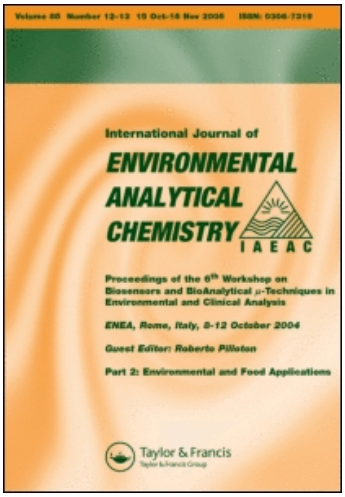

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Understanding Variations in Pollution Levels of Marine Biota: The Particle Concentration Effect

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UNDERSTANDING VARIATIONS IN POLLUTION LEVELS OF MARINE BIOTA: THE PARTICLE CONCENTRATION EFFECT

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Important seasonal variations in contamination levels of marine biota by lipophile organic compounds are noted when overviewing pollution data, even when data are normalized on lipid content. We therefore tried to understand part of the observed variations in contamination levels between watermasses (different geographic areas or seasons) by studying lipophile pollutant bio-concentration at the origin of the food chain.

The uptake kinetics and bioconcentration of ^{14}C-DDT, by five species of marine phytoplankton were investigated in laboratory experiments. An inverse relationship, representative for all species studied, was noted between the phytoplankton bioconcentration factor and the phytoplankton biomass (both normalized on organic carbon). No differences in bioconcentration factors among different phytoplankton species, with different cell sizes and biochemical characteristics, were noted, when data were standardized on organic carbon content. The importance of the Particle Concentration Effect (PCE) on the bioconcentration factor of micro-organic pollutants is, in this study, further illustrated with data on pollution of North Sea field samples. It is shown that within a specific range of organic matter, normalization of pollution data on particulate or phytoplankton biomass will account for part of the geographic and seasonal differences in organochlorine contamination levels noted for marine watermasses.

KEY WORDS: Bioconcentration, organochlorine residues, DDT, phytoplankton, biomass, particulate concentration effect.

INTRODUCTION

The fate of organic pollutants in aquatic environments has been a major study subject in environmental science. Field and experimental setups concerned with uptake, distribution and elimination of organic micro-pollutants by biota have led to the concepts of bioaccumulation, biomagnification (through food intake), and bioconcentration (through water). During studies concerned with mammal toxicity and pharmacokinetic compartmental models[1,2], it was observed that the distribution of many xenobiotic organic compounds among different biotic phases (bloodplasma, bloodcells, intra- and interstitial fluids, tissue cells, urine, faeces. . . .) is dominated by passive diffusion processes, regulated by the physiochemical interactions between the compounds studied and the body constituents. In these models, the central blood compartment acts as the medium, allowing equilibrium

distributions among the different body compartments. Due to partitioning processes, biomagnification in terrestrial environments is most pronounced for stable lipophile compounds such as organochlorine pesticides. At equilibrium state, a biomagnification factor (concentration animal/concentration food) exists depending on the physicochemical characteristics of the compounds.

This concept of physicochemical partition and pharmacokinetic modelling has, for aquatic environments (freshwater and marine), been extended from the level of the organism toward the level of the ecosystem. An equilibrium partitioning between the organisms living in an aquatic environment and its surrounding water was noted for a wide range of organic compounds: bioconcentration factors, described as the ratio of the compound concentration in the organism (fish) and its concentration in the water, were derived. Through the body and cell walls and through the gill interfaces of larger organisms, aquatic organisms can reach a pseudo-equilibrium state with their environment. It must, of course, be realized that bioconcentration is limited to particles, cells and organisms having intensive contact or interaction with the watermass (e.g. through the breathing system (gills). No extrapolation towards sea mammals or birds can be done. Already in 1980, a general relationship between the bioconcentration factors of the compounds in fish and the partitioning coefficient octanol-water (K_{ow}) was established, considering 84 different organic micropollutants[3]. Similar relationships ($\log K_b = a \log K_{ow} - b$) were described by other scientists[4,5] and lead to the so called lipophilicity approach. The lipophilicity relationship has been further refined with the inclusion of steric hindrance coefficients[6]. Models have been developed predicting the fate of different organic pollutants among different compartments, including air, water, soil, sediments and biota. The fugacity models of Mackay[7], pharmacokinetic fish accumulation models[8] and the study of Quantitative Structure Activity Relationships (QSARs)[9] have really opened new perspectives in environmental science.

The models have quite some predictive comparative value, but could not yet adequately predict natural environmental pollutant levels, not even for the most conservative and well known organic pollutants (the organochlorine pesticides and PCBs), even when data are standardized towards the lipid content. Important variabilities are still noted between sexes, among species and seasons. These variabilities have been related to analytical limitations (lipid content determined gravimetrically[10]), biologically regulated uptake and elimination processes and environmental variabilities.

