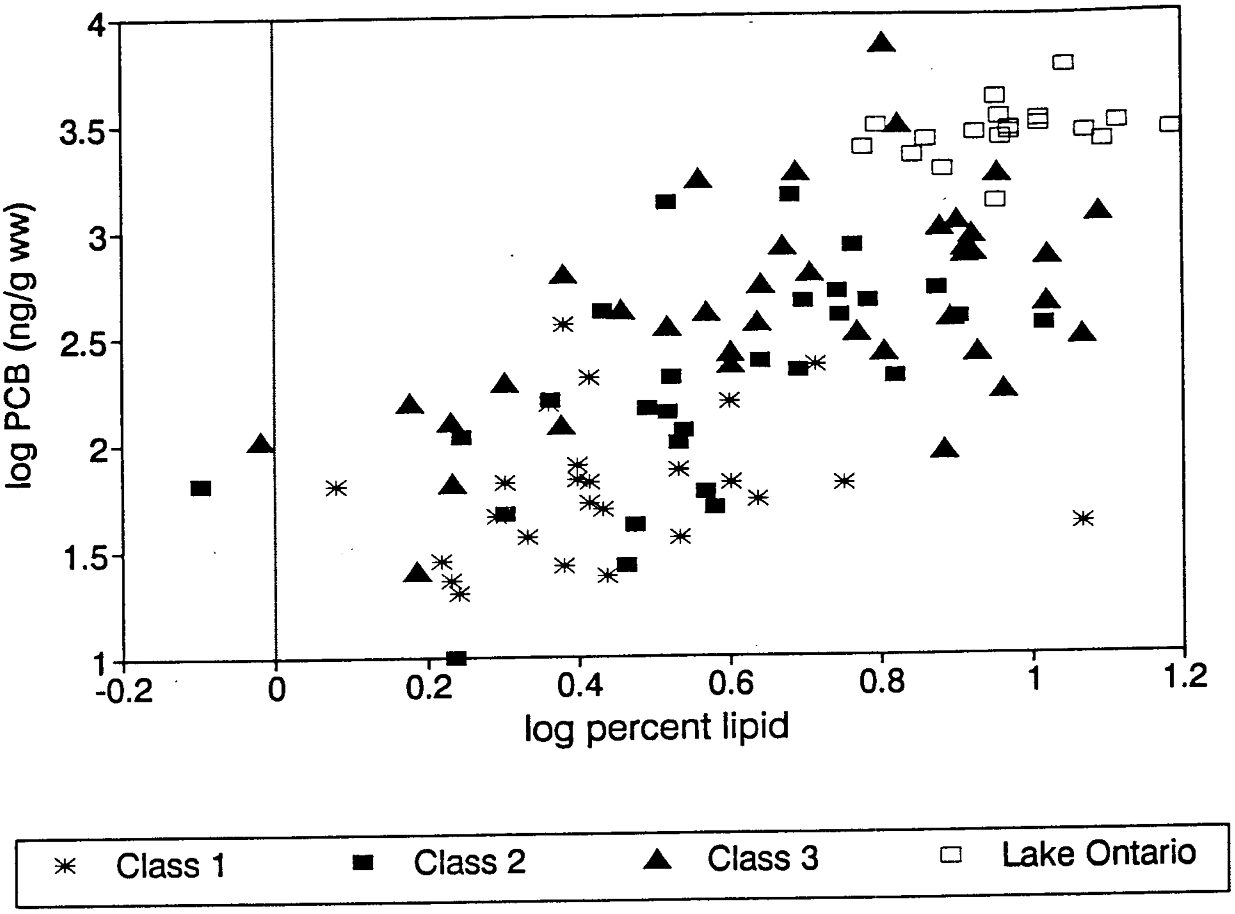

Fig. 4. Lakes with fatter fish have more contaminated fish, but there are significant differences in intercept for the lipid effect depending on food web type. Class 1 lakes have no visual planktivores, Class 2 lakes have planktivorous fish, usually lake herring, and Class 3 lakes have planktivorous fish and *Mysis relitca.*

Conclusive Discussion

The Woudschoten workshop was initiated by the National Institute of Public Health and the Environment in response to a request of the Netherlands Ministry of Housing, Spatial Planning and the Environment. Questions posed to the various invited participants were:

- What are the methods and/or models present with which interactions between toxic substances and nutrients can be evaluated?
- How quantitatively can we evaluate this interaction?
- To what extent can we expect problems with toxic substances during the process of recovery from eutrophication?

