A closer look at the sorption behavior of nonionic surfactants in marine sediment

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A closer look at the sorption behavior of nonionic surfactants in marine sediment

Een nadere beschouwing van het sorptiegedrag
van niet-ionogene oppervlakte-aktieve stoffen in marien sediment

(met een samenvatting in het Nederlands)

Proefschrift

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Everything should be made as simple as possible, but not simpler.
- Albert Einstein

We don't make mistakes here, we just have happy little accidents.
- Bob Ross

Chapter 1

General Introduction

GENERAL INTRODUCTION
1. Preface

There is a growing worldwide concern about the stress on the environment that is caused by human activities. However, as long as the benefits outweigh the costs of adverse effects on a short term, most of these activities will continue at the same rate, or will even be increased. Still, the past decades have shown that innovative technologies and improved regulatory guidelines can reduce the impact of human activities on the environment. The improved treatment of waste water (from both industry and households) has in many countries strongly reduced emissions of chemicals that are of ecological concern for the receiving environment. At the same time, several hazardous chemicals have been banned from large scale use, and have been replaced by more environmentally friendly chemicals. The ecological quality of several environments bordering industrialized and urbanized areas, such as rivers, lakes and estuaries, has been improved by lower input of chemicals.

Many developing countries, however, lack costly treatment systems for waste and waste water. Countries where this is better regulated still have a legacy of heavily polluted areas from the past century, and still deal with complicated mixtures of contaminants at relatively low but not insignificant concentrations. Active cleaning of contaminated areas, such as remediation or storage of dredged sediment, as well as many other action taken to solve pollution issues, are costly operations. Clearly, this requires that risk assessment should be based on scientific sound data with a thorough understanding of the most important processes.

This thesis concerns surfactants, well known as chemicals that are for example the active components in washing powder, and how the risk assessment of these chemicals could or should be refined. More specifically, this thesis focuses on the occurrence of an important group of surfactants, alcohol ethoxylates, in the sediment of coastal environments. Several monitoring studies around the coasts of Spain demonstrated that alcohol ethoxylates are commonly present in sediment, though in low concentrations. The most likely sources are the outflow of rivers in which sewage effluents and/or sewage sludges are discharged, but also via direct effluent discharges in the sea from urban areas along the coast, and more diffuse sources such as run-off from agricultural fields. Most organic contaminants in sediments are associated (sorbed) with the solid phases, whereas only a minor fraction (often far less than 1%) is really dissolved in the pore water of the sediment phase. The sorption behavior more or less describes why and with which affinity dissolved chemicals sorb to the sediment phase. Already more than 500 years ago, Paracelsus (1493–1541) stated that “solely the dose determines that a thing is not a poison” (*1*). In the current view on the risk assessment of sediments this may be translated as “organic contaminants only induce adverse toxic effects above a certain freely dissolved concentration”. Clearly, the ratio between the dissolved concentrations and the concentrations sorbed to sediment is a key element in the risk assessment of contaminated sediment, because it not only determines, a), the concentration to which biota that live in

the sediment are exposed, but also, b), the mobility of the chemical in the sediment phase, and c), the availability for microorganisms that can break down the chemicals.

Alcohol ethoxylates are only one type of surfactant within the plurality of other types, but they occur in complex mixtures of more than hundred different molecular structures. The sorption processes for all surfactants are currently poorly understood, which makes it difficult to properly assess the risk of concentrations measured in sediments. While several sorption studies exist for fresh water sediment and soil, sorption studies for nonionic surfactants in the marine environment are very scarce. The aim of this study was to obtain a detailed insight in the influence of sediment properties and molecular structure of the alcohol ethoxylates, under marine conditions. In other words, to have a closer look at the sorption behavior, in order to improve the risk assessment of these nonionic surfactants.

This introductory chapter provides an overview of information about surfactants, in order to relate the aim of this thesis to what is known already. A first part describes how surfactants enter the environment and what is known about the occurrence in the field, focusing on alcohol ethoxylates in marine sediment. A second part deals with commonly used risk assessment procedures and how these can be applied for surfactants. A third part summarizes the literature data relevant for the environmental behavior of alcohol ethoxylates, considering the sorption and toxicity of these chemicals. The last part of this introduction gives an outline of the research chapters in this thesis.

2. Environmental occurrence of alcohol ethoxylates

2.1 Surface active agents

Surfactants are chemicals that reduce the surface tension of water, because these chemicals accumulate at the air-water interface. Another characteristic of surfactants is that they can form micelles, aggregate structures that remain dissolved. Both processes are the result of the molecular structure of surfactants. In most cases, surfactants consist of a long hydrocarbon tail (chain of repetitive CH_2 units), that does not like to be surrounded by water molecules (hydrophobic), and an ionic or polar head group that does likes to be surrounded by water molecules (hydrophilic), as shown in Figure 1. There are several classes of surfactants depending on the type of hydrophilic head group.

The accumulated amount of surfactants at the air-water interface, with the hydrocarbon tail in the air and the polar head group in the water, will increase when the dissolved concentrations increase. Because the surfactants break up the tight connections between water molecules, the surface tension of the water is reduced by increasing concentrations of surfactants. When a certain concentration in the water is reached, the maximum amount of dissolved surfactant monomers is reached (*2,3*). This is specific for every individual surfactant chemical and called the critical micelle concentration (cmc). At higher concentrations, surfactants form micelles, which are aggregates of individual molecules that remain dissolved in the water because the hydrophobic tails are shielded

off from the water and the head groups together create a hydrophilic outer layer. The graph in Figure 2 shows that at dissolved concentrations above the cmc, the surface tension is not further decreased. The functioning of detergents is partly based on the presence of such micelles, as these allow for the solubilization of fatty molecules and other dirt from the fabrics of clothes. The required concentrations of surfactants in the application of detergents has to be high, above the cmc. As a result, household waste water will therefore on average contain high concentrations. Surfactants are also used in a wide variety of other household and industrial applications, such as cosmetics, shampoos and conditioners, oil drilling fluids, corrosion inhibitors, pesticides, paints and laquers and disinfectants.

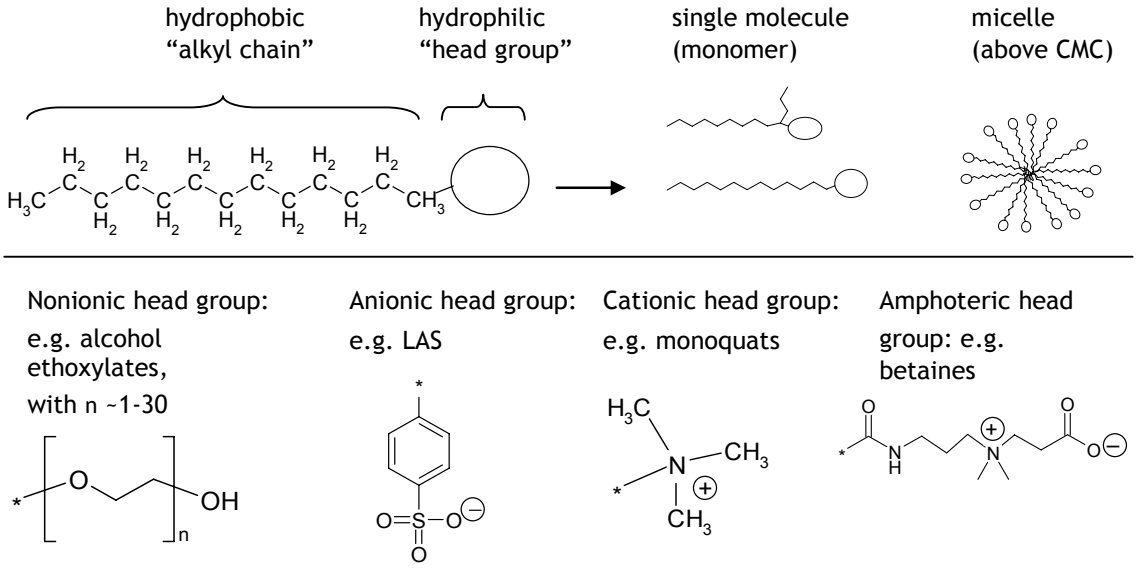

Figure 1. Examples of molecular structures of various surfactants, * indicates the alkyl chain which can be of variable length.

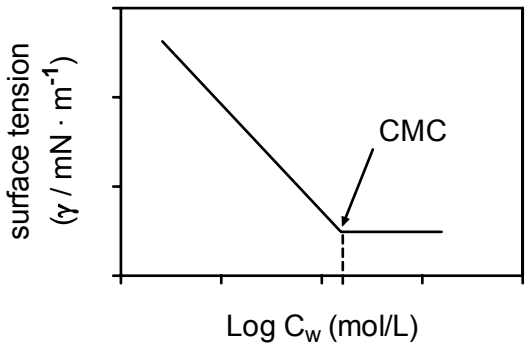

Figure 2. Theoretical plot of the surface tension (in (γ/mN·m^{-1}) of a solution against the dissolved concentration (C_w) of a surfactant.

2.2 Waste water treatment

As shown in Figure 3, the nonionic ethoxylates and the anionic surfactants are the most produced surfactants, and with over a million metric tonnes produced in Western Europe annually amongst the most produced synthetic substances in chemical industry. A relatively strong reduction of the concentrations of surfactants in waste water already occurs in the sewer systems, with half lives in the orders of hours (*4*). Sewage treatment and waste water treatment installations play a crucial role in avoiding a large input of surfactants in the environment via effluent discharges. Most of the recently designed multi-stage types of waste water treatment plants reduce the most common classes of surfactants with 95-99% or even more before discharging the effluents (*5,6*). In the waste water treatment installations, an adapted microbial community reduces the initial load of dissolved surfactants. Sorption to the organic rich sewage sludge, which is separated from the effluent, is also an important route of removal of surfactants from waste water (*7,8*).

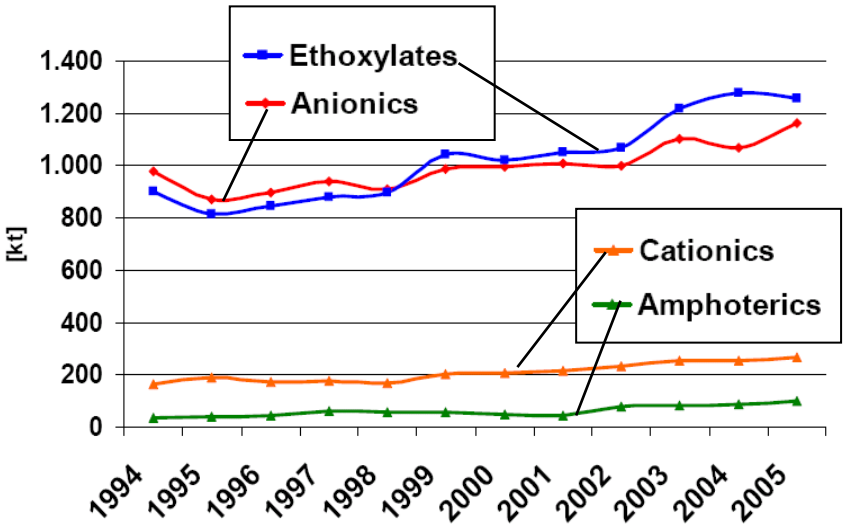

Figure 3. Production of surfactants in Wester Europe, adapted from a picture on the CESIO website. (http://www.cefic.org/files/Publications/CESIOSurf005.pdf)

For surfactants there are several examples on the reduced environmental impact due to technical improvements and regulatory actions. In the nineteen fifties, the first synthetic surfactants were poorly broken down by microbial organisms (biodegradation) in sewage treatment plants, due to a branched alkyl chain structure. The foam present on receiving environments was a clear indicator that these chemicals were abundantly present. By replacement with surfactants with linear alkyl chains a much higher biodegradability was achieved, and thus a lower environmental impact. A comparable voluntary replacement by the surfactant industry, in combination with national or international restrictions, has occurred in the last 15 years for the nonionic group of nonylphenol ethoxylates (NPEO, (*9*)) and for the cationic fabric softner dioctadecyl-dimethylammonium chloride (DODMAC, (*10,11*)). Some of the possible degradation

products of NPEO are suspected to cause endocrine disruption (affecting sexual development or reproductive systems of organisms) and are relatively persistent (*12,13*). DODMAC is poorly degradable, resulting in elevated environmental concentrations (*7*). Both compounds have been replaced on a large scale by compounds that are much more readily degraded into relatively harmless degradation products.

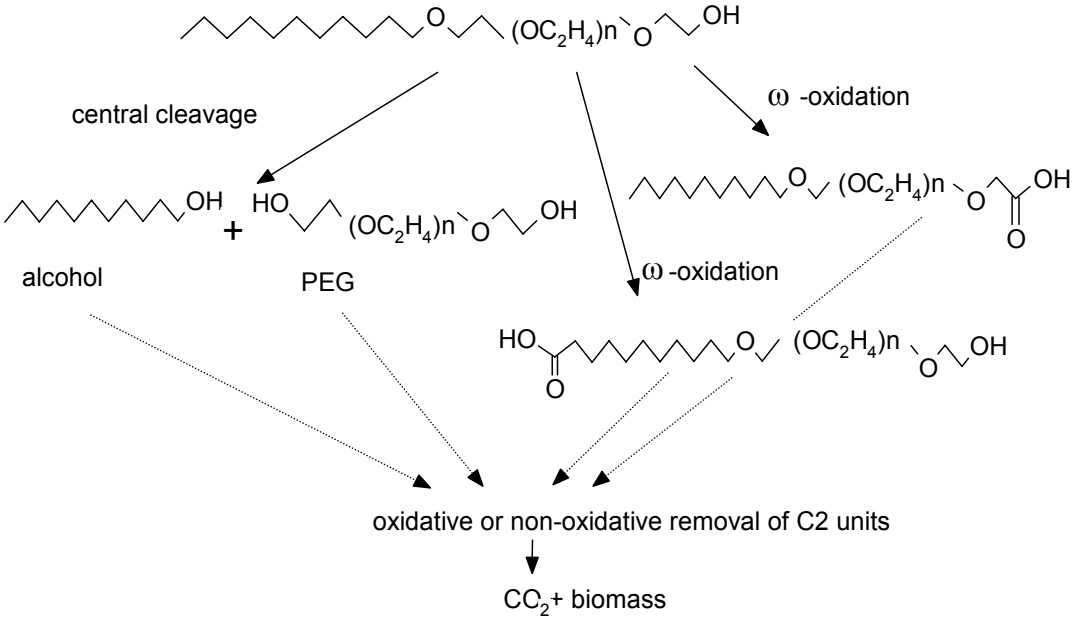

Figure 4. Basic steps in degradation processes for linear alcohol ethoxylates, where $(OC_2H_4)n$ indicates the EO units in the ethoxylate chain, and PEG is polyethylene glycol that is formed by scission of an AE at the first ether bond.

2.3 Alcohol ethoxylates

In Europe and several other parts of the world, the alkylphenol ethoxylates, to which the NPEOs belong, have been largely replaced by alcohol ethoxylates (AEs). These AEs are the main surfactants investigated in this thesis (presented in Figure 1). Technical commercial AE is comprised of mixtures of homologues with varying alkyl chain lengths and number of ethoyxlate units (CH_2CH_2O). During the production process of AE, the primary alcohols that are used are derived from petrochemical sources (mainly C_{10}, C_{11}, C_{12}, C_{13} and C_{14}) or from oleochemical products (animal fats and vegetable oils, only C_{10}, C_{12}, C_{14}, C_{16} and C_{18}) (*14*). Although the majority of the alkyl chains in AE are linear, an important fraction (5-95%) may have monobranched chains in the 2 position (also presented in Figure 1). An estimated 10% of the AE produced are multibranched alkyl chains, synthesized via ethoxylation of isotridecanol (C_{10}-C_{13} homologues mixture) (*15,16*). Most technical AE mixtures have an average number of ethoxylate (EO) units between 5 and 15, while the distribution of EO chains in AE homologues may range between 2 and 30 units. In this thesis, the tested AE

homologues were obtained as single compounds of high purity, which supposedly have linear alkyl chains only and a known absolute number of EO units.

The branched fraction is important for the risk assessment of AE because they differ in their biodegradation pathways from linear AE and short (methyl and ethyl) 2-alkyl substituents (Figure 4). Central cleavage by micro-organisms, which results in an alcohol and a polyethylene glycol (PEG) for the linear AE, is strongly reduced when length of the branching chain is increased. For these branched AE, ω-oxidation of the alkyl chain or ethoxylate chain is the most important step, resulting in carboxylated compounds (*16*). After this, alkyl chains can be further shortened by β-oxidation, in which in steps C_2 units are removed, while carboxylated EO chains are shortened via hydrolytic processes. The alcohols, PEG or carboxylated products that are formed via microbial degradation or via biotransformation in biota, are rapidly further degraded (*17*). Another factor related to the environmental safety of AE is that biodegradation occurs rapidly in the presence of oxygen (aerobic conditions), as well as in the absence of oxygen (anaerobic conditions), and these anaerobic conditions often occur in the sediment phases below the first few centimeters (*16-18*). As shown by Knaebel *et al*. (*19*), the sorbent phases in soil or sediment, such as clay minerals, sand and organic matter, strongly influence the extent and rate of biodegradation of AE.

2.4 Environmental occurrence of alcohol ethoxylates

After the input of surfactants in the environment via treated waste water effluents or direct discharges, the concentrations will be strongly reduced by dilution in the receiving water bodies. Using sewage sludge for enrichment of agricultural fields is another route of AE input into the environment (*8*). Because of ongoing microbial degradation and binding processes to suspended matter and sediment, the dissolved concentrations will be further reduced in time and as the distance from the source increases, as shown for NPEO by Jonkers *et al*. (*20*). At places with a relatively low stream velocity, however, suspended particles with surfactants sorbed to them may settle on the sediment and locally increase the surfactant concentration sorbed to the sediment phase. As long as there is a relatively continuous input of surfactants via effluent discharges, the environmental concentrations will be a balance between desorption fluxes from the sediment, biodegradation processes and fresh input.

The data on concentrations of AE in the environment are scarce. Detailed information is available for concentrations in waste water, sewage sludge and sewage effluents. Increased AE concentrations have been detected in the freshwater sediment downstream of several sewage treatment plants in the US (*21*), while another study reported the AE concentrations in the water phase at many points along the river Ter in the North East of Spain (*22*). For AE in coastal sediments and seawater, presently, only data are available from around Spain (*23-25*). Due to analytical limitations, only the most recent studies have been able to determine concentrations of each individual AE structure that occur in technical mixtures. Semi-specific analysis of AE grouped all ethoxymers for a

single alkyl chain length together (*26*). Another complicating factor is that the concentrations of the individual structures in the complex mixtures are also so low that sophisticated analysis is required to measure signals above detection limits. Reported total AE concentrations in the river and seawater sampled since 1999 were below 20 µg/L, total AE concentrations sorbed to marine sediment were up to 2 mg/kg.

3. Risk assessment

3.1 Risk assessment guidelines

From a national or international level, regulative guidelines have been set to facilitate risk assessment procedures, such as those listed in the Technical Guidance Document on Risk Assessment from the European Chemicals Bureau (*27*). Such guidelines on chemicals often directly state, or provide estimation models for the maximum allowable concentrations for the environmental compartments, i.e. water, air, soils and sediments. The most widely applied model to assess the risk of sediment contaminated with organic chemicals is based on the equilibrium partitioning (EqP) theory (Figure 5). The main assumptions in this model are (a) that the partitioning of a chemical between the sediment phase, the pore water and the tissues of biota is in equilibrium, and (b), that the equilibrated concentration in the tissue of organisms depends only on the freely dissolved concentration in the pore water. Di Toro *et al*. (*28,29*) showed that the theory closely predicts experimental data for a wide variety of organic chemicals. As a result, water quality criteria can be converted to sediment quality guidelines if the sorption behavior is understood.

This model also allows for risk assessment of mixtures of chemicals that have an additive mode of action, i.e. for which the concentrations at the target site where the effect occurs (e.g. membranes of cells) can be added up. For example, narcosis, or baseline toxicity occurs for all organic compounds at roughly the same critical concentration in the cell membranes. The total internal concentration for narcotic compounds can thus be compared with the critical body burden (CBB) at which narcosis occurs. This is only possible when internal concentrations are measured or when bioconcentration factors (BCF) are available. Alternatively, the toxic unit concept can be applied for additive mixtures. This concept is based on the concentration of a single compound relative to its effect concentration (e.g. where 50% mortality occurs for a population of the same test organism). In this way, the toxic concentration of a single compound equals 1 toxic unit, and if the concentration is 10 times lower, that compound contributes to the overall mixture for 0.1 toxic units. If the sum of all toxic units of the compounds with additive toxicity in a mixture reaches 1 toxic unit, this suggests that the total concentration of the mixture is at the effect level.

In line with the EqP approach, it is generally assumed that the partitioning of freely dissolved organic chemicals in the pore water to both sediment and organisms is driven by the hydrophobicity of the compounds. The reason for this is that the organic matter fraction in sediment and the lipid fraction in the tissue of biota are in most cases the dominant sorption phases for organic chemicals, and both are relatively hydrophobic

organic phases. The octanol-water partition coefficient (K_{ow}) is a commonly measured parameter to describe the hydrophobicity of organic chemicals. The K_{ow} is therefore in many models linked to the partition coefficient between water and the organic carbon fraction in sediment or soil (K_{oc}), and to the lipid corrected bioconcentration factor (BCF_{lip}). Assuming that, with some uncertainty, the K_{oc} is similar to BCF_{lip}, the sediment concentrations is directly related to the concentration in lipid fractions of biota, via a biota-sediment accumulation factor (BSAF). This would also allow a direct extrapolation of the CBB to maximum permissible concentrations in the sediment.

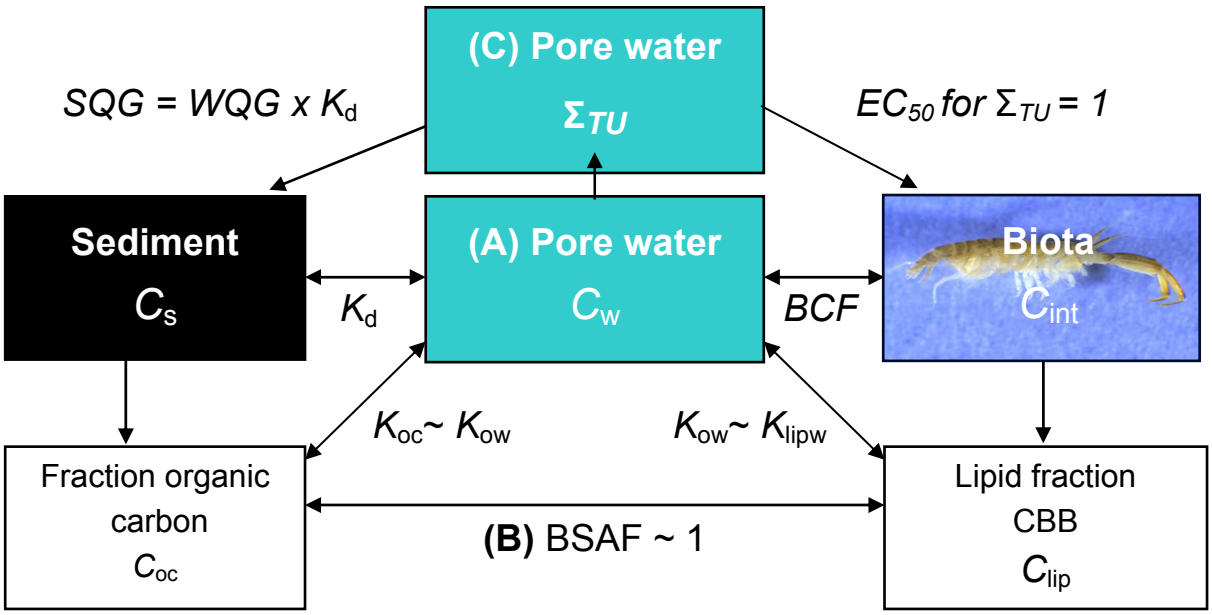

Figure 5. Combined schemes of common risk assessment procedures for contaminated sediment:
(A) Equilibrium partioning theory - the partitioning of the organic contaminant between sediment, pore water and biota is in equilibrium, and the internal concentration in the organism depends fully on the freely dissolved concentration;
(B) the hydrophobicity of the organic contaminant is assumed to drive both the affinity to sorb to the organic phase in the sediment (Koc) and the affinity to sorb into the lipid fraction of biota (Klipw). Adverse effects for the organism occur once a critical body burden (CBB) is reached. Via relationships of Koc and Klipw with the octanol-water partition coefficient (Kow), the concentration in sediment is indicative for the lipid corrected concentration in biota (Clip);
(C) the sum of the toxic units (ΣTU) for the freely dissolved concentration of compounds with additive toxic mode of action, and water quality guidelines (WQG) of individual compounds, can be used to derive sediment quality guidelines (SQG).

3.2 Exceptions to risk assessment guidelines

The guidelines are based on widely accepted scientific state of knowledge. Because the analytical tools are constantly being further developed, the insight in the environmental behavior of chemicals has also rapidly increased. Several exceptions to the currently most applied guidelines have been observed in the past decade. Many systems are not in

equilibrium, as is visible for example in the phenomena of biomagnification. The uptake via food is faster than exchange with the surrounding medium and excretion pathways, and internal concentrations are higher than predicted by EqP. Another important factor affecting the equilibrium distribution, is metabolic transformation of the compound inside the organism.

During the past decade it further became clear that the bioavailability of polycyclic aromatic hydrocarbons can be much lower compared to calculations based on the fraction of organic matter and K_{oc} values, due to a much higher sorption affinity for black carbon fractions like soot or coal (*30,31*). For such specific cases, the guidelines should be revised to incorporate these processes in the risk assessment models, so that decisions are based on more realistic predictions of the risk.

Another point that risk assessors have to deal with is that for many chemicals the basic input parameters that are required for the model calculations, are not available. For example, the octanol-water partition coefficient (K_{ow}) is a key parameter, but there are no direct measurements available of the K_{ow} for surfactants. This complicates the risk assessment of these chemicals via standard guidelines, because the K_{ow} of surfactants has to be estimated indirectly. The outcome of the available methods may differ substantially, as is obvious by comparing estimates from the method of Roberts (*32*) with KowWIN predictions (*33*).

There are other aspects of surfactants that raise questions on the applicability of models that are developed based on apolar or slightly polar organic contaminants. Tolls *et al*. (*34-37*) showed that many surfactants are readily biotransformed in fish, which resulted in a lower equilibrium distribution between water and tissue. Secondly, many studies have shown that the sorption to sediment does not increase linearly with the aqueous concentrations of cationic surfactants (*38,39*), anionic surfactants (*40-42*) and nonionic surfactants (*43-46*). This means that the sorption coefficient, that relates the concentration in the pore water to the sorbed concentration in the sediment, is concentration dependent. In contrast, the partitioning coefficient to organic matter is expected to be linear for all organic chemicals. This suggests that binding to organic matter may be related to sorption sites at the surface of organic matter, or it indicates that sorption phases other than organic matter in the sediment are contributing substantially.

4. Environmental behavior of alcohol ethoxylates

4.1 Sediment properties

To better understand the nonlinear sorption behavior of surfactants, and in particular that for the nonionic alcohol ethoxylates, a closer look at the sediment phases is required. A marine sediment is a complex mixture of a wide variety of materials (Figure 6). The easiest way to start a theoretical fractionation of these materials, is probably to discern between an organic fraction, a mineral fraction, metal oxides and carbonates. The organic fraction in the top-layer of marine sediments is made up of strongly weathered organic molecules,

often lignin rich, coming from algae, mucus secreted by benthic organisms and for example sorbed proteins, and bacteria that live in the sediment phase. Close to the coast, terrestrial organic input may be part of the organic fraction, and this has minor differences with marine organic matter. After marine algal blooms, the organic content may temporarily increase. Oily residues also occur in many coastal regions, as well as soot, coal and other black carbon material.

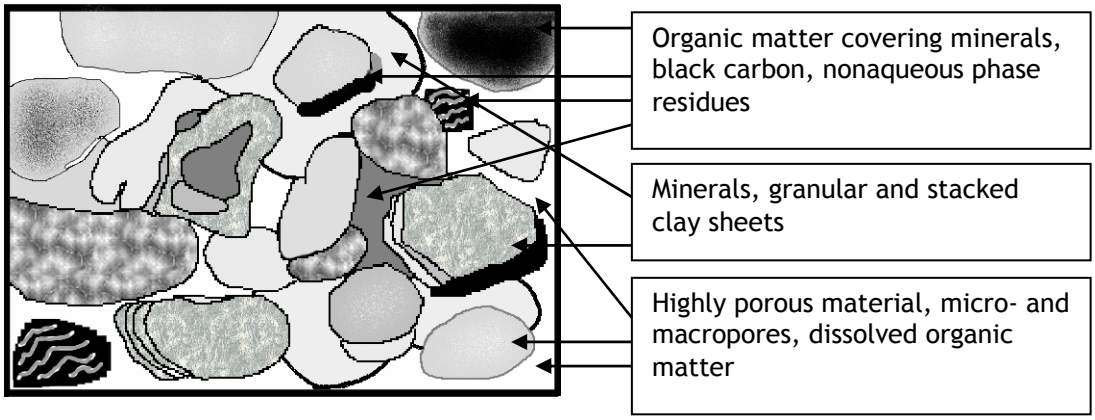

Figure 6. Conceptual microscopic sediment structure, inspired by Luthy *et al*. (*47*).

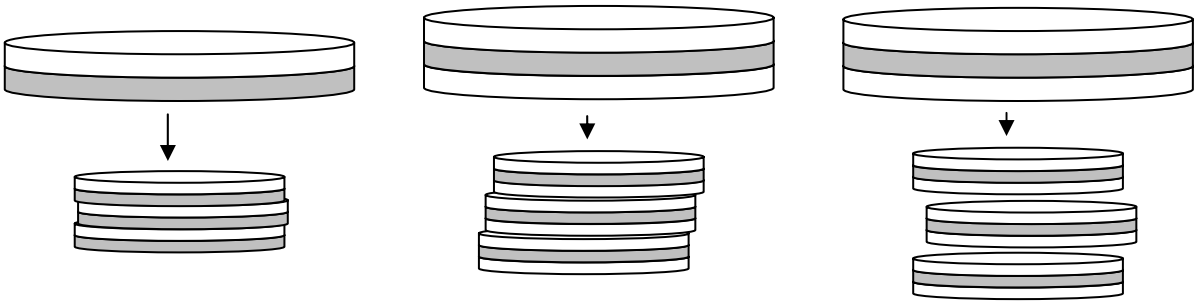

Figure 7. Conceptual model of individual silicate clay sheets and stacked formations in solution, for a 1:1 clay (left), 2:1 nonexpanding mineral (middle), 2:1 expanding mineral (right). Layers of aluminum hydroxyde are colored grey, silicium oxide layers white.

The mineral fraction consists of a wide variety of clay minerals and silicates, which differ strongly in the molecular crystal structure. An important difference between “sand” and “clay minerals” is that sand silicates are granular whereas clay minerals are stacked layers of clay “sheets” (Figure 7). The type of clay minerals and granular silicates depends on the origin, which can be terrestrial (fluvial input), from other remote marine areas via strong currents, from volcanic activity at the sea bottom, or old sediment layers that reach the surface due to movement of continental sheets or erosion. The clay minerals are classified in widely branched groups, depending on the molecular structure. This molecular structure is in almost all cases an average structure that includes a certain degree of

impurity. The basic structures are layers of silicon oxide and layers of aluminum hydroxide. The clay mineral kaolinite consists of sheets with a layer of silicon oxide on top of a layer of aluminum hydroxide (1:1). An ideal 2:1 mica mineral sheet consists of a layer of aluminum hydroxide sandwiched between two silicon oxide layers.

The wide variety of these minerals is related to the substitution of a silicon (Si^{4+}) or aluminum (Al^{3+}) ion with another cation. If this substitute has a lower valence (i.e. Mg^{2+} instead of Al^{3+}, or Al^{3+} instead of Si^{4+}), this results in a charge deficit of -1. Depending on the amount of such "impurities", almost all minerals have a permanent negative layer charge, that is balanced by adsorption of cations on the outside of the sheets, or between two adjacent sheets. These cations on the surfaces are highly hydrated (surrounded by H_2O molecules), and therefore hold only by weak electrostatic interactions (Coulombic forces). As a result, they can be exchanged for other cations, also cationic surfactants for example, and the capacity of a mineral to exchange cations is called the *CEC*. For 2:1 minerals with mainly substitutions in the Al-layer in the middle of the sheet, the layer charge (per so called unit) is relatively low (<0.6) and spread out over the surface oxygens on both sides of the sheet. Because of this low charge, two adjacent sheets are not held so tightly together via the cations, and water can enter the interlayer between two sheets. Such expandable clay minerals are used in many industrial applications that often also involve surfactants, and include amongst many others substrates called "smectites", montmorillonite, or bentonite. Besides the permanent charge, many clay minerals can bear a pH dependent charge. In the environmentally relevant pH range, the proton on surface hydroxyl groups (-OH) is often dissociated, though this depends on the mineral or metal oxide type. Metal oxides may form a substantial fraction of coastal sediments, since metals readily precipitate as a result of the higher pH in seawater compared to pH in the freshwater input (*48*).

A problem with such a subdivision in different materials for marine sediments, is that the organic fraction is often strongly associated with the mineral fraction, just as many metal oxides are precipitates on minerals surfaces, and clay minerals may be present in amorphous mixtures or form mixed layer minerals. A strong, linear and narrowly defined (factor of two) relationship between mineral surface area and organic carbon content has been demonstrated for a wide variety of bulk marine sediments, ranging 0.5-1.0 mg OC per m^2 surface worldwide (*49-51*). Exceptions to this relationship are pelagic and deltaic regions with concentrations significantly below this range and in nutritious zones with oxygen depleted sediments with significantly higher OC loadings (e.g. Peru Margin sediments with 2.3 mg/m^2 (*52*)). Keil *et al*. (*53*) demonstrated that the organic carbon to mineral surface area ratio from several sediments on the Washington coast was nearly constant at ~0.76 mg/m^2. In most marine sediments, less than 10% of the organic matter is only loose organic debris, unbound to the sediment (*54,55*).

4.2 Freely dissolved concentrations

In tests performed to study the sorption behavior of organic contaminants, ideally the concentration freely dissolved in the aqueous phase and the concentration sorbed to the test substrate (sorbent) are measured. Classically, the aqueous phase is separated from the sorbent via centrifugation. It is not easy, if not impossible, to separate dissolved organic matter (DOM) and the finest clay fractions from the aqueous phase by centrifugation. Several studies during the nineteen nineties showed that for very hydrophobic compounds, that strongly sorb to DOM, co-extraction of this fraction in water samples can strongly overestimate the freely dissolved concentrations (e.g.(*56,57*)). This is important because the chemicals bound to DOM or proteins are not able to cross membranes, and thus do not contribute to the equilibrium distribution between the water phase and biotic tissues (*58-60*). These wrongly sampled aqueous concentrations should therefore be avoided when possible.

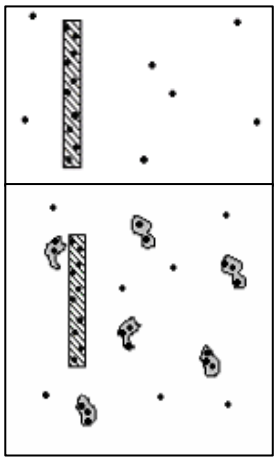

Figure 8. Passive sampler in equilibrium with freely dissolved concentration in clear solution (top) and in a solution with a third phase (e.g. DOM), adapted from Ter Laak (*61*).

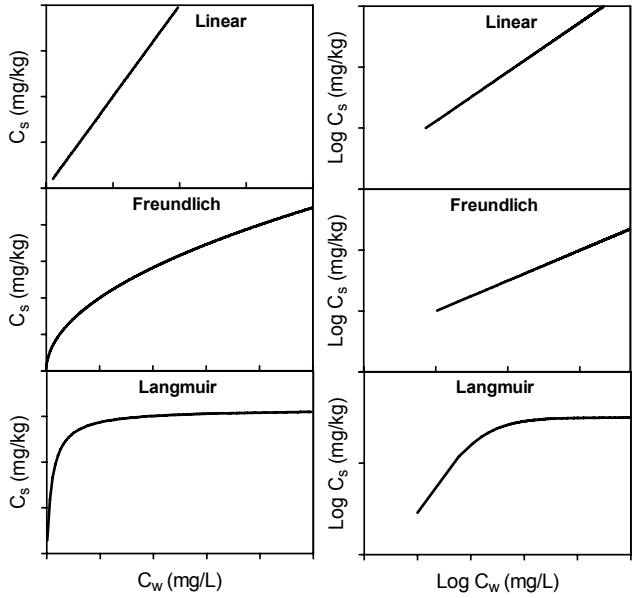

Figure 9. Theoretical sorption models on a linear scale (left) and logarithmic scale (right).

In the sorption studies that Westall *et al*. (*38,40,44*) performed with surfactants, a rigorous (and time consuming) washing procedure was applied for the test sediments to reduce the nonseparable fraction. Instead of active separation of the aqueous phase and the sorbent, dialysis membrane devices can be employed as passive separation devices: only freely dissolved compounds cross the membrane and the aqueous phase on the other side of the membrane can be sampled. The hydrophobic compounds, however, will also sorb to the membrane phase, which may cause additional problems during these tests. An alternative method is the use of passive samplers, which equilibrate only with the freely

dissolved concentration, and can be easily redrawn from the test system. If the relationship between the concentrations in the sampler and the aqueous phase is known, the measured concentration in the sampler can be used to determine the freely dissolved concentration.

There are several tools available, and nice results are obtained for a wide variety of organic chemicals in a wide variety of matrixes (*61-66*). The main prerequisites for testing in the aqueous phase are that the extraction phase is (a) a solid phase to assure that chemicals partition into it, and have a single affinity constant, instead of adsorb to sorption sites which may have a wide energetic distribution, (b) as thin as possible, since this exponentially increases equilibrium kinetics, but still with a volume that results in a suitable sensitivity.

The solid-phase microextraction (SPME) method uses the protective polymer coating around glass fibers (normally used as optical fibers in data communication) as a passive extraction phase (Figure 8). There are several types of polymer coatings available, in different thicknesses that can vary between 7 and 100 µm.