One must realize that in natural environments, no steady state conditions exist. The fate of the pollutants are constantly influenced by environmental factors (watercurrents, temperature, salinity, pH . . .) and ecological factors such as biomasses. It is evident that these factors are reflected in the distribution of the pollutants among the different abiotic and biotic compartments. During field studies, important differences in bioconcentration factors of hydrophobic pollutants between different regions and seasons were observed. Increased contamination levels in biota (not related to pollutant inputs) and increased bioconcentration in winter compared to summer were sometimes observed[11,12,13].

Similar observations were made in laboratory experiments[14,15]. The importance of the particle concentration on sorption and partitioning of organic compounds is mathematically described in literature under different forms:

A particle dependent adsorption is described in the Freundlich adsorption isotherm

$$Cp = K_{ads} \cdot C_w^{1/n} \cdot$$

when: C_p = concentration of the pollutant in the particles, K_{ads}= adsorption coefficient; C_w= concentration of the pollutant in the water and n= Freundlich adsorption constant.

Similar particle density dependent sorptions were described in Di Toro[16] as:

$$\text{Fraction sorbed} = \frac{K_{ads} \cdot S}{1 + K_{ads} \cdot S}$$

with: S = sorbent fraction

This latter equation is very similar to the Nernst law of partitioning described as:

$$P = \frac{a \cdot D}{1 + a \cdot D}$$

with:
P = fraction in nonpolar phase
a = relative volume of nonpolar phase compared to polar phase
D = partition coefficient.

These relations illustrate the nonlinearity of the adsorption/partitioning phenomenon and therefore suggest that from a certain amount of apolar phase or particle density some saturation takes place. The importance of this "saturation" depends on the adsorbed compounds and partitioning coefficients, the compounds watersolubility and the particle densities.

Di Toro[16] and Di Toro *et al.*[17] translated this observation into a particulate interaction model (PIM) and hypothised that a particle concentration effect exists due to additional desorption processes induced by particle-particle interactions. They described a reversible component partition coefficient:

$$kp^* = \frac{\mu g / kg \text{ dry weight}}{\mu g / L}$$

$$kp^* = \frac{f_{oc} \cdot K_{oc}}{1 + m \cdot f_{oc} \cdot K_{oc} / V_x}$$

with:
f_{oc} = particulate organic carbon weight per dry weight (kg OC/kg DW)
K_{oc} = organic carbon partition coefficient of the pollutant (L/kg OC)
m = particle concentration in suspension (kg/L)
v_x = an imperical constant = 1.4

The particle concentration effect has however often been classified as an artefact and different reasons have been suggested: an apparent increased water contamination level induced by a third sorbing phase or by complexing components, being part of the particulates

but measured as part of the dissolved concentration[18]. This apparent increased pollutants' concentration in water, leading to an apparent decrease in bioconcentration factor could be more important in summer compared to winter when plankton (producing exudation products) and bacterial activities are high. Particles not separated from the dissolved fraction and dissolved organic matter present in the water phase do most probably play a role in the existing discrepancies among observed bioconcentration factors. The importance of the "truly" dissolved organic matter for the bioavailability of the organic pollutants is another aspect of scientific interest[19]. Particle aggregation has also been suggested as a possible reason for the observed particle concentration effect[16].

It was now aimed to investigate this PCE for a well known hydrophobic pollutant (DDT), under well defined laboratory conditions (excluding possible artefacts, especially concerning the dissolved contamination levels in the water), using different phytoplankton species (with different biochemical characteristics and cell sizes), different phytoplankton biomasses and to compare the observation with field data from the North Sea.

MATERIALS AND METHODS

Materials used

Five species of marine phytoplankton were obtained from different Belgium laboratories and cultured under artificial daylight, at 20°C, using aseptic conditions. The species used belong to different classes of phytoplankton: *Tetraselmis sp.* (class Prasinophyceae), *Dunaliella tetriolectica* (Chlorophycea); *Chlorella sp.* (Chlorophiceae); *Chaetoceros sp.* (Bacillariophycea); *Isochrysis sp.* (Prynesiophycea).

A ^{14}C-DDT in hexane solution (29.7 mCi/mmol) was obtained from the Radiochemical Center Amersham, England.

Beckman Readysafe liquid scintillation cocktail was used as scintillation liquid in the experiments.

All samples were analyzed in a Beckman LS 7500 scintillation counter. All data were expressed in disintegration parts per minute (dpm).