The most important question for policy-makers in the Netherlands is: What is the best action a manager can take to obtain a clear ecosystem and not a "green soup", as happens in a lot of Dutch shallow waters like ditches and lakes? These bodies of water show two distinct states: firstly, more-or-less mesotrophic, with clear water, and diatoms and green algae, and secondly, after N and P enrichment , eutrophic, with turbid water and various algae (cyanobacteria). How will measures with respect to nutrients and contaminants interact in these systems?

The main question in the Baltic Sea is: What will happen if nutrients are reduced in the future? The situation with respect to contaminants is far better than 20 to 25 years ago: concentrations of toxicants in biota having dropped considerably. Will a reduction in nutrients undo these improvements?

The following set of questions served to structure the discussion. Since the questions were devised before the workshop, possible answers were in some cases given during the workshop but still reported here. The questions were subdivided into three subgroups: 1. bioaccumulation, 2. toxicity for zooplankton and other grazers and 3. management measures.

1. Bioaccumulation

Questions:

- Will different trophic states give rise to different rates of bioaccumulation in the foodweb (less grazed blue-green algae *vs.* more "edible" species)?
- Will this give rise to problems during the process of recovery from eutrophication?

It was clear that in answering these questions, a distinction had to be made between different types of toxicants. A main problem in the Netherlands, for instance, is the extensive use of pesticides. Most pesticides have a low log K_{ow} and thus show little bioaccumulation, but can be very toxic to certain organisms like zooplankton. This is different from the Swedish or Great Lakes situation. In the case of non-persistent pesticides, there will be less interaction with nutrients and one can proceed with reducing both emissions. For PAH, found in high concentrations in Dutch waters as well, one can draw more-or-less the same conclusion. Locally, there might be high concentrations, but PAH do not bioaccumulate or biomagnify to a large extent. However, in an indirect way, pesticides may show interaction with nutrients. Pesticides can be very toxic to certain species or functional groups. They may therefore alter the food web structure which may affect the way trophic status influences the levels of hydrophobic organic compounds or heavy metals (also in biota). A change in food web structure wil also have its effect on the partitioning of the pesticides themselves. To what extent the above occurs is not clear, for this has not yet been investigated.

Although it might be better to look at effects of these compounds on the community level, bioaccumulation or biomagnification will be seen when PCB or comparable hydrophobic organic compounds are considered. Here, a more direct interaction with nutrients will occur than in case of pesticides. Various mechanisms influence the way nutrient concentrations will affect the fate and effects of contaminants and vice versa, viz. through changes in partitioning behaviour (organic material and lipids), algal cell density ("particle concentration effect"), biomass and growth dilution, transformation, sedimentation, atmospheric exchange, lipid content of organisms and food web structure. Overall eutrophication will probably lead to a decreased bioavailability and less bioaccumulation and biomagnification, although an increased trapping capacity of the water with increased organic carbon concentration may cause an increase in total contaminant concentration on a volumetric basis. This will apply to heavy metals as well, which are still present in both Dutch waters and in the U.S.A and Canada, where mercury is becoming a serious problem.

In certain cases changing the trophic status from eutrophic to mesotrophic or even oligotrophic, one can expect higher levels of toxicants in biota. It will depend not only on concentrations of nutrients and toxicants but also on the ecosystem structure. Whether this will lead to changes within the ecosystem has to be considered in each specific case. Each situation should be analysed on organic material, lipids, food web structure, etc. However, it may be possible to generate a basic set of rules for the Dutch situation based upon relationships found, enabling an evaluation of possible effects of reducing either nutrients or contaminants or both.

2. Toxicity for zooplankton or other grazers

Questions:

- Zooplankton or other grazers can be affected by toxic substances in different ways (directly or indirectly via food uptake). Is this the same with different trophic states?

A distinction between mussels, on the one hand, and zooplankton, chironomids and worms, on the other, was suggested. Mussels and comparable grazers select material before digesting what they have filtered, thus creating pseudofaeces. Therefore mussels have to filter large quantities of water to get enough food. Thus, a correlation might be found between the concentration of a chemical in the water phase and the concentration in the mussel. Zooplankton, chironomids and worms, unlike mussels, digest all the material they have filtered. This way particle-bound toxicants become more available and the route through the food chain increases in importance. The exposure of these organisms may be underestimated regarding only the dissolved fraction.