4.3 Sorption studies with nonionic surfactants

The sorption behavior of organic contaminants to sediment depends on the sorption affinity to the different sorption phases in the sediment. Several basic relationships between the dissolved concentration and the sorbed concentration are commonly used, as presented in Figure 9. Organic matter is considered as the dominating sorption phase in risk assessment of organic contaminants (Figure 5), and interactions with other sediment phases are considered to have a negligible contribution. The overall sorption affinity for the sediment will thus depend on the percentage of organic matter in the sediment, often expressed as fraction organic carbon (f_{oc}), and the sorption coefficient of the compound between the organic phase and water (K_{oc}), according to:

$$C_s = C_{oc} \cdot f_{oc} = C_{aq} \cdot K_{oc} \cdot f_{oc} \qquad (1)$$

where C_s is the total sediment sorbed concentration, C_{oc} the concentration in the organic phase, and C_{aq} the freely dissolved concentration. The sorption isotherm of such a system is linear with a slope of K_{oc}. Karickhoff (*67*) showed for a wide variety of compounds that the K_{oc} was related to the K_{ow}:

$$K_{oc} = 0.41 \cdot K_{ow} \qquad (2)$$

The adsorption of a compound to a homogenous surface, with one type of adsorption sites and a maximum adsorption capacity ($C_{S,max}$), can be modeled by the Langmuir equation:

$$C_s = \frac{C_{S,max} \cdot b \cdot C_{aq}}{1 + b \cdot C_{aq}} \qquad (3)$$

where b is a constant related to binding energy. From this equation it follows that the adsorption coefficient is constant when $b \cdot C_{aq} << 1$, and is equal to the product ($C_{S,max} \cdot b$). When C_{aq} increases so that $b \cdot C_{aq}$ influences the curvature, the isotherm becomes nonlinear and when $b \cdot C_{aq} >> 1$, C_s will equal $C_{S,max}$.

In most sorption studies with surfactants to soils and sediments, however, the nonlinear sorption is described by the empirical Freundlich equation:

$$C_s = K_F \cdot C_{aq}^{n_F} \qquad (4)$$

where n_F is the Freundlich exponent defining the nonlinearity of the curve, and K_F the Freundlich coefficient, which depends on the measurement units of C_{aq} and C_s. The popularity of this model lies in the fact that it describes the sorption as the filling of sorption sites with a broad distribution of binding energies, i.e. it is the sum of an endless amount of Langmuir equations, and on a logarithmic scale fits as a linear regression:

$$\text{Log } C_s = \text{Log } K_F + n \cdot \text{Log } C_{aq} \qquad (5)$$

Most of the nonlinear sorption data for surfactants are described by this Freundlich equation. Both Brownawell *et al*. (*44*) and Cano and Dorn (*46*) showed that the nonlinearity parameter n decreased for AE with longer ethoxylate chains. At the tested concentration range, the sorption of the longest ethoxylate chain was stronger than the AE with smaller ethoxylate chains. Still, the alkyl chain seemed to dominate the sorption coefficient. These studies also showed for a small set of sediments that the sediment order based on fraction of organic matter did not correspond to the order based on the Freundlich coefficients. In studies with organic rich soil and sediments (f_{oc} >0.1) and sewage sludge, however, most reported sorption isotherms are relatively linear for nonionic surfactants (n = 0.8-1.2) (*43,68,69*), although also nonlinear isotherms are reported for sludge (*70*). A recently published review of sorption data for AE attempted to construct simple relationships between the molecular structure of AE homologues and sediment-water distribution coefficients for a concentration range between 0.1-50 µg/L (*69*). The K_d values were then corrected for the organic carbon content of the sorbents to obtain estimated K_{oc} values. The K_{oc} values were related to alkyl chain length and number of EO units as molecular descriptors of AE. The resulting relationship, however, showed an even weaker correlation coefficient (r^2 = 0.53) than the relation of the descriptors with uncorrected K_d values (r^2 = 0.64). The problem with the Freundlich parameters is that they are generic parameters, that neither translate clearly in sediment properties nor relate to molecular characteristics of the contaminants. Furthermore, extrapolating a generic nonlinear curve to environmental concentrations that are much lower than the measured concentration range in sorption studies, is not readily accepted in risk assessment procedures.

4.4 Adsorption of surfactants

It becomes clear from the multitude of industrial applications of surfactants that many types of surfactants adsorb to the mineral surfaces. Most of the studies related to the

adsorption of surfactants focus on the high concentration range where surfaces become saturated with surfactant. Often this is the interesting range for the application of surfactants, e.g. to prevent flocculation in paints, but on the other hand the analytical techniques used also do not allow to test at much lower concentrations. Luckham and Rossi (*71*) reviewed the adsorption behavior of nonionic polymers to mineral surfaces in 1999, and summarize the state of scientific knowledge and theory to a large extent. Since the sorption behavior at relatively low concentrations is not well studied, the authors can only describe the most popular model for either hydrophobic surfaces or hydrophilic surfaces. Figure 10 shows that the adsorption of surfactants can be divided in several stages. Both the hydrophobic tail and hydrophilic head group interact with the surface at low concentrations (L1). This is thought to occur with a constant affinity, i.e. linear sorption, since there is no competition for adsorption sites. When concentrations are increased, surfactants may cluster as soon as adsorption sites become saturated (L2). For hydrophobic surfaces, the hydrophilic head groups of surfactants will protrude into the solution. For hydrophilic surfaces, however, the ionic or polar head groups of surfactants will displace the weakly bound alkyl chains, and the clusters will have the hydrophobic alkyl chains sticking out into the aqueous solution. This hydrophobic layer will create a secondary sorption phase for the surfactants in solutions. Via sorbate-sorbate interactions the adsorbed layer is transformed to micellar structures on the surfaces (L3). Once the critical micelle concentration is reached, the sorption processes reach a maximum and additional surfactants will only create more micelles in solution (L4).

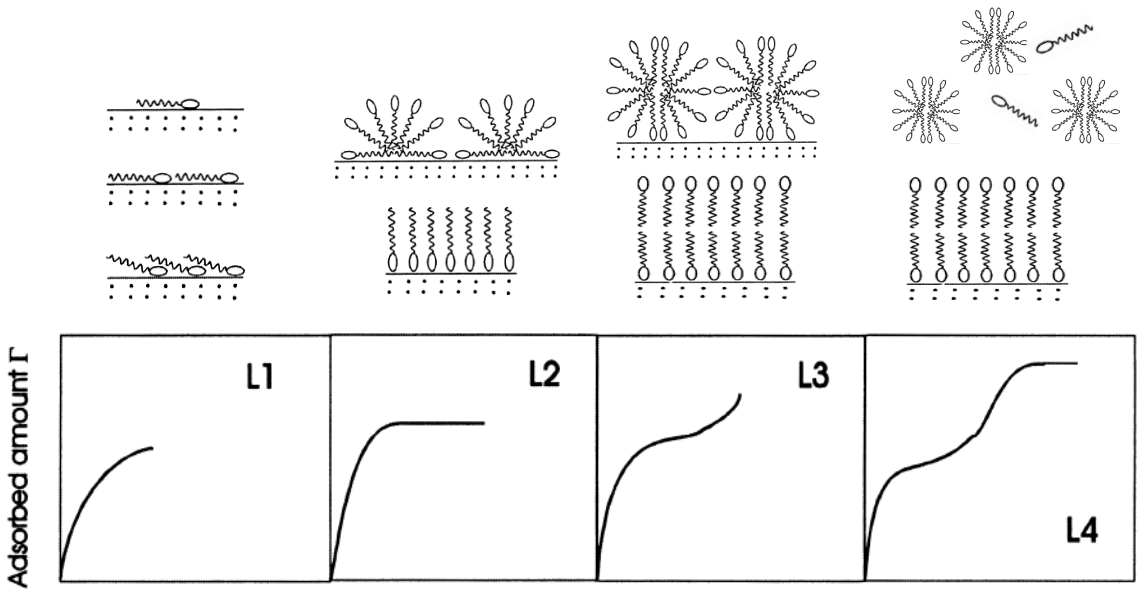

Figure 10. Theoretical representation of the adsorption behavior of surfactants, adapted from Luckham and Rossi (*ref* (*71*)).

4.5 Toxicity of alcohol ethoxylates

The toxic mode of action of alcohol ethoxylates is most likely nonspecific, basic toxicity, also referred to as narcosis. Most toxicity studies indicate that test organisms like daphnids and fish (*72,73*) and tadpoles (*74*) become immobile above a certain concentration. After prolonged exposure with such narcotic effects the organisms often die within several hours to days. The chronic exposure of daphnids (21 days) to various AE solutions did not result in much higher toxicity (factor 0.41 - 10.9) compared to acute toxicity tests (2 days)(*73*). When immobilized organisms are transferred to clean solutions, the effects appeared to be readily reversible (*74*). These studies suggest that the effects in acute tests are most likely due to accumulation of the compounds in the membrane structures. At a critical concentration in the membrane, the basic functioning of the membrane is hindered (*75,76*). This could result in a wide array of more specific effects, such as the teratogenic effects and mitochondrial malfunctioning observed for tadpoles (*74*), or gill permeability (for NPEO in ref (*77*)). Due to rapid biotransformation of surfactants in the tissues of the organisms, the test organisms may cope with high exposure concentrations which are close to the critical concentrations. Most dose-effect plots for AE indeed show an all-or-nothing effect, with a steep slope at the effect concentrations (*72*). When organisms are transferred to clean(er) water, the internal concentration decreases to below the critical concentration and the organisms will display normal functioning.

As shown in the risk assessment scheme in Figure 5, the internal concentration depends on the freely dissolved concentration. With increasing hydrophobicity, the affinity of AE for the membrane phase also increases, resulting in higher bioconcentration factor (BCF) (Figure 5). The available number of high quality BCF values for AE is limited, however, and biotransformation in the organism strongly influences the experimental data (*34*). Predicting the total internal AE concentration for complex mixtures based on BCF values, and comparing this with the critical body burden is therefore not possible. There are more data for toxicity of AE to aquatic biota (*72,73,78*), and these data provide better relationships between molecular structure and effect concentrations. Because the individual compounds in the mixtures are additive narcotics, the toxic unit concept can be applied to AE mixtures if the freely dissolved concentrations can be calculated.

5. Scope and outline of this thesis

Following the equilibrium partitioning theory, the freely dissolved concentration plays a key role in the risk assessment of contaminated sediment, as it links sediment sorbed concentrations to internal concentrations. However, the sorption behavior of surfactants to environmental matrixes is still poorly understood. From the currently available sorption data for surfactants it is not clear to which extent the various sorption phases in a sediment contribute to the overall sorption coefficient. Furthermore, the generic sorption models that are fitted to the sorption data for surfactants make it impossible to incorporate the chemical properties of surfactants into meaningful relationships. The measured concentrations in field sediments from monitoring studies are therefore difficult

to interpret. The relatively low concentrations of total AE mixtures in field sediments present another challenge for sorption studies with individual concentrations.

On the other hand, it has also not been carefully examined whether the equilibrium partitioning (EqP) theory also works for nonionic surfactants. There are no published data on sediment toxicity tests with AEs or other nonionic surfactants. The AEs are known to be readily biodegradable under both aerobic and anaerobic conditions, while many test organisms also have the capacity to biotransform AE once these have accumulated in their tissues. The presence of sediment sorbed AE may thus be an additional route of exposure for organisms inhabiting in the sediment phase.

The aim of the thesis is to improve the understanding of the sorption behavior of AE, to provide a more scientific basis for the risk assessment of AE concentrations that have been detected in coastal sediments. Passive samplers facilitate the analysis of the freely dissolved concentrations, but have not yet been optimized for the analysis of surfactants. Though, once these are validated, they could be used in sorption studies without having to worry about inseparable fractions in the aqueous phase. Furthermore, passive samplers could be used to determine freely dissolved concentrations in sediment toxicity tests with AE, and thereby allow a more detailed investigation of the equilibrium partitioning theory. The following stepwise approach was therefore used in this thesis with the objectives:

1. to investigate whether solid phase microextraction (SPME) can be used as a passive sampler method to analyze the freely dissolved concentrations of surfactants in environmental matrixes at marine conditions.

2. to study the sorption behavior with a broad set of AE homologues on marine sediments. An understanding of the most relevant sediment properties should provide more insight in the influence of the surfactant's molecular structure, and explain the varying sorption affinity to different sediments.

3. to apply the knowledge of the sorption behavior for one sediment together with the benefit of the passive sampler, in order to investigate whether the assumptions made in the EqP approach are valid for a single AE homologue.

Chapters 2 to 4 provide a more technical section of this thesis, and together show how, and to what extent, the SPME method can be applied to measure chemicals with a complicated molecular structure like surfactants. **Chapter 2** describes the applicability of SPME for a series of individual alcohol ethoxylates in varying matrixes, including the presence of micelles, sediment and simple mixtures of AE homologues. **Chapter 3** investigates whether the SPME method can also be applied for surfactants with a negatively charged head group. This research was focused on some individual linear alkylbenzene sulfonate structures (LAS), the most widely applied anionic surfactant. In **Chapter 4**, the partition coefficients of AE to the polymer coating of the SPME fiber itself are studied, since these partition coefficients may function as predictors of the hydrophobicity. In a preliminary study using a large dataset collected from literature with

additional experimental data, the SPME data are compared to K_{ow} data, by looking in detail at the molecular interactions that drive the partitioning of organic chemicals to both the polymer phase and octanol.

Chapters 5 to 7 describe the outcome of a variety of sorption tests with AE. **Chapter 5** links the technical section to the studies on the sorption behavior of AE, and shows how the SPME can be applied in sorption experiments with AE. Furthermore, a sorption model is suggested based on the data of three individual AE homologues. **Chapter 6** presents data for an additional seven AE homologues and presents data for a single homologue on six marine sediments and two clay minerals. The sorption model presented in Chapters 5 and 6 is refined in **Chapter 7** to explain sorption behavior of mixtures of AE.

Chapter 8 presents data for sediment toxicity tests with a single AE homologue, in relation to the EqP assumptions. In the concluding **Chapter 9**, the results of the preceding work are discussed in the context of risk assessment of surfactants.

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Chapter 2

Analysis of Freely Dissolved Alcohol Ethoxylate Homologues in Various Seawater Matrixes Using Solid-Phase Microextraction

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ABSTRACT

Solid-phase microextraction fibers (SPME) were tested as tools to determine freely dissolved alcohol ethoxylate (AE) surfactants in seawater matrixes. Partitioning of a wide range of AE homologues into a 35-µm polyacrylate fiber coating was linearly related to aqueous concentrations as low as submicrograms per liter, with high reproducibility. The exposure time needed to reach equilibrium between aqueous phase and the SPME fiber depended on the fiber-water partitioning coefficient (K_{fw}) of the AE homologue. Specific attention was given to the influence of various matrixes on the analysis via SPME. The presence of sediment increases the uptake kinetics of AE homologues for which diffusion in the aqueous phase is rate-limiting. The K_{fw} in equilibrated systems was not affected by the presence of other homologues, micelles or varying amounts of sediment phase. SPME is therefore a suitable tool for analysis of AE in sorption studies and sediment toxicity tests. A strong linear relation was observed between K_{fw} and the hydrophobicity of the AE homologue, using estimated octanol-water partition coefficients. This relation can be used to predict the partitioning coefficient of any AE homologue to the SPME fiber, which facilitates the analysis of complex mixtures.

INTRODUCTION

Alcohol ethoxylates (AE) are nonionic surfactants used worldwide in large quantities, mainly for laundry cleaning products. Commercial products are complex mixtures of AE homologues with alkyl chain lengths usually ranging between 10 and 16 carbon atoms and a polar chain of usually 1-20 ethoxylate (EO) units. The alkyl chain of AE is generally linear, but can consist up to 50% of mono-branched (2-alkyl substituted) alkyl chains, and ~10% of the total AE production has highly branched alkyl chains (*1*). The long alkyl chains make most AE relatively hydrophobic, and as a consequence, once in the environment they tend to accumulate in the sediment phase. Coastal sediments close to industrialized Spanish areas all contained AE with total concentrations ranging between 37 and 1300 µg/kg (*2*). A surface sediment from the interior of the Bay of Cadiz (southwest Spain) showed a AE distribution with enrichment of the longer alkyl chain AE, with total concentration of 35 µg/kg for the C_{12}-ethoxymers, up to 282 µg/kg for C_{18}-ethoxymers, including branched homologues (*3*). Although detailed studies on effluent concentrations in North America and Europe were recently published (*4,5*), data on AE concentrations in freshwater systems is very limited (*6*).

The sediment is the main environmental compartment where alcohol ethoxylates accumulate. From a risk assessment point of view, it is important to develop proper sampling techniques for analyzing concentrations of ethoxylates in sediment pore water, because this compartment is generally considered to be the main route of exposure to sediment dwelling organisms. Obtaining reliable aqueous concentrations (C_{aq}) in sediment phases is difficult though. When centrifugation of sediment samples is used to collect pore water, the supernatant may still contain nonseparable particulate matter (NSM) and dissolved organic matter (DOM) with a substantial amount of AE bound to it (*7*). As hydrophobic chemicals have a high affinity for DOM, and clay minerals can be strong sorbents for polar or ionized organic molecules, this appears to be a relevant problem when determining truly aqueous concentrations of AE from sediment suspensions or other matrixes.

The freely dissolved concentration in a sediment-water suspension can also be determined indirectly via passive samplers (*8-11*), which do not require separation of the water and sediment phase. Solid-phase microextraction (SPME) is a sampling technique based on passive diffusion of freely dissolved chemicals from the water phase into a thin polymer coating around a piece of glass fiber. The affinity of a chemical for the polymer phase depends mainly on the hydrophobic character of the molecule, resulting in a unique polymer-water partitioning coefficient (K_{fw}) for each chemical. With a well-established K_{fw}, the freely dissolved concentration in the suspension can be derived directly from the concentration in the polymer phase. The extraction phase volume for SPME is small compared to the sample volume. Consequently, in most cases, a negligible fraction from the aqueous phase will be extracted. In pure aqueous solutions, the depletion of the aqueous phase is determined by the fiber-water partition coefficient and the volume ratio fiber coating versus the volume of the aqueous phase. In sediment suspensions, negligible

depletion will also be obtained if the volume of sediment is high enough to balance the loss of chemical from the aqueous phase due to uptake into the fiber. In those cases, the depletion will often be completely negligible, because the fiber volume is often much lower than the volume of the sediment. The concentration in the aqueous phase can then simply be calculated from the concentration in the fiber and the fiber-water partition coefficient.

This specific tool to measure truly dissolved concentrations is therefore also called negligible depletion SPME (nd-SPME) (*8,12*). Furthermore, equilibrium is reached relatively fast compared to other passive samplers since the thickness of polymer coating is typically in the range of 7-100 µm. Although partitioning kinetics depends strongly on the compound's molecular properties and agitation of the test solution, several studies indicated that uptake kinetics of a contaminant from the aqueous phase to the SPME fiber can also be influenced by matrix effects (*13-16*). Particularly when tests are performed under nonequilibrium conditions, such phenomena may influence the outcome of SPME analysis. Since matrix effects often involve increased kinetics, for some compounds they could shorten the necessary equilibration times.

Although well validated for many nonpolar organics (e.g. refs (*8,17-19*)), SPME has only once been applied to a single alcohol ethoxylate in solution (*20*). In that study SPME was part of an on-line detection system. Several studies using SPME have been performed on nonylphenol ethoxylates (NPEO). However, these studies include either only the shortest ethoxylates (*21,22*) or the complex mixtures (*23*).

The aim of this study was to test the ability of the SPME method to analyze the freely dissolved concentration of individual nonbranched AE homologues in seawater and marine sediment-water systems via nd-SPME. The optimization of the method included first the selection of an appropriate polymer phase. Subsequently, equilibration times of several AE were determined in seawater via kinetic studies. Testing a set of individual alcohol ethoxylates, differing in either ethoxylate chain length or alkyl chain lengths, allowed us to examine the relationship between the partition coefficient to the SPME and the hydrophobicity of the compounds. The calibration of the SPME relative to the dissolved concentration was extended for several alcohol ethoxylate homologues to aqueous concentrations above the critical micelle concentration (cmc), to determine how measurements of freely dissolved analytes are affected in the presence of micelles. Further investigations on possible matrix effects on the SPME method included experiments with simple and more complex mixtures of pure homologues, and studying the effects of the presence of varying amounts of a sediment phase, and therewith suspended particles and dissolved organic matter.

MATERIALS AND METHODS

Experimental Design

A small set of pure alcohol ethoxylate homologues were used as model compounds for the development of the SPME method. The first goal of this study was to determine which polymer phase could best be used as a partioning based extraction phase. Because we would like to apply the technique to environmental samples as well as in laboratory studies, we are in particular interested in a technique that can cover a broad range of concentrations. Moreover, because we want to avoid the possibility of competition effects in case of application to mixtures, the sampling method should be based on absorption. After examination of the time needed to reach equilibrium for one of the compounds, $C_{14}EO_{8,}$ between three different types of custom made SPME fiber materials, the fibers were then exposed to a broad range of concentrations of $C_{14}EO_8$ in seawater for a sufficiently long equilibration period. Based on these findings, one of the SPME fibers was selected to study the uptake kinetics of several other homologues, $C_{10}EO_8$, $C_{12}EO_8$, $C_{14}EO_4$, $C_{14}EO_{11}$, and $C_{16}EO_8$. With the optimized equilibration periods, measurements obtained for individual solutions of $C_{10}EO_8$, $C_{12}EO_8$, and $C_{14}EO_8$ were then compared to SPME extractions from mixtures of these three AE. Since commercial AE mixtures often contain up to hundreds of different AE homologues, we also examined the seawater-fiber partitioning coefficients of a complex mixture of AE, which consisted of C_{12} homologues with a range between 2 and 18 EO units. To test the influence of different seawater matrixes on the analysis of freely dissolved individual AE with SPME, we determined (i) isotherms covering concentrations both below as above cmc for $C_{14}EO_8$, $C_{12}EO_8$, and $C_{14}EO_{11}$; (ii) uptake kinetics for $C_{14}EO_8$ in sediment solutions; and (iii) isotherms for $C_{10}EO_8$, $C_{12}EO_8$, and $C_{14}EO_8$ in sediment slurries.

Chemicals, SPME fibers and sediment

The individual poly(ethylene glycol) alkyl ethers $C_{10}EO_8$, $C_{12}EO_8$, $C_{14}EO_4$, $C_{14}EO_6$, $C_{14}EO_8$, $C_{14}EO_{11}$, and $C_{16}EO_8$ and the AE mixture of C_{12}-ethoxymers ($C_{12}EO_{\sim 9}$) were purchased at Fluka Chemie GmbH (Buchs, Germany) and were of at least 98% purity (TLC) or higher. The actual molar EO distribution pattern of $C_{12}EO_{\sim 9}$ was determined experimentally using several pure homologues as reference standards. Except for KBr (Sigma-Aldrich, Zwijndrecht, The Netherlands), the salts used for the preparation of artificial seawater (GP2 in ref (*24*)) were from Merck (Amsterdam, The Netherlands). The biocide NaN_3 (Merck, Darmstadt, Germany) was added to the seawater at 100 mg/L, formaldehyde (37% solution without methanol) was from Fluka. Methanol was always HPLC quality (Labscan, Dublin, Ireland) and highly pure deionized water ($R \geq 18$ MΩ) was prepared by a water purification system (Millipore Waters, Amsterdam, The Netherlands). SPME fibers with an internal diameter of 110 µm and either a 28.5-µm poly(dimethylsiloxane) (PDMS) coating (volume 12.4 µL/m), 35-µm polyacrylate (PA) coating (15.4 µL/m) or a 7-µm PA coating (2.6 µL/m) were purchased from Polymicro Technologies (Phoenix, AZ), cut to the desired

length (generally 2.0-6.0 cm, depending on the expected partitioning coefficient) and further used as received. An off-shore North Sea sediment (north of the "Frisian Front" area) was collected using a box corer, and an estuarine sediment was collected at a mud flat in the Eastern Scheldt ("Oesterput" location) by wet sieving over 500 µm. Organic carbon contents (NA 1500 NCS elemental analyzer, Fisons) were 0.27% and 1.2% of the dry weight, respectively, and the fraction of particles of <8 µm (Malvern Laser Particle Sizer) were 11.0 and 14.7%, respectively.

Spiking aqueous solutions and extraction methods

For all tests in this study, a certain amount of AE dissolved in methanol was added to 40-mL glass test vials with PTFE-lined screw caps (Supelco, Bellefonte, PA), after which the solvent was evaporated off. Pilot experiments showed that sorption of $C_{14}EO_8$ from an aqueous phase to the glass wall was directly related to the amount of headspace, and could reduce the aqueous concentration by >90% of the nominal concentration (data not shown). Minimizing the air-water interface (and probably also contact time of this phase with the glass wall) to only a small air bubble strongly reduced this problem to a minimum. Test vials were therefore always filled up as much as possible. To dissolve AE from the glass wall and obtain steady concentrations, the test vials were kept for 48 h on a shaking device (Rock 'n' roller, Snijders Scientific B.V., Tilburg, The Netherlands), before introducing SPME fibers.

After taking out exposed SPME fibers, they were blotted dry on a tissue, quickly wiped along a wetted tissue, and put in HPLC vials with PTFE septum caps (Bester BV, Amsterdam, The Netherlands). The AE was extracted from the polymer phase in 0.5-1 mL of methanol and left at least 24 h at -20 °C before analysis. Negligible amounts of AE were found in repeated fiber extracts. SPME fibers were discarded after use.

To isolate the AE from seawater samples, SPE tubes (500 mg of C_{18} Supelclean™ ENVI™ from Supelco) were used that were activated by passing 5 mL of methanol followed by 5 mL of pure water. After elution of 10 mL of the aqueous sample, the columns were flushed with 10 mL of pure water to remove the excessive amount of salt, and taken to dryness by applying vacuum for a several seconds. AE was eluted with 8 mL of methanol, which was collected in glass vials and kept at -20 °C until analysis. The recovery of the SPE procedure was tested in triplicate for all AE by spiking a weighed amount of methanol stock (<0.5 mL) in 5 mL of clean GP2, which was transferred to a conditioned SPE column. After this solution was drawn through the column, another 5 mL of GP2 was added on the column and the SPE was further treated as described above. All solvent volumes were checked by weighing. Sampling of the fibers and aqueous phase was always performed as described above, unless stated otherwise. Except for kinetic studies, the SPME fibers were always equilibrated with the medium for 96 h.

Selection of fiber coating and thickness

The uptake of $C_{14}EO_8$ from the seawater in the fiber coatings was performed in duplicate at 20 µg/L. Several SPME fibers were sampled during 150 h. Based on this initial equilibration experiment, a 96 h exposure was selected to obtain seawater-SPME isotherms. For the isotherms, test vials were spiked in triplicate from 0.5 to 900 µg/L in which a 7-µm PA fiber, a the 35-µm PA fiber, and a 30-µm PDMS fiber were exposed simultaneously, each fiber with a different length to identify them afterward.

Kinetics of uptake to SPME in seawater

The extractions with the 35-µm PA fibers gave the best reproducibility of the tested fibers. Fiber concentrations were linearly related to aqueous concentrations of $C_{14}EO_8$ (Figure S1 in the Appendix). The PA fiber was selected to study the uptake kinetics of $C_{10}EO_8$, $C_{12}EO_8$, $C_{16}EO_8$, $C_{14}EO_4$, and $C_{14}EO_{11}$. A separate test vial was prepared for each time point with initial concentrations of 100 µg/L, except for $C_{10}EO_8$, for which 500 µg/L solutions were prepared because the affinity of this compound for polyacrylate was relatively low. Two fibers were added to each test vial.

Calibration of SPME in seawater: effect of mixtures and micelles

Isotherms for $C_{10}EO_8$, $C_{12}EO_8$, $C_{14}EO_6$, and $C_{14}EO_{11}$ were obtained using seawater solutions ranging from as low as the detection limit allowed (depending on the fiber-water partition coefficient) to just below the expected cmc (Table 1). Detection limits in the aqueous samples in the setup used in this study vary from 0.02 µg/L ($C_{16}EO_8$) to 14 µg/L ($C_{10}EO_8$). For all compounds, except for $C_{14}EO_6$, two fibers were exposed per test vial. Only one SPME fiber was used for $C_{14}EO_6$ to minimize the depletion of the aqueous phase to ~11%. To test the influence of multiple compounds present in a sample, first a simple AE mixture composed of $C_{10}EO_8$, $C_{12}EO_8$, and $C_{14}EO_8$ was used. Duplicate fibers were exposed to three different samples where concentrations of the compounds in this mixture were kept equal (30, 80, and 300 µg/L). These SPME data were compared to results obtained with solutions of each individual AE homologue in seawater. The isotherms of most ethoxymers present in the mixture of C_{12}-ethoxymers were obtained using two SPME fibers per vial, with total AE concentrations ranging between 78 and 27500 µg/L.

For $C_{12}EO_8$, $C_{14}EO_8$, and $C_{14}EO_{11}$, solutions were prepared with concentrations ranging from a factor of 100 below the cmc and up to 2-fold above the cmc in fresh water (Table 1). For $C_{14}EO_8$, one fiber was added to each test vial while for $C_{12}EO_8$ and $C_{14}EO_{11}$ two SPME fibers were added.

The effect of sediment on uptake kinetics

To test the uptake rate of AE in 35-µm PA SPME fibers in sediment-seawater suspensions, 10 µg of $C_{14}EO_8$ was spiked in two vials as described above. To the first vial, 60 mg of wet estuarine sediment was added (63% dw) and 200 mg of wet marine sediment (79% dw) was added to the second vial. Both were filled up with 39 mL of GP2, and 0.4 mL of a 37%

formaldehyde solution was added to inhibit microbial degradation. After 48-h shaking, four SPME fibers were added to the test vials, which were taken out of the suspensions after 1, 4, 24, and 78 h. Any sediment particles still attached to the fibers, were wiped off with on the wetted tissue. When the last SPME fibers were taken out, the vials were centrifuged at 2000 rpm, after which 10 mL of the supernatant was analyzed after elution on a SPE column (see above). The uptake kinetics in the presence of sediment were compared to that in the seawater solution of $C_{14}EO_8$.

Potential role of suspended particles and dissolved matter on the analysis of the aqueous concentration in a marine sediment-water system

Isotherms for 35-µm PA fibers in seawater in the presence of sediment were obtained from a sorption experiment, which followed the sorption of AE on the same marine sediment as used in the kinetic study described above. The sorption study has been described in detail in another paper (*25*). Briefly, solutions with either $C_{10}EO_8$, $C_{12}EO_8$, and $C_{14}EO_8$ were prepared in the presence of varying amounts of the marine sediment similar to the procedures described in the previous paragraph. Fibers were exposed during 96 h, after which fibers and aqueous samples were extracted as described above.

Analysis of alcohol ethoxylates using LC-MS

Concentrations of AE in the methanol extracts were analyzed on a LC-MS system consisting of a Perkin Elmer (Norwalk, CT) Series 200 degasser, PE 200 LC pump, and a PE 200 LC autosampler connected via a reversed-phase C_{18} column (Chromspher 5, 100x3 mm, Chrompack International BV, Middelburg, The Netherlands) to a high performance, hybrid triple-quadrupole/linear ion trap mass spectrometer (Q-TRAP®, MDS Sciex Applied Biosystems/MDS Sciex Instruments, Foster City, CA). The interface was a TurboIonSpray® source, used in the positive mode. A 20 µl sample was injected using an eluent flow of 0.6 mL/min. Eluent consisted of 90% methanol and 10% water. It further contained 5 mM NH_4^+ (as ammonium acetate) in order to detect most of the AE as a positive adduct composed of the parent compound with NH_4^+ $[m + NH_4]^+$. Further details are on the detection of AE via LC-MS are given in the Appendix (section B). The software used for operating the LC-MS and quantifying of the peak areas was Analyst 1.4.1 (AB/MDS Sciex Instruments). Several calibration series were run during one batch analysis to correct for increased or decreased response of the MS. Carry-over of the compound from a highly concentrated sample to a blank was negligible, but still blanks were inserted after each calibration series.

Data analysis

Details on data analysis are presented in the Appendix. The derived K_{fw} values were compared with estimates of the octanol-water partitioning coefficient according to atom/fragment contributions used by SRC's KowWin Program (v1.67), which uses data from Meylan and Howard (*26*) and is part of the EPI-Suite package (US-EPA, 2000).

RESULTS AND DISCUSSION

Selection of fiber coating and thickness

In order to select the most appropriate SPME fiber, we tested two different coating polymers, both of which are nonporous materials. For polyacrylate, we studied fibers with a 35-µm coating as well as fibers with a thinner, 7-µm, coating. Detailed results are presented in Figure S1 and accompanying text in the Appendix. A 35-µm polyacrylate fiber was selected for further studies because (i) the sorption was linear, (ii) acceptable equilibration time, and (iii) acceptable sensitivity.

Kinetics of uptake to SPME in seawater

The water-SPME partitioning kinetics of a set of AE homologues ($C_{14}EO_4$, $C_{14}EO_{11}$, $C_{10}EO_8$, $C_{12}EO_8$, and $C_{16}EO_8$) was followed over time in order to test whether 96 h was sufficient to ensure equilibrium. The concentrations in duplicate fibers corresponded well with each other; in each test vial they differed between 2 and 5%, except for $C_{14}EO_4$, where duplicate fibers differed 17% on average. For the two most hydrophobic ethoxylates, $C_{16}EO_8$ and $C_{14}EO_4$, the two fibers in the test vial of 30 h contained respectively 22% and 42% of the total initial amount of AE in the test vial. Since the final aqueous concentration was lower than the initial concentration for these two compounds, the initial kinetics were faster (*27*), with a shorter time until equilibrium as a result. Details on calculation of the true elimination rate constant are presented in section A of the Appendix. From the true elimination rate constant $k_{e,true}$ and the fiber-water partitioning coefficient, the uptake rate constant was calculated (Table 1).

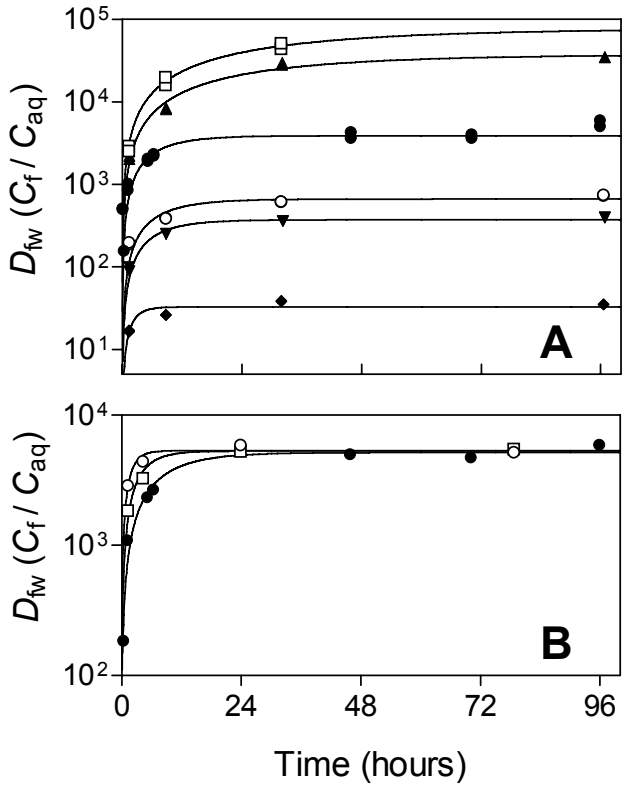

Figure 1. The fiber-water distribution coefficient (D_{fw}) as a function of time, for: **(A)** Seawater solutions of $C_{14}EO_4$ (□), $C_{16}EO_8$ (▲), $C_{14}EO_8$ (●), $C_{14}EO_{11}$ (○), $C_{12}EO_8$ (▼), and $C_{10}EO_8$ (◆). **(B)** Sediment suspensions compared with seawater solutions (●), using $C_{14}EO_8$ and either a marine sediment (○) or a estuarine sediment (□). The solid lines represent the fits of a modification of eq S2 (in the Appendix) by using D_{fw} instead of C_f.

In Figure 1A the accumulation of the different AE homologues in the fiber until equilibrium is shown. Clearly, the K_{fw} depends on molecular properties of AE. In Figure S2 in the Appendix, the log-transformed rate constants are plotted against the corresponding fiber-water partition coefficients (log K_{fw}).

Table 1. Critical Micelle Concentrations (cmc) in Seawater and Buffer, Uptake Rate Constants (k_u), Polyacrylate-Seawater (K_{fw}), and Octanol-Water (K_{ow}) Partition Coefficients of Alcohol Ethoxylates.

	cmc [a] seawater (mg/L)	cmc [b] buffer (mg/L)	k_u [c] (L $kg^{-1}h^{-1}$)	Log K_{fw} [d] ± SE	n [d] ± SE	N [e]	Log K_{ow} [f]
$C_{10}EO_8$		554.6	19	1.49 ± 0.01 [g]	0.97 ± 0.01	16	1.59
$C_{12}EO_8$	42	59.6	67	2.51 ± 0.01 [g]	0.95 ± 0.01	22	2.57
$C_{14}EO_8$	2.9	6.4	614	3.62 ± 0.01 [g]	1.01 ± 0.01	23	3.56
$C_{16}EO_8$		0.7	717	4.57 ± 0.03 [h]		1	4.54
$C_{14}EO_4$		2.9	836	4.89 ± 0.09 [h]		1	4.65
$C_{14}EO_6$		4.4		4.02 ± 0.03 [i]	0.95 ± 0.02	4	4.11
$C_{14}EO_{11}$	5.8	10.6	103	2.84 ± 0.04 [j]	1.03 ± 0.02	9	2.73
$C_{12}EO_2$				4.22 ± 0.02 [k]	0.98 ± 0.03	3	4.22
$C_{12}EO_3$				3.91 ± 0.01 [k]	0.95 ± 0.01	3	3.95
$C_{12}EO_4$				3.68 ± 0.02 [k]	0.94 ± 0.01	3	3.67
$C_{12}EO_5$				3.38 ± 0.01 [k]	1.00 ± 0.01	3	3.40
$C_{12}EO_6$				3.03 ± 0.03 [k]	1.10 ± 0.02	3	3.12
$C_{12}EO_7$				2.74 ± 0.06 [k]	1.14 ± 0.05	3	2.85
$C_{12}EO_9$				2.46		2	2.30
$C_{12}EO_{10}$				2.20		2	2.03
$C_{12}EO_{11}$				1.95		2	1.75
$C_{12}EO_{12}$				1.76		1	1.48

[a] Critical micelle concentration (cmc) in artificial seawater. [b] Calculated according to:
log cmc = 1,65 - 0.496#C + 0.0437#EO (29). [c] k_u = calculated uptake rate constant to 35-µm PA fiber, see section A of the Appendix.[d] Determined using
Log C_f = Log K_{fw} + n·Log C_{aq}, *with both C_f and C_{aq} in µg/L. [e] Number of samples used in the isotherm to obtain Log K_{fw}. [f] Calculated using atom/fragment contributions from (26).[g] from isotherm for data on single compound and mixed AE solutions in Figure 2.[h] from kinetic data in Figure 1A.[i] data not shown [j] from data < cmc in Figure 3 [k] determined with the C_{12}-ethoxymer mixture*

Although limited data are available for these surfactants, a similar pattern is visible as demonstrated by Verbruggen *et al*. (*28*), who plotted the rate constants against polyacrylate-water distribution coefficients for a broad set of organics. Up to log K_{fw} 3.5, the uptake rate constant increases with K_{fw} (Table 1), because the diffusive resistance in

the polyacrylate phase is limiting the uptake process (*18*). Above log K_{fw} 3.5, the rate-limiting step is diffusion through the aqueous diffusion layer and the uptake rate constant is constant. A more detailed discussion about rate-limiting steps in fiber uptake is given by Vaes *et al*. (*18*). Using the "depletion-corrected" true elimination rate constants, $C_{10}EO_8$ and $C_{14}EO_8$ required 6 and 24 h, respectively, to reach 95% of the equilibrium concentration in the polyacrylate phase. For $C_{16}EO_8$ and $C_{14}EO_4$, however, 180 and 315 h are required to reach 95% steady state in nondepletive solutions with similar stirring regime. To decrease the equilibration time for AE homologues with a high K_{fw}, the rate of diffusion in the aqueous phase surrounding the fiber should be increased, e.g., through faster stirring of the solution, or, as discussed below, by facilitated transport.