Contamination of the water

In most experiments dealing with accumulation of highly hydrophobic contaminants, the contaminants are dissolved in the water through an organic solvent (often aceton)[20,14,21]. The influence of aceton on bioaccumulation of hydrophobic contaminants was however described by Mac and Seeylye[22]. The ^{14}C DDT solution was therefore dropped on a glass microfibre and kept in a vapor chamber for 12 hours to evaporate the hexane. After evaporation, saline water (32–35%) was added to the flask and the solution kept for 24 hours. This pre-contaminated seawater was then transferred to the experimental flasks and the phytoplankton cultures were added. The thus obtained DDT contamination levels in the pre-contaminated seawater ranged between 0.015 and 0.150 µg/l.

Separation of algae and water

A pre-test was done to investigate the extend of adsorption of DDT on the materials used (filters, filtration sets, centrifugation tubes) during separation of the contaminated phytoplankton cultures from the contaminated water (3 hours incubation with pre-contaminated water). Two methods (filtration of 10 ml sample on Whatman glass microfibre filters and centrifugation of 10 ml sample at 3000 rpm for 15 minutes) were used to separate the phytoplankton cells from the water. The radioactivity (dpm counted inscintillation counter) in water and cells were measured respectively in filters, filtrate, supernatant and cells after addition of 10ml scintillation liquid to every subsample. No difference in phytoplankton contamination nor in reproducibilities between the two methods was observed. The filtration method was therefore used for all further experiments. For each experiment, blank contamination of all glassware and filtration set was controlled.

To evaluate the amount of radioactivity adsorbed in the filters from the solution (not associated to the phytoplankton cells), different volumes (5, 10 and 20 mls) of pre-contaminated DDT solution (without culture) were filtered on Whatman Glassfiber filters and the radioactivities measured in the filters and filtrates. A constant part (due to a specific K_{ads}) of the radioactivity was retained by the filters. During the experiments with contaminated cultures, the amount of radioactivity adsorbed on the filter paper from the solution was therefore each time deducted from the additive curves of 5, 10 and 20 mls contaminated culture. This allowed us to obtain the real amount of radioactivity incorporated in the phytoplankton cells.

To have an estimation of the influence of the dissolved or/and colloid organic matter in solution, possibly increasing the apparent water associated pollutant fraction, part of the non-contaminated *Dunaliella tetriolectica* culture was centrifuged (3000 rpm for 30 minutes), the supernatant (containing dissolved and colloid organic matter) discarded and the phytoplankton cells reinoculated in saline water of the same salinity as the original culture. This culture was then used in a contamination experiment (3 hours incubation). The results were compared with data obtained from the normal procedure (no pre-centrifugation of the culture), using the same experimental setup (volume of phytoplankton culture . . .). The radioactivity measured in the filtered water from both sets of data were comparable indicating that, during this experiment (with growing cultures) the dissolved and colloid organic matter does not play an important role in the contamination level of the water compartment.

Incubation time

The uptake kinetic of DDT by phytoplankton was very rapid. An equilibrium between the phytoplankton cells and the surrounding water was reached within 10 minutes. No further uptake by phytoplankton was observed up till 24 hours. Similar fast uptake rates of DDT in phytoplankton were observed before[20,14]. A 3 hours incubation time was therefore used as standard procedures.

Recovery

The adsorption of DDT on the walls of the experimental flasks was calculated for every experiment. 30 to 50% of the total DDT input was adsorbed on the flask walls. Similar adsorptions were observed in other experiments with highly hydrophobic contaminants.

Biological characteristics of the cultures

For each experiment, 2 ml of algae culture was taken for microscopic counting and sizing of the cells.

The particulate organic carbon content was measured for every culture prior to contamination. 20 ml of algae solution was filtered on glass microfibre filters and the particulate organic carbon measured in a Carbon analyser[23].

Normalization of DDT contaminations in phytoplankton

Due to the hydrophobic character of DDT, the DDT concentrations in phytoplankton were normalized for the organic carbon content of the cultures.