In general, grazers have to filter less in the eutrophic state because of the higher food concentration. The toxicant concentration adsorbed onto organic material (including phytoplankton) on a mass basis is decreased in eutrophic situations. Although it is assumed that the filtering will not decrease linearly with increased food availability because of less efficient grazing, in eutrophic situations the bioaccumulation of toxic substances will be less than in mesotrophic or oligotrophic situations. A change in trophic state may also induce a change in zooplankton composition which may lead to different contaminant concentrations in zooplankton. It is not clear to what extent this changes the food web structure and if this will affect the contaminant levels in other organisms.

3. Management measures

Questions:

- In the Netherlands both toxicants and nutrients are attacked simultaneously in applying measures, reducing their emissions. Is this the right way of working?
- What is the proper order of importance in the working method? Priority to toxicants? Priority to nutrients? Or both?
- Does it make sense to abuse a eutrophic system in reducing the effects of toxic substances?

The Baltic showed high levels of contaminants in the seventies, but reduction of these contaminants has prevailed. While eutrophication still increased, there has been a significant improvement in the concentrations of toxic substances. However, now, concern about algal blooms is growing and nutrient reduction has become more important, even though there is anxiety about possible relapse, leading to the situation of the seventies, with higher contaminant concentrations. In the Netherlands both toxicants and nutrients have been reduced over the past 15 years. Still, chlorophyll-*a* levels have remained high in most Dutch waters and the decrease in chlorophyll-a is less than might be expected based on the reduction of N and P. This might be due to an increased availability of toxicants and toxic effects on grazers. In certain Dutch waters the effects of eutrophication might further decrease when the toxicant input is reduced. Overall, there may be two mechanisms with which it is possible to manage effects on ecosystems. Which mechanism is most promising depends on the type of toxicant, as previously explained, as well as the trophic state of the ecosystem.

In the case of bioaccumulating substances with a log K_{ow} of 6 and higher, for instance, bioavailability will increase with decreasing eutrophication. In this conflicting situation research is needed on the kind of ecosystem preferred to the one at present. Information on the nutrient status and the properties of the contaminants is also necessary to analyse what can be expected when the loadings are reduced. If one is able to classify what kind of system is aimed at after nutrient-reducing measures, it may be possible to estimate DOC concentrations in this system. In this way one may be able to calculate the effects of the present toxicant concentrations and even necessary contaminant reductions to avoid effects on the food chain. However, in most cases relationships will not be as linear as assumed with this approach. Complex interactions and feedback mechanisms will make it more difficult to estimate the effect of nutrient state on the DOC concentration and hence on the bioavailibility of contaminants. In the described conflicting circumstances it will be necessary to look at the case-by-case situation. However, as stated above, it may be possible to generate a basic set of rules for the Dutch situation based upon relationships found, enabling an evaluation of possible effects of reducing either nutrients or contaminants or both.

Major conclusions & recommendations

- Reducing eutrophication will increase the importance of interactions between nutrients and toxicants.
- Interaction is particularly important with persistent hydrophobic compounds and heavy metals.
- Despite the fact that eutrophic systems will act as a sink for pollutants, it is not recommended to keep them eutrophic.
- Priority of nutrients over contaminants in reduction measures are irrelevant; both should be reduced vigorously.

- Due to complex interactions and feedback mechanisms it will be difficult to estimate the effect of nutrient state on bioavailability, bioaccumulation and toxicity of contaminants. Although a case-by-case evaluation is best, it may be possible to generate a basic set of rules for some typical Dutch situations based upon relationships found. This may enable an evaluation of possible effects of reducing either nutrients or contaminants or both.

Research questions remaining

It will be clear from the previous discussion that in specific cases detailed research is needed to estimate the interactive effect of nutrients and toxicants on the various levels of the ecosystem. However, one other topic was raised at this workshop. Even though most models assume a constant incoming flux of pollutants to the water from the air, independent of the organic carbon concentration in the water phase, some recent research has brought forward that the trapping capacity of water may rise with increasing organic carbon concentration. In the Experimental Lakes Area, where the lakes were completely atmospherically driven, it was found that in one experimentally fertilised lake, the PCB concentration in particles was lower than in a comparable, but oligotrophic, lake, while the dissolved concentrations were similar. However, the total volumetric concentration of the contaminants was higher in the eutrophic situation. Further research on this particular subject is needed.