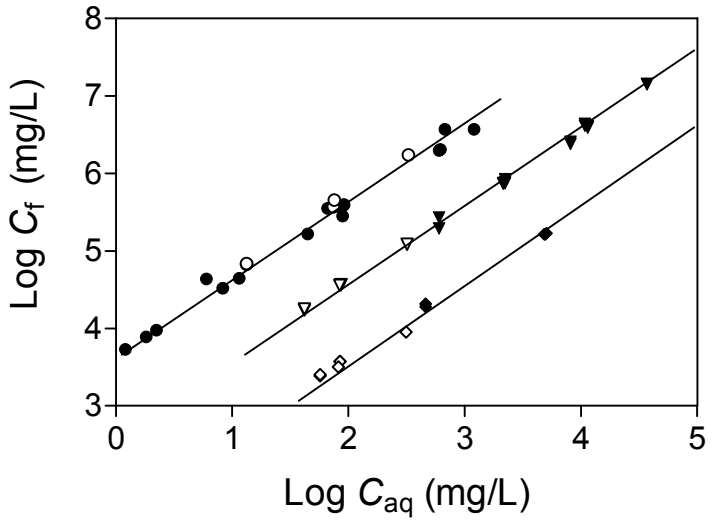

Figure 2. Concentrations of $C_{10}EO_8$ (◇,◆), $C_{12}EO_8$ (▽,▼), and $C_{14}EO_8$ (○,●) in 35-µm polyacrylate SPME fibers (C_f) plotted against seawater concentrations (C_{aq}). Measurements from single-compound solutions are presented as closed symbols; open symbols are data from extractions from solutions with a mixture of the three compounds.

Calibration of SPME in seawater: effect of mixtures and micelles

The linear isotherm found for $C_{14}EO_8$ indicated that the extraction of AE into the polyacrylate is a simple partitioning process. Also the uptake of $C_{14}EO_6$ in the SPME fibers was linearly related to the aqueous concentration (Table 1). Hence, there should be no competition for specific binding sites in the polyacrylate when AE were present in a mixture. The uptake of AE homologues from the mixtures confirmed this assumption as the data overlap with measurements from single compound solutions (Figure 2). The isotherms obtained from the data of both single compound and mixtures of $C_{10}EO_8$, $C_{12}EO_8$ and $C_{14}EO_8$ were nearly linear, with slopes (±SE, *n*) of 0.94 (±0.015, 16), 0.97 (±0.01, 22) and 0.99 (±0.02, 23), respectively (Table 1). C_{12}-AE with more than 12 EO units were not detected in the fiber extracts exposed to the complex mixture, probably due to low concentrations in combination with a low affinity of these compounds for polyacrylate (K_{fw}). Those

homologues in the mixture for which isotherms were obtained, also showed slopes close to unity (Table 1).

When AE concentrations in water are increased above the critical micelle concentration (cmc), the concentration of AE in the monomeric form remains constant and all extra added AE will form micelles (*29*). A similar pattern was observed with the SPME fibers. The concentration of the AE in the fiber (C_f) increased linearly with aqueous concentration (C_{aq}) when SPME fibers were exposed to a series of increasing concentrations of $C_{12}EO_8$, $C_{14}EO_8$ and $C_{14}EO_{11}$ in artificial seawater, until at some point a maximum was reached and no further increase of C_f was observed with increasing C_{aq} (Figure 3). The aqueous concentration where the maximum concentration in the fiber is reached in Figure 3, is the cmc in seawater. These values are 1.4-2.2 times lower than the calculated cmc for these compounds in pure water according to Huibers *et al*. (*29*) (Table 1). Such a decrease in the cmc of alcohol ethoxylates was not found when artificially prepared "hard" river water was used (*30*).

Usually, cmc are determined by the analysis of the surface tension. This study showed that the SPME analysis is an alternative and simple method to determine cmc values for AE homologues based on measured concentrations of the monomeric form. As far as we know, these cmc values are the first published for seawater. Micelles are either too large to partition into the polymer phase, or too polar since the ethoxylate chains form the outside of the micelles. The tests with concentrations above the cmc also clearly showed that only the freely dissolved, monomeric form, of the nonionic surfactants contributed to the concentration in the polymeric phase on the SPME fibers. This again shows the strength of the SPME analysis performed in the nondepletion mode for measuring freely dissolved concentrations in complex matrixes.

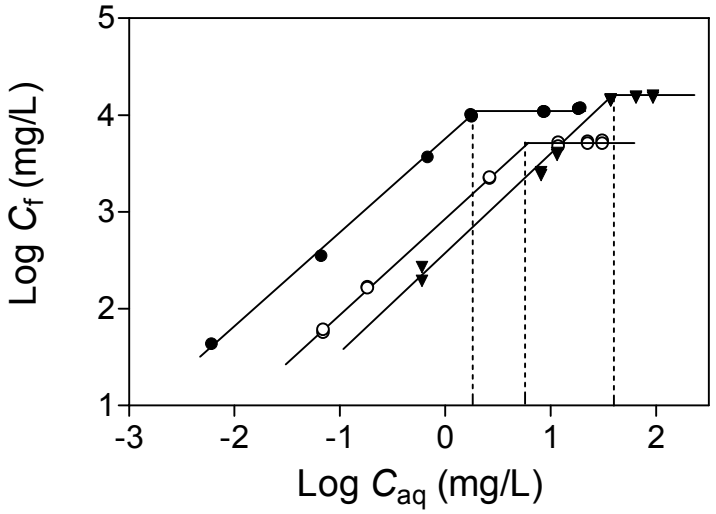

Figure 3. SPME measurements (C_f) at seawater concentrations (C_{aq}) from below to above critical micelle concentrations (cmc) for $C_{14}EO_8$ (●), $C_{12}EO_8$ (○), and $C_{14}EO_{11}$ (▼). The broken lines indicate the derived cmc values.

The effect of sediment on uptake kinetics

Before we could test the influence of sediment on the isotherms of AE to SPME fibers, information on the partitioning kinetics in the presence of sediment was needed, to confirm that the exposure period was sufficient for establishing an equilibrium between fiber and seawater sediment suspensions. This is, in particular, relevant because other studies have shown that the kinetics can be influenced by the matrix (presence of humic substances for example) (*13-15*). The effect of the presence of sediment on the uptake kinetics was studied for $C_{14}EO_8$. A plot of the fiber-water distribution coefficient D_{fw} (C_f / C_{aq}) against the exposure time is presented in Figure 1B. The uptake of $C_{14}EO_8$ in the fiber in the presence of sediment appeared to be faster than uptake in seawater alone: the time at which 95% of equilibrium was reached, was 5.5 and 11.6 h for marine and estuarine sediment, respectively, while 23.8 h were needed to reach this in seawater only. Although the amount of $C_{14}EO_8$ extracted by SPME was ~25% of the amount dissolved in the aqueous phase, the extracted amount was readily compensated for by desorption from the sediment. This depletion of the aqueous phase did not disturb the sediment-water equilibrium since ~99% of the AE in the system was bound to the sediment. The observed effect of the sediment phase on the kinetics of the partitioning of chemicals in SPME fibers has also been observed for fiber uptake of fluoranthene in the presence of dissolved organic matter (DOM) (*14*). The uptake rate constant of $C_{14}EO_8$ (log K_{fw} = 3.67) is already at the maximum plateau (see Figure S2 in the Appendix), and diffusion in the aqueous phase is therefore the rate-limiting step (*18*). Enhanced kinetics has been observed previously. One explanation is direct contact, but a more likely explanation is facilitated transport. A detailed study on facilitated transport by Mayer et al. (*16*) mentions that "(…) those medium constituents that improve the solubilization properties of the medium, for instance by complexation, can increase the diffusive mass transfer". Both particulate-bound or DOM-bound chemicals may enhance uptake kinetics, because of facilitated transport in the aqueous diffusion layer surrounding the fiber. Therefore, AE homologues with a high K_{fw} will thus have a strongly reduced equilibration time when sediment is present, which is very convenient for the use of SPME to analyze concentrations of individual AE homologues in sediment-water systems.

Potential role of suspended particles and dissolved matter on the analysis of the aqueous concentration in a marine sediment-water system

Since fiber uptake kinetics were at least not retarded by the presence of sediment, an exposure time of 96 h was considered sufficient to determine isotherms for $C_{10}EO_8$, $C_{12}EO_8$, and $C_{14}EO_8$ between the polymer and aqueous phase in sediment-seawater solutions. In Figure 4, the concentrations in the SPME fibers (C_f) are plotted against the AE concentrations measured in the supernatant (C_{aq}) of these sediment-seawater systems. The isotherms are almost linear and overlap with SPME measurements in vials with only seawater solutions, which were run in the same series. Although the amount of sediment in

the test systems varied considerably, no effect on K_{fw} was observed. Apparently, the influence of nonseparable matter (NSM) on the concentration of AE in the supernatant was negligible for the amounts of sediment, up to 50 g dw/L, used in the test systems. In bulk sediment phases, however, depending on the affinity of the AE homologue for the various types of NSM, the fraction of bound AE present in the pore water may be so large that supernatant-derived C_{aq} will overestimate freely dissolved concentrations. For example, in a system with 10 mg/L dissolved organic carbon (DOC), 10% of a compound with a K_{oc} of 10^4 is bound to DOC. The data in Figure 4 also show that the measured C_f can be used to determine the freely dissolved concentration of AE in the sediment-seawater solutions, using the K_{fw} established for each AE homologue in seawater only systems. SPME might therefore be a more suitable tool to determine freely dissolved aqueous concentrations compared to analysis of the concentration in pore water collected after centrifugation of a sediment phase.

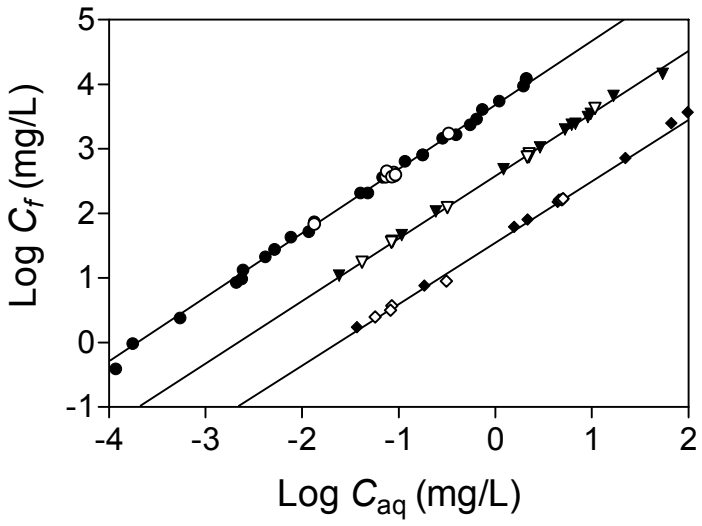

Figure 4. Concentrations of $C_{10}EO_8$ (◇,◆), $C_{12}EO_8$ (▽,▼), and $C_{14}EO_8$ (○,●) in 35 -µm polyacrylate SPME fibers (C_f) plotted against aqueous concentrations (C_{aq}). Measurements from vials with sediment suspensions are presented as closed symbols; open symbols are data from vials with seawater solutions of the single homologues (for experimental details see text and ref (*25*) or Chapter 5).

Dependency of fiber-water partition coefficients on physico-chemical properties

A plot between estimated octanol-water partition coefficients and measured fiber-water partition coefficients is shown in Figure 5, using K_{fw} (at 1 mg/L) and EPI-Suite-K_{ow} values (Table 1). Similar to predicted K_{ow} values, each carbon atom in the C-chain contributes positively to the K_{fw}, while additional EO units decrease the affinity of AE homologues to the polyacrylate. Although several data points in Figure 5 are based on one or two single measurements, a clear correlation between K_{fw} and estimated K_{ow} values exists:

$$\text{Log } K_{fw} = 1.04\ (\pm 0.02) \cdot \text{Log } K_{ow} - 0.16\ (\pm 0.06);\ (\pm SE,\ n = 11,\ r^2 = 0.997) \quad (6)$$

The EPI-Suite™ K_{ow} values are excellent indicators of the K_{fw} values measured with the polyacrylate SPME fibers, for AE homologues with a wide range of EO-units and carbon chain lengths. The measured K_{fw} values are of the same magnitude as the estimated K_{ow} values. For other polar organics such as phenols, substituted anilines and nitrobenzenes, which all have well-established K_{ow} values, the polyacrylate-water partition coefficients were also of the same magnitude as the K_{ow} (*18*). Like AE, these polar compounds can form hydrogen bonds.

Remarkably, however, the EPI-Suite-derived K_{ow} values for AE are 2-3 orders of magnitude lower than the K_{ow} values often used (*31-33*) and which are based on work by Leo and Hansch (*34*) with modifications by Roberts (*35*). A more detailed analysis of the influence of the structure of AEs on partitioning behavior is presently ongoing.

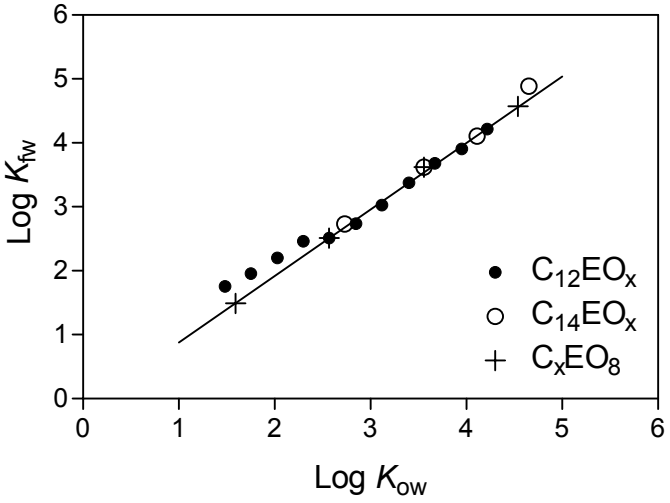

Figure 5. Correlation between log polyacrylate-water partition coefficients (Log K_{fw}) and log octanol-water partition coefficients (Log K_{ow}) estimated with EPI-Suite (*26*). The open circles are the four C_{14}-AE with 4-11 ethoxylate units, black dots represent data from the $C_{12}EO_x$ mixture and individual $C_{12}EO_8$, and plus signs are values obtained for all AE with 8 EO units.

Application of the SPME method

The linearity of the isotherms for individual AE homologues and the independency of the partitioning on the matrix demonstrate that the SPME method can serve as a suitable analytical tool for more complex AE mixtures of chemicals, as long as (i) K_{fw} values are known, and (ii) analytical tools have adequate discriminative power and sufficient sensitivity for quantification and (iii) equilibration times are short enough. The Log K_{fw} for every AE homologue can be well estimated from EPI-Suite K_{ow} values. This study clearly showed that the K_{fw} is not sensitive to competition effects or matrix effects, which facilitates studies with complex AE mixtures.

ACKNOWLEDGMENTS

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APPENDIX

Equations used in the data analysis and details on the LC-MS analysis are presented here, as well as results on the selection of the fiber coating and thickness (Figure S1), and partitioning rate constants plotted against K_{fw} values (Figure S2). This material is available as Supporting Information via the Internet at http://pubs.acs.org.

A. Data analysis

The polyacrylate-water partition coefficient (K_{fw}) at 1 µg/L was determined from the log-linear regression (Freundlich isotherm) according to:

$$\mathrm{Log}C_f = n \cdot \mathrm{Log}C_{aq} + \mathrm{Log}K_{fw} \qquad \text{(s1)}$$

where C_f and C_{aq} were both expressed as µg/L and the parameter n defines the nonlinearity of the isotherm. For n = 1, C_f is linearly related to C_{aq} via the partition coefficient K_{fw}. For the AE mixture, K_{fw} values could only be calculated for the AE homologues detected in the SPME samples, and isotherms could be obtained when data was obtained for at least 3 different concentrations. From the kinetic data, a value of K_{fw} was obtained by dividing the calculated $C_f(\infty)$ by C_{aq}.

A one-compartment, first order kinetic model (eq s2) was used to calculate the equilibrium concentrations in the fiber ($C_f(\infty)$) and elimination rate constant of the fiber (k_e) from the concentrations in the fiber in time ($C_{f(t)}$). The model was fitted with GraphPad Prism™ 3.0 (San Diego, CA).

$$C_{f(t)} = C_{f(\infty)} \cdot \left(1 - e^{(-k_e \cdot t)} \right) \qquad \text{(s2)}$$

For fibers which deplete the aqueous phase considerably, the rate constant calculated in this way overestimates the true elimination rate constant. In a study on the bioconcentration of hydrophobic compounds in fish, Banerjee *et al*. (*27*) demonstrated that, depending on the bioconcentration factor and the mass of fish per unit mass of water, uptake of toxicants in fish could decrease aqueous concentrations. The equation which describes how the aqueous concentration $[S]_t$ relative to the initial concentration $[S]_0$ decreases over time, can be derived from a simple first-order two-compartment model. As can be seen in eq s3 (*27*), the kinetics depends on the uptake rate constant (k_u), the fish-to-water mass ratio F and k_e:

$$\frac{[S]_t}{[S]_0} = \frac{1}{k_u F + k_e}\left(k_e + k_u F e^{-(k_u F + k_e)t}\right) \qquad \text{(s3)}$$

In a similar way, the apparent elimination rate constant ($k_{e,app}$) for depletive fiber extractions, depends on the true uptake rate constant (k_u), the fiber-to-water volume ratio and the true elimination $k_{e,true}$:

$$k_{e,app} = k_{u,true} \cdot \frac{V_f}{V_w} + k_{e,true} \qquad \text{(s4)}$$

where V_f and V_w are the volumes of the fiber and aqueous phase, respectively. This can be rewritten as the equation Jager (2003) (*36*) derived from the mass balance in such a two-compartment system under depletion:

$$k_{e,app} = k_{e,true}\left(\frac{V_f}{V_w} \cdot K_{fw} + 1\right) \qquad \text{(s5)}$$

with K_{fw} as the polyacrylate-water partition coefficient. From the true elimination rate constant $k_{e,true}$ (Table 1) and the fiber-water partitioning coefficient, the uptake rate constant can be calculated:

$$K_{fw} = \frac{k_u}{k_{e,true}} \qquad \text{(s6)}$$

To calculate the time needed to reach 95% of steady state (SS), equation (s2) can be rearranged to:

$$t_{(95\%\,SS)} = \frac{\ln(0.05)}{-k_e} \qquad \text{(s7)}$$

B. Details on the detection of AE on LC-MS

The mass of $[m + NH_4]^+$ was, for all AE homologues, observed as the highest peak in the first mass spectrometer (Q1), whereas also $[m + Na]^+$ ion adducts were identified, and to a much lesser extent $[m + K]^+$ and $[m + H]^+$. The $[m + NH_4]^+$ peaks were used for quantitation as they were always clearly identified, showed a good sensitivity (limit of quantitation ~5 pg per injection of 20 µL sample) and were clearly separated from any interference. The $[m + Na]^+$ mass peak was always present in the samples at a 1-10 times lower peak area due to background traces of sodium and analyzed in the same run, serving as an extra identification of the AE at the specific retention time. The peak area ratio ($[m + NH_4]^+$ / $[m + Na]^+$) served as an indication of the quality of the sample, since e.g. incomplete removal of salt during SPE immediately resulted in high $[m + Na^+]$ peaks, thereby lowering the $[m + NH_4]^+$ peak area.

C. Selection of fiber coating and thickness

Initial experiments showed that within 30 min exposure to $C_{14}EO_8$ in sea water, the 7 µm PA fiber showed a maximum uptake plateau. For the 35-µm PA fiber, 95% of the equilibrium was reached within 22 h. The AE concentration in the 30-µm PDMS coating showed no increase after 5 h exposure (data not shown). As no decrease of the aqueous AE concentration (C_{aq}) was observed over more than 200 hours, 96 h was chosen to be a

sufficiently long equilibration time to determine isotherms between the three types of polymer coating and concentrations in the sea water. The concentrations of $C_{14}EO_8$ in both the 7-µm and the 35-µm PA fibers appeared to increase almost linearly with concentrations in the sea water ranging from 0.6 - 1300 µg/L, with the slope (±SE, n = *29*) on a log-scale of 0.976 (±0.022) and 0.968 (±0.006), respectively (Figure S1). Concentrations in the 35-µm PA fiber at 100 µg/L were already ten times higher than could be explained by adsorption on the surface of the fiber alone, based on an estimated (*37*) surface area of an adsorbed molecule of $C_{12}EO_6$ of 0.95 nm^2. The linear increase over a broad concentration range also showed that uptake of AE in polyacrylate is very likely a partitioning driven process, or absorption, into the polymer phase, which has also been demonstrated for fluoranthene in SPME-fibers (*38*). The isotherm of $C_{14}EO_8$ in PDMS fiber coating was distinctively nonlinear with a slope (±SE, n = 29) of 0.731 (±0.013). This nonlinearity for PDMS was assumed to be due to the strongly nonpolar properties of the polymer phase. This makes it a less attractive phase for AE with its long polar ethoxylate chains, while substantial adsorption of AE on the fiber surface may occur with the alkyl chains in the polymer phase. Because of the nonlinear isotherm, the fiber-water partitioning coefficient (K_{fw}) with PDMS is concentration dependent. For polyacrylate however, a fairly constant K_{fw} can be used to determine the C_{aq} from a fiber extract, making it a far more robust extraction phase. Tests on other AE and matrix effects were performed with the SPME fibers with the 35-µm PA coating, because the 35-µm PA fibers appeared to be more accurate than the 7-µm PA coated fibers over the whole concentration range, and gave a higher sensitivity due to the higher volume of polyacrylate phase.

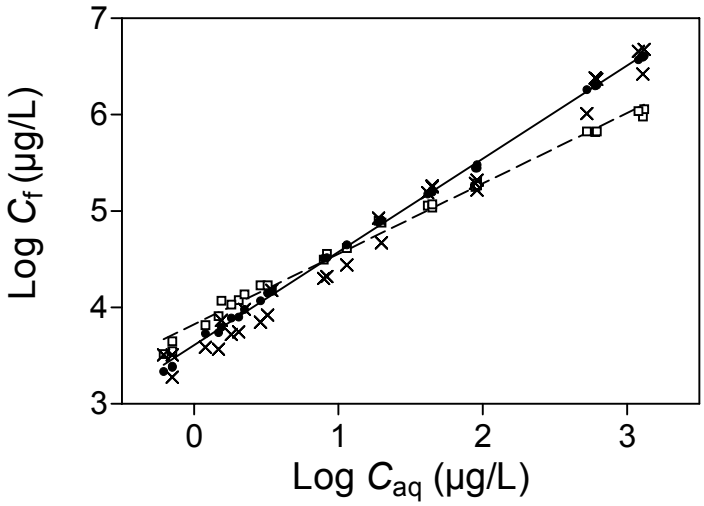

Figure S1. Concentrations of $C_{14}EO_8$ in the polymer phase (C_f) of the SPME fiber after 96 h exposure to different concentrations in sea water (C_{aq}). Data from SPME fibers coated with 30-µm PDMS are presented as open squares, 7-µm PA-coated fibers as crosses and 35-µm PA-coated fibers as closed circles. The solid lines shows the linear regression through the log transformed data obtained with the 35-µm PA-fiber, the broken line the linear regression through the log transformed data for the 30-µm PDMS-fiber.

Chapter 3

Analysis of Anionic Surfactant Homologues in Seawater With a Glassy Polymer: From Nonlinear to Linear Extraction Isotherms

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Analysis of Anionic Surfactant Homologues in Seawater With a Glassy Polymer: From Nonlinear to Linear Sorption Isotherms

ABSTRACT

The solid-phase microextraction (SPME) method was optimized to determine the freely dissolved concentration of a single linear alkylbenzene sulphonate (LAS) in seawater. The uptake kinetics of this ionized organic compound in custom-made SPME fiber with a 7-µm thick polyacrylate (PA) coating showed an apparent equilibrium after 3-5 days, but the sorption isotherm after this "equilibration period" was nonlinear. The uptake profile over a period up to 4 months revealed an initial excessive uptake of LAS which gradually decreased in time until a concentration independent fiber water distribution coefficient was observed between 2 and 4 months. Results indicate that a slow hydration of the PA lowers the glass transition temperature (T_g), which turns the PA phase from a glassy to a rubbery state at room temperature. The suggested rubbery state of PA, at which sorption isotherms for various LAS compounds were linear, was also achieved after thermal conditioning. A plasticizing effect of high concentrations of the LAS itself may also play a role. The concentration independent fiber-water sorption coefficients increase with alkyl chain length and may be closely related to the hydrophobicity of this type of anionic surfactants.

INTRODUCTION

Solid-phase microextraction (SPME) has been used as a partitioning based analytical tool for many polar and nonpolar organics in many types of aqueous matrixes (*1*). Chemicals sorbed to suspended particles or dissolved organic matter, including humic acids (*2*), clay minerals (*3*), and proteins (*4,5*), cannot partition into the polymer coating of the SPME fibers, either by size exclusion or because of the fact that these particles strongly favor the aqueous phase. The ability to rapidly determine the freely dissolved concentration is one of the main advantages of SPME, and the free concentration is a main entity in toxicological studies as well as in other environmental processes and applications. The concentration of a compound in a polymer phase, after reaching an equilibrium, depends on the freely dissolved concentration via the compound's fiber-water partitioning coefficient (K_{fw}).

The partitioning based SPME method has rarely been applied to the analysis of ionized organics and often porous polymer phases were considered preferable because of a greater yield and faster kinetics (*6*). Two previous studies have used SPME to extract linear alkylbenzene sulphonates (LAS), an anionic surfactant, from environmental samples. Alzaga *et al*. (*7*), however, used tetrabutylammonium as an ion-pairing reagent to extract LAS into PDMS coatings to maximize the extraction efficiency. The ion-pair clearly has a different partitioning behavior compared to the single anion. Furthermore, it is not likely that this method is able to determine the freely dissolved concentration of LAS when samples contain considerable amounts of substrate with LAS sorbed to it. Ceglarek *et al*. (*8*) used a porous polymer (Carbowax/Templated Resin) and extractions were performed at pH 3, but extraction isotherms were not provided. Porous polymers will mainly adsorb the anions. Nonlinear extraction isotherms are expected over a broad concentration range for adsorptive extraction phases, because adsorption sites may vary energetically and, when reaching saturation, ions will compete for these sites. Escher *et al*. (*9*) studied the partitioning of several organic bases and acids to the 85-µm polyacrylate coated SPME fibers in the kinetic phase, and concluded that for solutions of different pH the neutral species accounted for the accumulated concentration. As shown for studies with chloro- and nitrophenols in an octanol-water system, ionized organics do partition into organic phases, but with a 2 to 4 orders of magnitude lower octanol-water partition coefficient (K_{ow}) than the neutral species (*9,10*). The K_{ow} of the ionized organics furthermore depended stronger on salinity and composition of counterions.

For ionizable organics with a dissociation constant in the common range of environmental pH values, the overall partition coefficient in most samples will depend on the pH controlled ratio between neutral and ionized species. Analysis of freely dissolved species by SPME will therefore require detailed insight in these equilibria. The linear alkylbenzene sulphonates (LAS) are totally dissociated at pH > 2. Commercial LAS is used widespread in detergents, and consists of homologue mixtures with alkyl chain lengths of 10-14 C-atoms, and isomers with varying positions of the *p*-sulfophenyl group within the alkyl chain. The alkyl chain and benzene ring are assumed to render most LAS homologues

as relatively hydrophobic, despite the negative charge and polar groups. Direct measurements of K_{ow} for these structures are complicated by the interfacial properties of surfactants, and the possibility to form micelles and emulsify both solvents, and therefore have not been performed. It has recently been shown that it is possible to obtain linear extraction isotherms for nonionic surfactants to polyacrylate coated SPME fibers, and therefore single homologue specific partition coefficients (*11*). The SPME method facilitates many studies on environmental processes for compounds with a sufficiently high, and constant, SPME affinity coefficient. Therefore, this study investigated whether polyacrylate SPME fibers could be used as partitioning based analytical tools for LAS. The medium for which SPME was tested is seawater, which was convenient because of the constant pH and high salinity. The tendency of LAS to precipitate with dissolved calcium strongly limited the range of test concentrations, but regarding the widespread occurrence of (low concentrations of) LAS in coastal environments (*12,13*), and the limited amount of studies on processes in this system, it was considered very relevant.

The first aim was to study the uptake kinetics and determine the exposure time required to equilibrate the distribution between the aqueous phase and polyacrylate SPME fibers. The second aim was to obtain extraction isotherms at equilibrium for several pure LAS structures to derive the fiber-water distribution coefficient. Adsorption to the surface of the SPME fibers, with the alkyl chains sticking in the polymer phase, was considered as a possible process which could lead to nonlinear extraction isotherms. To maintain electroneutrality, LAS may partition along with different cations, or in ion-pairs, from the artificial seawater (*10*). Such a set of different processes may influence nonlinearity as well, but varying cation compositions were not further tested in this study. As will be shown in this study, and to our surprise, the polymer structure of PA had a major impact on the extraction process and understanding some of the mechanisms played an important role in the development of the SPME method for LAS.

Although the polyacrylate (PA) SPME coating has been successfully used for a wide variety of organics as an absorption phase, it is not a well defined polymer. The commercially available 85 µm PA coating in SPME fibers is according to the provider a partially crosslinked, glassy polymer (Supelco, Bellefonte, PA). Lord and Pawliszyn (*14*), however mention that "it is believed to be an acrylate co-polymer (…) existing as an amorphous rubbery compound" at room temperature. The PA coating in SPME fibers indeed probably does not consist of pure poly[acrylate] (*14*). The deprotonated polyacrylate polymer, with sodium counterions, is used as a superabsorbent in diapers, readily absorbing many times its own weight of water (*15*). This swelling is not observed for PA coated fibers. The discussion on glassy or rubbery state provides further clues on the composition of the polymer phase. Because it plays a key role in understanding the extraction of LAS with PA fibers, and relevant for some of the procedures used in this study, it is necessary to elaborate on it to some detail.

Amorphous polymers, in contrast to crystalline polymers, have a specific small temperature range where the polymer structure changes from a glassy, rigid state, to a rubbery state. The temperature at the interval between these states is defined as the glass

transition temperature (T_g), and depends on the polymer structure. Crosslinking itself does not increase the T_g (*16*), although the crosslinking agent may strongly affect the polymer composition and therewith the T_g (*17*). Poly(alkyl acrylates) are all rubbery at room temperature, with a T_g below 5 °C (*18*). Several poly(alkyl methacrylates) are glassy polymers at room temperature, with T_g between 120 °C and 20 °C for methyl- to butyl-methacrylates, respectively. It seems likely that the PA SPME coating consists of (a mixture of) the latter type of monomers. The T_g of amorphous polymers can furthermore be strongly decreased by plasticizers (*19*) or absorbed water (*20*). This occurs via several mechanisms, for example by the filling of free volumes, microcracks, that exist in the rigid polymer structure, through sorption to polar groups on the polymer chains.

The PA coating in the 7 and 35-µm SPME fibers which were used for the nonionic surfactants (alcohol ethoxylates, AE) in ref (*11*), was the same material as for the 85-µm PA fibers, according to the supplier. The 35-µm PA fibers, however, showed leaking droplets at the fiber surface at the conditioning temperature of 300 °C that is recommended for 85-µm fibers (Theo Sinnige, personal communication), suggesting weaker crosslinking. In the study with AE, the fibers were therefore used as received without conditioning and these gave satisfying linear extraction profiles. AE was not detected in blank unconditioned fibers, so conditioning at high temperatures to reduce background contamination was not considered important. As will be demonstrated in this study, for LAS the conditioning of the PA phase plays a crucial role on the applicability of the SPME method, which involves the temperature, plasticizing and hydration effects on T_g mentioned above. The uptake kinetics and extraction linearity for both unconditioned fibers and fibers treated with varying conditioning methods were investigated for a single LAS structure, whereas the extraction isotherms of several other pure LAS compounds were studied with the optimized method.

EXPERIMENTAL SECTION

Test compounds, seawater, solvents and SPME fibers

The pure homologues $C_{n\text{-}m}$-LAS, with alkyl chain length *n*, and position of p-sulphobenzene at alkyl chain carbon number *m*, $C_{10\text{-}2}$-LAS, $C_{11\text{-}2}$-LAS, $C_{12\text{-}2}$-LAS and $C_{13\text{-}2}$-LAS, were provided by J. Tolls, and were synthesized as sodium salts with 97% purity as reported in ref (*21*). Artificial seawater (GP2) was prepared according to standard procedures (*22*). Except for KBr (Sigma-Aldrich, Zwijndrecht, The Netherlands) the salts used for the seawater were from Merck (Darmstadt, Germany). To prevent biodegradation of AE during the tests, 100 mg/L sodium azide (NaN_3) (Merck) was added to the seawater. Methanol was always HPLC-quality (99.9% Labscan, Dublin, Ireland) and highly pure deionized water was used (Millipore Waters, Amsterdam, The Netherlands). The solid-phase microextraction (SPME) fibers were custom made by Polymicro Technologies (Phoenix, AZ), with a 108 µm diameter glass core and a 7.5-µm PA coating (volume 2.72 µL/m) and were cut to pieces of the desired length.

Overview of tests and PA conditioning treatments

For unconditioned "7 µm" PA coated fibers, uptake profiles of $C_{12\text{-}2}$-LAS were obtained for several aqueous concentrations for a period of up to three months. In these kinetic studies, a separate vial was prepared for each time point, in which both the aqueous phase and SPME fiber were analyzed, as described below. Extraction profiles for the widest possible concentration range were obtained for the 7 µm fibers for a four day exposure period (short term), when an apparent equilibrium was observed, and for a three months exposure period (long term). For $C_{12\text{-}2}$-LAS the upper limit of the aqueous concentration was ~2 mg/L, after which it precipitates, presumably with calcium. Besides these initial tests, three different conditioning treatments were applied for which uptake kinetics were followed in time and short term extraction profiles were obtained. The first treatment consisted of storage of fibers for a month in either clean artificial seawater or pure water (both with 25 mg/L NaN_3) before starting the exposure to LAS solutions. In the second treatment, fibers were autoclaved for 4 h in pure water (120 ºC at 15 psi), after which the samples were left to cool down slowly inside the machine. In the third treatment, fibers were kept in the oven of a gas chromatograph (GC) under a flow of helium at 120 ºC overnight, after which the fibers were kept in pure water for at least a day until used in the experiments. The latter treatment was used to obtain extraction isotherms in seawater for all four LAS homologues.

Exposure conditions and sampling

All tests were performed in 20 mL scintillation vials (Perkin Elmer, Boston, MA) with polyethylene lined screw caps at room temperature (19 ± 1 °C). Only $C_{12\text{-}2}$-LAS was used to study the uptake kinetics and to compare the effect of the conditioning treatments. In these experiments, LAS was spiked using stock solutions in pure water with 25 mg/L NaN_3, always using less than 1 mL stock per vial. The extraction isotherms for all four isomers were only determined using the thermally conditioned fibers. To spike the aqueous phase for these tests, methanol stock solutions were used, always with less than 0.1 mL per vial. Test vials were filled up as much as possible to minimize the air-water interface, and a 40 mm fiber was added. Gentle agitation of the SPME fibers in the solutions was established on Rock and Rollers (Snijders Scientific BV, Tilburg, The Netherlands).

The fiber was taken out by a pair of tweezers, blotted dry on a tissue and then wiped along a wetted (millipore water) tissue. About 20% less LAS was desorbed from wiped fibers compared to fibers that were only dried on the tissue (data not shown). Replicates of wiped fibers also showed smaller variation. A possible explanation could be a film of loosely adsorbed LAS when the fiber passes the water-air surface of the sample. The fibers were cut to pieces of <10 mm and LAS was desorbed from the fibers in 0.5 mL of a solution with the same composition as the LC-MS eluents, consisting of 10 mM ammonium acetate (Fluka, Buchs, Switzerland) in 80/20 (v/v) methanol-water. The HPLC vials (Chromacol, Herts, UK) were capped with aluminum foil and closed with the cap without the septum.

Five mL of seawater was sampled from nearly all test vials with pipette tips pre-flushed three times with methanol. The seawater was drawn through 3 mL ENVI^{TM} C_{18} SPE columns (Supelco, Bellefonte, PA), which had been conditioned with 5 mL methanol and pure water. The salt from the seawater sample was flushed by 3 x 5 mL pure water, after which vacuum was applied to the column for 5 seconds. LAS was eluted from the column with 8 mL of the LC-MS eluents. Samples were stored at -20 ^{o}C until analysis.

Chemical analysis

LAS is a known background contaminant in laboratory equipment (*23,24*), and also in this study elevated concentrations of all isomers and homologues existing in commercial LAS were found in a wide variety of old and new glassware, septa of HPLC-vials, SPME fibers, solid phase extraction (SPE) columns, disposable pipette tips, methanol and pure water, and analytical system. All glassware was checked for background peaks, and the cleanest were selected. Repetitive rinsing of glassware and SPME fibers with methanol was often not very successful. The presence of LAS in eluents was clearly demonstrated when gradient elution of HPLC column was used, as used for example in ref (*25*). The problem is that LAS does not elute from the column below a certain methanol:water ratio, and will be trapped at the head of the column until a threshold ratio is reached. Even without injection, a peak will therefore be osberved when the right ratio has been reached. Working as clean as possible, with isocratic HPLC-conditions, resulted in a very low, but always present and variable, background noise on the LC-MS, leading to a detection limit of ~20-40 pg per injection. The random like nature of contamination was most apparent for the lowest tested concentration, where often relatively high variation is obtained in replicate samples.

LAS isomers were measured by LC-MS/MS, consisting of a Perkin Elmer (Norwalk, CT) liquid chromatography system and triple quadrupole/linear ion trap mass spectrometer (Q-TRAP®, MDS Sciex Applied Biosystems, Foster City, CA). At an isocratic flow of 0.4 ml/min with premixed eluents (80/20 methanol:water with 10 mM NH_4^+), samples passed an Alltech RP-C_{18} column (3 µm Econosphere, 50 x 3 mm, Alltech, Deerfield, IL). A turboIonSpray® source used in the negative mode (-1200 mV ionspray voltage at 450°C) introduced LAS in the Q-TRAP, and the fragment m/z 183 (ethyl-p-sulphobenzyl) was detected from the [M-H]- parent ions m/z 297, 311, 325, and 339 for the LAS structures with increasing C-chain in this study, comparable to ref (*26*).