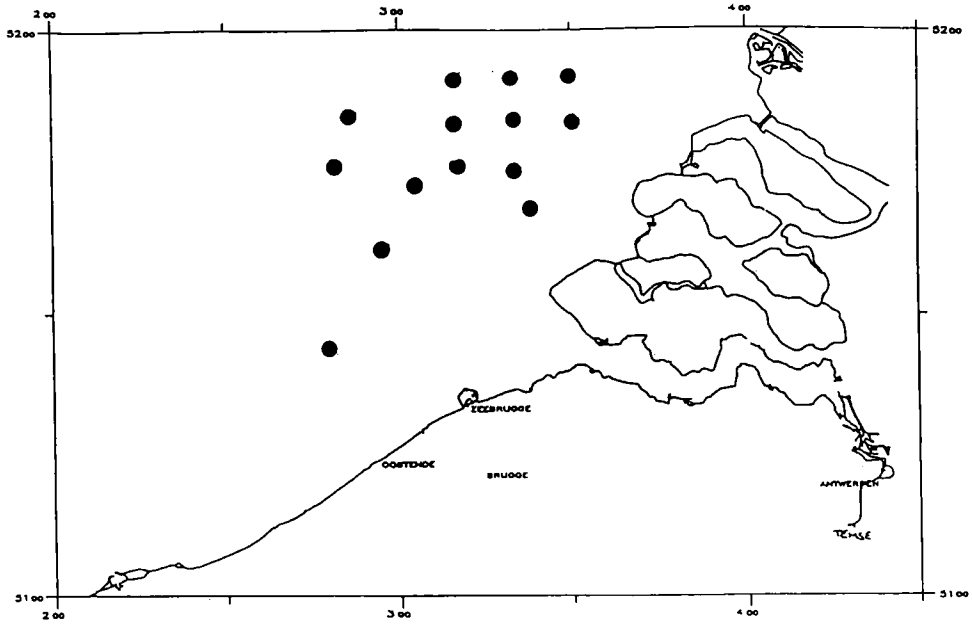

Figure 1 Sampling stations of suspended particulate matter on the Belgium Continental shelf of the North Sea.

Extrapolation towards natural ecosystems

^{14}C-DDT pre-contaminated water was added to water samples collected at different stations on the Belgium continental shelf of the North Sea (Figure 1) between 17 and 18 May 1993. All samples were taken on board of the research vessel "Belgica" using Niskin Bottles. The incubations (3 hours incubation in pre-contaminated water (1/1)), filtrations and addition of scintillation liquid were done on board of the R.V. "Belgica". The measurements of the radioactivity of the particulate matter and the filtered water were done after transportation of the samples to the laboratory.

250 -600 ml sample was filtered and the filters frozen on board of the R.V. "Belgica" to obtain data on particulate organic carbon and chlorophyll (in triplicate). Particulate organic carbon was measured in a carbon analyzer Chlorophyll a was measured by HPLC as described in [23].

RESULTS AND DISCUSSION

DDT bioconcentration factors in different phytoplankton species

During the ^{14}C-DDT bioconcentration experiment, different species of marine phytoplankton (*Tetraselmis sp.; Dunaliella tetriolectica; Chlorella sp.; Chaetoceros sp.; Isochrysis sp.*) were used in cell concentrations varying between 356000 to 1088600 cells/ml (Table 1). The experimental DDT contamination levels ranged between 0.015–0.150 µg/l. To account for differences in phytoplankton contamination levels due to differences in cell size and organic content, phytoplankton contamination levels were expressed in µg DDT/g particulate organic carbon (POC). Significant covariances between the DDT contamination levels in phytoplankton (µg DDT/g POC) and in water (µg DDT/ml water) were noted for each phytoplankton species and bioconcentration factors were calculated for every species (Table 1). As can be expected from a log K_{ow} of 6.2 for DDT[24], high DDT phytoplankton BCF were noted for the different marine phytoplankton species considered in this study. The data showed, as a confirmation of data obtained from literature[24,20,25], considerable interspecies variations possibly due to the existing differences in cell size and cell density among the phytoplankton cultures (Table 1).

Table 1 DDT Bioconcentration factors (µg DDT per g phytoplankton organic carbon/µg DDT per ml water) and correlation coefficients (r) for the relation between phytoplankton contamination and watercontamination for 5 species of marine phytoplankton; n = number of samples; conc. = concentration.

Phytoplankton species	*n*	*BCF*	*r*	*Cell concentr. (10^3 cells/ml)*	*Cell volume (μm^3)*
Tetraselmis sp.	8	35418	0.97	644	407
D. tetriolectica	13	26666	0.82	1088	250
Chlorella sp.	15	13745	0.85	364	59
Chaetoceros sp.	8	28270	0.93	400	113
Isochrysis sp.	8	13202	0.96	356	78

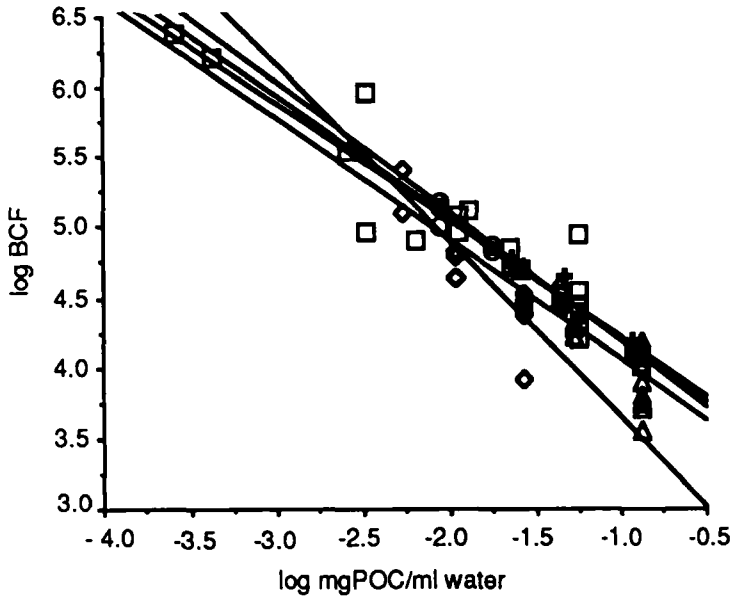

Figure 2 The effect of particle biomass (mg POC/ml water) on the POC normalized bioconcentration factors (μg DDT per g POC/μgDDT per ml water)(BCF) of DDT in different species of marine phytoplankton (○ tetraselmis, ❑ Dunaliella, ▲ Chlorella, ◊ Chaetoceros, + Isochrysis).

Relation between DDT bioconcentration factor in phytoplankton and phytoplankton biomass

To better evaluate the importance of respectively cell size and cell density on the observed differences in bioconcentration factors (Table 1), additional contamination experiments were carried out, with a broader range in culture densities. The culture biomasses were expressed as particulate organic carbon (POC) per ml water and ranged between 0.5–130 mg POC/liter water. Inverse nonlinear relationships were observed between the calculated bioconcentration factors (normalized on their POC content) and the phytoplankton biomass (organic carbon concentrations). Significant linear relationship, with similar density dependent bioconcentration factors, were noted when the data were transformed on logarithmic scales (Figure 2 and Table 2). The noted interspecies differences in regression slopes were not related to differences in cell size (Table 2).

The similarity in the observed relationships between the different species allows one to investigate the generality of the relationship for marine phytoplankton. A highly significant inverse linear relationship was observed between the bioconcentration factor of DDT in marine phytoplankton and the phytoplankton biomass (Figure 3). The relationship was described by the following equation:

$$\log BCF = -0.88 \log \text{biomass} + \log 3.24 \; (r^2 = 0.87;\; P < 0.001))$$

Table 2 Relation between the particle biomass (mg POC/ml water) and the POC normalized bioconcentration factors (μg DDT per g POC/μg DDT per ml water) of DDT for different species of marine phytoplankton expressed as log BCF = A log biomass +log B. All correlation coefficients (r) are highly significant ($P < 0.001$); n = number of samples.

Phytoplankton species	*n*	*A*	*log. B*	*r*	*Cell volume* (μm^3)
D. tetriolectica	25	–0.83	3.38	0.94	250
Chlorella sp	24	–0.86	3.21	0.83	59
Tetraselmis sp.	15	–0.87	3.34	0.98	407
Isochrysis sp.	12	–0.92	3.26	0.97	78
Chaetoceros sp.	15	–1.26	2.38	0.91	113

or

$$BCF = 1737 \,.\, C_{poc}^{-0.88} \qquad \text{(eq 1)}$$

The data clearly showed that a large amount of variability in BCF can be understood through this particulate concentration effect (PCE). A similar observation was noted for PCBs by Richer and Peters[21]. The observed phenomenon is related to the extremely important association of DDT with phytoplankton: 40–70% of the DDT administered was usually associated with the phytoplankton cells even at very low phytoplankton concentrations

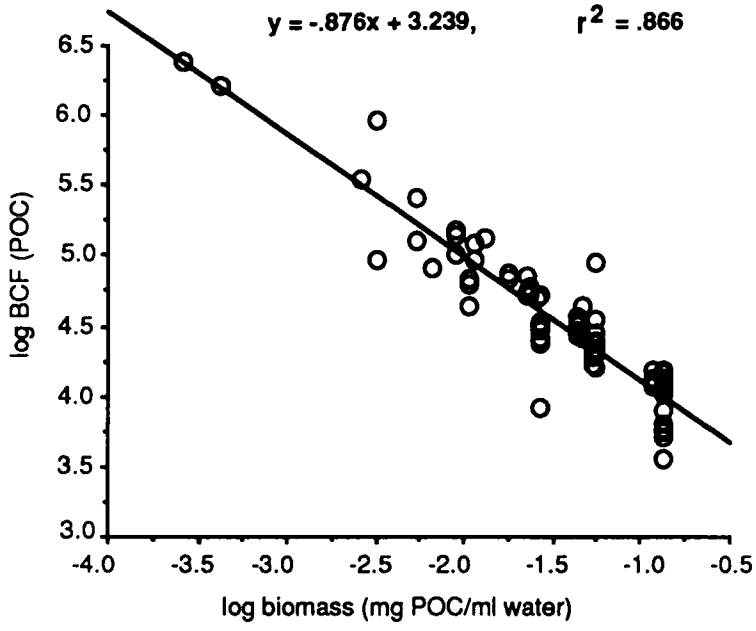

Figure 3 The effect of particle biomass (mg POC/ml water) on the POC normalized bioconcentration factors (μg DDT per g POC/μg DDT per ml water) (BCF) of DDT in marine phytoplankton ($p < 0.001$).