RESULTS AND DISCUSSION

Uptake kinetics and extraction isotherms of $C_{12\text{-}2}$-LAS in unconditioned SPME fibers

There are two common ways to determine the SPME fiber-water partition coefficient (K_{fw}). The first and most used method is based on measured uptake profile during a certain period, assuming a one compartment model with first-order kinetics as discussed by Vaes *et al.* (*4*). More reliable data are obtained using measurements of the aqueous phase and nonporous polymer phase when an equilibrium has established, preferably at various concentrations as was for example done for alcohol ethoxylates (*11*). Knowledge on the required equilibration period is important for both methods. For alcohol ethoxylates with a K_{fw} up to ~5000, the required equilibration time for 35-µm PA fibers was 2-4 days (*11*). In a pilot study with unconditioned fibers exposed to $C_{12\text{-}2}$-LAS, there was still no equilibrium observed for 35-µm PA fibers within 20 days, even though most test conditions were similar and the fiber distribution coefficient was not much higher than 5000.

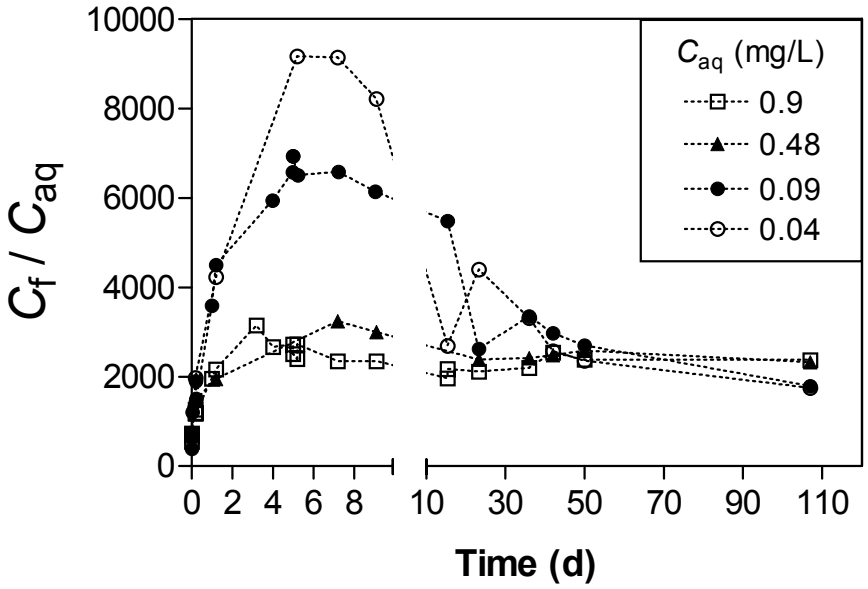

Figure 1. Uptake kinetics of $C_{12\text{-}2}$-LAS in unconditioned 7-µm PA fiber for 4 different aqueous concentrations in seawater, plotted as the ratio of the concentration in the fiber (C_f) to the measured aqueous concentration (C_{aq}) against days of exposure. Note that the x-axis consists of two parts, from 0-10 and 10-120 days. Connecting dotted lines are presented as visual guidance only.

Because of a higher surface to volume ratio, the kinetics for the thinner 7-µm PA fibers are in most cases much faster. The first tests with $C_{12\text{-}2}$-LAS concentrations of 0.09 and 0.9 mg/L with unconditioned 7-µm PA fiber showed that an apparent equilibrium was reached within 4 days (Figure 1). The average fiber-water distribution coefficients (C_f/C_{aq}) between days 3 and 5, however, were $10^{3.9}$ and $10^{3.4}$ for the low and the high test

concentration, respectively. The extraction isotherm determined after an exposure period of 4 days with the unconditioned fiber, presented in Figure 2, confirmed that the K_{fw} was indeed dependent of the aqueous concentration: the concentration in the fiber clearly did not increase linearly with aqueous $C_{12\text{-}2}$-LAS concentrations. Log (C_f/C_{aq}) values decreased from 4.2 to 3.4 from the lowest to the highest tested concentration, respectively. This concentration dependency indicated that the SPME extraction of LAS was not, or not only, a partitioning processes.

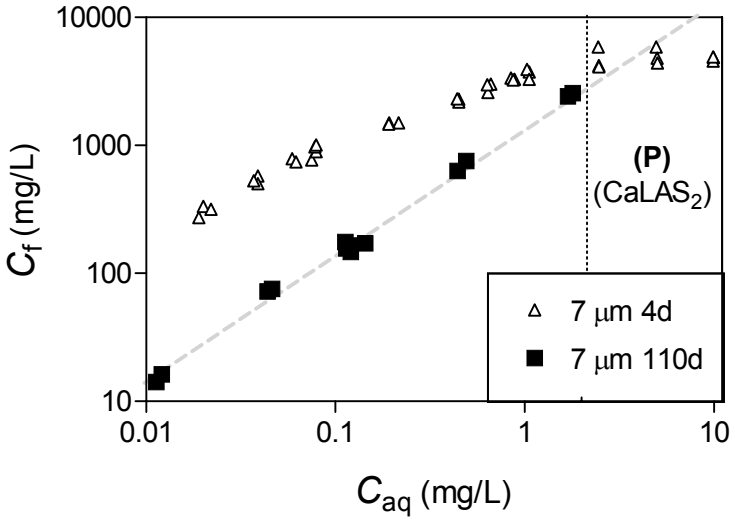

Figure 2. Concentration of $C_{12\text{-}2}$-LAS in unconditioned SPME fibers plotted against measured aqueous concentration. Data is presented for the 7-μm PA fiber sampled after 4 days (Δ), when an apparent equilibrium was observed for (C_f / C_{aq}), and after exposure for 110 days (■). The dashed grey line has a slope of 1, indicating linearity for the long term exposure of the 7-μm PA fiber. The area **(P),** right of the dotted line, indicates the concentrations above which $C_{12\text{-}2}$-LAS precipitates were observed in seawater, presumably as (Ca-LAS_2) salt (*36*).

Accidentally, test vials with a 7-μm PA fiber at varying concentrations of $C_{12\text{-}2}$-LAS in seawater were left to equilibrate for ~4 months. When these were analyzed, the concentrations in the 7-μm PA fibers showed a clear, linear relationship with the aqueous concentrations, with Log K_{fw} of 3.15 ± 0.04 (Figure 2). Apparently, the extraction isotherm for the 7-μm PA fibers changed from nonlinear, after a short term exposure, to linear after long term exposure. To understand this change in time better, the uptake kinetics were studied for four different concentrations of $C_{12\text{-}2}$-LAS in more detail by including more time points after 5 days. Results are presented in Figure 1. Each time point was obtained from a separate test vial, but aqueous concentrations did not differ significantly for each test concentration throughout the 4 months exposure period. The uptake curves for the fiber-water distribution coefficient demonstrated that an apparent equilibrium was indeed reached between day 3 and 7. As the nonlinear extraction isotherm already indicated, the

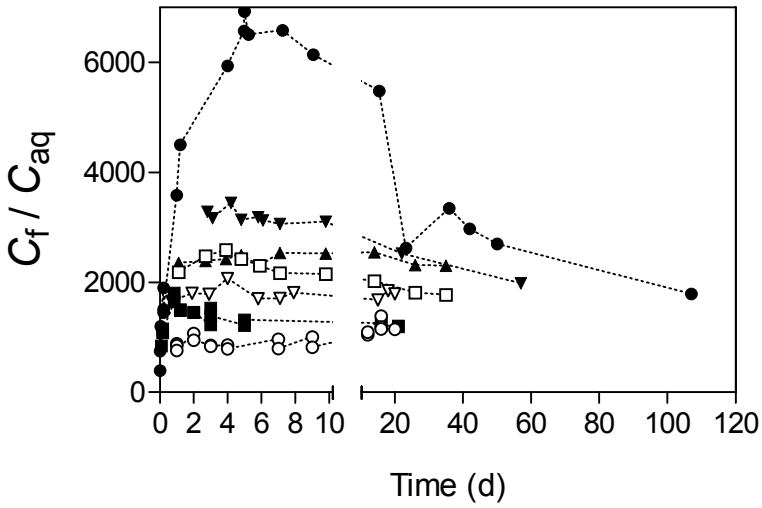

Figure 3. SPME uptake kinetics of $C_{12\text{-}2}$-LAS from seawater in unconditioned (●: 90 µg/L) and several pretreated 7-µm PA fibers: (▼) 30 days stored in seawater, 70 µg/L; (□ and ▲) one cycle autoclaving (AC) in pure water or GP2, respectively, both 80 µg/L; (▽) five AC cycles, 70 µg/L; (■) 8 hours AC, 30 µg/L; (○) GC-oven heated, 25 µg/L. Data points are the ratios of the concentration in the fiber (C_f) to the measured aqueous concentration (C_{aq}) against days of exposure. Note that the x-axis consists of two parts, from 0-10 and 10-120 days. Connecting dotted lines are presented as visual guidance only.

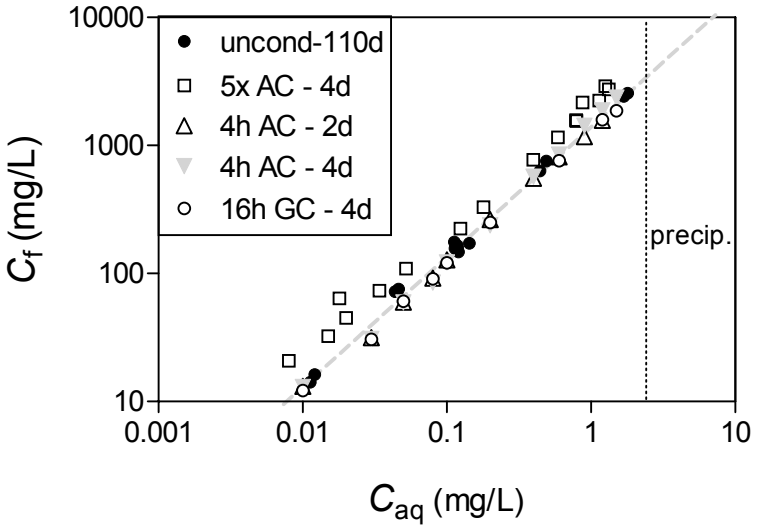

Figure 4. Concentration of $C_{12\text{-}2}$-LAS in conditioned 7-µm PA fibers plotted against measured aqueous concentration. (●) unconditioned fibers exposed for 110 days; (□) fibers autoclaved (AC) in 5 cycles of 20 minutes and exposed for 4 days; (Δ) and (▼) fibers with 4 hours AC before exposure for 2 and 4 days, respectively; (○) fibers thermally conditioned in GC-oven overnight at 120 °C and exposed for 4 days. The dashed grey line has a slope of 1, indicating linearity, the dotted line indicates the concentration above which $C_{12\text{-}2}$-LAS precipitates in seawater.

fiber-water distribution coefficient at this apparent equilibrium was higher for lower aqueous concentrations. The uptake profile clearly show an "excessive uptake" of LAS in the 7-µm PA fibers for the lower concentrations, after which the C_f/C_{aq} ratio slowly decreased in time. Between days 60 and 110 the C_f/C_{aq} ratio became more or less constant for the four tested concentrations, and more or less overlap with the data from the linear extraction isotherm obtained after 110 days exposure.

Uptake kinetics of $C_{12\text{-}2}$-LAS in conditioned PA fibers

The linearity of the isotherm after 110 days of exposure is a first indication that SPME analysis of LAS in aqueous samples is related to an absorption process. Insight in the process that caused the shift from nonlinear to linear extraction isotherms was required to further optimize the 7-µm SPME as a tool for the analysis of LAS. The first clue that the abnormal behavior at short exposure times was related to a change in the polymer phase, was obtained from the uptake kinetics of $C_{12\text{-}2}$-LAS in 7-µm PA fibers that had been stored for a month in seawater prior to exposure to the LAS solution. The data, presented in Figure 3, showed a reduced, but still apparent, excessive uptake of LAS compared to unconditioned fibers exposed to similar concentrations. Apparently, some property of the polymer phase slowly changes in time when they are exposed in seawater. Figure 3 further shows the reduction of the excessive uptake by the various other tested conditioning treatments. The change in the polymer phase, judging from the reduction of the excessive uptake, was markedly enhanced in time when the fibers were autoclaved, either in seawater or pure water, for a single cycle of 20 minutes at 120 °C and 15 psi. Five of these cycles reduced excessive uptake further, and when fibers were autoclaved for 4 or 8 h, and slowly cooled down, the ratio C_f/C_{aq} after 4 days exposure was not significantly different from the ratio at the long term exposure. Finally, the fibers were also thermally treated by overnight heating at 120 °C under a flow of helium in a GC-oven. This way of conditioning gave similar results as the long periods of autoclaving. The fibers had to be kept in (clean) water for another day to reduce some interfering background signals which disturbed the analysis of samples taken from the lowest test concentrations.

Extraction isotherms of $C_{12\text{-}2}$-LAS in conditioned PA fibers

The reduction of the excessive uptake due to conditioning was confirmed by performing short term extraction experiments with fibers that were autoclaved for several hours, at high temperature in water, and those that were (only) thermally conditioned in the GC-oven. Figure 4 shows the data obtained after 2 and 4 days exposure of the autoclaved fibers, which are indistinguishable from the data obtained with the unconditioned fibers exposed for 110 days. Also the data for the thermally conditioned fibers give the same linear isotherm (slope of 1 in the log-log plot). This last procedure was considered to be the most reproducible and convenient method, because a batch of hundred fibers of e.g. 50 mm can be conditioned simultaneously in basically any GC-oven. With this method, the extraction isotherms of four pure LAS structures were determined in two separate series.

In one of these series aqueous concentrations were checked by analysis, while nominal concentrations were used in the second series. Linear isotherms with a slope of 1 were fitted through the data as presented in Figure 5. The fiber-water distribution coefficients of the individual LAS homologue structures are presented in Table 1. Although some scatter of the data around the isotherms appeared to be inevitable due to various background sources of LAS and drift of the LC-MS signal, narrow confidence intervals could be realized. As expected, the affinity of LAS homologues for the fiber increases with increasing length of the alkyl chain. The addition of one (CH_2) unit to the alkyl chain adds 0.5 log units to the K_{fw}, except for the step between $C_{10\text{-}2}$-LAS and $C_{11\text{-}2}$-LAS. This fragment value for an aliphatic (CH_2) fragment coincides with those observed for partition coefficients to hydrophobic, organic phases like octanol (*27*) and organic matter (*28*). A comparable incremental value of 0.4 and 0.45 per CH_2 unit were observed for the sorption coefficients of LAS compounds to sediments by Westall *et al*. (*29*) and Hand and Williams (*30*), respectively, both suggesting that organic matter controlled sorption. Also the KowWIN software from the EPI-Suite package (v3.12) uses 0.5 log units per aliphatic CH_2 fragment to calculate the octanol-water partition coefficient (K_{ow}) for nonionic organics. Whether this SPME method indeed is a partitioning process should become clear from future experiments with mixtures of LAS structures, because partition coefficient are supposed to be independent of co-solutes. If the K_{fw} values for LAS are indeed partition coefficients, they can be considered also as a measured value indicative for the hydrophobicity of such compounds.

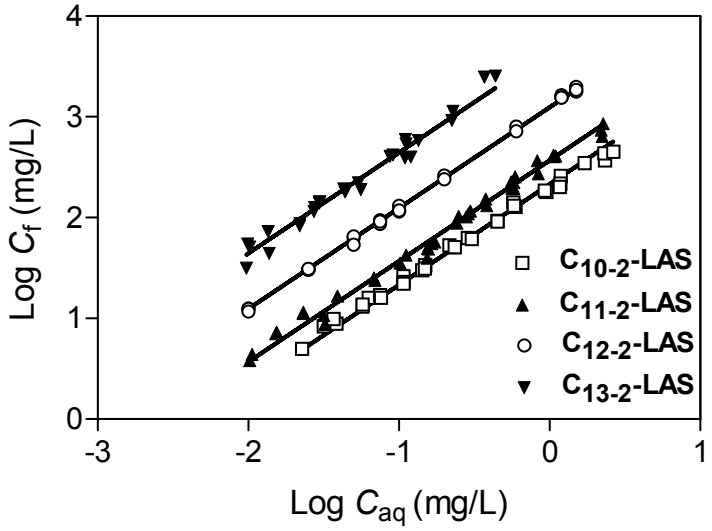

Figure 5. Concentration of several pure LAS homologues in thermally conditioned (16h at 120 ºC) 7-µm PA fibers plotted against dissolved concentration in seawater, for (▼) $C_{13\text{-}2}$-LAS, (○) $C_{12\text{-}2}$-LAS, (▲) $C_{11\text{-}2}$-LAS and (□) for $C_{10\text{-}2}$-LAS.

Table 1. Partition Coefficients Between Seawater and Thermally (16h at 120 °C) Conditioned 7-µm PA SPME Fibers (K_{fw}).

	Log K_{fw} (*n*, 95% c.i.) [a]
$C_{10\text{-}2}$-LAS	2.33 (*34*, 2.31-2.35)
$C_{11\text{-}2}$-LAS	2.57 (*38*, 2.55-2.59)
$C_{12\text{-}2}$-LAS	3.09 (*25*, 3.08-3.10)
$C_{13\text{-}2}$-LAS	3.64 (*26*, 3.61-3.68)

[a] obtained by fitting linearized isotherm, as Log C_f = Log C_{aq} + Log K_{fw}, n = number of data points used, 95% c.i. are 95% confidence limits.

A tentative interpretation of the conditioning process

From the results with the various conditioning treatments it was hypothesized that the underlying mechanism was related to a transition of the polymer phase from a glassy to a rubbery state. In the glassy state, via a yet unknown mechanism, LAS adsorbs relatively strongly to adsorption sites in the rigid polymer structure or at the fiber surface. When the polymer has become fully rubbery, due to a lowering of the glass transition temperature (T_g) because of hydration, LAS absorbs into the polymer phase with a constant affinity coefficient. By heating, and slowly cooling down, the polymer phase is also brought to the rubbery state and maintains this state after the conditioning. The C_f/C_{aq} ratio for fiber exposed to the highest test concentrations does not show an excessive uptake (Figure 1) and, furthermore, after four days is similar as the concentration independent C_f/C_{aq} ratio in the fibers exposed for 110 days (Figure 2). This could be interpreted as a plasticizing effect of LAS itself, lowering the polymer's T_g to below room temperature, so that only the absorption affinity for the rubbery state drives the C_f/C_{aq} ratio. Apparently, the plasticizing effect of LAS is much faster than that the effect of hydration.

Whether the linear extraction isotherms indicate that the LAS homologues truly partition into the polymer phase cannot be concluded from the data presented in this study. A follow-up study will amongst others discuss the effect of the presence of other LAS homologues on the extraction isotherm of a single homologue. If the extraction of LAS with conditioned PA fibers still involves significant adsorption to specific sites in or on the surface of the polymer phase, competition for these sites will occur when they become filled with co-solutes. The sensitivity of the SPME method is limited by background levels of all LAS homologues in the SPME fiber at the low level, and by the precipitation with salts in the seawater at the high concentration range. Still, within this window, SPME can be used as a valuable tool to determine freely dissolved concentrations of these anionic surfactants in a wide variety of test systems.

The effect of the glassy PA structure on the K_{fw} is absent for nonionic surfactants, where linear extraction isotherms were obtained for unconditioned PA fibers (*11*). As far as we have encountered, all studies using commercial 85 µm PA fibers report preconditioning at 300 °C, and it is not known whether the fibers returned to a glassy state when used in the experiments. Since we can not provide a mechanistical interpretation for the strong

adsorption to glassy PA polymer, it is not possible to speculate whether this is only related to LAS. Xing and Pignatello (*31*) showed that the sorption of 1,3-dichlorobenzene (DCB) to the polymer PVC (which has a sharp T_g at 85 °C) was nonlinear at room temperature but linear at 90 °C, with the slope of a linear isotherm on a log-log plot of 0.88 and 1.00, respectively. The polymer-water distribution coefficient in that study was higher with the rubbery PVC (at 90 °C) than that in the glassy PVC (at 23 °C), but due to the different test temperatures, it is difficult to compare the activity coefficient of DCB in the glassy and rubbery PVC phase. In our study all tests were performed at the same temperature, and LAS showed a higher affinity for the glassy PA polymer than for the rubbery PA. An interesting consequence of this behavior of LAS is that recent studies have shown that macromolecular structure of natural organic matter may also contain glassy domains (*31-33*). The glass transition temperature for organic matter is much less clearly defined as for polymers, but may range between 40 and 90 °C. The effect of hydration on the T_g is much more complex for organic matter than for polymers, and it is not clear organic matter will be rubbery at room temperature in field wet sediment. Furthermore, nonionic organics can react differently on the hydration state of organic matter (*34,35*). The effect of glassy domains on sorption of LAS may however be relevant when dried sediment or organic matter is used to study sorption. This study showed that this may result in nonlinear, short term sorption isotherms, which could become linear after a sufficiently long hydration period.

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Chapter 4

Estimating K_{ow} Values for Nonionic Surfactants Based on Polymer-Water Partition Coefficients and a pp-LFER Approach: A Preliminary Study

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Estimating K_{ow} Values for Nonionic Surfactants Based on Polymer-Water Partition Coefficients and a pp-LFER Approach: A Preliminary Study

ABSTRACT

Experimental octanol-water partition coefficients (K_{ow}) for alcohol ethoxylates (AE) are not available. The partition coefficient to the polyacrylate coating of solid-phase microextraction (SPME) fibers (K_{fw}) in Dutch standard water are established experimentally. This study discusses whether these experimental K_{fw} values for AE could replace K_{ow} as hydrophobicity parameters in risk assessment. SPME partition coefficients for organic compounds were collected from the literature and a few new data were generated experimentally. The polyacrylate K_{fw} values are within a factor 10 of K_{ow} values for all 70 chemicals in the data set. The chemical domain, however, does not include the ethoxylated surfactants. A polyparameter linear free energy relationship (pp-LFER) approach would allow for a detailed comparison between K_{fw} and K_{ow} values. Pp-LFER models explain the partition coefficient of organic compounds between two bulk phases via the molecular interactions between the compound and the bulk phases. From the data set of K_{fw} values, a pp-LFER model for the water-polyacrylate system is established. A comparison of the pp-LFER models shows that there are both similarities, but also differences in the properties of octanol and polyacrylate. A full comparison of the two phases will only be possible if the data set is extended to cover a broader variety in structures and descriptor space.

INTRODUCTION

K_{ow} values for surfactants

The shake flask method, described in OECD guideline 117 (*1*), is a simple test to determine the octanol-water partition coefficient (K_{ow}) of organic compounds. As mentioned in Guideline 117, the method is not suitable for "surface active agents" in general, because surfactants accumulate at the interface between two phases, and furthermore readily emulsify with both phases (*2-4*). The slow-stirring method (*5*) may be a more suitable method for surfactants because the formation of micro-droplets of octanol in the aqueous phase is prevented (*6-8*). This method has already been applied for positively charged imidazoles (ionic liquids) (*9*) and is patented for surfactant mixtures (*10*). Still, there are no directly measured K_{ow} values available in peer reviewed literature for the majority of surfactants. In June 2007, the EU-legislation on bulk-produced chemicals (REACH) went into force. All chemicals used and produced in the EU have to be registered and will be assessed on potential environmental risk. Within REACH, the K_{ow} functions as a key parameter and is for example used to classify a chemical as having a potential to bioaccumulate or not.

In the absence of direct K_{ow} measurements, reliable estimates are required for surfactants. Two common methods to estimate K_{ow} values for organic compounds are:

(A) A fragment based approach where an organic compound is divided into small molecular fragments for which the contribution to the overall Log K_{ow} is known.

(B) Apply the measured sorption coefficient between water and another organic phase to the relationship between K_{ow} and the coefficient for that specific organic phase, which has been established for comparable compounds.

This study investigates whether it is possible to estimate the K_{ow} of nonionic surfactants (alcohol ethoxylates) from measured sorption coefficients between water and a polymer phase, i.e. via method (B). In a previous study it was shown that alcohol ethoxylates have a concentration independent affinity for the polyacrylate coating of solid-phase microextraction (SPME) fibers (*11*). The experimental fiber-water partition coefficients (K_{fw}) were highly correlated to the estimated K_{ow} values of alcohol ethoxylates obtained via fragment values (EPI-Suite's KowWIN software). Interestingly, the polyacrylate-water partition coefficient (K_{fw}) has been determined for a wide variety of polar and nonpolar organic compounds, and good correlations with measured K_{ow} values have already been reported (*12*). The main focus of this study was therefore to better understand whether the sorption properties of polyacrylate are indeed comparable to those of octanol. Once this is established, it will become clear whether the K_{fw} for surfactants are representative of K_{ow} values.

Estimating K_{ow} of surfactants based on molecular fragments with KowWIN

Estimating K_{ow} based on the contribution of specific molecular fragments is used for example in EPI-Suite's KowWIN software. This is possible because the database of compounds for which K_{ow} values are established is large enough (13058 compounds for KowWIN) to cover almost all possible molecular fragments (*13*). The fragment value that is derived from this database for (CH_2) units in alkyl chains of surfactants can be considered as very accurate. The fragment value for aliphatic ether fragments, which are present in the ethoxylate chains of most nonionic surfactants (alcohol ethoxylates and alkylphenol ethoxylates) and some ionized surfactants (e.g. ethoxysulfates), are clearly less abundantly covered in the database. Because commonly used commercial mixtures of nonionic surfactants include compounds with up to 20 or more ethoxylate units, a small error in the fragment value for aliphatic ether can result in large deviations from the "actual" K_{ow}. Furthermore, since ethoxylated surfactants are not included in the K_{ow} database, it is not clear whether the ether fragment in a repetitive ethoxylate unit (C_2H_4O) requires an additional correction factor compared to a single aliphatic ether fragment.

Estimating K_{ow} of surfactants via sorption data for comparable organic phases

In theory, hydrophobicity parameters for surfactants could be derived indirectly from other sorption data, for example from sorption coefficients to organic matter (K_{oc}) or from the bioconcentration factors (BCF) measured for example in fish (*14-16*). At the moment, however, neither sorption data with natural sorbents nor uptake studies with living organisms are serious options for surfactants. First of all, there are hardly any high quality data in peer-reviewed literature on the direct sorption of surfactants to organic matter (*17*). Secondly, it is not possible to derive organic carbon-water partition coefficients (K_{oc}) from data on sediment-water distribution coefficients. Sorption of surfactants to sediment is often a nonlinear process (*18-21*), and, in contrast to many other organic contaminants, most of these studies showed that the organic matter fraction in sediment is not the dominant sorption phase for most surfactant types. Third, it does not make sense to derive hydrophobicity parameters from sorption data with biota, because the few existing accumulation studies of surfactants in organisms showed that most surfactants are readily biotransformed within the organism. Because of this elimination process, the measured bioconcentration factors are lower than the actual affinity of surfactants for membranes. Extrapolating the few available results to the wide variety of other surfactant homologue structures will furthermore be hampered when the biotransformation rates substantially vary within a group of chemicals or test species.

The affinity for liposome structures, which are considered artificial biomembranes, decreased (on average) with 0.1 log units per ethoxylate (EO) unit for a series of alcohol ethoxylates (*4*). This value is comparable to the value that Roberts *et al*. (*2,22*) deduced from toxicity data, which seems to confirm that toxicity was related to the accumulation

of surfactants in membrane structures. For heptane-water systems, however, the EO unit fragment value appeared to be -0.45 log units at room temperature (*23-25*). The sorption coefficients of a series of alcohol ethoxylates to the polyacrylate coating of SPME fibers showed a very constant fragment value of -0.27 log units per EO unit (*11,21*). These results show that the effect of a single ethoxylate unit on the partition coefficient can be quite different for varying organic phases. When deciding which sorption phase is most representative to octanol, this effect should be taken into account.

Explaining partitioning behavior by molecular interactions between the solute and a solvent

The reason that organic chemicals can have varying partition coefficients between water and different organic phases is neatly described in the polyparameter linear free energy relationship (pp-LFER) approach. The pp-LFER approach is used to compare the octanol-water system with the polyacrylate-water system, and therefore it needs to be described to some detail first before clarifying the aims of this study. The pp-LFER approach has been worked out in detail since the early nineteen nineties by Abraham and co-workers (e.g. (*26*)), and is based on the molecular interactions between a solute in a solvent (e.g. water) and those in the second bulk phase (e.g. octanol). Goss and Schwarzenbach (*27*), Nguyen *et al*. (*28*) and Niederer *et al*. (*29*) demonstrated with pp-LFERs for natural organic matter that this approach can be a valuable tool for environmental risk assessment. pp-LFER models combine information of the properties of the two phases with the characteristics of the compound.

The possible molecular interactions of the solute are Van de Waals forces (both dipole and induced dipole interactions) and polar interactions (hydrogen bond formation). To describe the partitioning between two bulk phases, these interactions have been reduced to five descriptors that are solute specific. These descriptors have been determined experimentally for more than 1000 compounds, published over several papers in scientific journals. The descriptors that seem to cover most molecular interactions for nonionic organics, are the molecular volume V, the excess molar refraction E (which stands for the difference in polarizability compared to an alkane of the same size), the ability for stable charge interactions via dipole-dipole interactions S, the overall hydrogen-bond acidity (or electron acceptor) A, and overall hydrogen-bond basicity B (electron donor). The solute can interact via these descriptors with both phases, and the difference between the two phases for each descriptor results in a coefficient specific for the system of the two phases. The system specific coefficients *v, e, s, a,* and *b* thus describe the influence of the solute specific descriptors (V, E, S, A, and B, respectively) on the overall partition coefficient between phases '*i*' and '*j*', according to:

$$\text{Log } K_{i,j} = v \cdot \text{V} + e \cdot \text{E} + s \cdot \text{S} + a \cdot \text{A} + b \cdot \text{B} + \text{c} \qquad (1)$$

where c is a constant obtained from multiple regression of a data set with sufficient values of Log $K_{i,j}$ and values for the descriptors of the compounds. The quality of the coefficients

depends on the quality of the data set and the (co-)variation between the descriptors in the set used in the regression. All descriptors have been scaled to a certain range. Descriptors V and E can be calculated, whereas S, A and B can be measured in several ways, although there is no consensus yet on the best way to measure or estimate them (*30-32*). If the specific interaction (descriptor) of a solute is very similar for both phases then that coefficient will be almost zero. If the hydrogen acidity coefficient *a* in an octanol-water system is comparable to coefficient *a* for a different organic phase-water system, then apparently octanol and the other organic phase have a similar hydrogen-bond donor ability. Molecular volume (V) is an important descriptor because it determines the energy required for cavity formation, breaking up the solvent molecules in order to create space to dissolve the solute. Water has very strong interactions with itself, via hydrogen bonding, often much stronger than an organic phase such as octanol. Therefore coefficient *v* is often positive and relatively high, and the product (*v*·V) strongly contributes to the partition coefficient. The pp-LFER coefficients have been established for a wide variety of biphasic systems with water and air, including octanol and hexadecane (*26*), various types of organic matter (*28,29*), polymer-air systems (*33*) and blood-brain barrier system (*34,35*). The pp-LFER for K_{ow} has been established using more than 600 different chemicals with K_{ow} values ranging over 10 orders of magnitude (*26*), and therefore considered to be of high quality.

Establishing a pp-LFER for sorption coefficients to polyacrylate SPME fibers

To investigate whether polyacrylate has the same capacity for specific molecular interactions with solutes as octanol, the pp-LFER coefficients for the polyacrylate-water system should be directly compared with those for the octanol-water system. A pp-LFER for partitioning behavior of organics in a polyacrylate-water system is therefore constructed in this study. For this purpose, a sufficient number of polyacrylate-water partition coefficients (K_{fw}) are required, and the organic compounds should cover a wide variety of chemical classes to avoid co-variation between the five pp-LFER descriptors in the data-set. Polyacrylate SPME fibers have been used in a considerable number of studies, but many studies focused on short exposure times during the kinetic phase of uptake in the fiber. To ensure the quality of the pp-LFER, reported K_{fw} values are only useful when the studies explicitly demonstrate that they have been derived after reaching equilibrium, or are corrected for this in the right way.

Aims of this study

The first aim of this study was to compile a high quality K_{fw} data set from literature sources that used polyacrylate SPME fibers. Based on this data set, K_{fw} values can be directly compared with K_{ow} values, as has also been done by Vaes *et al.* (*12*) and Leslie (*36*) for smaller data sets. For the compounds in this data set experimental pp-LFER descriptors were obtained from several published databases.

The second aim was to enhance the variety of structures in the K_{fw} data set for which pp-LFER descriptors were available. The data on aliphatic organics was considered to be too limited in order to compose a pp-LFER model, and therefore the K_{fw} values were determined for six compounds in one mixture. Pure alkanes have no polar molecular interactions with a solvent, and therefore only the descriptor V contributes to the pp-LFER and the other descriptors are scaled to zero. Because alkanes were not part of the data-set obtained from literature sources, n-heptane, n-nonane, and n-decane were chosen. Cyclohexane was also chosen since it only has a small value for descriptor E besides V. 1-Heptanol and 1-octanol were also included to complement several other aliphatic alcohols present in the literature database. Again, in a series of aliphatic alcohols molecular volume varies while the other parameters are constant, thus increasing the variety in the descriptor set.

The third aim was to establish the pp-LFER from the available polyacrylate SPME partition coefficients and to determine the quality of the polyacrylate-water pp-LFER. The system coefficients of the polyacrylate-water systems can then be compared to those for the octanol-water system, in order to (i) see at which molecular interactions polyacrylate differs from octanol, and (ii), if these differences can explain for which compound classes sorption to the polyacrylate SPME fibers is a good indicator of the K_{ow}.

The final aim of this study is to discuss to what extent the pp-LFER can be used for alcohol ethoxylates. First, K_{fw} values will be determined for the alcohol ethoxylates in standard fresh water, since previously reported SPME coefficients were determined in artificial seawater (*11*). Because of the application of SPME coefficients in environmental research, Dutch standard water was chosen as a low salinity test medium. A major shortcoming in this study is that the pp-LFER descriptors are not available for AE. Accordingly, it will not be possible to determine whether the pp-LFER for K_{fw} values explain the experimental K_{fw} values for AE. Platt *et al*. (*37*) and Endo and Schmidt (*38*) calculated contribution factors for all five pp-LFER descriptors for a wide variety of molecular fragments, including alkyl chains and aliphatic ether bonds. With the pp-LFER for polyacrylate it is possible to determine whether these fragment values can be used for nonionic surfactants.

EXPERIMENTAL SECTION

Data collection on K_{fw} values for polyacrylate SPME fibers

To select only high quality K_{fw} values for use in the pp-LFER, several criteria were set that should be met in the reported studies. Extractions should be performed at room temperature (20-25 °C), at low salt contents (≤0.1 M) and below solubility at all concentrations. If aqueous concentrations were not measured, mass balance assumptions should be valid and corrections applied, with reported volume size of the test solution. The uptake profiles (see equation 2) should be presented when kinetic data are used to determine K_{fw} values. Uptake rate constants should be reported, or circumstantial evidence provided that at least 70% of the equilibrium distribution (K_{fw}) was reached when fitting a first-order one-compartment uptake curve. This value was chosen because with a common analytical error of 5%, the fitted K_{fw} value can be off more than 2-fold because of the large error in the fitted elimination constant (k_e):

$$\frac{C_f}{C_{aq}}(t) = K_{fw}\left(1 - e^{(-k_e t)}\right), \text{ and} \qquad (2)$$

$$t_{(70\% \text{ of } K_{fw})} = \frac{\ln(0.3)}{-k_e} \qquad (3)$$

Constructing the pp-LFER for a polyacrylate-water system

For the compounds for which K_{fw} values were available, the pp-LFER descriptors were collected from the literature. Only measured descriptors were used as far as this was possible to reconstruct. This resulted in a data set for 64 substances, with three independently determined values for 5 compounds, and 15 compounds with two reported values of K_{fw} (Appendix A). For these 20 compounds, the average difference between reported Log K_{fw} values is 0.25±0.24 (SD), with a maximum of 0.9 (chlorobenzene). With each reported value treated as a separate value, the coefficients for each descriptor in the LFER model for Log K_{fw} values were determined via multiple linear regression.

Chemicals, test medium and SPME fibers

The polyethylene glycol alkyl ethers $C_{10}EO_8$, $C_{12}EO_3$, $C_{12}EO_5$, $C_{12}EO_6$, $C_{12}EO_8$, $C_{14}EO_6$ and $C_{14}EO_8$ (all >98% TLC) were from Fluka Chemie AG (Buchs, Switzerland), $C_{14}EO_{11}$ and $C_{14}EO_{14}$ were custom made by J. Tolls (>97% GC, HPLC, ^{1}H-NMR). Cyclohexane (99.5%), n-heptane (95%) and dichloromethane (99.8%) were from Labscan Ltd (Dublin, Ireland), n-nonane (99.7%) from Riedel-deHaën AG (Seelze, Germany), n-decane (>99%) from Sigma-Aldrich Chemie (Steinheim, Germany), 1-heptanol (98%) from Merck (Hohenbrunn, Germany) and 1-octanol (>99.5%) from Fluka. n-Pentane (>99%, Riedel-deHaën) was distilled once to reduce background peaks that coincided with cyclohexane and heptane. For the test with

surfactants, Dutch Standard Water (DSW) was used, prepared according to NEN 6503 (pH 8.2, 2.1 mM $CaCO_3$). The test solution for the hydrocarbons and aliphatic alcohols consisted of 0.1 M $CaCl_2$ (Fluka). For both solutions, highly pure deionized water was used (Millipore Waters, Amsterdam, The Netherlands) with 100 mg/L NaN_3 as biocide. The solid-phase microextraction (SPME) fiber, with a 108 µm diameter glass core and a polyacrylate (PA) coating of 34.5 µm thickness (volume 15.4 µL/m), was custom made by Polymicro Technologies (Phoenix, AZ).

Sorption isotherms

Sorption isotherms were determined for all compounds in this study, using at least 4 different concentrations. The surfactants were tested individually in 40 mL vials, filled almost completely with DSW. Two fibers of 40 mm were exposed per test vial, and fibers were exposed for 3 days. Surfactants were spiked via a stock solution in methanol, which was evaporated before the test solution was added to the test vial. The fibers were desorbed in 1 mL of methanol, while AE was extracted from 10 mL aqueous phase using C_{18} SPE columns, according to ref (*11*).

The hydrocarbons and aliphatic alcohols were prepared as a mixture in acetone, in such a composition that the initial aqueous concentration, before introduction of the SPME fiber, would be within a factor 2 below the maximum solubility of each compound (Table 1) at the highest test concentration. Dilutions of the acetone stock were prepared for lower test concentrations, and from each stock 0.8 mL was added to 250 mL of test medium, leaving 3 mL of headspace. Aluminum foil was used within the screw cap to prevent sorption to the teflon septum. After gentle shaking of these test solutions overnight, a single SPME fiber of 115 mm was added to the test solutions (1.8 µL polyacrylate volume). Three series of 4 different test concentrations were prepared and after 2 weeks the fibers were sampled from the first series. After 3 weeks the second series was sampled, and the final series after 4 weeks.