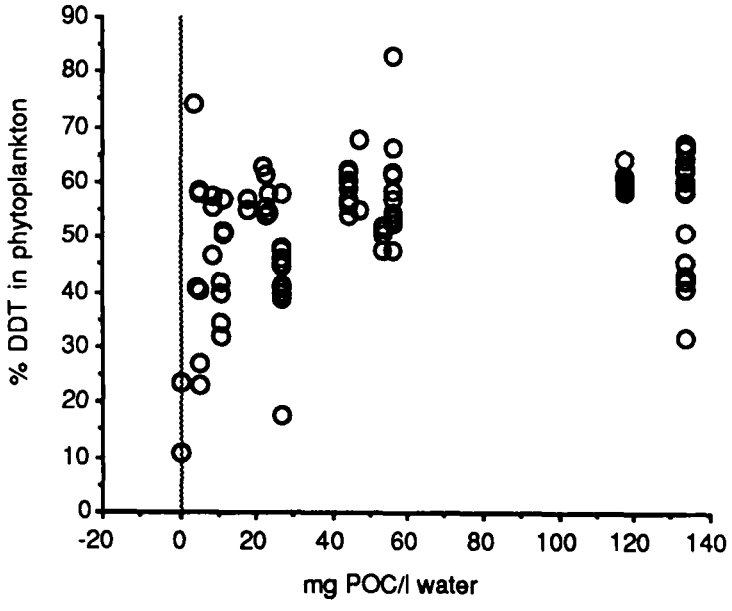

Figure 4 The relative uptake of DDT by phytoplankton.

(Figure 4). Extrapolation of this phenomenon towards a broader range of particle concentrations, especially including infinitely diluted biomass levels could end into the absurd fact that with very small amounts of particulate organic matter, enormous concentrations and bioconcentration factors could be observed. A decline in the amount of DDT taken up (10–30%) by phytoplankton was however noted for low phytoplankton concentrations (less than 10 mg POC/liter water). The relative importance of this lower association of DDT to phytoplankton can however not be seen from Figure 3 due to the remaining importance of the PCE and the logarithmic nature of the phenomenon. The importance of this association with particulate organic matter is not only dependent on the amount of particulate organic matter but also on the K_{ow} of the compound considered as illustrated for colloid organic matter by Brownawell[26] (Figure 5).

The importance of the PCE in natural marine ecosystems

The extrapolation of this observation towards natural ecosystems was furthermore tested for North Sea samples by adding pre-contaminated water to watersamples collected at different stations in the North sea in May 1993 (see materials and methods). One must realize that although during the sampling period there was clearly a *Phaeocystis sp.* bloom, the nature of the natural particulate organic carbon in natural marine samples is very diverse compared to the culture mediums. The POC pool included phytoplankton (essentially *Phaeocystis sp.*), zooplankton, detritus, bacteria and anthropogenetic organic carbon. The obtained bioconcentration factors (normalized on their organic carbon content)ranged between 8 and