When sampling the fiber, it was quickly blotted dry once taken out of the solution, and cut to pieces which were collected in vials containing 1.5 mL pentane. To analyze cyclohexane, heptanol and octanol in the aqueous phase, for which the aqueous concentrations were relatively high, 1 mL was sampled from the test vial, and compounds were extracted in 4 mL pentane. Heptane, nonane, and decane were extracted from the remaining 249 mL test solution using 3 mL pentane. A teflon 8 mm spinbar was added and after rigorous shaking by hand, the solutions were stirred during at least 4 hours. Pentane was sampled, and stored at 4 ^{o}C until analysis.

Chemical analysis

The nonionic surfactants from the fiber extracts and aqueous SPE extracts were analyzed on a Perkin Elmer (Norwalk, CT) HPLC system connected via a RP-C_{18} column (Chromspher 5, 100x3 mm, Chrompack, Middelburg, The Netherlands) to a API 3000 triple quad mass

spectrometer (MDS Sciex Applied Biosystems/MDS Sciex Instruments, Foster City, CA). Eluent consisting of 90:10 (v/v) methanol/water with 5 mM NH_4^+ was used isocratic at 0.6 mL/min, and introduced in the MS via a Turbo IonSpray source in the positive mode. The peaks of adducts of the parent compound with NH_4^+ were integrated for analysis, whereas adducts with Na^+ were used to identify the surfactant peak along with external standards.

The aliphatic compounds were analyzed in the pentane extracts of fiber and water, by injection of 1 µL sample in a Carlo Erba 5360 gas chromatograph with a flame ionization detector (FID, 50 kPa hydrogen). Compounds were separated on a 30 m x 0.53 mm SE-54 column (Alltech, df = 1.2 µm), with a temperature program of 1 min at 30°C, then with 10°C/min to 165°C, and were quantified using external standards. For sorption isotherms with a linear slope of 0.95-1.05 on a log-log plot, a linear line with a fixed slope of 1 was fitted to the data to obtain a concentration independent partition coefficient.

Table 1. Properties of Alcohol Ethoxylates and Partition Coefficients for Octanol-Water (estimated), Polyacrylate-Seawater (ref (*11*)) and Polyacrylate-Freshwater (this study).

AE	MW	cmc [a] (mg/L)	log K_{OW} est. [b]	log K_{fw} (SW) [c]	C_{aq} tested range (mg/L)	n [d]	log K_{fw} (DSW) [e]	ΔLog K_{fw} (SW- DSW)	Log K_{fw} via pp-LFER [f]
$C_{10}EO_8$	510	553.6	1.60	1.49	9.2 – 215.0	10	1.17 ± 0.10	0.32	-2.06
$C_{12}EO_3$	318	21.3	3.95	3.97	0.01 – 1.0		3.28 ± 0.13		2.10
$C_{12}EO_5$	407	33.2	3.40	3.43	0.01 – 1.0	5	2.81 ± 0.05	0.62	0.80
$C_{12}EO_6$	451	40.8	3.12	3.09	0.004 – 41.0	20	2.74 ± 0.01	0.35	0.15
$C_{12}EO_8$	539	59.6	2.58	2.50	0.29 – 44.0	10	2.08 ± 0.04	0.42	-1.15
$C_{14}EO_6$	479	4.4	4.11	4.07	0.15 – 1.4	8	3.94 ± 0.01	0.13	1.05
$C_{14}EO_8$	567	6.4	3.56	3.62	0.09 – 2.5	10	3.17 ± 0.01	0.45	-0.25
$C_{14}EO_{11}$	698	10.6	2.73	2.80	0.17 – 4.8	8	2.32 ± 0.01	0.48	-2.21
$C_{14}EO_{14}$	830	17.1	1.91	2.06	0.24 – 6.3	10	1.48 ± 0.01	0.58	-4.16

[a] in purified water according to Log cmc = 1.65 – 0.496·#C + 0.0437·#EO (mol/dm^3) in ref (*47*); [b] estimated via KowWIN in the EPI-Suite software package; [c] measured in artificial seawater (SW) in refs (*11*) and (*21*) where concentration independent values were reported; [d] Number of SPME fiber measurements; *e* determined in this study in artificial freshwater (DSW, 0.5 g salt/L) as concentration independent coefficients ± standard error; [f] calculated using estimated descriptor values for AE (as further explained in text) and the pp-LFER in eq 6.

RESULTS AND DISCUSSION

Polyacrylate-water partition coefficients database for pp-LFER modeling

The selected K_{fw} values were obtained from fourteen different literature sources, which differed considerably in experimental setup. The K_{fw} values for eight compounds reported in the paper of Verbruggen *et al.* (*39*) and one from Vaes *et al.* (*12*), were discarded because the kinetic data did not include measurements above 70% of the equilibrium. For almost none of the K_{fw} values for more than 50 pesticides, reported by Valor *et al.* (*40*) and Magdic *et al.* (*41*), pp-LFER descriptors could be found, which clearly is a pity for the quality of the K_{fw} database. The K_{fw} data for the most hydrophobic PCBs from Paschke and Popp (*42*) were not used because the data for PDMS fibers with varying thicknesses showed that equilibrium may not have been reached. The pp-LFER descriptors of the 64 selected chemicals are presented in Appendix A.

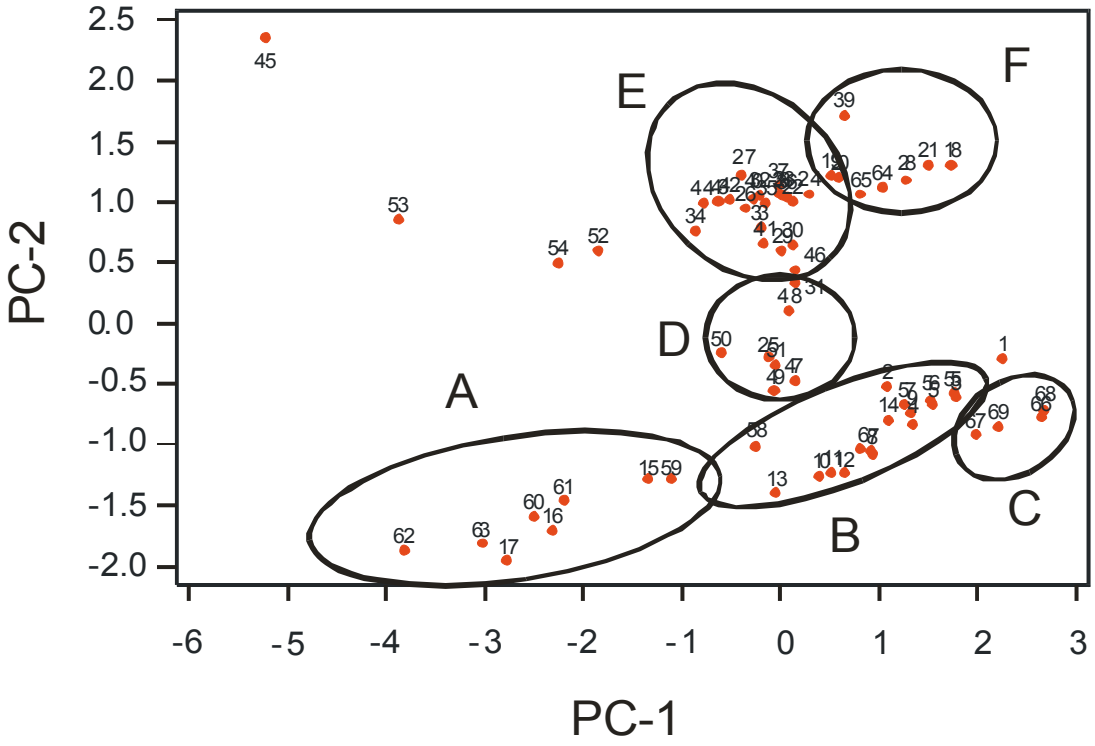

Figure 1. Principle components score for the data set with K_{fw} values, with clusters of polyaromatics (A), halogenated hydrocarbons (B), alkanes (C), polar organics containing nitrogen (D), hydroxylated polar organics (E) and hydroxylated aliphatics (F). Compounds 52 and 54 are phthalates, 53 is atrazine, 45 estradiol.

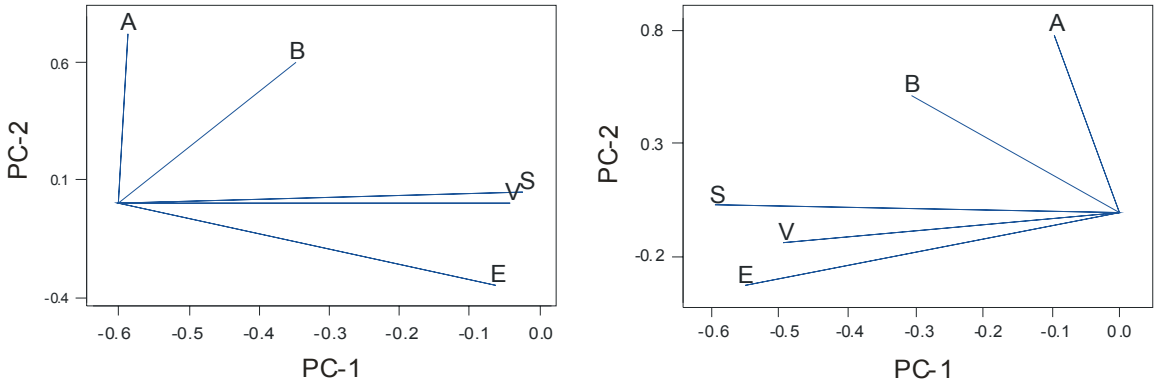

Figure 2. Principle components loading plots for the K_{fw} values data set according to the descriptors for molecular volume (V), molar refraction (E), polarisability (S), and hydrogen bond acidity (A) and basicity (B). The plot on the left side shows the variation of descriptors for data set of literature values, the plot on the right shows the variation when the 6 K_{fw} values for the aliphatic alcohols and alkanes are included.

The variation for each descriptor (lowest and highest values are presented at the end of Appendix A) do not cover the total ranges that are possible. Nevertheless, the highest descriptor values are comparable to those in the data set that Nguyen *et al*. (*28*) used to construct a pp-LFER for sorption coefficients between organic matter and water. The lower range of descriptors E and S will be improved by including the new data for alkanes in this study, as values for both descriptors are zero for alkanes. The database would be further improved when fluorinated compounds are included too, as the Van der Waals descriptors E and V are even below zero, but these compounds were not tested in this study.
The variation in the descriptors for the compounds present in the K_{fw} data set is shown in a principle components plot (Figure 1), in which the alkanes and several other chemical classes are clearly clustered. Figure 2 shows the loading plot of the first and second component for the descriptors. In the loading plot of the literature data set (2A), descriptor V shows a clear overlap with descriptor S. This is probably related to the over-representation of polycyclic aromatic compounds in the data set, since both S and V increase with the amount of rings in these compounds. Including the few extra alkanes that were investigated in this study separates descriptors S and V to some extent (2B), showing that the variation of the data set can be slightly improved.

K_{fw} values for alkanes and aliphatic alcohols

The average mass balance for 1-heptanol and 1-octanol, based on the fiber extracts and water samples for the 13 test vials were 104±9 and 109±9%, respectively. The calibration curve for cyclohexane determined along with the samples could unfortunately not be used, because the samples were probably contaminated with hexane while being stored. The calibration curve measured a week prior to the samples was used, after correction for a 10% difference in sensitivity. Only the samples obtained in the first series also showed this contamination. Based on measured fiber and water samples for the cyclohexane samples from the second and third series, the mass balances were 100 ± 13%. The extraction of alkanes from 250 mL water in 3 mL pentane was not successful. Although the heptane and

nonane were clearly presents in the aqueous samples, the total mass balances were 27±15, 17±9%, respectively. Whereas the peak of decane was clearly separated and identified in calibration standards and the fiber extracts, the much higher peak of 1-heptanol in the total extracts from the aqueous phase disturbed the detection of decane. The concentrations of the alkanes in the fibers, however, showed the expected range as expected from nominal concentrations. Given the good recovery for the mass balances of the alcohols, the aqueous concentrations of the alkanes were calculated assuming a 100% mass balance. The weight fraction of heptane, nonane, and decane, that the fiber extracted from the aqueous phase, was 2, 11 and 22% respectively. Since other major sorption phases were not expected in the test solutions, it was assumed that the calculated mass balances are valid. However, further experimental work is needed to confirm this assumption and the sorption data for the alkanes should be considered as tentative values.

Figure 3A shows the fiber concentrations of the alkanes and alcohols plotted against the measured or estimated aqueous concentrations for the samples after 2, 3 and 4 weeks exposure of the fibers. The regressions with a slope of 1 fit the data for all compounds well for all series. The y-intercepts in these regressions are the K_{fw} values and are presented in Table 2. The K_{fw} values for the 2, 3 and 4 weeks series, and for none of the test compounds, significantly increase in time, indicating that equilibrium was reached within 2 weeks. As expected from aqueous solubility and K_{ow} values of these values, the affinity for the polyacrylate phase increased with increasing alkyl chain length. Comparing heptanol with heptane, the K_{fw} was lowered with more than 1.5 log units by the presence of the hydroxyl group.

Table 2. Properties of Hydrocarbon Compounds and Aliphatic Alcohols in This Study.

	Log K_{ow} [a]	Log K_{ow} [b]	S_w (mg/L) [c]	Log K_{fw} [f]
cyclohexane	3.44	3.38	58.3 [d]	2.82 ± 0.01
n-heptane	4.50	4.26	3.39 [d]	3.34 ± 0.03
n-nonane	5.65	5.34	0.171 [c]	4.19 ± 0.03
n-decane	6.25	5.88	0.046 [c]	4.57 ± 0.04
1-heptanol	2.62	2.52	1750 [e]	1.72 ± 0.01
1-octanol	3.07	3.05	585 [e]	2.27 ± 0.01

[a] K_{ow} values recommended by Sangster (*43*); [b] K_{ow} values predicted with the pp-LFER model (*26*), using the descriptors in Appendix A; [c] maximum aqueous solubility (S_w) from 298 K in ref (*48*); [d] experimental at 298 K from Plyasunov and Shock (2000) as reported in ref (*49*); [e] at 298 K taken from ref (*50*); [f] determined in this study in aqueous solution with 0.1 mM $CaCl_2$ and 8 mM NaN_3 as concentration independent coefficients ± standard error.

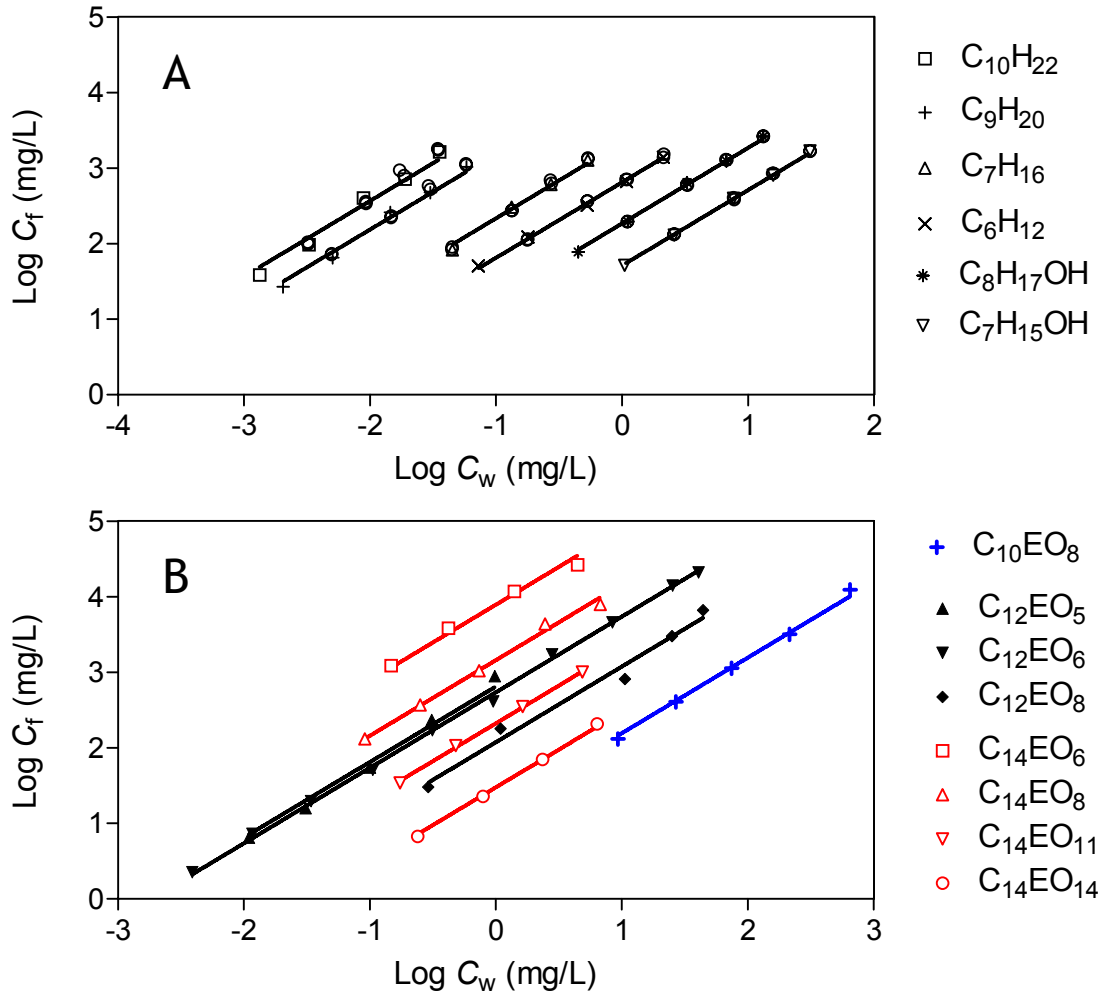

Figure 3. Linearized SPME sorption isotherms for (A) hydrocarbons and aliphatic alcohols in 0.1 M $CaCl_2$ and (B) individual alcohol ethoxylate homologues in artificial freshwater (DSW).

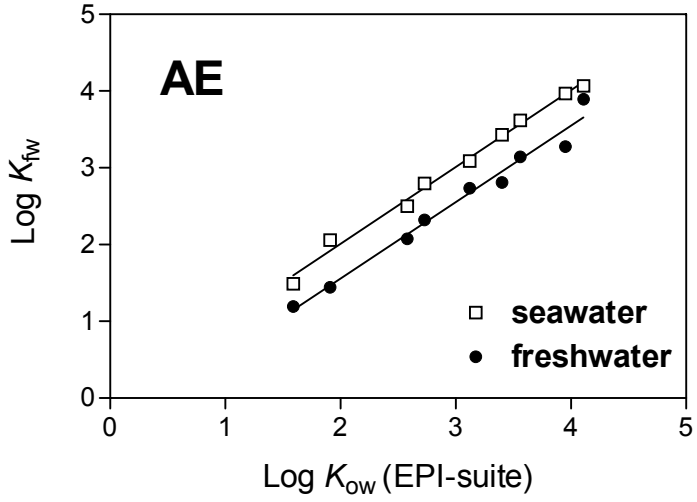

Figure 4. Experimental K_{fw} values for alcohol ethoxylates in freshwater (DSW), from this study, and seawater (SW) from ref (*11*), plotted against estimated K_{ow} values from KowWIN.

Approach 1: A direct comparison between K_{fw} and K_{ow} values

Figure 5 presents the relationship between polyacrylate K_{fw} and K_{ow} values for all compounds that were considered good values (≤2007). For 64 out of 134 compounds, no pp-LFER descriptors could be retrieved from literature (Appendix D). For the remaining 70 compounds, including the alkanes and aliphatic alcohols, the K_{fw} values are almost linearly related to K_{ow} values:

$$\text{Log } K_{fw} \text{ (pp-LFER set)} = 0.993\ (\pm 0.036)\ \text{Log } K_{ow} - 0.166\ (\pm 0.116) \qquad (4)$$

$n = 70$, $r^2 = 0.93$, s = 0.334

On average, the K_{fw} of compounds in the pp-LFER data set are almost similar to the K_{ow}. Some compound classes considerably deviate though, e.g., both literature data as the experimental data in this study show that the K_{fw} values of the alkanes and alcohols are more than an order of magnitude lower than the reported K_{ow} values. The K_{ow} of decane recommended by Sangster (*43*), however, is 0.5 log units higher than the K_{ow} predicted by the pp-LFER for octanol-water (Table 2).

The group of compounds without pp-LFER descriptors, which comprise mainly highly polar pesticides, significantly deviates ($p<0.01$) from the K_{ow} relationship in equation 4:

$$\text{Log } K_{fw} \text{ (without descriptors)} = 0.518(\pm 0.052)\ \text{Log } K_{ow} + 1.51\ (\pm 0.19) \qquad (5)$$

$n = 64$, $r^2 = 0.61$, s = 0.518

Partly this could be due to erroneous values in the set of compounds without descriptors, although the described procedure passed our criteria for this set of data. For example, values from Valor *et al*. (*40*) are down to 1.5 log units lower compared to replicates for some compounds from other studies, e.g. for chlorpyriphos. On the other hand, K_{ow} values may also include considerable uncertainty for such compounds. Still, it is possible that the partition coefficients differ between octanol and polyacrylate because of the complex polar structures of the pesticides which may interact differently with these two phases.

Approach 2: A comparison between the pp-LFERs for polyacrylate-water and octanol-water

Including the K_{fw} data for the alkanes and alcohols, multiple regression of the 70 experimental K_{fw} values with the five pp-LFER descriptors resulted in the following coefficients for the polyacrylate-water relationship:

$$\text{Log } K_{fw} = 3.20(\pm 0.11) \cdot \mathbf{V} + 0.38(\pm 0.11) \cdot \mathbf{E} + 0.084(\pm 0.16) \cdot \mathbf{S} + 0.048(\pm 0.099) \cdot \mathbf{A} - 3.93(\pm 0.14) \cdot \mathbf{B} - 0.13(\pm 0.11) \qquad (6)$$

$n = 70$; $r^2 = 0.97$; SE = 0.215

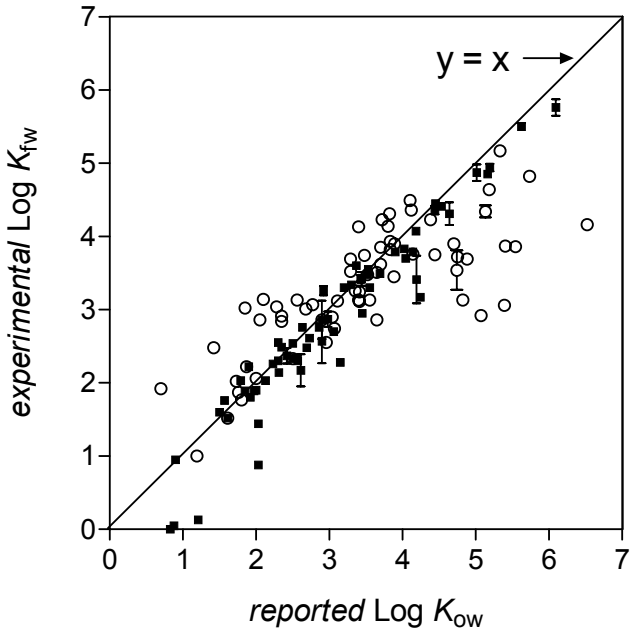

Figure 5. Experimental Log K_{fw} values (±SD) versus Log K_{ow} values reported in the literature sources. The data set used in the pp-LFER model are indicated with (o), K_{fw} values for which no pp-LFER descriptors were retrieved are presented as (■).

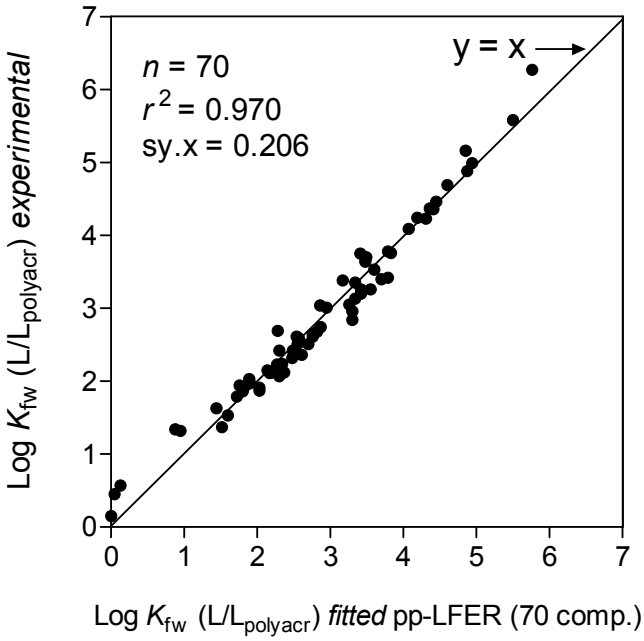

Figure 6. Experimental K_{fw} values versus pp-LFER calculated K_{fw} values including the 6 additional compounds from this study.

Figure 6 plots the experimental K_{fw} values against the K_{fw} values calculated via the pp-LFER. The K_{fw} values calculated for the 70 compounds with the obtained pp-LFER deviated on average 0.16(±0.13) log units from the experimental K_{fw} values. The estimated K_{fw} for ten of the compounds (out of 70) deviated more than a factor 2 (0.3 log units) from the experimental value, while the largest deviation was a factor 3 (0.5 log units, PCB 52). The pp-LFER for K_{ow} values has been determined already in 1994 (*26*):

$$\text{Log } K_{ow} = 3.81 \cdot \mathbf{V} + 0.56 \cdot \mathbf{E} - 1.05 \cdot \mathbf{S} + 0.034 \cdot \mathbf{A} - 3.46 \cdot \mathbf{B} - 0.88 \quad (7)$$

n = 613; r^2 = 0.997; SD between fitted and experimental Log K_{ow} = 0.12

When comparing the pp-LFER coefficients, the most obvious deviations are for the coefficients for descriptor V (molecular volume) and S (polarizability). These two descriptors, however, are still relatively strong correlated in the data set (see loading plot in Figure 2). Applying the LFERs for polyaromatics, the partition coefficients from water to polyacrylate do not strongly deviate from those to octanol. The lower value for the coefficient *v* for polyacrylate compared to octanol does explain the lower K_{fw} for alkanes, and probably also aliphatic alcohols, which do not contribute strongly via S.

Octanol and polyacrylate are comparable phases regarding hydrogen bond acidity. The polyacrylate-water system, however, has a higher coefficient for hydrogen bond basicity descriptor B, indicating that the polyacrylate is a weaker electron donor than octanol. Most likely, this is due to the presence of hydroxyl groups in octanol, whereas these are probably not present in polyacrylate. The polyacrylate in PA coated SPME fibers probably consists of a mixture of poly(alkyl methacrylates), which contain ester bonds. Because of the rather subtle differences between the system coefficients, the question whether the K_{fw} of a compound is representative for the K_{ow} (or vice versa) depends on the combination of all solute descriptors.

K_{fw} values for nonionic surfactants in freshwater

Figure 3B shows that the fiber concentrations of all alcohol ethoxylates increase linearly with the measured aqueous concentrations. Similar to the results in seawater, the affinity of AE for the polyacrylate fibers increases with alkyl chain length, and decreases with each additional ethoxylate unit. The K_{fw} values that are obtained from the linear regressions with a slope of 1 in Figure 3B are presented in Table 1. The partition coefficients in DSW are lower than those in seawater, on average 0.42±0.16 log units. The increasing affinity of the AEs for the SPME fiber with salinity corresponds with the decrease in critical micelle concentration (cmc) with salinity (*11,44*), although the cmc did not differ more than a factor 2. The regression between K_{fw} values for AE in freshwater and estimated K_{ow} values, presented in Figure 4, shows that the regression line for freshwater is parallel to the relationship for K_{fw} values in seawater, but with a lower cut-off (0.44 log units) with the Y-axis. Multiple regression of the freshwater Log K_{fw} values with alkyl chain length (#C) and number of ethoxylates (#EO) gives the same coefficients as observed for the seawater, 0.52 and -0.27, respectively, and only a different constant (Chapter 6 and ref (*21*)):

Log K_{fw} (DSW) = 0.516(±0.038)· #C – 0.268(±0.017)· #EO – 1.93(±0.45) (8)

The K_{fw} data for both seawater and freshwater show that there is, up to 14 EO units, no limit on the contribution of these polar fragments to the partition coefficient. Furthermore, the contribution of a single EO fragment to the overall partition coefficient appears to be fairly constant.

Comparing K_{fw} values for nonionic surfactants with pp-LFER predictions

As already mentioned in the introduction, there are no experimental values for the pp-LFER descriptors for AE. Similar to the contribution values of molecular fragments for K_{ow}, some studies have derived the contribution values of molecular fragments for the pp-LFER descriptors (*37,38*). The types of molecular fragments in AE are not complex, basically CH_2 groups, aliphatic ether bonds and a hydroxylgroup. Especially for the repetitive ethoxylate units, however, it is not clear if the fragment values can be used for AE. If the pp-LFER for the polyacrylate-water system is correct, and the fragment values can be used to derive the descriptors for AE, they should accurately predict the experimentally derived K_{fw} values of AE in freshwater.

In general, the descriptors for molecular volume (V) and molar refractions (E) are easily calculated from other structures. Just as for alkanes, the alkyl chain of the AE will only contribute to the overall K_{fw} via the descriptor V. Each CH_2 unit increases the molecular volume descriptor with 0.141, and in combination with system coefficient v (+3.20) in Equation 6, this shows that the contribution to Log K_{fw} of each CH_2 unit (v·V) is +0.451. This contribution factor already differs from the fragment value for #C from multiple regression of the K_{fw} data of AE in freshwater (+0.52, eq 8). Still, equation 8 can also be readily adapted so that the value for #C becomes +0.45.

The fragment values of ether bonds in the ethoxylate units may be comparable to those obtained for di-ethyl ether, 0.041 for the descriptor E, 0.25 for S, 0 for A, and 0.45 for B (*38*). It is more difficult to include the fragment value for the hydroxylgroup at the end of the ethoxylate chain. For example, the descriptor values E, S, A, and B for the hydroxyl group in butanol and 2-ethoxyethanol are different when corrected for the ether fragment in 2-ethoxyethanol. Apparently, the contribution of the hydroxyl fragment to the molecular descriptors for polarity is clearly influenced by the last ether bond. Therefore the contribution values for the fragment of the last ether bond and hydroxylgroup are approximated by those of 2-ethoxyethanol: 0.237 for E, 0.5 for S, 0.3 for A, and 0.83 for B. The last column in Table 1 presents the pp-LFER predicted K_{fw} values for AE based on equation 6 and the descriptors that are derived with the fragment values. Clearly, the deviation between the predicted K_{fw} values and experimental K_{fw} values in freshwater (DSW) increases with an increasing number of ethoxylate units. With the pp-LFER-descriptors estimated above, the pp-LFER predicts a decrease of 0.65 per EO unit for Log K_{fw} values, which is much more than the decrease of 0.27 per EO unit observed for

experimental Log K_{fw} values. Whether this is due to an error in the system coefficients of the pp-LFER (equation 6) or one or more of the descriptor values is not known.

With the correct descriptors for the fragments of AE homologues, it would be possible to draw conclusions on whether K_{fw} values are really representative for the K_{ow} values. This is not yet possible based on the results of this study. It is still interesting to further establish accurate fragment values for AE, because in the future these could even be used to estimate organic carbon partition coefficients (K_{oc}) or membrane partition coefficients for AE. The pp-LFERs for such phases have already become available (*28,29,35,45,46*) and will constantly be improved by additional data. This will also further clarify whether K_{ow} are really good indicators of partition constants for surfactants to biomembranes or natural organic matter.

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Appendix A. Properties of nonionic organic compounds reported in literature (<2007) used to construct the pp-LFER.

	Log K_{ow} *	Log K_{fw} (experim.)	Ref (resp.)	Max. ΔLog K_{fw} (experim.)	V	E	S	A	B
1,2,3,4-tetrachlorobenzene	4.64	4.15, 4.47	(*42*), (*51*)	0.32	1.206	1.180	0.920	0.000	0.000
1,2,3-trichlorobenzene	4.14	3.79	(*52*)		1.084	1.030	0.860	0.000	0.000
1,2,4-trichlorobenzene	4.02	3.83	(*52*)		1.084	0.980	0.810	0.000	0.000
1,3,5-trichlorobenzene	4.19	3.08, 3.73	(*53*), (*52*)	0.65	1.084	0.980	0.730	0.000	0.000
1,2-dichlorobenzene	3.43	3.47, 3.37	(*52*), (*54*)	0.1	0.971	0.872	0.780	0.000	0.040
1,3-dichlorobenzene	3.53	3.55	(*52*)		0.971	0.847	0.730	0.000	0.020
1,4-dichlorobenzene	3.44	3.51, 3.33	(*52*), (*54*)		0.971	0.825	0.750	0.000	0.020
1-butanol	0.88	0.05	(*53*)		0.731	0.224	0.420	0.370	0.480
1-hexanol	2.03	0.88	(*53*)		1.013	0.210	0.420	0.370	0.480
1-iodobutane	3.06	2.70	(*55*)		0.930	0.628	0.400	0.000	0.150
1-iodohexane	4.04	3.70	(*55*)		1.212	0.615	0.400	0.000	0.150
1-iodopentane	3.55	3.30	(*55*)		1.071	0.621	0.400	0.000	0.150
1-iodopropane	2.57	2.30	(*55*)		0.790	0.634	0.400	0.000	0.150
2-butoxyethanol	0.83	0.00	(*53*)		1.072	0.201	0.500	0.300	0.830
2,4,6-trichlorophenol #	3.69	3.49	(*56*)		1.142	1.010	1.010	0.820	0.080
2,4,6-trimethylphenol	2.73	2.61	(*56*)		1.198	0.860	0.780	0.370	0.440
2,4-dimethylphenol	2.42	2.26, 2.47	(*56*), (*57*)b	0.21	1.057	0.843	0.800	0.530	0.390
2,4-dichlorophenol	2.92	3.34, 3.13, 3.30	(*58*), (*56*), (*57*)b	0.21	1.020	0.970	0.990	0.580	0.140
2,5-dichlorophenol #	3.20	3.30	(*56*)		1.020	0.970	0.880	0.560	0.190
2,6-dichlorophenol #	2.86	2.76	(*56*)		1.020	0.900	0.900	0.380	0.240
2-chloroaniline	1.9	2.22	(*52*)		0.939	1.033	0.920	0.250	0.310
2-nitrophenol	1.79	2.03	(*58*)		0.949	1.015	1.050	0.050	0.370
2-nitrotoluene	2.30	2.55	(*53*)		1.032	0.866	1.110	0.000	0.270

Appendix A (cont.)	Log K_{ow} *	Log K_{fw} (experim.)	Ref (resp.)	Max. ΔLog K_{fw} (experim.)	**V**	**E**	**S**	**A**	**B**
3,4-dimethylphenol	2.23	2.26	(*58*)		1.057	0.830	0.860	0.560	0.390
3,4-dichlorophenol	3.37	3.60	(*56*)		1.020	1.020	1.140	0.850	0.030
3,5-dichlorophenol	3.52	3.48	(*56*)		1.020	1.020	1.170	0.770	0.000
3-pentanol	1.21	0.13	(*53*)		0.872	0.218	0.360	0.330	0.560
3-chlorophenol	2.5	2.60, 2.51, 2.51	(*58*), (*56*), (*52*)	0.09	0.898	0.909	1.060	0.690	0.150
3-methoxyphenol	1.57	1.76	(*56*)		0.975	0.879	1.170	0.590	0.380
4-bromophenol	2.63	2.76	(*56*)		0.950	1.080	1.170	0.670	0.200
4-chloro-3-methylphenol	2.98	2.97, 2.76	(*56*), (*53*)	0.21	1.038	0.920	1.020	0.650	0.230
4-chlorophenol	2.35	2.49	(*56*)		0.898	0.920	1.080	0.670	0.200
4-ethylphenol	2.50	2.33	(*56*)		1.057	0.800	0.900	0.550	0.360
4-fluorophenol	1.92	1.80	(*56*)		0.793	0.670	0.970	0.630	0.230
4-iodophenol	2.90	2.60, 3.12	(*55*), (*56*)	0.52	1.034	1.380	1.220	0.680	0.200
4-methylphenol	1.97	1.88, 1.90	(*56*), (*58*)	0.02	0.916	0.820	0.870	0.570	0.310
4-t-butylphenol	3.45	2.95	(*58*)		1.339	0.810	0.890	0.560	0.390
4-t-pentylphenol	4.24	3.17	(*53*)		1.480	0.810	0.890	0.560	0.410
aniline	0.9	0.95	(*53*)		0.816	0.970	0.970	0.260	0.410
anthracene	4.45	4.45	(*42*)		1.454	2.290	1.340	0.000	0.260
atrazine	2.61	2.38, 1.95	(*40*), (*52*)	0.43	1.620	1.950	1.640	0.320	0.970
benzene	2.13	2.03	(*57*)b		0.716	0.610	0.520	0.000	0.140
bromoform	2.30	2.30	(*55*)		0.775	0.974	0.680	0.150	0.090
chlorobenzene	2.90	2.87, 2.87, 1.97	(*54*), (*57*)b, (*53*)	0.90	0.839	0.720	0.650	0.000	0.070
Chloroform	2.00	1.90, 1.90	(*55*), (*57*)b	0.00	0.617	0.425	0.490	0.150	0.020
diethylphthalate	2.54	2.34	(*59*)		1.711	0.729	1.400	0.000	0.880

Appendix A (cont.)	Log K_{ow} *	Log K_{fw} (experim.)	Ref (resp.)	Max. ΔLog K_{fw} (experim.)	**V**	**E**	**S**	**A**	**B**
dimethylphthalate	1.61	1.52	(*59*)		1.429	0.780	1.410	0.000	0.880
estradiol	3.9 **	3.79	(*60*)		2.199	1.800	1.770	0.860	1.100
fluoranthene	5.16	4.85	(*42*)		1.585	2.377	1.530	0.000	0.200
fluorene	4.18	4.07	(*57*)a		1.357	1.588	1.030	0.000	0.200
N,N-dimethylaniline	2.31	2.14	(*53*)		1.098	0.957	0.840	0.000	0.420
naphthalene	3.30	3.37, 3.34, 3.30	(*61*), (*57*)a, (*57*)b	0.03	1.085	1.340	0.920	0.000	0.200
nitrobenzene	1.85	1.92, 1.85	(*57*)b, (*53*)	0.07	0.891	0.871	1.110	0.000	0.280
PCB-1	4.53	4.41	(*57*)a		1.447	1.530	1.120	0.000	0.200
PCB-15	5.33	5.17	(*57*)a		1.569	1.640	1.180	0.000	0.160
PCB-28	5.62	5.46, 5.55	(*42*), (*57*)a	0.09	1.691	1.800	1.390	0.000	0.120
PCB-52	6.09	5.65, 5.88	(*42*), (*57*)a	0.23	1.814	1.930	1.520	0.000	0.060
pentachlorophenol #	5.01	4.98, 4.75	(*56*), (*57*)b	0.23	1.389	1.217	0.880	0.970	0.000
phenanthrene	4.44	4.47, 4.29, 4.33	(*42*), (*57*)a, (*57*)b	0.18	1.454	2.055	1.290	0.000	0.260
phenol	1.50	1.60	(*56*)		0.775	0.805	0.890	0.600	0.310
p-xylene	3.15	2.28	(*53*)		0.998	0.613	0.520	0.000	0.160
pyrene	5.19	4.89, 4.99	(*42*), (*57*)a	0.10	1.585	2.808	1.710	0.000	0.290
quinoline	2.03	1.44	(*53*)		1.044	1.268	0.970	0.000	0.540
toluene	2.69	2.48	(*57*)b		0.857	0.601	0.520	0.000	0.140
Min.	**0.83**	**0.00**			**0.62**	**0.20**	**0.36**	**0.00**	**0.00**
Max.	**6.09**	**5.88**			**2.20**	**2.81**	**1.77**	**0.97**	**1.10**

(*57*)a: Table 1 in ref (*57*), (*57*)b: Table 2 in ref (*57*); # corrected for concentrations of neutral species at tested pH in ref (*56*) or sufficiently below pKa in ref (*57*)b. * K_{ow} taken from the study itself, or ** estimated value based on calculating software (*62*).