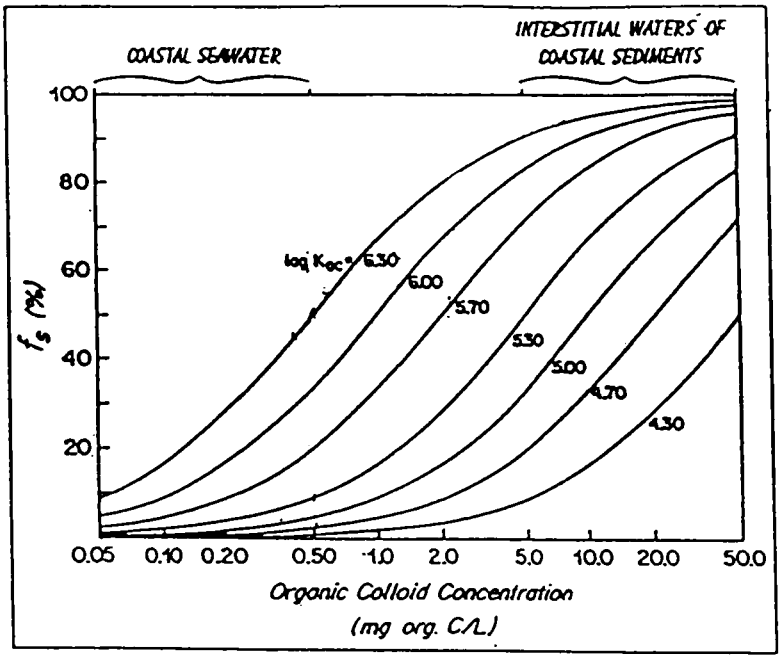

Figure 5 Relationship between fraction (f_s) of a given hydrophobic compound sorbed to organic colloids, organic colloid and log K_{oc} of the compound. From Brownawell[26].

21.10^5. They were significantly related to the particulate organic carbon content of the water (Figure 6). A less significant relationship was obtained between the bioconcentration factors (normalized on their organic carbon content) and the chlorophyll a present in the water (r^2=0.38; P< 0.05). This means that the partitioning phenomenon and the PCE also included other suspended matter than phytoplankton. The observed relationship for natural samples (Figure 6) was very similar to the one observed during the laboratory experiments (Figure 3) and the bioconcentration factors predicted from the model (eq 1) were closely related to the real bioconcentration factors (Figure 7). The real BCFs were however 2 times higher than the predicted ones. This factor is probably related to the diverse nature of the marine POC compared to phytoplankton cultures. The POC pool in marine systems contained more lipids (per POC) in higher trophic levels. A somewhat higher BCF, due to the contribution of e.g. zooplankton (with higher lipid content compared to phytoplankton) in the water samples was indeed expected. A detailed qualitative and quantitative study of the POC and lipid pool (different lipid classes) of the particulate and soluble fraction of watermasses will allow further model refinement.

In order to further evaluate the validity of the observed BCFs for the North Sea, we compared the observed BCFs for the North sea with the ones predicted from the particle interaction model (PIM)[16,17]. The formula of PIM was slightly modified to enable comparison with our data (BCF on organic carbon base).

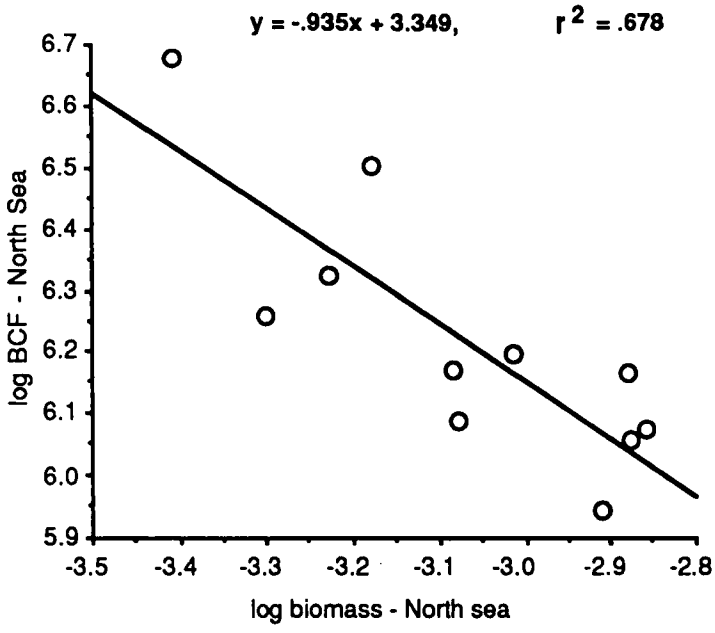

Figure 6 The effect of particle biomass (mg POC/ml water) on the POC normalized bioconcentration factors (µg DDT per g POC/µg DDT per ml water) (BCF) of DDT in marine phytoplankton collected from the North Sea in May 1993. ($P<0.002$)