Appendix B. Partition coefficients and pp-LFER descriptors of alkanes and alcohols used in this study.

	Log K_{ow} *	Log K_{fw} (experim.)	Log K_{fw} (pp-LFER 70 comp.)	**V**	**E**	**S**	**A**	**B**
n-heptane	4.50	3.34	3.35	1.09	0.00	0.00	0.00	0.00
n-nonane	5.65	4.19	4.24	1.38	0.00	0.00	0.00	0.00
n-decane	6.25	4.57	4.69	1.52	0.00	0.00	0.00	0.00
cyclohexane	3.44	2.82	2.68	0.85	0.31	0.10	0.00	0.00
1-heptanol	2.62	1.72	1.79	1.15	0.21	0.42	0.37	0.48
1-octanol	3.07	2.27	2.23	1.30	0.20	0.42	0.37	0.48

* K_{ow} recommended by Sangster 1989 (*43*)

Appendix C. Eigenvectors for Principle component (SVD) analysis of the K_{fw} data set in Appendix A including 6 aliphatics in Appendix B analyzed in this study.

Variable	PC1	PC2
V	-0.493	-0.137
E	-0.550	-0.327
S	-0.593	0.027
A	-0.095	0.780
B	-0.306	0.514

Appendix D. K_{ow} and seemingly good experimental K_{fw} values for nonionic organic compounds reported in literature (<2007) for which no pp-LFER descriptors were found in literature. * K_{ow} taken from the study itself.

Compound	Log K_{ow} *	Log K_{fw}	Ref (resp.)	Compound	Log K_{ow} *	Log K_{fw}	Ref (resp.)
1-iodoheptane	4.70	3.90	(*55*)	dimethylphthalate	1.61	1.52	(*59*)
2(3h)-benzothiazolone	1.76	1.87	(*52*)	di-n-butylphthalate	3.29	3.69	(*59*)
2,3,4,6-tetrachlorophenol	4.10	4.49	(*56*)	di-n-propylphthalate	2.68	3.01	(*59*)
2,3,6-trichlorophenol	3.88	3.45	(*56*)	endosulphan i	3.83	3.93	(*40*)
2,4,5-trichlorophenol	3.72	4.23	(*52*)	endosulphan ii	3.83	3.82	(*40*)
2,4,6-trinitrotoluene	2.05	2.86	(*63*)	endrin	4.88	3.69	(*40*)
2,4-diamino-6-nitrotoluene	0.70	1.92	(*63*)	ethion	5.07	2.92	(*40*)
2-amino-4,6-dinitrotoluene	1.85	3.02	(*63*)	ethylazinphos	3.40	3.13	(*40*)
3,5-dichlorophenol	3.52	3.48	(*56*)	fenthion	4.12	4.36	(*40*)
4-amino-2,6-dinitrotoluene	2.10	3.14	(*63*)	fonofos	3.89	3.90	(*40*)
4-chloro-3,5-dimethylphenol	3.48	3.74	(*56*)	h,epoxide	5.40	3.87	(*40*)
4-ethylphenol	2.50	2.33	(*56*)	heptachlor	5.54	3.86	(*40*)
4-iodophenol	2.90	2.60, 3.12	(*55*)	hexachlorobenzene	5.73	4.82	(*52*)
α-HCH	3.80	4.14	(*40*)	lindane	3.70	3.85	(*40*)
β-HCH	3.82	4.31	(*40*)	methyl-4-chloro-2-nitrobenzoate	2.35	2.84	(*53*)
δ-HCH	4.14	3.76	(*40*)	methyl-parathion	2.56	3.13	(*40*)
aldrin	6.52	3.78, 4.53	(*40,52*)	methyl-trithion	4.82	3.13	(*40*)
ametryn	3.07	2.74	(*40*)	parathion	3.41	3.24	(*40*)
carbophenothion	5.39	3.06	(*40*)	pentachlorobenzene	5.18	4.64	(*52*)
chlorpiryphos	5.13	3.51, 5.18	(*40*) (*41*)	phenitrothion	3.40	4.13	(*40*)
cyanazine	1.73	2.02	(*40*)	phenthoate	3.70	3.62	(*40*)
diazinon	3.35	2.75, 3.78	(*40*)	prometryne	3.41	3.11	(*40*)
dibenzo-p-dioxin	4.38	4.23	(*52*)	propazine	2.96	2.55	(*40*)
dibutylphthalate	4.74	3.81, 3.27	(*52,53*)	quinalphos	4.44	3.75	(*40*)
dibutylsuccinate	3.65	2.86	(*53*)	simazine	2.00	2.06	(*40*)
dichlorvos	1.42	2.48	(*41*)	terbuthylazine	3.04	2.90	(*40*)
dieldrin	4.75	3.72	(*40*)	terbutryn	3.65	3.51	(*40*)
diethyladipate	1.8	1.77	(*53*)	tradimephon	2.77	3.07	(*40*)
diethylmalonate	1.19	1.00	(*53*)	triazophos	3.55	3.13	(*40*)
diisobutylphthalate	3.29	3.52	(*59*)	trietazyne	3.11	3.12	(*40*)
dimethyl-2-amino-p-phtalate	2.28	3.04	(*53*)				

Chapter 5

Nonlinear Sorption of Three Alcohol Ethoxylates to Marine Sediment: A Combined Langmuir and Linear Sorption Process?

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Nonlinear Sorption of Three Alcohol Ethoxylates to Marine Sediment: A Combined Langmuir and Linear Sorption Process?

ABSTRACT

Alcohol ethoxylates (AE) are nonionic surfactants mainly used in laundry cleaning products. The relation between particle bound and freely dissolved concentrations is an important entity in risk assessment. The mechanistic understanding of AE sorption is still poor, hampering extrapolations from laboratory studies to the field. We studied the sorption of three AE with 8 EO units but with increasing alkyl chains (C_{10}, C_{12}, and C_{14}) to a marine sediment. Solid-phase microextraction, using polyacrylate as the extraction phase, was applied to measure freely dissolved concentrations in pore water. A model that combines a Langmuir and a linear sorption term fitted the nonlinear sorption data to sediment well. At low aqueous concentrations, adsorption dominates over absorption leading to higher distribution coefficients for AE at low field concentrations. This dual-mode model offers the possibility to extrapolate to other AE homologues and other marine sediments and also from high to low field concentrations.

INTRODUCTION

Alcohol ethoxylates (AE) are nonionic surfactants that contain a hydrophobic alkyl chain connected via an ether bond to a hydrophilic chain of ethoxylate (EO) units. They are used worldwide in domestic and commercial detergents, household cleaners and personal care products. In these commercial products, AE is always a mixture of molecules with different chain lengths, represented by the molecular formula $CH_3(CH_2)_n(OCH_2CH_2)_yOH$ where *n* usually is 11-16 or 18, and *y* varies between 1 and 18. Typical concentrations of each individual AE in sewage treatment plant (STP) influents are 5-10 µg/L for the lowest (EO<3) and the most (EO>17) ethoxylated AE, and up to 100 µg/L for AE with an intermediate EO chain length. Individual AE concentrations in STP effluents range between 1 and 200 ng/L (*1,2*). Although very limited data exists on AE field concentrations, one study showed that all marine sediment samples from several industrialized zones along the Spanish coast contained AE, with total concentrations between 37 and 1300 µg/kg, while concentrations in seawater in the same regions were always (well) below 15 µg/L (*3*).

Although most monitoring data are for sediment, an evaluation of potential risk based on sediment concentrations is not straightforward because the bioavailability may depend on specific sediment properties. The freely dissolved concentration in the pore water is an important entity in evaluating the availability of AE for biodegradation processes (*4*) and likely also for bioaccumulation and toxicity to sediment inhabiting organisms. The relation between sediment sorbed and pore water dissolved concentrations is specific for each AE homologue and also depends on the type of sediment (*5-7*). Especially for AE with long ethoxylate chains isotherms can be nonlinear (*6*), and the sorption coefficients are thus concentration-dependent. This complicates the extrapolation of existing sorption data to the real environment, where concentrations of individual homologues in the sediment are in the order of µg/kg (*8*), whereas the lowest concentrations in sorption experiments with spiked sediment are in the mg/kg range. Furthermore, existing sorption data cover only a few individual AE homologues and a small selection of freshwater sediments. There are no sorption studies on marine sediments. Direct extrapolation of data from freshwater sediments to marine sediments seems inappropriate, because characteristics specific of the marine environment, such as high salinity, high pH, and low organic carbon content, can influence sorption processes.

Sorption coefficients can be derived from the measurement of the aqueous concentration (C_{aq}) only (*9*), assuming a 100% mass balance. This is only valid when (i) there are no uncontrolled losses to additional sorption phases, such as the glass surface of the test vial, (ii) loss due to biodegradation is negligible, and (iii) the freely dissolved concentration is measured. This last issue is relevant, because after centrifugation of sediment suspensions, the supernatant can still contain nonseparable particles or dissolved organic matter (DOM). For compounds with a high affinity for this so-called "third phase"(*10*), substantial amounts of third phase in supernatant could lead to overestimation of the true aqueous concentrations (*11*). An incomplete mass balance and an overestimation of the aqueous concentration could thus lead to systematic errors in

sorption data. Such artifacts may have been the cause for the solids concentration effect observed in a sorption study with a mixture of C_{15}-ethoxymers (*12*). No influence of the solids concentration was observed for the sorption of pure AE homologues on a natural sediment, which was washed to reduce the material that would remain suspended after centrifugation (*6*).

In this study, the sorption of three pure alcohol ethoxylates to a marine sediment was examined. Complementing existing studies in which a series of AE with varying ethoxylate chains were tested (*5-7*), this study tested AE homologues for which only the alkyl chain length differed. Specific objectives were (i) to investigate whether the mass balance approach is appropriate for estimating sorption coefficients for AE, (ii) to generate sorption isotherms over a broad range of aqueous concentrations, and (iii) explore which sorption model fits the data best.

Aqueous concentrations in the sorption studies were measured via solid-phase microextraction (SPME). We have recently developed and tested this method to analyze freely dissolved AE concentrations in seawater matrixes (*13*).

Sorption models for alcohol ethoxylates

The dependency of concentrations sorbed to the sediment (C_s) on aqueous concentrations (C_{aq}) is often analyzed with different models. In linear sorption models, the sorption coefficient (K_p) is the concentration independent ratio between the concentration in sediment and the aqueous concentration:

$$K_p = \frac{C_s}{C_{aq}} \qquad (1)$$

Nonlinear sorption of AE to natural sediment has so far only been modeled via the Freundlich isotherm:

$$C_s = K_F \cdot C_{aq}^{\,n} \qquad (2)$$

in which n is a constant parameter describing the degree of nonlinearity, and K_F is a unit-dependent partition coefficient. Although the Freundlich isotherms generally fit the sorption data for AE reasonably well, it is nearly impossible to extrapolate the sorption parameters K_F and n to other AE homologues, other sediments with different properties, or to concentrations outside the range of tested concentrations. An understanding of the sorption mechanism and sorption sites will highly increase the possibility of extrapolations. Sorption studies of ethoxylates have shown several trends, from linear to nonlinear isotherms. AE and nonylphenol ethoxylates (NPEO) sorb strongly to organic-rich sorbents such as sewage sludge, shale, and humic acids (*14-18*) and often fairly linear isotherms have been observed. Ethoxylated structures also have a high affinity for pure clay minerals, especially clays with expandable sheets such as smectites (*15,17,19*). The importance of the clay fraction in sediments with fairly low organic carbon content to sorption of AE has been discussed in several papers (*5,6,12*). Some sorption studies with

NPEO demonstrated that sorption coefficients increased when the organic matter of native sediment was removed (*15,17*). Adsorption of AE to hydrophilic surfaces of pure clay minerals is generally modeled using the Langmuir equation:

$$C_s = \frac{C_{S,max} \cdot b \cdot C_{aq}}{1 + b \cdot C_{aq}} \quad (3)$$

In eq 3, b is a constant related to binding energy, and $C_{S,max}$ represents the maximum concentration of the sorbing analyte on the solid. At infinitely low C_{aq}, this model assumes a constant sorption coefficient of $C_{S,max} \cdot b$. An opposite nonlinearity (increase in sorption at high concentrations), at aqueous concentrations near or just above the critical micelle concentration (cmc), has also been observed for AEs. This phenomenon is likely related to adsorbate-adsorbate interactions, reaching a maximum when a bilayer has been formed (*20*).

As suggested by John *et al*. (*15*), sorption of alkylethoxylates to sediments is likely a combination of interactions with both organic matter and clay minerals. In that case, sorption to the sediment, for aqueous concentrations below the cmc, can be described by a dual-mode model (eq 4), combining the Langmuir term for adsorption to (clay) mineral surfaces and a linear sorption term, with coefficient K_p, for sorption to organic matter.

$$C_s = \frac{C_{S,max} \cdot b \cdot C_{aq}}{1 + b \cdot C_{aq}} + K_p \cdot C_{aq} \quad (4)$$

This dual-mode model (DMM) has previously been used to explain the sorption and competition behavior of organic contaminants to carbonaceous materials such as peat, cellulose, or “glassy” polymers (*21-24*). In these studies, it was suggested that the Langmuir part represented adsorption to micropores in the organic structure. For the sorption of AE to the marine sediment in our study, we propose that the two terms are related to different phases in the sediment. We refer to an adsorption site which is described by the Langmuir term, and an absorption site which is related to the linear sorption term. A more detailed description of these sorption models is given in the Appendix (Figure S1).

EXPERIMENTAL SECTION

Sediment, chemicals, solvents and fibers

Sediment was sampled just north of a sedimentation area in the North Sea (Frisian Front, roughly 54 °N, 4.5 °E) from a ship using a box corer. The 30 L sample was kept as received at 4 °C. A sub sample was taken from below the aerobic upper layer and used as wet sediment in all sorption tests. The dry weight of this sub sample was determined in triplicate by drying at 105 °C. The organic carbon (OC) content (0.27%), grain size distribution (1.2% <2 µm, 19.2% 2-63 µm, and 79.6% > 63 µm, average diameter 113 µm) and specific surface area (EGME method, 27 m^2/g) were determined following standard procedures (*25*). A study by Irion and Zölmer (*26*) could serve as an indication of the mineral composition of the clay size fraction at the collection site (10-15% kaolinite, 20-40% smectite, <50% illite, and 10-15% chlorite).

The polyethylene glycol alkylethers $C_{10}EO_8$, $C_{12}EO_8$, and $C_{14}EO_8$ (>98% TLC) were from Fluka Chemie GmbH (Buchs, Germany). Artificial seawater was prepared according to a standard procedure (*27*). Except for KBr (Sigma-Aldrich Chemie BV, Zwijndrecht, The Netherlands) the salts used for the artificial seawater were from Merck (Amsterdam, The Netherlands). To prevent biodegradation of AE during the tests, 100 mg/L sodium azide (NaN_3) (Merck, Darmstadt, Germany) and 1% of a formaldehyde solution (37%, Fluka), were added to all test vials. Methanol was HPLC-quality (Labscan, Dublin, Ireland) and water taken from a water purification system (Millipore Waters, Amsterdam, The Netherlands). For analytical purposes, ammonium acetate (≥99%, Fluka) was used in the eluents at 5 mM. Glass fibers with an internal diameter of 110 µm and a 35-µm polyacrylate (PA) coating (volume 15.4 µL/m) were obtained via Polymicro Technologies (Phoenix, AZ), cut to the right length and used as received.

Setup of the sorption tests

For each alcohol ethoxylate, two test series were prepared with sediment. In the first series, varying amounts of AE were added to test systems with a constant amount of sediment. In the second series, the amount of sediment added to each test vial was varied while all containers contained a similar dose of AE. Details are summarized in Table 1. Aqueous equilibrium concentrations were aimed to range from 1 µg/L up to concentrations close to the cmc of each homologue. Both series consisted of single measurements over a broad range of concentrations. For $C_{10}EO_8$, a third series was tested with a varying amount of sediment (180-5900 mg ww) but with a much lower amount of AE spiked to each vial (initial concentration of 0.01 mg/L). To each empty 40 mL glass test vial (Supelco, Bellefonte, PA), a weighed amount of a methanol stock containing AE was added, after which the methanol was evaporated out of the vial. Wet sediment was added and the vial was filled up with artificial seawater and 0.4 mL formaldehyde until only a small air bubble was left as headspace, to reduce possible losses due to sorption to the glass walls (*13*). Vials were closed off with PTFE lined screw caps. The test systems were left to equilibrate

at 20 °C for 48 h on a shaking device (Rock 'n' roller, Snijders Scientific BV, Tilburg, The Netherlands). After this period, two SPME fibers of 4 cm were added to the test vials with $C_{10}EO_8$ and $C_{12}EO_8$. To keep the depletion of the aqueous phase by uptake in the fiber within 10%, only one 4 cm SPME fiber was added to the test vials with $C_{14}EO_8$. The systems with SPME fibers were left for another 4 days on the shakers to equilibrate the water and the polyacrylate phase. After this the SPME, water and sediment phases were analyzed as described below.

Five vials were prepared for each AE with seawater only to determine the polyacrylate water partitioning coefficient at different concentrations. Table 1 presents the range of solid concentrations and initial as well as measured equilibrium concentrations of the test chemicals.

Extractions of AE from fiber, water and sediment

After 4 days, the SPME fibers were taken out, quickly blotted dry on a tissue, and wiped clean from any sediment particles using a wet tissue. The AE in each fiber was desorbed in 1 mL of methanol and kept at -20 °C until analysis. The test vials with sediment were then centrifuged at 1700*g* for 20 min. The first 5 mL supernatant were used to flush the pipet tip and 10 mL of supernatant was transferred to conditioned SPE tubes (Supelclean™ ENVI™ 500 mg C_{18}, from Supelco) for analysis of the aqueous concentration. Subsequently, 10 mL of pure water was used to flush the salt from the columns, after which the water was removed by applying vacuum for several seconds. The AE were eluted from the SPE with 8 mL of methanol and kept at -20 °C. The remainder of the supernatant was carefully decanted from the test vials after which the vial was weighed and frozen at -20 °C. The vials with frozen sediment were freeze-dried and weighed again to calculate the amount of salt remaining from sublimated pore water. Either as much as possible or, in case of a high amount of sediment phase, sub samples of 200 mg were transferred to 5 mL vials. AE was extracted from the sediment by two subsequent sonication steps of 1 h in 5 mL methanol (35 kHz 180/840 W, Bandelin electronic, Berlin, Germany). The methanol extracts were transferred to a new vial, evaporated to dryness and redissolved in 0.5 mL of methanol and 9.5 mL of pure water. The AE in this solution was further treated comparable to the supernatant samples using SPE columns. All extracts were diluted with methanol if concentrations in the pure extract were too high.

The fraction AE bound to the glass wall was analyzed in two of the vials without sediment by flushing the emptied test vials with 5 mL pure water first and subsequently with two times 3 mL methanol. The water sample was run over a preconditioned SPE to remove excess salt, and the methanol fractions were used to elute the SPE followed by another 3 mL of clean methanol.

The recovery of the SPE method for extraction and/or clean up of the aqueous and sediment extractions was tested using external standards in four replicates, by applying a weighed amount of methanol stock (~0.5 mL) on a conditioned SPE column on which first 5 mL of seawater was added. These samples were treated further as supernatant samples

described above. Potential losses during the sediment extraction and cleanup procedure were checked without sediment first. The recovery of the sediment extraction procedure was further checked using sediment which was spiked by equilibrating 150 µg in a slurry of 2 g sediment with 2 mL seawater for 2 days. Assuming that the sediment would contain >99% of the total amount of spiked AE, four sub samples of 200 mg were analyzed from this batch.

Analysis of samples

The analytical procedure was similar as described in (*13*). Briefly, concentrations of AE in the methanol extracts were analyzed on an LC-MS system consisting of a Perkin-Elmer (Norwalk, CT) Series 200 degasser, PE 200 LC Pump, and a PE 200 LC autosampler connected to a high performance, hybrid triple-quadrupole/linear ion trap mass spectrometer (Q-TRAP®, MDS Sciex Applied Biosystems/MDS Sciex Instruments, Foster City, CA). The interface was a TurboIonSpray® source used in the positive mode. 20 µL sample was injected into a Chrompack Varian (Chrompack International BV, Middelburg, The Netherlands) RP-C_{18}-column (Chromspher 5, 100x3 mm) using an eluent flow of 0.6 mL/min. MS-conditions were similar as those reported in Droge *et al*. (*13*). Several calibration series were run during one batch analysis to account for increased or decreased response of the MS. Calibration curves of the analysis of the aqueous phase with SPME are presented in Droge *et al*. (*13*), and equations are given in Table 1.

Calculation of sorption data and modeling the sorption isotherms

In case of a complete mass balance (no biodegradation nor adsorption on the test vial), the concentration in the sediment could also be determined via the SPME, since C_{aq} can be derived from C_f. However, when the mass fraction of the total AE that is in the solid is too small, only a slight uncertainty in C_{aq} could lead to a large error in the estimated C_s. The reproducibility of SPME-derived C_{aq} was determined from duplicate SPME fiber extractions. This information was used to determine which fraction of AE should be sorbed to estimate C_s within 10% accuracy. In case these conditions were met, the SPME-derived sediment water distribution coefficients could be compared with data based on solvent extracts.

GraphPad Prism v3.00 for Windows (GraphPad Software, San Diego, CA) was used to fit the Freundlich and dual-mode model to the sorption data. Equation 2 was used to determine the Freundlich parameters. For the dual-mode model, the data was weighed as $1/y^2$, and instead of using eq 4, we used log transferred parameters to facilitate fitting to the data in GraphPad:

$$C_s = \frac{10^{\mathrm{Log}(C_{S,max})} \cdot 10^{\mathrm{Log}(b)} \cdot C_{aq}}{1 + 10^{\mathrm{Log}(b)} \cdot C_{aq}} + 10^{\mathrm{Log}(K_p)} \cdot C_{aq} \qquad (5)$$

The deviation of the fitted regressions of the Freundlich model and the dual-mode model with the sorption data was assessed with a runs test using the GraphPad software.

To assess which model was most likely to be correct, the best fitting regression of both models were compared using the Akaike's information criterion (AIC) method in GraphPad, since the two models were not related (nonnested). This method uses the sum of squares, but corrects for the number of parameters in each model and the number of data points.

TABLE 1. Molecular Properties of the AE Homologues and Experimental Details During the Sorption Studies

Properties	**$C_{10}EO_8$**	**$C_{12}EO_8$**	**$C_{14}EO_8$**
Mw	511	539	567
cmc (mg L^{-1}) [a]	510	53	5.7
Calibration curves for SPME analysis [b]			
Sea water only [b]	*a* = 0.95 (±0.025) *b* = 1.55 (±0.023) *n* = 7	*a* = 0.97 (±0.013) *b* = 2.58 (±0.011) *n* = 8	*a* = 0.99 (±0.053) *b* = 3.68 (±0.061) *n* = 9
Experimental details during sorption studies			
Series 1: mg of wet sediment added (RSD [c])	83.7 (4.6)	93 (3.6)	82.2 (4.8)
Series 2: nominal initial C_{aq} in mg L^{-1} (RSD)	5.2 (3.4)	10.3 (1.0)	0.99 (2.5)
Series 2: range of solids concentration (g L^{-1})	0.5 - 188	0.65 - 63	0.5 - 20
Range of equilibrium concentrations			
C_{aq} *(mg* L^{-1}*)*	0.005 - 111	0.03 - 40.1	0.0004 - 2.77
C_s *(mg* kg^{-1}*)*	0.4 - 1250	2.6 - 5080	1.7 - 4400
Distribution coefficient range [d]	530 - 11	2780 - 120	35200 - 1120
Mass balance (RSD)	100 (5.3)	102 (4.7)	96.6 (7.8)
Recovery (±SD) for C_{aq} via SPE (%) [e]	92.3	91.5	89.8 (3.3)
Recovery (±SD) for C_s via SPE (%) [f]	92.8 (4.4)	89.0 (3.3)	85.7 (6.2)
Recovery (±SD) for C_s via SPE (%) [g]	91.7 (2.3)	92.5 (1.8)	90.7 (1.8)

[a] In AgCl saturated water at 25 °C, in (32). [b] Calibration curves are presented in (13), according to Log C_f = a (±SE of best fit values)· Log C_{aq} + b (±SE) *(using mg* L^{-1}*). [c] RSD = relative standard deviation in %. [d] at the lowest and highest equilibrium concentrations. [e] n=2 for $C_{10}EO_8$ and $C_{12}EO_8$, n=4 for $C_{14}EO_8$. [f] for solvent spiked sediment (n=4). [g] for sediment loaded via aqueous phase (n=4).*

RESULTS AND DISCUSSION

Measured concentrations, extraction recoveries and analytical accuracy

The recovery of the analysis of C_{aq} via SPE was ~90% (Table 1), comparable to the recoveries for the clean up procedure for the sediment extraction procedure, which also included a SPE step. When corrected for this loss in the SPE step, complete recoveries were achieved for sediment extractions from samples spiked via the aqueous phase (Table 1). No AE were detected in blanks.

We have used SPME-derived aqueous concentrations, using the calibration curves in seawater solutions (Table 1), as well as aqueous concentrations measured after SPE extractions in those cases where the SPME method was not sensitive enough, to derive the sediment sorption isotherms. Part of the underlying data for the concentrations in the SPME fiber itself and total concentrations in the aqueous phase after centrifugation are presented in a recent publication (*13*) with a focus on the development of the SPME technology for ethoxylates. In ref (*13*), several matrix effects were investigated, including the potential effect of dissolved organic matter on aqueous concentration measurements. The data presented in ref (*13*), show that the SPME-derived C_{aq} was almost identical to the C_{aq} determined in the supernatant via SPE. Apparently, for these AE and at the tested solid to water ratios (Table 1), overestimation of aqueous concentrations due to coextraction of AE sorbed to third-phase matter was not significant (*13*). Therefore, both SPME-derived and direct measurements of the aqueous concentrations are appropriate for measuring the freely dissolved concentration in a sediment suspension sample.

The concentrations of AE in the duplicate fibers used in tests with $C_{10}EO_8$ and $C_{12}EO_8$ differed on average 2.8 ±2.4% (n = 35). From this, as a rule of thumb, we considered that SPME-derived concentration in the sediment (C_s) should be accurate within 10% when at least 35% of the spiked AE was sorbed to the sediment. The mass fraction of AE that a 4 cm polyacrylate fiber extracted from the aqueous phase was 0.09, 0.95, and 5.7% for $C_{10}EO_8$, $C_{12}EO_8$, and $C_{14}EO_8$, respectively. Some depletion itself is not problematic, because the calibrations were based on measured fiber and measured aqueous concentrations after equilibration. The disturbance of the sediment-water equilibrium by introduction of SPME fibers was limited, in the worst case, for $C_{14}EO_8$ with the smallest amount of sediment, C_s decreased by 3.0%. Losses in the system due to sorption to the glass wall were negligible because the fractions AE bound to the glass were less than 1.5% of the total mass of AE spiked to all test systems.

Distribution coefficients derived via SPME and a mass balance approach

For almost all test vials in this study, the total amount of AE present in the sediment phase, supernatant, and polyacrylate together closely matched the spiked amount (Figure S2 in the Appendix). Average mass balances (±SD) were 100% (5.3), 102% (4.7) and 97.0%

(7.5) for $C_{10}EO_8$, $C_{12}EO_8$, and $C_{14}EO_8$, respectively (Table 1). Biodegradation was apparently sufficiently inhibited during the 7 day test period. Hence, it is possible to accurately predict the sorbed concentration (C_s) on the basis of only C_f. Because for some test vials less than 35% of the total amount of $C_{10}EO_8$ was sorbed to the solid phase, or aqueous $C_{10}EO_8$ concentrations were too low to detect with the SPME fiber, for only four out of fourteen test vials with $C_{10}EO_8$, the C_s could be accurately estimated from C_f. For the remaining samples, aqueous concentrations were measured after SPE extraction. The sediment-water distribution coefficients (D_{sa}) derived from the estimated C_s and SPME-derived C_{aq} were plotted against the D_{sa} based on measured C_s and SPME-derived C_{aq} (Figure 1). On average, the estimated values for D_{sa} were 96% (±10% SD) of the D_{sa} based on measured C_s. This shows that with a well-defined fiber-water partitioning coefficient, accurate sorption data for AE can be obtained using the polyacrylate SPME fibers and a mass balance approach, making tedious solvent extractions of both aqueous and sediment phases redundant.

In Figure 2, the measured sediment concentrations (C_s) are plotted against aqueous concentrations (supernatant derived C_{aq} for $C_{10}EO_8$ and SPME-derived C_{aq} for $C_{12}EO_8$ and $C_{14}EO_8$). The sorption data from the series with varying amounts of sediment (Figure 2, open symbols) overlap with the data from test vials with a constant amount of sediment (Figure 2, closed symbols). In line with the sorption study with AE by Brownawell *et al.* (*6*), and the outcome of our earlier study (*13*), this implies that the solids concentration had no effect on measured aqueous concentrations and the sorption coefficients of the AE in our test systems.

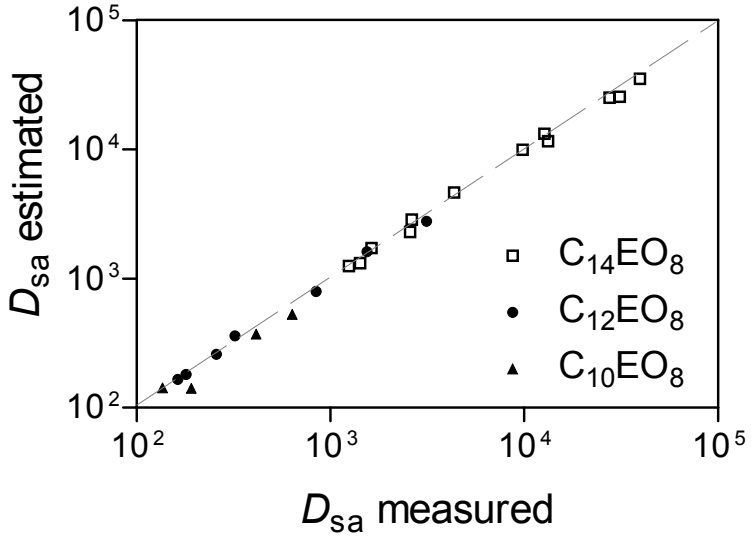

Figure 1. Comparison of sediment-aqueous phase distribution coefficients (D_{sa}) calculated from measured concentrations in the sediment (C_s) and aqueous concentrations (C_{aq}) versus distribution coefficients estimated from C_{aq} only and a mass balance approach. The broken gray line represents the 1:1 relationship.

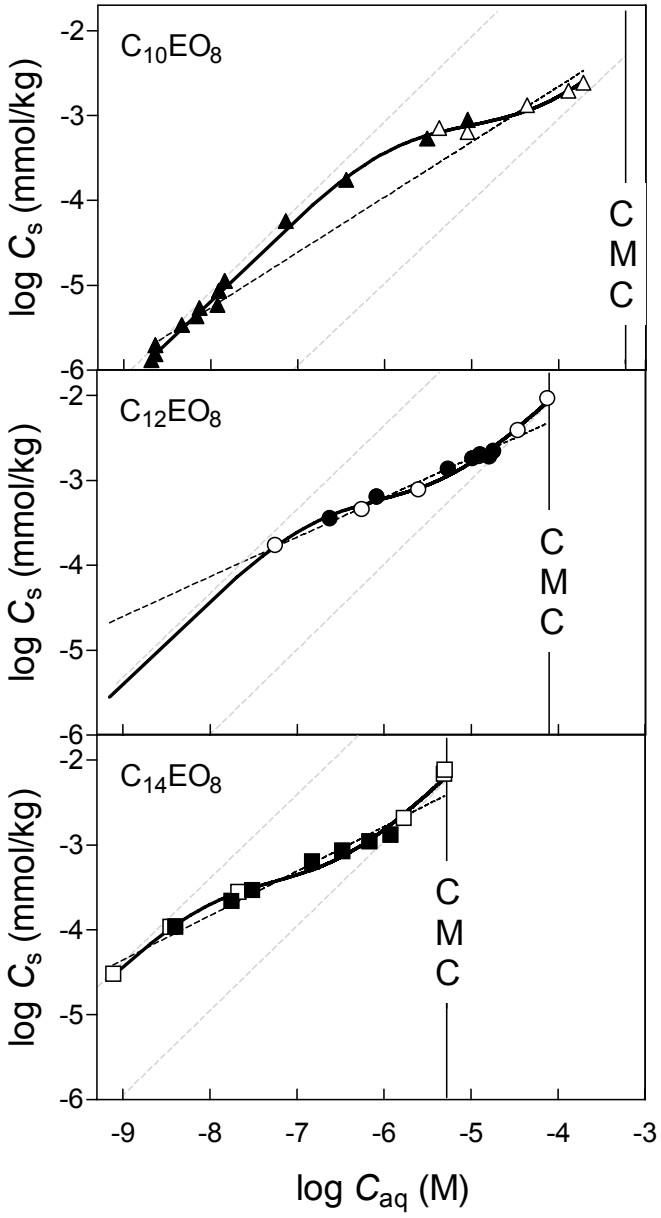

Figure 2. Sorption data for $C_{10}EO_8$, $C_{12}EO_8$, and $C_{14}EO_8$ on a marine sediment. Data from the series with constant amount of solid phase are indicated with open symbols, data from the test series with varying amounts of solid phase with closed symbols. The dashed black lines represent Freundlich model fits (eq 2), the solid black lines are fits of the dual-mode model (DMM). For $C_{10}EO_8$ supernatant derived C_{aq} were used, for $C_{12}EO_8$ and $C_{14}EO_8$ SPME-derived C_{aq} were used. The dotted gray lines have a slope of 1 and coincide with the linear sorption coefficient at low concentrations ($C_{S,max} \cdot b$) and high concentrations (K_p) according to the DMM fitted parameters. The vertical lines indicate the critical micelle concentrations (cmc) in seawater ($C_{12}EO_8$ and $C_{14}EO_8$, in (*13*)) or estimated cmc in seawater ($C_{10}EO_8$).

Nonlinearity of the sorption isotherms

Figures 1 and 2 show that, over the whole range of tested concentrations, the sorbed concentration of the three AE used in this study is not linearly related to the aqueous concentration. The sediment-water distribution coefficients are 20-50 times higher for the lowest tested aqueous concentrations compared to those at high concentrations (Table 1). Both the Freundlich model (dashed lines in Figure 2) and the dual-mode model (DMM) (solid lines in Figure 2) were fitted to the sorption data. The DMM is for all three AE the preferred model according to a comparison of the fits via the AIC method (p<0.0014). Also a run test shows that the data significantly deviate from a Freundlich model, which is not the case for the DMM. The DMM assumes that sorption isotherms become linear both below and above the concentrations where saturation of adsorption sites occurs ($C_{S,max}$). From eq 4, it follows that the sediment water distribution coefficient (D_{sa}) at infinite dilution is equal to ($C_{S,max} \cdot b + K_p$), and D_{sa} equals K_p at concentrations well above $C_{S,max}$. These sorption constants calculated from the DMM fits (see Table 2) for the three AE, are indicated in Figure 2 by gray dotted lines with a slope of 1.

Although we only present data for three AE homologues to one single marine sediment, the DMM appears to fit the sorption data very well. Still, predictions from the Freundlich regressions deviate at most only about 3-fold from the measured data ($C_{10}EO_8$), which are minor differences for risk assessment purposes. The real benefit of the DMM model will be in providing a better mechanistic understanding of the nonlinear sorption of these AE homologues to the marine sediment, since it distinguishes two separate sorption phases which are described by simple processes. This will strongly facilitate comparisons of sorption data to various sediment types and different AE homologues. Furthermore, Figure 2 shows that the lowest tested concentrations in the sediment are still several orders of magnitude above concentrations which can be expected in the real environment (*8,28*). Extrapolating both the Freundlich and the DMM sorption isotherms to 1000 times lower concentrations will result in sorption coefficients which differ by a factor of ~30. Extrapolations based on the mechanistic approach of the DMM may be the preferred choice to derive such values.

However, we want to emphasize that the assumptions based on which we apply the DMM (adsorption to (clay) mineral surfaces and absorption to organic matter), remain unvalidated. Further validation of the DMM should include studies on whether sorption to marine OM is indeed linear, to what extent it is possible to generalize the adsorption to the mineral surfaces in a natural marine sediment to a single Langmuir relationship, and for example, to what extent bilayer formation on the mineral surfaces contributes to the overall sorption close to the cmc.

TABLE 2. Values of Parameters for Freundlich Model and Dual-mode Model (Combined Langmuir-Linear Sorption)

	$C_{10}EO_8$ [a]	$C_{12}EO_8$ [b]	$C_{14}EO_8$ [b]
Freundlich parameters [c]			
n (95% c.i. [d])	0.671 (0.61 - 0.73)	0.491 (0.42 - 0.56)	0.560 (0.50 - 0.61)
Log K_F (95% c.i.)	0.192 (-0.20 - 0.56)	-0.248 (-0.62 - 0.12)	0.669 (0.25 - 1.09)
r^2	0.970	0.962	0.973
Average difference (±SD) measured vs. predicted D_{sa}	114% (±29%)	103% (±26%)	100% (±61%)
Dual-mode model parameters [c]			
LOG $C_{S,max}$ (95% c.i.)	-3.12 (-3.21 - -3.02)	-3.21 (-3.39 - -3.03)	-3.46 (-3.75 - -3.18)
LOG K_L (95% c.i.)	5.94 (5.83 - 6.05)	6.76 (6.17 - 7.34)	8.06 (7.31 - 8.81)
LOG K_p (95% c.i.)	0.972 (0.82 - 1.13)	2.01 (1.95 - 2.07)	3.15 (3.09 - 3.20)
r^2	0.991	0.988	0.978
Average difference (±SD) measured vs. predicted D_{sa}	110% (±15%)	103% (±11%)	97% (±14%)
K_p	9.4	103	1402
$K_{ad}=C_{S,max}\cdot b$	663	3540	39170
Ratio $C_{S,max}\cdot b$ / K_p	71	34	28

abbreviations:
D_{sa}: sediment-water distribution coefficient (L kg^{-1}) at a certain concentration
n: exponent of the Freundlich equation
Log K_F: *Freundlich constant (L kg^{-1} at 1 mol L^{-1})*
$C_{S,max}$: *maximum adsorption concentration (mol kg^{-1})*
b: Langmuir constant related to the binding energy (L mol^{-1})
K_p: *linear absorption coefficient (L kg^{-1})*
$C_{S,max}\cdot b$: *linear adsorption coefficient at* $C_s << C_{S,max}$ *(L kg^{-1})*

[a] *C_{aq} from supernatant and measured C_s.* [b] *SPME-derived C_{aq} and measured C_s.* [c] *data were transformed to mol L^{-1} en mol kg^{-1} dw.* [d] *c.i. = confidence intervals.*

Interpretation of sorption parameters according to the DMM

The dual-mode model (DMM) distinguishes two (homogenous) sorption sites, presumably organic matter and mineral surfaces. We assume that a certain AE homologue has a specific affinity for each sorption site. The DMM will only display a nonlinear isotherm for compounds for which adsorption significantly contributes to the overall sorption. If the absorption process dominates the overall sorption ($K_p > C_{S,max}\cdot b$), the isotherm will be linear. Furthermore, we assume that the sorption isotherm for such compounds is only nonlinear in the concentration range around the maximum capacity of the adsorption sites, $C_{S,max}$ (see Appendix). According to the DMM fitted regressions (see Table 2), the sorption isotherms of the tested AE homologues are nonlinear because the adsorption coefficients are a factor of 28-71 higher than the absorption coefficients, and the maximum adsorption capacities (204-390 mg/kg) occur in the range of tested concentration.

The high affinity of AE for the adsorption sites at low concentrations can be explained as the result of various molecular interactions of the EO chain with specific

binding sites on the surface of sediment particles, and van der Waals interactions of the alkyl chain, as reviewed by Luckham and Rossi (*20*). The adsorption energy will, therefore, increase with every additional carbon atom in the alkyl chain, as well as for each additional ethoxylate unit. Furthermore, if we use the cmc (Table 1) as a relative indication of the subcooled liquid solubility, the aqueous activity coefficient is lower for $C_{14}EO_8$ than for $C_{10}EO_8$, so it is not surprising that the order in adsorption coefficients is as follows: $C_{14}EO_8 > C_{12}EO_8 > C_{10}EO_8$.

In a study on the sorption of nonylphenol ethoxylates (NPEO) on silica gel, the cross-sectional area occupied by an NPEO molecule, *at saturation*, was proportional to the length of the EO chain, and was ~0.85 nm^2 for each EO unit (*29*). Although the standard deviations for the values of $C_{S,max}$ are rather high (Table 2), the maximum adsorption capacities for these three AE homologues, with similar EO chain lenghts, are indeed in the same range. Based on the specific surface area for this marine sediment and the surface area of the total ethoxylate chains of these AE (6.8 nm^2), this corresponds to a rough estimate of a single layer surface coverage of 5.4-11.6%. This is lower than that observed for pure clay minerals, but it is likely that the organic matter fraction covers some part of the mineral surfaces, and the adsorption capacity does not necessarily imply complete coverage of the surface.

The values for absorption coefficient (K_p) obtained with the dual-mode model increased with a factor 10 when the alkyl chain of the AE increased with 2 carbon atoms. This coincides with the K_{ow} fragment value for two additional -CH_2 groups (KowWin v1.66), and with the observed increase in partitioning coefficient of AE to other organic phases such as liposomes (*30*) or the polyacrylate SPME fiber (*13*). We suggest that this linear sorption process represents absorption of AE into organic matter, which could become the dominant sorption process at concentrations above the saturation point of the Langmuir like sorption type. This implies that the organic carbon-water partition coefficient (K_{oc}) of the AE can be calculated by dividing the values for K_p by the fraction of organic carbon in the sediment. These K_p values result in Log K_{oc} values of 3.5, 4.6, and 5.6 for $C_{10}EO_8$, $C_{12}EO_8$, and $C_{14}EO_8$, respectively. The K_{oc} of an AE homologue is related to the total change in Gibbs free energy (ΔG_{oc}) to transfer one mole of that specific AE homologue from aqueous solution to the organic carbon phase. This change in Gibbs free energies includes terms for cavity formation in both phases to dissolve the solute, as well as terms for both phases related to the molecular interactions between the solute and each phase (*31*).

The DMM sorption parameters should be obtained for an extended set of AE homologues on a single marine sediment to understand the influence of the AE structure on both the adsorption and the absorption coefficient. With accurate predictions on the ratio between these two coefficients to a certain sediment, it should be possible to predict whether sorption isotherms for certain AE homologues will be nonlinear or not. A sorption study using $C_{13}EO_3$, $C_{13}EO_6$, and $C_{13}EO_9$ demonstrated that the sorption isotherms were more linear for AE with shorter EO chains (*6*).

We still would like to emphasize that our interpretations are based on the assumption that the DMM represents two sorption phases (clay and organic matter).

Although this is not proven, it is tempting to postulate this hypothesis and the data support this hypothesis. The advantage of the DMM is that it enables the extrapolations of sorption to lower concentrations, but also will assist in further studies into the effect of chemical structure as well as sediment properties on the sorption behavior of this class of surfactants.

Comparison with literature data for freshwater sediments

Comparisons between the sorption data to marine sediment from this study with sorption data in other studies are difficult because the exact sorption sites and their relative contribution remain unclear for AE, and the isotherms are often nonlinear. It is only possible to compare the sediment-water distribution coefficient (D_{sa}) data from this study with other literature at the lowest tested concentrations, 1 µg/L for example. Sorption coefficients for $C_{10}EO_8$, $C_{12}EO_8$, and $C_{14}EO_8$ on a freshwater sediment (11% OC and a 1% clay fraction) were presented by Kiewit *et al*. (1996) (*7*). Although difficult to interpret their data at 1 µg/L, since only initial aqueous concentrations were given and merely linear isotherms were assumed, the D_{sa} were 126, 1230 and 3548, respectively. The D_{sa} at 1 µg/L (calculated with parameters from the dual-mode model) for $C_{10}EO_8$, $C_{12}EO_8$, and $C_{14}EO_8$ in our study are up to an order of magnitude higher; 650, 3600 and 34800, respectively, in spite of the much lower OC content of the marine sediment in this study (0.3% OC versus 1.2% clay). The only other sorption data on natural sediment with slightly comparable AE homologues is from the sorption of $C_{13}EO_6$, and $C_{13}EO_9$ on a river sediment (2.3% OC and 35.4% clay) (*6*). Using the Freundlich parameters presented in that study, the D_{sa} at 1 µg/L were calculated to be 1100 and 5040, respectively. These values are also distinctively lower than the values for D_{sa} observed in this study, despite the higher OC content and the much higher clay content. The marine sediment in this study may have contained up to 40% smectites in the clay fraction (*26*), whereas other sediments used in sorption studies may not have had such minerals at all. To our knowledge, no sorption studies with AE under marine conditions have been reported before.

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APPENDIX

Theoretical plots and interpretation of the Freundlich model and the dual-mode model (Figure S1), as well as a plot of the mass balance for AE in the sorption tests (Figure S2) are presented here. This material is available as Supporting Information via the Internet at http://pubs.acs.org.

A. Theoretical plots of nonlinear isotherms

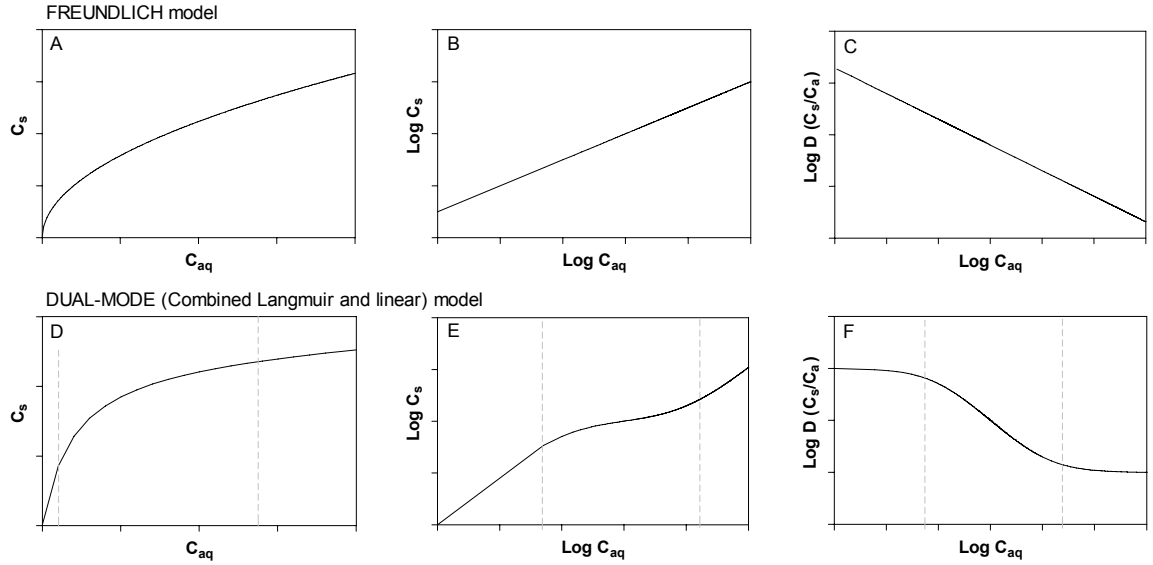

Figure S1. Theoretical plots of nonlinear sorption data according to the Freundlich model and the dual-mode model (combined Langmuir and linear sorption, see text). The theoretical plots are presented both on a linear scale (A and D, respectively) and on a logarithmic scale (B and E, respectively), as well as the resulting distribution coefficient plotted against aqueous concentration (C and F, respectively).

The Freundlich isotherm is exponentially nonlinear over the whole scale, in this example with (n) <1, and thus is a linear line with slope (n) on the log-log plot. The dual-mode model is linear at the low and high concentration ranges, shown in the log-log plot with two regions where the slope = 1, representing 2 sorption sites with different affinities. The broken grey lines in the panels of the dual-mode model (D-F) show the regions with linear relationship between concentrations in the aqueous phase (C_{aq}) and sediment bound concentrations (C_s). The nonlinear part occurs in the concentration range where the Langmuir related sorption sites become saturated, until at saturation of these sites the sorption at higher concentrations only occurs at the sites with the sorption coefficient K_p. Performing sorption studies at the low concentrations of AE in the field is often practically impossible. The consequence of the models for extrapolating to low concentrations can be shown by the logarithmic plots of C_{aq} against distribution coefficient (D_{sa}). Using the Freundlich equation, an ever-increasing distribution coefficient is assumed at decreasing concentrations, whereas the combination model has a constant distribution coefficient at

low concentrations with a value of ($C_{S,max} \cdot b$). The Freundlich model assumes exponentially increasing affinity for lower concentrations, while the combination model assumes a constant affinity for the sediment at concentrations one order of magnitude below the saturation point of the Langmuir equation ($C_{S,max}$). We aimed at following the (non)linearity at equilibrium concentrations as low as sub µg/L, up to concentrations of maximum solubility, which for nonionics is the critical micelle concentration (cmc). The dual-mode model could further provide a more mechanistic view on the sorption on natural sediment, since it discriminates between and provides direct parameters for absorption (linear) and adsorption (nonlinear) processes.

B. Mass balance of AE in the sorption tests

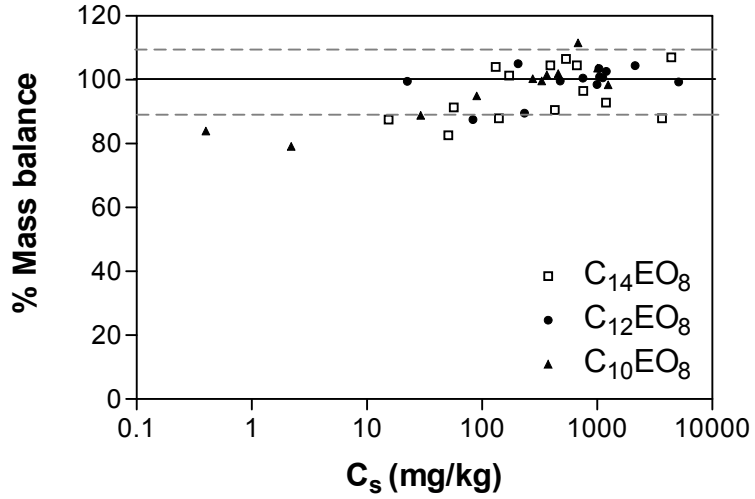

Figure S2. Mass balances for all test vials in which concentrations of AE in the sediment phase, supernatant and SPME-fiber were determined. The broken gray lines indicate 90 and 110% values. Only for very low concentrations 80-90% of all AE added to the system was recovered, which was considered to be caused by low extraction efficiency rather than losses due to biodegradation.

Chapter 6

Nonlinear Sorption of Alcohol Ethoxylates to Marine Sediment: Modeling the Influence of the Surfactants' Structure and Sediment Properties

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Nonlinear Sorption of Alcohol Ethoxylates to Marine Sediment: Modeling the Influence of the Surfactants' Structure and Sediment Properties

ABSTRACT

The nonlinear sorption of individual alcohol ethoxylate (AE) homologues was studied as a function of the chemical structure of AE and properties of six marine sediments and three clay minerals. A dual-mode model (a combined Langmuir and linear sorption isotherm), fits the sorption data well and, based on this outcome, the sorption is discussed as a combination of two sorption processes. Adsorption to mineral surfaces dominates the sorption of most AE homologues to the tested marine sediments. Good correlations between chemical descriptors of AE and sorption coefficients were obtained. The Langmuir sorption coefficient increases, while the linear sorption coefficient decreases, with the number of ethoxylates. The linear term is most likely related to the affinity for sorbate-sorbate interactions, forming bilayers on the mineral surfaces. The models explain and quantify the increased nonlinearity of the isotherms for AE with longer ethoxylate chains that is observed in the region of the maximum adsorption capacity of the substrate. The variation between isotherms of a single homologue for the different substrates was strongly reduced when sorbed concentrations were expressed per specific surface area. Organic matter may only become an important sorption phase for AE homologues with short EO chains for organically enriched marine sediments.

INTRODUCTION

Alcohol ethoxylates (AE) are nonionic surfactants of which worldwide more than one million metric tons are consumed annually (*1,2*). The AE in commercial products are comprised of complex mixtures of homologues, varying in alkyl chain length and with wide distributions of the number of ethoxylate (ethylene oxide) units. Although concentrations are strongly reduced by normally functioning sewage treatment plants (*3,4*), still small fractions will be discharged into the environment. Trace levels of AE have been observed in coastal and freshwater sediments in the vicinity of discharge locations (*5-7*).

Current risk assessment procedures for AE in sediments assume that hydrophobic interactions with the organic matter fraction in the sediment dominate the ratio between the sediment sorbed and freely dissolved concentrations (*5*). Accordingly, the concentrations in the pore water of sediments are often calculated with estimated organic carbon/water partition coefficients (K_{oc}), and compared with predicted no effect concentrations in the aqueous phase. However, several studies have shown that sorption is not simply a function of K_{oc} and the fraction of organic matter in the sediment (*8-11*). Observations that sorption isotherms are nonlinear show that the sediment-water distribution coefficient (K_d) is not a single, constant value. The organic matter content can also not explain differences in sorption parameters of individual AE homologues for different sediments (*9,11,12*).

As suggested by John *et al*. (*13*), sorption of alkyl ethoxylates to natural sediments is likely a combined process with contribution of multiple sorption phases. Sediment water distribution coefficients for AE are sometimes better correlated to the percent of clay (*9,10*). Especially the contribution of the amount of swelling clays is considered important (*11*), because ethoxylated compounds sorb also to the surface area between sheets of expandable clay minerals (e.g. refs (*14,15*)). This internal specific surface area is often more than tenfold larger than the external surface area of such clays. Adsorption to clay mineral surfaces is an important industrial application of AE, and therefore extensively studied, as reviewed by Luckham and Rossi (*16*) Because the long alkyl chains render most AE homologues rather hydrophobic, it is not surprising that AE also sorb to organic rich phases such as sewage sludge (McAvoy and Kerr, 2001 in (*17*)) and sediment with more than 10% OC (*18*).

In a previous study on the sorption of three individual AE homologues to a marine sediment (*8*), the sorption data were accurately described by a dual-mode sorption model, which combines a single Langmuir adsorption component and a linear term:

$$C_s = \frac{C_{S,max} \cdot b \cdot C_{aq}}{1 + b \cdot C_{aq}} + K_p \cdot C_{aq} \qquad (1)$$

In eq 1, $C_{S,max}$ is the maximum sorption capacity of the adsorption phase in the sediment, b a parameter related to the binding affinity, and K_p the sorption coefficient of the linear sorption component in the sediment. The dual-mode model (DMM) distinguishes

two separate sorption phases in sediment, and it was hypothesized that the nonlinear sorption term represents the affinity to mineral surfaces, and the linear term represents absorption into organic matter (*8*).

The sorption parameters of the dual-mode sorption model (DMM) provide an explanation for nonlinear sorption isotherms of AE. From eq 1 follows that $C_{S,max} \cdot b$ represents the constant adsorption coefficient (K_{ad}) when $b \cdot C_{aq} << 1$. The overall sorption coefficient in this low concentration range is the sum of the adsorption and absorption coefficient, $K_{ad} + K_p$. At concentrations above the maximum adsorption capacity, absorption (via K_p) dominates the overall sorption coefficient. This region is limited at higher concentrations by the critical micelle concentration (cmc). The DMM isotherms will only be nonlinear in the range around the maximum adsorption capacity, since then the overall sorption coefficient will shift with increasing concentrations from ($K_{ad} + K_p$) to (K_p). If the assumptions of the DMM are valid, the DMM sorption parameters K_{ad} and K_p describe the affinity of the tested AE homologue for the two suggested sorption phases in the sediment.

The first objective of this study was to examine how the two sorption coefficients from the dual-mode isotherms (K_{ad} and K_p) vary with the chemical structure of AE homologues, in particular with the alkyl chain length and number of ethoxylate units. Therefore, sorption experiments were performed with several individual AE homologues on the same sediment that was used in a previous study (*8*). The second objective was to examine, or better explore, the influence of varying sediment properties on the sorption coefficients. The sorption of a single homologue was therefore studied as a model compound on a set of relatively fine marine sediments with varying properties. To investigate the sorption of the model alcohol ethoxylate in the absence of organic matter, sorption isotherms were also determined for the clay minerals illite, kaolinite and bentonite. These minerals represent the most common types of clay minerals present in marine sediments. Because bentonite is a swelling clay and illite and kaolinite not, these clays differ considerably in specific surface area when the interlayer is included. Because specific surface area and organic matter content were considered key characteristics for the sorption of alcohol ethoxylates, it was tested to what extent these parameters could explain the variation in the sorption coefficients. Finally, the sediment-water distribution coefficients measured for the marine sediments in this study, and those calculated via the structure-activity relationships derived in this study, were compared with sorption coefficients predicted following currently available risk assessment guidelines. Predictive models based on the individual sorption processes may result in more realistic predictive sorption models, as compared to the K_{oc} based sorption models used in current risk assessment.

EXPERIMENTAL DESIGN

Chemicals, solvents, SPME fibers and sorbents

The polyethylene glycol alkyl ethers $C_{12}EO_1$, $C_{12}EO_3$, $C_{12}EO_5$, $C_{12}EO_6$, and $C_{14}EO_6$ (>98% TLC) were from Fluka (Buchs, Switzerland), $C_{14}EO_{11}$ and $C_{14}EO_{14}$ were synthesized by J. Tolls and H.C. Kwint in 1996 (>97% GC, HPLC, ^{1}H-NMR). Artificial seawater (GP2) was prepared according to standard EPA procedures (*19*). Except for KBr (Sigma-Aldrich, Zwijndrecht, The Netherlands) the salts used for the seawater were from Merck (Darmstadt, Germany). To prevent biodegradation of AE during the tests, 100 mg/L sodium azide (NaN_3) (Merck) as well as 0.4 ml of a 37% methanol free formaldehyde solution (Sigma-Aldrich) were added to all test vials. Methanol was always HPLC-quality (Labscan, Dublin, Ireland) and highly pure deionized water was used (Millipore Waters, Amsterdam, The Netherlands). The solid-phase microextraction (SPME) fiber, with a 108 µm diameter glass core and a 34.5-µm polyacrylate (PA) coating (volume 15.4 µL/m) was custom made by Polymicro Technologies (Phoenix, AZ) and cut to pieces of the desired length.

Three marine sediments were sampled in the Dutch North Sea using a box corer, at locations 'Oyster grounds' (OG), 'Frisian front' (FF) and just North of the Frisian front (NFF), all three considered sedimentation areas. Three intertidal sediments were sampled by hand using a 500 µm sieve, at an intertidal mudflat (Oesterput, OP) in the Dutch Eastern Scheldt estuary, on a mudflat near the city of San Fernando (SF) in the bay of Cadíz, and at La Antilla (LA), close to Huelva (Spain). All sediments were stored wet at 4 ^oC. Subsamples for sorption tests were taken from below the aerobic upper layer, and used as wet sediment in all sorption tests. Kaolinite and bentonite were obtained from Keramikos (Haarlem, The Netherlands), illite was purchased as fine powdered French green clay from Argiletz. The clay fractions that passed a 63-µm sieve were first hydrated for one day in artificial seawater (with 100 mg/L NaN_3), then centrifuged for 30 minutes at 3000 rpm (1670 *g*) after which the supernatant was carefully decanted. The wet clays were mixed to achieve a homogenous grain size distribution. The dry weight of the sediments and clays was determined by drying at 105 ^oC overnight for triplicate subsamples, which were taken just before the sorbents were added to the test vials.

The fraction organic carbon (f_{OC}) in the sorbents was determined after acid treatment (1M HCl) using a NA 1500 NCS elemental analyzer (Fisons, Milan, Italy). Grain size distribution was measured using a Malvern Mastersizer-S (Malvern Ltd, Malvern, UK). Because the nitrogen adsorption BET (Brunauer-Emmett-Teller) method only determines the external specific surface area, the EGME adsorption method (ethylene glycol monoethyl ether; Sigma-Aldrich) was used. This was done by gravitational analysis on P_2O_5 (Sigma-Aldrich)-dried samples according to standard ISRIC methods (*20*). A drawback of this method is that organic matter may retain some EGME during the analysis (*21*), and thereby overstimate the actual surface area. Table S2 in the Appendix provides an overview of the sediment properties.

Sorption experiments and extractions

Sorption tests were performed in similar set-ups as described in a recent study (*8*). SPME fibers were used in all tests to determine freely dissolved concentrations. For $C_{14}EO_6$ and $C_{14}EO_{11}$ previously published fiber-water partition coefficients (K_{fw}) were used (*22*). For $C_{12}EO_3$, $C_{12}EO_5$, $C_{12}EO_6$, and $C_{14}EO_{14}$, K_{fw} values were determined in duplicate using at least four concentrations. Analysis of the aqueous concentrations was performed after an extraction with ENVI 500 mg C_{18} SPE columns (Supelco), as described in ref (*22*). Table S1 in the Appendix shows the results for these 7 alcohol ethoxylates and those presented in previous studies (*8,22*). Based on the available data for AE, this SI section also presents the strong relationship between the K_{fw} values and alkyl chain length and number of ethoxylate units, in addition to the previously established relationship with estimated K_{ow} values (*22*).

In the sediment sorption tests for $C_{12}EO_1$, $C_{12}EO_3$, and $C_{14}EO_6$, one fiber was used per test vial to minimize the depletion of the aqueous phase by uptake in the SPME fiber. Duplicate fiber measurements were used for the other AE homologues. The sediment sorbed concentration can be calculated from the SPME measurements assuming a 100% mass balance (*8*). The relative standard deviation (RSD) of fiber replicates obtained from the various concentrations was <3% for all tested compounds. To assure that the error in the calculated C_s was within 10%, only results from test vials in which the amount of AE sorbed to the sediment phase was more than 30% of the total amount of AE in the test system, were used to derive the isotherms. No significant losses were observed to the glass in a previous study (*8*), while biodegradation was shown to be adequately prevented by formaldehyde and NaN_3.

The sorption isotherms of the set of AE homologues were all obtained on the NFF sediment, using 95 to 130 mg (dw) sediment per 40 ml seawater. $C_{12}EO_8$ was the model alcohol ethoxylate for which isotherms on the different sediments and the three clay minerals were obtained. The amount of sorbent for each test series was kept constant within 10% RSD. The sorbents for which a relatively high affinity was expected, solids concentrations of at least 1 g/L (40 mg dw in 40 ml) were used. For sorbents with relatively low sorption affinity, up to 11 g/L was used in order to achieve that at least 30% of the total amount of AE was sorbed. The clays were dispersed by sonication before the SPME were added to the suspensions.

The exposure of the SPME fibers, extraction of the AE homologues from the fibers, and the analysis by LC-MS were performed as described in previous studies using the same analytical equipment (*8,22*). Briefly, with $NH4^+$ added to the eluents at 5 mM, all AE homologues could be quantified by the mass of the parent AE with $NH4^+$ (m/z_i + 18). The adduct (m/z_i + 23), formed together with Na^+ which is present at background levels in the analytical system, was used as an additional identifier of the ethoxylate peaks.

Data analysis

The dual-mode model was fitted to the data using weighted nonlinear regression, with Log($C_{S,max}$), Log(b) and Log(K_p) as adjustable parameters. Applying linear regression with a least squares method, the regression coefficients for the molecular descriptors were calculated that best described the sorption parameters, as well as the correlation coefficient and the standard error for the y estimate.

RESULTS

Sorption data for individual AE homologues to the NFF sediment

Figure 1 shows the sorbed concentrations (C_s) of the AE homologues on the NFF sediment plotted against the freely dissolved concentrations (C_{aq}) after 72 h equilibration period, which is sufficiently long to ensure equilibrium (*9*). The dual-mode model (DMM; eq 1) fits well to the sorption data of all homologues. The data confirm the predicted linearity (slope of 1 in Figure 1) of the isotherms for both the low and high concentration ranges of AE. A summary of the DMM parameters is presented in Table 1, along with those for $C_{10}EO_8$, $C_{12}EO_8$ (including new data points) and $C_{14}EO_8$, which were presented in a previous study with the same sediment (*8*).

It was not possible with the currently used set-up to study the sorption of $C_{14}EO_{14}$ at concentrations lower than 200 mg/kg. Due to the strong sorption to the sediment and a relatively low affinity towards the polyacrylate of the SPME fiber (Table S1), the aqueous concentrations were then below the detection limits. For $C_{12}EO_1$ and $C_{12}EO_3$, the sorption isotherms are nearly linear, with a slope of 0.98±0.05 and 0.89±0.07, respectively, on a log-log scale. Therefore, the obtained Langmuir parameters for these two homologues have high standard errors.

The DMM distinguishes an adsorption phases and an absorption phase, for which each AE has a specific affinity depending on the chemical structure. These affinities follow directly from the DMM parameters K_p and $C_{S,max} \cdot b$ (K_{ad}). These values are also presented in Table 1, except for the unreliable K_{ad} values for $C_{12}EO_1$ and $C_{12}EO_3$. The predicted maximum adsorption capacity of the NFF sediment varies within a factor of 4, between 0.28 ($C_{14}EO_6$) and 1.02 ($C_{14}EO_{14}$) mmol/kg.

Sorption data for $C_{12}EO_8$ to clay minerals and six different sediments

Sorption data for $C_{12}EO_8$ to the three clay minerals and the six sediments are presented in Figure 2A, with the sorbed concentration as mol AE per kg dry weight. The lowest tested aqueous concentrations with clay were 4 orders of magnitude below the critical micelle concentration (cmc) and this is, to our best knowledge, considerably lower than in any other sorption study with AE on clay. Sorption to both clays was strongly nonlinear, and

adsorption to bentonite was much stronger than to kaolinite clay. In the low concentration range, adsorption to bentonite shows the linear trend predicted by the Langmuir term, but this was not observed for the data of kaolinite and illite. Furthermore, the data for all three clays did not show a distinct maximum sorption capacity that is associated with adsorption processes following the Langmuir isotherm. Especially for kaolinite, an apparent increase in the sorbed concentrations was observed at concentrations close to the cmc.

Table 1. Dual-Mode Sorption Model (eq 1) Parameters of Sorption Isotherms of Individual AE Homologues on Marine Sediment (NFF) and $C_{12}EO_8$ on Different Sediments.

	Log *b* (L/mol)	Log $C_{S,max}$ [a] (mol/kg)	Log K_p (L/kg)	*n* [b]	Log K_d [c] DMM (L/kg)	Log K_d [d] Eq 2+3 (L/kg)	Log K_d [e] Ref (*5*) (L/kg)	Log K_d [e] Ref (*17*) (L/kg)
Sorption of AE on sediment NFF								
$C_{10}EO_8$ [g]	5.94 (± 0.05)	-3.12 (± 0.05)	0.97 (± 0.07)	19	2.8	2.8	-4.3	2.1
$C_{12}EO_1$	5.67 (± 3.30)	-4.04 (± 4.11)	2.12 (± 0.34)	9	2.2	3.1	-0.5	2.8
$C_{12}EO_3$	6.99 (± 0.65)	-4.67 (± 0.57)	2.44 (± 0.06)	10	2.7	3.2	-1.5	2.8
$C_{12}EO_5$	6.30 (± 0.12)	-3.29 (± 0.11)	1.88 (± 0.13)	16	3.0	3.4	-2.4	2.8
$C_{12}EO_6$	6.76 (± 0.11)	-3.46 (± 0.09)	2.16 (± 0.05)	17	3.3	3.5	-2.9	2.8
$C_{12}EO_8$ [h]	7.00 (± 0.10)	-3.31 (± 0.06)	2.06 (± 0.03)	18	3.7	3.6	-3.7	2.8
$C_{14}EO_6$	7.82 (± 0.06)	-3.55 (± 0.04)	3.30 (± 0.02)	20	4.3	4.4	-2.3	3.5
$C_{14}EO_8$ [g]	8.00 (± 0.11)	-3.46 (± 0.06)	3.10 (± 0.04)	14	4.6	4.5	-3.3	3.4
$C_{14}EO_{11}$	7.89 (± 0.12)	-3.01 (± 0.07)	2.94 (± 0.09)	7	4.9	4.8	-4.6	3.4
$C_{14}EO_{14}$	7.71 (± 0.08)	-2.99 (± 0.04)	2.67 (± 0.04)	11	4.7	5.0	-6.0	3.4
Sorption of $C_{12}EO_8$ on marine sediments								
OG (0.28; 19 [j])	6.84 (± 0.16)	-3.21 (± 0.12)	1.93 (± 0.14)	8	3.6	3.7	-3.8	2.8
NFF [f] (0.27; 19)	7.00 (± 0.10)	-3.31 (± 0.06)	2.06 (± 0.03)	18	3.7	3.7	-3.8	2.8
FF (0.54; 25)	7.20 (± 0.13)	-3.11 (± 0.06)	2.28 (± 0.06)	12	4.1	3.8	-3.5	2.8
OP (1.4; 46)	7.22 (± 0.10)	-2.73 (± 0.04)	2.66 (± 0.05)	18	4.5	4.1	-3.1	2.8
SF (1.2; 68)	6.86 (± 0.10)	-2.87 (± 0.08)	2.48 (± 0.11)	10	4.0	4.2	-3.1	2.8
LA (0.84; 60)	6.88 (± 0.07)	-2.75 (± 0.05)	2.51 (± 0.07)	11	4.1	4.2	-3.3	2.8

[a] maximum adsorption capacity in mol/kg; [b] *n* = number of data points; [c] highest sorption coefficients according to the DMM sorption isotherms in this study, with Log K_d = Log (K_{ad} + K_p) = Log ($C_{S,max}$·*b* + K_p); [d] sorption coefficients at environmentally relevant concentrations predicted by Log K_d = Log (K_{ad} + K_p) using equations 2 and 3. For the different sediments, equations 2 and 3 are used after which the sorption coefficients are corrected for the differences in surface area; [e] according to PcKocWIN values recommended by ref (*5*), which calculates Log K_{oc} = 0.265·#C - 0.46·#EO - 0.66; [f] according to Kd relationship recommended by ref (*5*), which calculates Log K_d = 0.33·#C - 0.01·#EO - 1.1; [g] data from ref (*8*); [h] data from ref (*8*) with additional 6 data points in this study. [j] sediment properties of the tested sediments (percentage organic carbon in dried sediment; specific surface area in m^2/g dw).

The DMM sorption parameters of $C_{12}EO_8$ on the 6 sediments (isotherms are presented in Figure S2 in Appendix) are presented in Table 1. The data for all sediments (Figure 2A) cover aqueous concentrations over at least 3-4 orders of magnitude, and include the lower and upper linear regions of the isotherms for sediments OP, NFF and OG. There are no data for sediments LA, OG and SF in the concentration range between 10 mg/L and the cmc of $C_{12}EO_8$ (42 mg/L, (*22*)). As this appeared to be the region where the sorption became linear, the fitted K_p values for these three sediments do not rely on many data points. As a result of a limited sediment batch, additional sorption data were not obtained.

Relation between sorption coefficients (K_{ad} and K_p) and chemical structure

Including the results of a previous study (*8*), sorption data for ten AE homologues were available on the same batch of one marine sediment. K_{ad} and K_p, calculated using eq 1, are given in Table 1. Because the isotherms for $C_{12}EO_1$ and $C_{12}EO_3$ are linear, no data are available for K_{ad} for these two chemicals. A multiple linear regression of Log K_{ad} values with the alkyl chain length (#C) and number of ethoxylate units (#EO) gives:

$$\text{Log } K_{ad} = 0.430(\pm 0.061)\cdot\#C + 0.0903(\pm 0.030)\cdot\#EO - 2.31(\pm 0.71) \qquad (2)$$

$n = 8$, $r^2 = 0.95$, $p<0.001$, s (s.e. for the y-parameter) = 0.22

The positive coefficient for #EO indicates that the adsorption affinity increases with each additional ethoxylate unit. This is shown by the isotherms in Figure 1 at the low concentration range where adsorption is the dominant sorption process. Whereas eq 2 would predict a higher adsorption coefficient for $C_{14}EO_{14}$ compared to $C_{14}EO_{11}$, this was not observed in our data (Table 1). Because the low concentration range was not well covered in the isotherm for $C_{14}EO_{14}$, the fitted K_{ad} might underestimate the actual adsorption coefficient. The positive contribution of the ethoxylate chain length on sorption at low concentrations coincides with other sorption studies of individual AE on freshwater sediments (*11*) and ethoxylates mixtures on soils (*23*) and clay (*13*). The contribution of a single CH_2 fragment to K_{ad} is stronger than a single EO unit, but the adsorption coefficients within a group of alkyl-homologues will vary substantially given the broad range in EO units in commercial AE mixtures.

The influence of the ethoxylate chain length on the linear sorption coefficient clearly differs from the influence on the adsorption coefficient. Multiple linear regression of the fitted Log K_p values with #C and #EO shows that K_p is dominated by the alkyl chain length, and that the effect of the number of EO units on K_p is opposite to the effect on K_{ad}:

$$\text{Log } K_p = 0.539(\pm 0.046)\cdot\#C - 0.0471(\pm 0.017)\cdot\#EO - 4.10(\pm 0.54) \qquad (3)$$

$r^2 = 0.95$, $n = 10$, $p<0.001$, $s = 0.17$

Equations 2 and 3 indicate that the affinity coefficients for the two sorption phases that are hypothesised by the dual-mode sorption model, K_{ad} and K_p, diverge with an increasing number of ethoxylate units. As the sorption data for different AE show in Figure 1, the isotherms for longer ethoxylates therefore are more nonlinear in the range around $C_{S,max}$, because there the sediment-water distribution coefficients shift from (K_{ad} + K_p) to (K_p). Such an increase in nonlinearity with longer ethoxylate chains has also been reported in previous studies on the sorption of AE to freshwater sediments, where a decrease in the exponential Freundlich parameter was observed for AE with higher numbers of EO units (*10,11*). We would like to emphasize that equations 2 and 3 have been obtained for a single marine sediment and for a limited set of AE homologues. Extrapolation to other sediments and ethoxylates should therefore be performed with care.

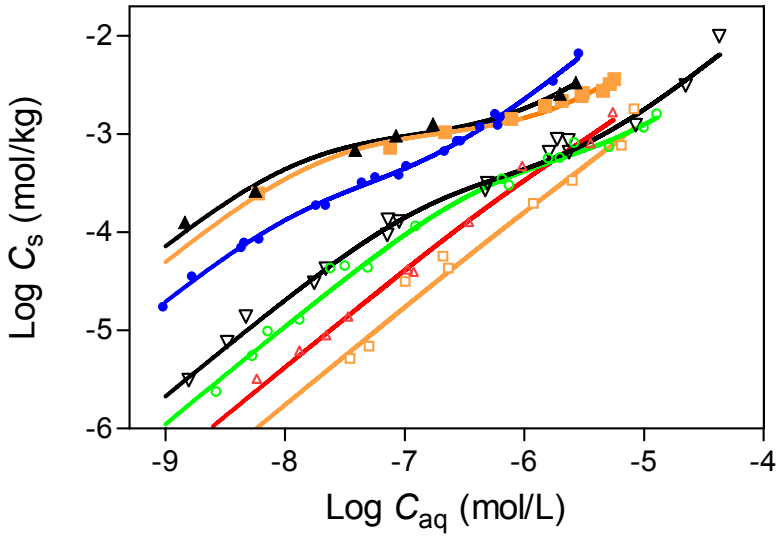

Figure 1. Sorption data and best fitting dual-mode isotherms (eq 1) of individual AE homologues ($C_{12}EO_1$ (□), $C_{12}EO_3$ (Δ), $C_{12}EO_5$ (o), $C_{12}EO_6$(▽), $C_{14}EO_6$ (●), $C_{14}EO_{11}$ (▲), $C_{14}EO_{14}$ (■)) on the marine NFF sediment. The fitted dual-mode model parameters are presented in Table 1.

Relation between sorption coefficients (K_{ad} and K_p) and sediment characteristics

Ideally, the sediment properties related to the two sorption phases would have varied widely throughout the set of six sediments tested in this study. The previous study that described the sorption of AE by the dual-mode model (*8*), hypothesized that K_{ad} was related to the clay fraction, more specifically the specific surface area (SSA) determined via EGME, while K_p should be related to the fraction organic matter. The variance in these two properties for the six tested sediments was limited, also because the sediment

chracteristics are often highly colinear. The fraction of organic carbon (f_{oc}) ranged from 0.27 to 1.4%, and the SSA ranged from 14 to 68 m^2/g (Table 1 and more detailed sediment properties in Table S2 in the Appendix. These two properties also covary significantly in the six tested sediments (Figure S1-A in SI; r^2 = 0.68, p <0.05), as has been observed for marine sediments in general (*24,25*). This complicates the interpretation of the outcome of correlations between sorption coefficients and these two sediment properties.