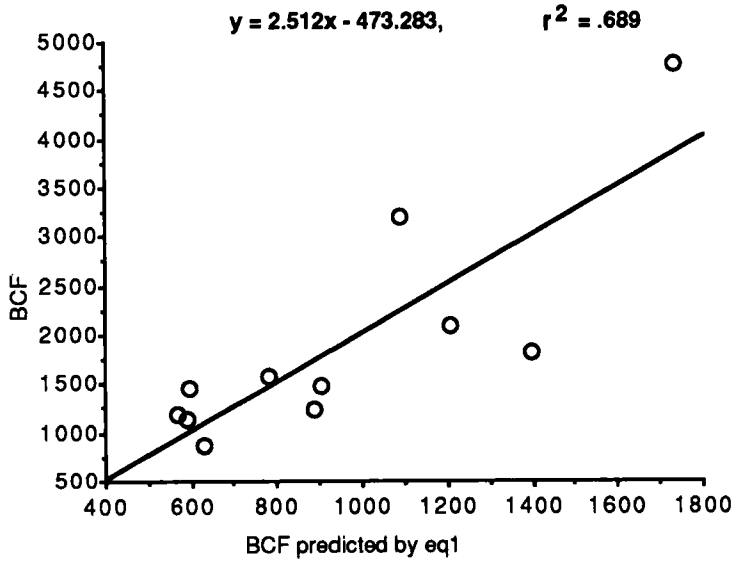

Figure 7 Comparison between the observed BCF and the BCF predicted from the model described in eq1. (BCF = observed or predicted BCF/10^3)

$$K_{p(oc)} = \frac{\mu gDDT / kgoc}{\mu gDDT / lwater} = \frac{Kow}{1 + \text{biomass (kg poc / liter water). Kow / 1.4}}$$

with:
$K_{p(oc)}$ = reversible component partition coefficient normalized on organic carbon = POC normalized BCF.

Both sets of data are related and very similar values are observed, when comparing the calculated and the measured BCFs. (Figure 8). Our data thus clearly illustrated the importance of a particle density bioconcentration factor for natural seawater suspended matter, corresponding to the model described as the PIM[16,17].

It is therefore believed that this phenomenon should be considered in future monitoring strategies.

CONCLUSION

Within a certain watermass, with a specific concentration of particulate matter, POC and lipids, a pseudo-equilibrium between the contamination of the organisms and the surrounding water exists. This equilibrium situation can be described in terms of BCFs. The BCFs for lipophile compounds such as DDT were however inversely related to the particulate

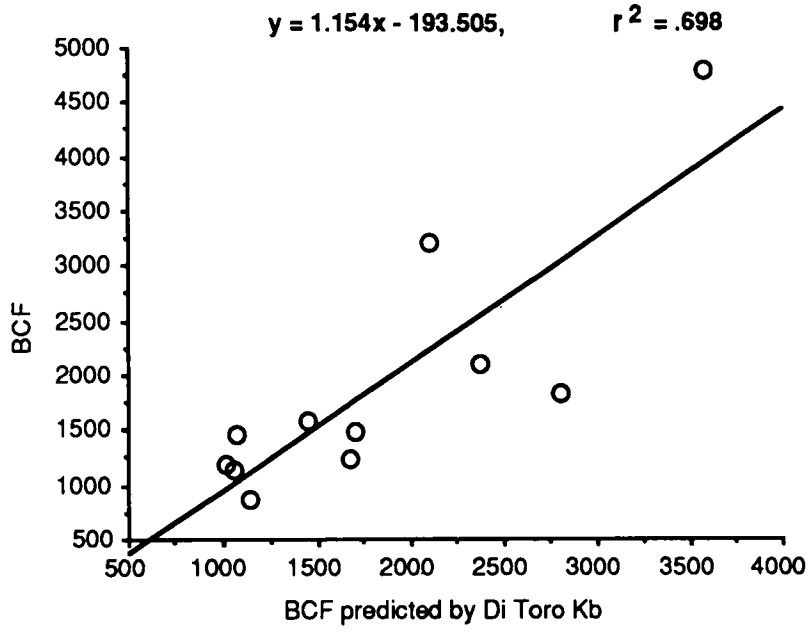

Figure 8 Comparison between the observed BCF and the BCF predicted from the PIM model described in Di Toro[17]. (BCF = observed or predicted BCF/10^3)

matter concentration. This means that, although so often described in literature, no general BCF (as a function of the compounds K_{ow}) exists for DDT. A dilution or concentration of the organic contaminants over the particulate organic matter pool (irrespective of the phytoplankton species considered) was observed. The extend of this phenomenon depends on the amount and composition of the POC pool present in the watermass and on the K_{ow} of the compounds. The particle concentration effect (PCE) as generally described by the Particle Interaction Model[16,17] fit the data observed for the North Sea.

A particle concentration effect (PCE) must thus be considered in order to understand and predict bioconcentration in aquatic systems. The data clearly illustrated that part of the differences in contamination levels observed among different watermasses (different geographic areas or seasons) were related to the particle concentration effect. It therefore seems extremely important to include PCEs in pollution models and pollution monitoring.

Quantification of the POC and lipid pool (different lipid classes) of the particulate and soluble fraction of the watermass will allow further model refinement.

The extrapolation of the model towards other pollutants, on the base of laboratory and field experiments and the Particle Interaction Model[16,17] will also add important information for the prediction of pollution levels and impact of organic compounds on marine ecosystems.

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