Figure 2B shows the sorption data to the three clay minerals and the six sediments with C_s expressed as the amount AE sorbed per m^2 surface area. Comparing Figure 2B with 2A clearly demonstrates that correcting for the SSA of the substrates, including the interlayer surface area, strongly reduces the variation in the sorption data between the three clay minerals. The difference in sorption coefficients for the three clay minerals at the tested range of aqueous concentrations is reduced from a maximum factor of 48 in Figure 2A to within a factor 5 in Figure 2B. The variation in K_{ad} for the sediments is reduced from a factor 7.4 to 4.7 after correcting for the SSA, as presented in Figure 2B. Plots of the log transformed sorption parameters K_{ad}, K_p and $C_{S,max}$, against log transformed sediment properties, SSA, f_{oc} and fraction of particles <63 µm ($f_{<63}$) are presented in Figure S1 (in the Appendix). Surprisingly, the correlation between the adsorption coefficient and SSA is the weakest of all the tested correlations (r^2 = 0.4, standard error for the y-estimate (s) = 0.25). The correlations of Log K_{ad} with f_{oc} and $f_{<63}$ are even considerably better (both r^2 = 0.7). The remaining variation in K_{ad}, that cannot be explained by differences in surface area, may well be related to more specific sediment characteristics that reflect the electrostatic interactions of the AE's with clay minerals.

Figure 2B also shows a reduced variation in the plateau in the middle region of the isotherms, representing $C_{S,max}$, compared to Figure 2A. Log $C_{S,max}$ does show a relatively strong relation with Log SSA (r^2 = 0.83, s = 0.10). The maximum adsorption capacity per surface area varies within a factor 2 for the sediments and is on average 30±7 $nmol/m^2$.

The linear sorption coefficient K_p is stronly related with organic carbon content (r^2 = 0.91, s = 0.08). Although the correlation with SSA is less strong (r^2 = 0.77, s = 0.14), Figure 2B shows that the variance in the sorption coefficient at the highest concentrations is also reduced when the data is corrected for surface area, from a maximum factor 5.4 to a factor 2.2.

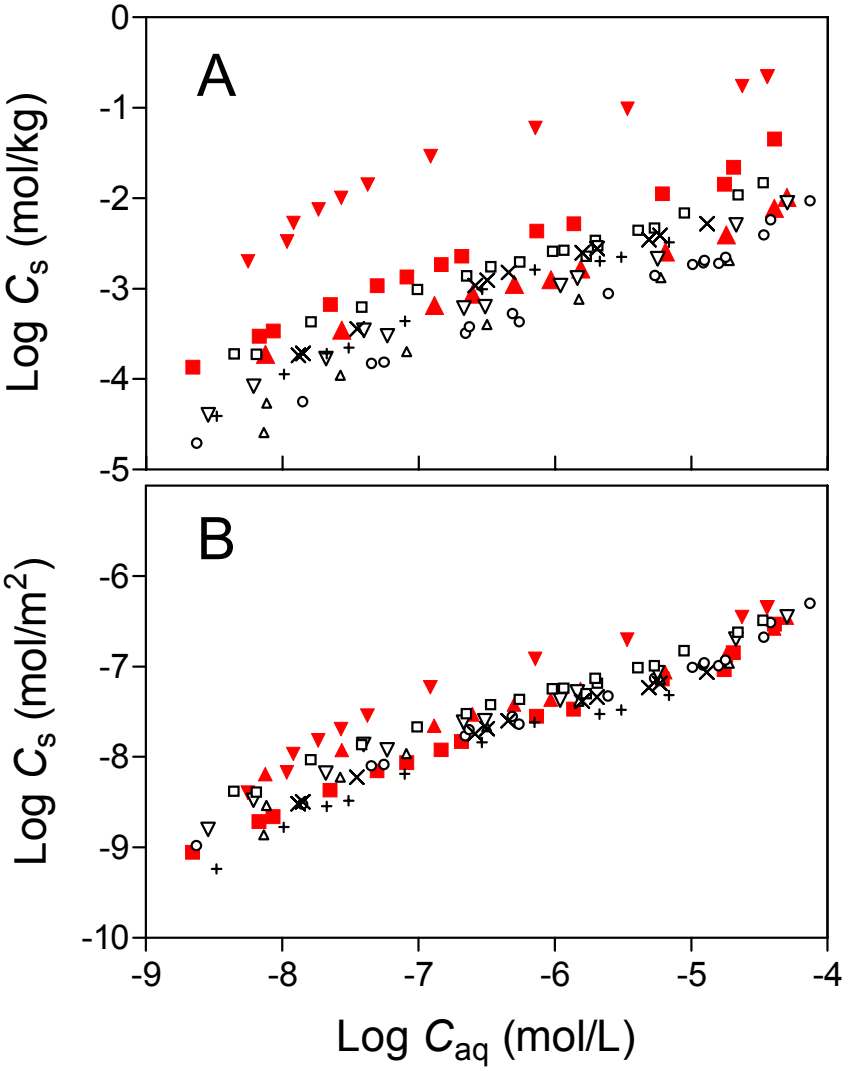

Figure 2. Sorption data of $C_{12}EO_8$ to bentonite (▼), illite (■), kaolinite (▲), three marine (FF (V), NFF (o), OG(Δ)) and three intertidal sediments (OP (□), SF (+), LA (X)). Sorbed concentrations in the upper panel (A) are expressed as mol/kg dry weight, in the lower panel (B) the sorbed data are transformed to the sorbed concentrations per m^2 specific surface area (Table S1 in Appendix). Best fitting DMM sorption parameters for the sediments are presented in Table 1.

DISCUSSION

Interpretation of K_{ad}

In the absence of organic matter, a strong sorption affinity of $C_{12}EO_8$ to the clay minerals was observed. The sorption affinity normalized for the SSA is almost the same for these three clay minerals. The sorption isotherms for the sediments also overlap with the sorption data for the clays when the data is corrected for differences in surface area. This suggests that most of the nonlinear sorption in the sediments can be explained by adsorption to mineral surfaces. On the other hand, using a single Langmuir term for sediments is likely to render some variation, since different adsorption affinities can be expected for the mixture of substrates that comprise the total specific surface area. This may already be the case for kaolinite, of which the clay sheets consist of aluminum hydroxides on one side and a silicium oxide surface on the other side. Several studies suggest that ethoxylates have a weaker affinity for alumina and calcite compared to silica surfaces (*26,27*). Still, based on the SSA corrected data, at lower concentrations sorption to kaolinite is stronger than to illite. This may be due to a stronger surface charge for illite compared to kaolinite. Furthermore, metal oxides may form a substantial fraction of coastal sediment, since metals readily precipitate as a result of the higher pH in seawater compared to pH in the freshwater input (*28*). Eq 2 shows that K_{ad} increases for AE with longer ethoxylate chains, likely because of an increased strength of electrostatic interactions between the ether oxygens and the mineral surface. There are, however, no systematic sorption data with clay minerals for individual AE with increasing ethoxylate chains that can confirm this. One of the reasons for a lack in data is the fact that it has not been possible to determine the freely dissolved concentrations at sorbed concentrations readily below the maximum adsorption capacity. The present study shows that studies at such low concentrations could be performed with a passive sampling extraction technique (such as the SPME method) in combination with LC-MS analysis.

The affinity of $C_{12}EO_8$ for the clay mineral with the larger surface area was much higher. This indicates that the contribution of adsorption to the total affinity of AE for sediment will increase with the total surface area of the sediment. This is in line with previously observed positive relations between sorption affinity of ethoxylates to soils or sediments and clay content (*9,10,13,15,29,30*) and the presence of swelling clays, which have a relatively large surface area to which AE could adsorb (*11,31*). While the variation in K_{ad} was reduced for the sediments when corrected for the surface area, the sediments with the highest SSA in this study did not have the highest K_{ad} values (Figure S1-F in the Appendix). As mentioned earlier, also other sediment characteristics may affect the adsorption affinity.

Interpretation of K_p

In our earlier study (*8*), we interpreted the linear term (K_p) in the dual-mode model as absorption to organic matter. The strong relation of K_p with f_{oc} seems to confirm the

influence of organic matter on the sorption of AE. However, the sorption data with clay minerals also show an increase in sorption after reaching an apparent saturation plateau. In Figure 2B, this increase in sorption of $C_{12}EO_8$ to kaolinite and illite overlaps with the sorption of $C_{12}EO_8$ to the sediments in the high concentration range. These observations do not support our earlier interpretation of the dual-mode model with two sorption compartments (clay and organic matter). Another explanation for the increase in sorption at high surfactant concentrations is the formation of a bilayer of surfactants at the mineral surface. The degree of bilayer formation will be related to the surface area that is covered with surfactant molecules, and therefore with $C_{S,max}$ (Figure S1-A). The strong overlap of the sediment isotherms normalized to surface area for the three clay minerals suggest that the contribution of organic matter to the total sorption affinity for the tested marine sediments is negligible. For substrates with a high organic carbon content, relative to the mineral surface area, organic matter may still be an important sorption phase for AE homologues with relatively low adsorption affinity. This may explain the linear isotherms reported by Kiewiet *et al*. (*18*) for a freshwater sediment with 10% OC content.

The phenomenon of bilayer formation is well known in sorption studies with nonionic surfactants on hydrophilic surfaces like clay minerals, as for example reviewed by Luckham and Rossi (*16*). With increasing concentrations, the adsorbed AE molecules form aggregates on the surface with the alkyl chains extending to the aqueous phase. This, at some point, induces the formation of micelle-like aggregates (in bilayers) via an endothermic sorption process (*32*) and this process reaches a maximum at or just above the cmc (e.g. (*33*)). The results of sorption studies of simple AE mixtures for kaolinite and a marine sediment (see accompanying paper (*34*)) also support the hypothesis of bilayer formation. For both the clay minerals and the sediments, it is clearly demonstrated that when a strongly adsorbing AE homologue ($C_{14}EO_{14}$) is present at concentrations above the $C_{S,max}$, a weaker adsorbing AEs' ($C_{12}EO_8$ or $C_{14}EO_6$) show an almost linear sorption. This linear sorption coincides with the linear sorption at high concentrations for the individual homologue. The most obvious explanation for the linear sorption in the mixture experiment with clay is sorption to the adsorbed layer of the stronger adsorbing AE. This sorption process appears to have a constant affinity coefficient.

Theoretical considerations on bilayer formation

With bilayer formation contributing as a secondary sorption process for AE to clay minerals, it should be possible to fit a combined sorption model like the DMM to the data in this study, with K_p related to bilayer formation. The bilayer affinity term, however, will depend on the amount of AE adsorbed on the mineral surface. When adsorbed AE lie flat on the surface, it is not likely that sorbate-sorbate interactions will occur. However, as soon as small aggregates are formed, even below $C_{S,max}$, with alkyl chains protruding towards the solution, such interactions could already occur. As shown in the accompanying paper, sorption to the adsorbed layer is linear (K_p), but will also be proportional to the

adsorbed surface area relative to the maximum adsorbed area, $C_{S,max}$. The AE concentration "absorbed" to the bilayer ($C_{s,abs}$) should thus be described as:

$$C_{s,abs} = \left(\frac{\frac{C_{S,max} \cdot b \cdot C_{aq}}{1 + b \cdot C_{aq}}}{C_{S,max}} \right) \cdot K_p \cdot C_{aq} = \frac{b \cdot C_{aq}}{1 + b \cdot C_{aq}} \cdot K_p \cdot C_{aq} \qquad (4)$$

The nominator of the enclosed term represents the surface area occupied with adsorbed patches, and the first term at the right the relative surface area occupied with adsorbed patches. If the DMM in eq 1 is used to describe the adsorption and bilayer formation of AE to clay, this gives:

$$C_s = \frac{C_{S,max} \cdot b \cdot C_{aq}}{1 + b \cdot C_{aq}} + \frac{b \cdot C_{aq}}{1 + b \cdot C_{aq}} \cdot K_p \cdot C_{aq} = \frac{b \cdot C_{aq}}{1 + b \cdot C_{aq}} \left(C_{S,max} + K_p \cdot C_{aq} \right) \qquad (5)$$

Eq 5 represents a hypothetical relation and there are no data yet to confirm its applicability. Furthermore, while eq 5 may describe the sorption processes more correctly, the calculated sorption parameters hardly vary when eq 5 is fitted to the sorption data instead of eq 1. The adsorption and bilayer formation of AE to hydrophilic surfaces is further complicated because it is not clear to what extent AE adsorbed in the interlayer of swelling clays contributes to bilayer formation. If sorption to organic matter in sediments is a linear process, then the sorption of AE to sediments could be described by the sorption model in eq 5 extended with the K_{oc} multiplied with f_{oc}. At the moment, however, only estimates of K_{oc} via fragment contribution values are available for AE.

Applying the dual-mode model to predict sediment-water distribution coefficients: a comparison with classical models

This study shows that a combined Langmuir-linear model describes the sorption data of AEs to marine sediments. The strength of the dual-mode model is that it clearly recognizes that sorption at high concentrations is different from sorption at low concentrations because it concerns two different processes. Moreover, the effect of the ethoxylate chain length on sorption is clearly different at the low or high concentration range of the sorption isotherm. Because sediment characteristics are often correlated to each other, it is still difficult to correctly predict the sorption coefficients based on sediment properties. This study shows that for a single AE homologue the specific surface area, including the interlayer area, seems to predict sorption well within a factor of ~five. Perhaps the best indication of the adsorption capacity and adsorption affinity of ethoxylates for different sediments could be deduced from an isotherm over a broad concentration range with a reference AE, such as $C_{12}EO_8$. Such a reference compound can then be used to normalize the sorption data. The sorption parameters of other homologues could then be predicted

using equations 2 and 3. A similar approach has been proposed in the past for nonpolar organic contaminants (*35*).

Two approaches to estimate sediment-water distribution coefficients, and therewith the bioavailable concentrations required for risk assessment, have been presented in recent studies. Dyer *et al*. (*5*) used the fraction of organic carbon multiplied by the K_{oc} estimated with PcKocWIN under EPI-Suite v.3.11 to predict the homologue specific distribution coefficients. Van Compernolle *et al*. (*17*) recommend a fixed sediment-water distribution coefficients for sediments with low organic carbon content (<7-10%), calculated with an equation including the molecular descriptors #C and #EO. Both methods were used to predict AE sorption coefficients to the marine sediment (NFF, f_{oc} = 0.27%) for the AEs that were tested in this study. The predicted whole sediment sorption coefficients (Log K_d) are presented in Table 1.

To compare these two approaches with the experimental sorption data from this study, Table 1 presents the sorption coefficients for the lower linear part of the DMM isotherms on the NFF sediment, where Log K_d = Log (K_{ad} + K_p), in two ways: (i) based on the individual isotherms, and (ii) predicted via equations 2 and 3. The constant sorption coefficient at the low end of the isotherm is used in order to extrapolate to the much lower concentrations of individual homologues at locations where AE is detected (*5-7*).

The K_{oc} model recommended by Dyer *et al*. (*5*) clearly does not work for this marine sediment: the PcKocWIN software predicts a decrease in Log K_{oc} of 0.46 per EO unit and only increases 0.26 with each CH_2 group, and thereby predicts much lower K_d values compared to the observed sorption coefficient. The model is further limited by a maximum amount of EO-units that are corrected for, as well as a recommended lower limit to the K_{oc} of 10. Both limitations were not taken into account in the predicted values in Table 1, but if they were, a lower limit of the Log K_d of -1.54 is calculated for the NFF sediment. The PcKocWIN is not recommended for risk assessment of AE in marine sediments. The K_d model predictions recommended by Van Compernolle *et al*. (*17*) deviate more with experimental data with increasing ethoxylate chain lengths. Extending the calculations for an ethoxylate range of $C_{12}EO_1$ to $C_{18}EO_{18}$, the DMM predicted K_d values are 0.18 to 2.06 log units higher than the fixed K_d model from ref (*17*), respectively. For this sediment, the fixed K_d values from ref (*17*) can thus be considered as conservative for all AE homologues. The scientific approach with which these values are obtained is rather poor, though.

Equations 2 and 3 are constructed using the data for the NFF sediment only. Considering the results from the clay minerals, it seems that correcting for the surface area of the sediment should be sufficient to use equations 2 and 3 for other marine sediments. An uncertainty factor of 5 should taken into account in combination with the uncertainty that this has only been established for a single AE homologue. For the different marine sediments, the K_d values that should be representative for field situations with low environmental concentrations (K_{ad} + K_p) are obtained form the individually fitted isotherms, as well as those predicted from equations 2 and 3. Obviously, the fixed K_d values recommended by ref (*17*) predict similar K_d values for all these marine sediments.

This study suggests that the role of organic matter appears to be small for the tested marine sediments, whereas adsorption to mineral surfaces, and formation of bilayers, appear to dominate the affinity of AE for these sediments. Ignoring these phenomena may result in models that are unable to generate reliable predictions when extrapolating to (i) the wide range of AE homologues, (ii) concentration ranges below the tested sorption isotherms and (iii) the possible range of sediment properties. Although the processes behind the models presented in this article are not completely understood, and should be further validated, they are more realistic interpretations of the sorption processes and will likely supply more reliable predictions of sorption coefficients.

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APPENDIX

Table S1. SPME Fiber-Seawater Partition Coefficients (K_{fw}) Used in This Study

AE	Log K_{ow} [a]	Log K_{fw} ± s.e.[b]	n [c]
$C_{10}EO_8$ [d]	1.59	1.49±0.02	16
$C_{12}EO_1$ [f]	4.50	4.83±0.05 [f]	4
$C_{12}EO_3$ [e]	3.95	3.97±0.01	4
$C_{12}EO_5$ [e]	3.40	3.43±0.01	10
$C_{12}EO_6$ [e]	3.12	3.09±0.01	8
$C_{12}EO_8$ [d]	2.58	2.50±0.01	22
$C_{14}EO_6$ [d]	4.11	4.07±0.02	4
$C_{14}EO_8$ [d]	3.56	3.62±0.01	37
$C_{14}EO_{11}$ [d]	2.73	2.80±0.02	9
$C_{14}EO_{14}$ [e]	1.91	2.06±0.02	4

[a] K_{ow} = Estimated octanol-water partition coefficient obtained from SRC's KowWin Program (v1.67) within the EPISuite package; [b] K_{fw} = polyacrylate-water partition coefficient, obtained by a fit of Log C_f = log K_{fw} + Log C_{aq} through the available data for seawater at 20 °C. [c] n = number of data; [d] data previously published data (*22*); [e] from data obtained in this study; [f] K_{fw} obtained from data obtained during the sorption experiment, with aqueous phase sampled after centrifugation and C_{18} SPE columns, as in ref (*22*).

The fiber-water partition coefficients (K_{fw}) determined separate from the sorption tests in clear GP2 medium for $C_{12}EO_3$, $C_{12}EO_5$, $C_{12}EO_6$, and $C_{14}EO_{14}$, were highly comparable to values calculated with the previously established EPI-Suite K_{ow} based QSAR (*22*). Although the Log K_{fw} values correlated very well with the estimated Log K_{ow} values, it is probably better to relate Log K_{fw} to simple molecular descriptors of the AE, alkyl chain length (#C) and number of ethoxylate units (#EO). A linear regression was used on C_f against C_{aq} because for most AE the nonlinearity parameters n obtained with Freundlich isotherms were not significantly different from 1. Accordingly, K_{fw} can be estimated accurate within 0.073 log units:

$$\text{Log } K_{fw} \text{ (sea water)} = 0.520 \cdot \#C - 0.264 \cdot \#EO - 1.56 \qquad \text{(eq s1)}$$

$n = 9$, $r^2 = 0.995$, s = 0.073

Table S2. Properties of Three Clay Minerals and Six Sediments.

Abbreviation sorbent and sampling location (longitude, latitude)	%TOC	% clay [b]	% silt [b]	Mean grain size (μm)	Surface area,[c] (m^2/g)
Clay minerals					
BEN, bentonite	<0.05	n.a.	n.a.	n.a.	490 (±3)
ILL, illite	<0.05	n.a.	n.a.	n.a.	155 (±4)
KAO, kaolinite	<0.05	n.a.	n.a.	n.a.	30 (±3)
Dutch North sea marine sediments					
OG, Oyster grounds (54.5 °N, 4.5 °E)	0.28	1.0	21	117	19 (±1)
NFF, Northern Frisian Front (54 °N, 4.5 °E)	0.27	1.2	19	106	19 (±2)
FF, Frisian Front (53.65 °N, 4.5 °E)	0.54	1.2	26	123	25 (±1)
Intertidal sediments					
LA, Huelva (Spain) (37.13 °N, 7.10 °E)	0.84	1.6	43	186	60 (±4)
SF, San Fernando (Spain) (36.28 °N, 6.12 °E)	1.24	1.0	33	150	68 (±4)
OP, Eastern Scheldt (Netherlands) (51.36 °N, 3.47 °E)	1.38	1.5	52	73	46 (±4)

[a] m = marine sediment, i = inter tidal sediment, c = ceramics shop; [b] clay = fraction <2 μm, silt = fraction <8 μm, n.a. = not analyzed; [c] specific surface area determined via EGME method (±standard deviation, *n*=3).

The clay minerals were not checked for purity. The specific surface area of kaolinite was 1.5 times higher in this study than in a previous study, while that for bentonite was slightly lower than montmorillonite, a reference smectite (*36*). The kaolinite should mostly consist of 1:1 layered nonexpandable clay sheets, with an octahedral aluminumhydroxide layer on one side and tetrahedral siliciumoxide layer on the other side of the sheet, with a typically low charge. Both surfaces of bentonite and illite sheets consist of siliciumoxide. Bentonite, however, has mainly isomorphic substitutions of Al^{3+} by Mg^{2+} in the octahedral aluminum sheet, therefore the sheets are only moderately negatively charged and can expand. Illite has substitutions of Al^{3+} for Si^{4+} in the tetrahedral silicon layer, resulting in a stronger charge at the surface and nonexpandable clay sheets.

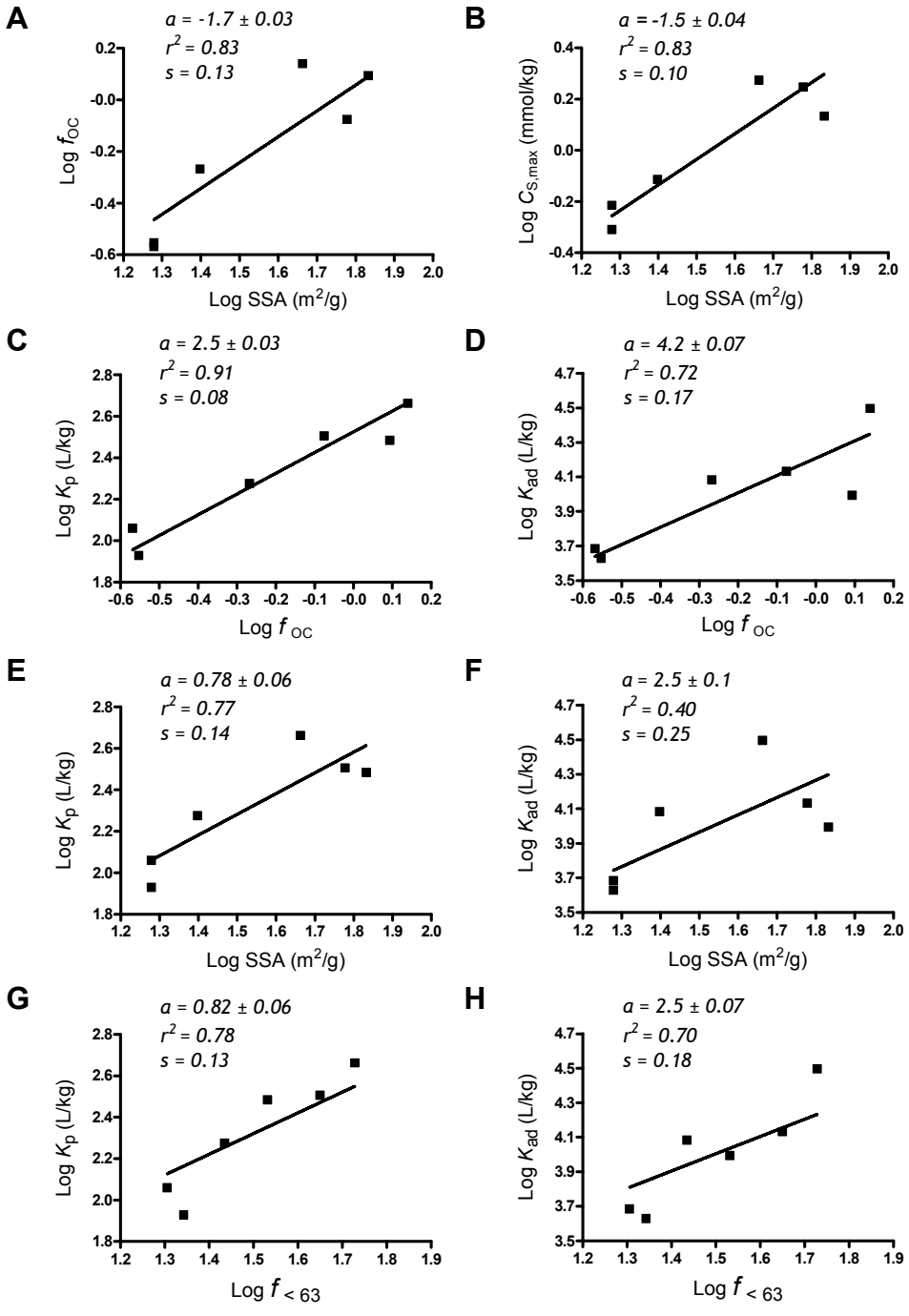

Figure S1. Correlations between dual-mode model sorption parameters and sediment properties. K_p and K_{ad} ($b^*C_{S,max}$) are fitted values using eq 1, and are listed in Table 1. SSA is specific surface area, f_{oc} is fraction organic carbon, both are listed in Table S2. The regressions are linear relationships with a slope of 1, according to and y = x + *a*, with *a* (±s.e.) presented together with correlation coefficient (r^2) and standard error for the y-estimate (s) above the plots.

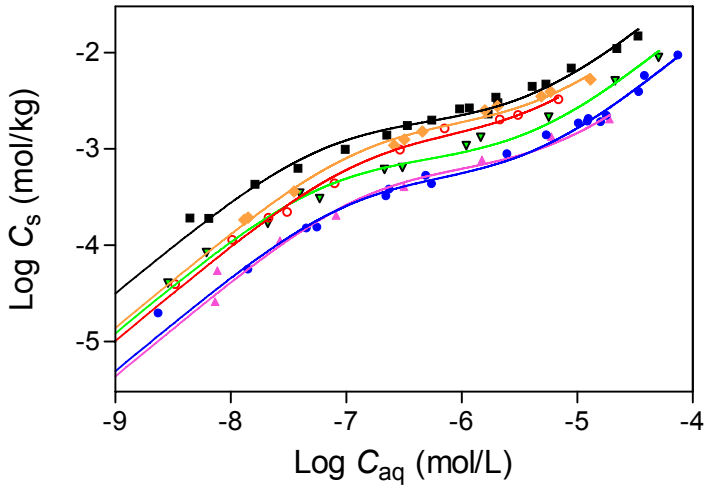

Figure S2. Dual-mode model (eq 1) isotherms on the sorption data of $C_{12}EO_8$ for the tested sediments, three marine (FF (▼), NFF (●), OG(▲)) and three intertidal sediments (OP (■), SF (○), LA (◆)), with abbreviations as in Table S2. Isotherm parameters are presented in Table 1.

Chapter 7

Nonlinear Sorption of Alcohol Ethoxylates to Marine Sediment: Modeling Competition Effects in Mixtures

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Nonlinear Sorption of Alcohol Ethoxylates to Marine Sediment: Modeling Competition Effects in Mixtures

ABSTRACT

The sorption of alcohol ethoxylates (AEs) to marine sediment and kaolinite clay is studied in binary and ternary mixtures of homologues with different number of ethoxylate units or alkyl chain lengths. A clear competition effect is observed in the isotherms obtained with these mixtures. The sorption data with kaolinite show that adsorption sites can be effectively blocked by a homologue with a stronger adsorption affinity. This adsorbed AE cosolute, however, likely forms a second sorption phase to which the homologue with the weaker adsorption affinity sorbs with a constant sorption coefficient. A Langmuir-linear dual-mode model extended for competition effects almost perfectly describes the observed competition in the isotherms for the sediment. Competition becomes apparent when the total adsorbed concentration reaches ~10% of the maximum adsorption capacity, and it depends on the affinity constants and homologue composition in the aqueous phase. Competitive sorption effects also depend on the solids concentration because the composition of the AE mixture in the aqueous phase strongly varies with the amount of substrate in closed test systems. Competition will not often occur in field contaminated sediments, where concentrations of AEs are relatively low, but will certainly be an issue in sorption studies and sediment toxicity tests with complex surfactant mixtures.

INTRODUCTION

Alcohol ethoxylates (AEs) are nonionic surfactants used in many household and industrial products, and consist of complex homologue mixtures with the molecular formula $CH_3(CH_2)_n(OCH_2CH_2)_yOH$, where n generally varies from 11–15,17 and y from 0–18. Once the compounds are released in the environment via effluents, often in strongly reduced concentrations due to sewage treatment (*1,2*), AEs may accumulate in the sediment layer via direct sorption from the aqueous phase or sedimentation of particular matter to which AEs are sorbed (*3-5*). The residence time, mixture composition, and resulting concentrations of AEs will be a balance between biodegradation processes, sorption and fresh input. The specific sorption affinity of each homologue for the sediment controls the freely dissolved concentrations of AEs in the pore water, to which organisms in the sediment layer are exposed. The sediment-water distribution coefficient (K_d) is therefore an important parameter for risk assessment.

The K_d of most AE homologues in natural sediments is not a constant value, but concentration dependent (*6-10*). The nonlinearity of the sorption isotherms of alkyl ethoxylates is likely the result of multiple types of sorption sites in natural sediments, such as various clay mineral surfaces and organic matter (*11*). In recent studies with individual AE homologues and various marine sediments (*6,7*), the sorption data could be well described by a dual-mode sorption model (DMM), which combines a Langmuir term and a linear sorption term:

$$C_s = \frac{C_{S,max} \cdot b \cdot C_{aq}}{1 + b \cdot C_{aq}} + K_p \cdot C_{aq} \qquad (1)$$

where $C_{S,max}$ is the maximum sorption capacity, expressed as the maximum concentration of an adsorbing contaminant, $C_{S,max} \cdot b$ the linear adsorption coefficient (K_{ad}) at sediment sorbed concentrations well below $C_{S,max}$ (where $C_{aq} << 1/b$), and K_p the sorption coefficient of a linear sorption component. Sorption data obtained for ten individual AE homologues on the same sediment, presented in the accompanying paper (*6*), showed a positive contribution of each additional EO unit to K_{ad}, and a slightly negative contribution to K_p. The increasing adsorption coefficient with longer ethoxylate chains can be explained by the increased strength of electrostatic interactions at the mineral surfaces. From the comparison between sorption data of a single AE homologue for pure clay minerals and a set of sediments, it was concluded that the K_p in the dual-mode model was most likely related to bilayer formation, and not to sorption to organic matter, as was suggested in an earlier study (*7*).

The general conclusion that sorption of AEs to sediment is dominated by adsorption to mineral surfaces, raises the question of what happens when multiple AE homologues are present in a sample. Since AEs are always used in complex mixtures of homologues, the sorption isotherms of individual homologues will likely be influenced by the presence of comparable structures. It would be very convenient to model this influence in order to

understand under which circumstances such competitive sorption effects become important. A detailed interpretation of the sorption processes and a fully descriptive sorption model for AE homologues in sediment is complex and at the moment there is insufficient high quality sorption data to incorporate all possible interactions. Still, the simple model in eq 1 fitted the AE data well, and it may function as an approximative model of the most important sorption processes.

The Langmuir part of the dual-mode model can be easily extended with additional compounds competing for similar adsorption sites. Sorption models based on the Langmuir equation have for example been described for the competitive binding of two ligands to serum proteins (*12*), chlorophenols to activated carbon (*13*), as well as for the sorption of mixtures of PAHs to organic matter in sediment, for which glassy (Langmuir) and rubbery (linear) sites within organic matter were suggested as two sorption phases (*14-16*). To include the influence of cosolutes on the adsorption of an AE homologue for a mineral surface area, eq 1 can be extended with an extra term in the Langmuir component, in a similar way as was done for sorption of PAHs to the glassy sorption sites (*15,16*):

$$C_{s,1} = \frac{C_{S,max} \cdot b_1 \cdot C_{aq,1}}{1 + b_1 \cdot C_{aq,1} + \sum_{i=2}^{n} b_i \cdot C_{aq,i}} + K_{p,1} \cdot C_{aq,1} \qquad (2)$$

where subscript *i* applies to competitive cosolutes 2 through *n* of an AE (compound 1), with *n* as the number of solutes. The parameters in eq 2 are compound specific sorption coefficients and can be derived from sorption isotherms with individual compounds. Even when K_{ad} would represent an average adsorption affinity for all mineral surfaces, eq 2 would mechanistically still make sense. The interpretation of the dual-mode model, applied in the accompanying paper (*6*), is that the Langmuir term describes adsorption to a phase with a certain maximum capacity, combined with a linear term that represents sorption to adsorbed aggregates, forming bilayers. If a stronger adsorbing AE homologue is present at concentrations above the maximum adsorption capacity, it should block all adsorption sites for a weaker adsorbing homologue, similar to observations for mixture studies with PAHs (*15*). In the case of these nonionic surfactants, however, the adsorbed high affinity AE homologue will provide a secondary sorption phase to which the weaker adsorbing homologue may sorb via bilayer formation.

In this study, sorption experiments with simple AE mixtures are performed on a marine sediment and kaolinite clay. Results are compared with individual sorption isotherms determined in previous studies with AE on the same sorbents (*6,7*). The first objective of this work was to verify that bilayer formation of alcohol ethoxylates is a linear sorption process. In sorption experiments with kaolinite clay and sediment, binary mixtures were therefore used in which the homologue with the stronger adsorption affinity was present at a constant high concentration.

The second objective was to understand competitive sorption in a ternary mixture at varying concentrations of the AE homologues. Based on these experiments, the ability of

the extended DMM (eq 2) to predict sorption isotherms for individual homologues in mixtures of AE was assessed. For this purpose mass balance based simulations of sorption tests were run, according to a mathematical model comparable to the model used in a competition study with serum protein (*12*). This mathematical model enables simulations of the effect on sorption of both a varying amount of sediment and the amount of each compound added to the test system. Finally, the implications of competitive sorption for risk assessment of AE are discussed.

EXPERIMENTAL SECTION

Chemicals, SPME fibers and sediment

The polyethylene glycol alkylether homologues $C_{10}EO_8$, $C_{12}EO_8$, $C_{14}EO_8$ and $C_{14}EO_6$ (all >98% TLC) were from Fluka (Buchs, Switzerland), whereas $C_{14}EO_{14}$ was synthesized by J. Tolls and H.C. Kwint in 1996 (>97% GC, HPLC, ^{1}H-NMR). The aqueous concentrations in the sorption experiments were determined by the same solid phase microextraction (SPME) method as described in previous studies with AE (*6,7,17*), using the measured fiber-water partition coefficients (K_{fw}) presented in those studies. Both the North Sea sediment (NFF) and the kaolinite clay, which had been hydrated in seawater for several days, were from similar batches as used in previous sorption studies with AE (*6,7*).

Sorption experiments

The sorption tests in this study were performed with similar chemicals, test systems, test conditions and analytical procedures as described in previous studies (*6,7*). Briefly, AE were added to empty 40 mL vials via stock solutions in methanol, and the added methanol was evaporated. Wet substrate and 0.4 mL formaldehyde solution was added, and seawater until less than a mL headspace was left. Two SPME fibers were added after 24 h and these were equilibrated in the systems for 72 h. Methanol extracts from fibers were analyzed by LC-MS. Using the SPME derived aqueous concentrations, sorbed concentrations were calculated for the binary mixtures assuming a closed mass balance. This approach has been validated for similar test conditions in a previous study (*7*). The amount of sediment in the ternary mixtures were sometimes too small to meet the requirement to have at least 30 % of the total amount of each AE homologue in the system sorbed to the sediment (*7*). Therefore, all sediment sorbed concentrations in these tests were measured directly, after extraction with methanol extraction as described in ref (*7*).

Several mixture systems were tested, and details of the test conditions used are presented in Table 1. To test whether a homologue with a high adsorption affinity could block all adsorption sites for a homologue with a weaker adsorption affinity, binary mixtures were studied with $C_{14}EO_{14}$ as the strong adsorbing homologue, present at concentrations above the maximum adsorption capacity ($C_{S,max}$). $C_{12}EO_8$ was used as the

weaker adsorbing homologue in the experiment with kaolinite clay, and $C_{14}EO_6$ in the experiment with marine sediment. The sorption isotherms of the individual homologues on the same substrates are presented in the accompanying paper (*6*). Two different sediment sorbed concentrations of $C_{14}EO_{14}$ on the kaolinite clay were tested in separate series.

Ternary mixtures were prepared using equimolar stock solutions of $C_{10}EO_8$, $C_{12}EO_8$, and $C_{14}EO_8$. In three test series, the amount of sediment in each vial (solids concentration W_s) was kept constant, while an increasing amount of the ternary spike solution was added. Different solids concentrations were used for each series. In a fourth series, all vials contained the same amount of the equimolar stock, while the solids concentration varied.

Table 1. Test Conditions and Measured Concentrations at Equilibrium.

Binary mixtures

Sorbent	AE mixture	Sorbent concentration (g/L)	C_s of $C_{14}EO_{14}$ (mg/kg)	C_{aq} test range of 2nd AE (mg/L)
Kaolinite clay	$C_{12}EO_8$ $C_{14}EO_{14}$	6.36±0.54	775±68	0.001 - 31.3
Kaolinite clay	$C_{12}EO_8$ $C_{14}EO_{14}$	6.74±0.27	1770±105	0.008 - 19.3
Marine sediment	$C_{14}EO_6$ $C_{14}EO_{14}$	2.60±0.04	1900±300	0.0015 - 0.35

Ternary mixtures with marine sediment

Variable	AE mixture	Sorbent concentration (g/L)	Amount of each AE in test system (µg)	C_{aq} test range used in Fig. 3 (mg/L)
Spiked amount of AE	$C_{10}EO_8$ $C_{12}EO_8$ $C_{14}EO_8$	0.26±0.05	0.13 - 89	0.011 - 1.28 0.0011 - 3.07 0.0001 - 1.98
Spiked amount of AE	$C_{10}EO_8$ $C_{12}EO_8$ $C_{14}EO_8$	1.36±0.05	0.5 - 110	0.011 - 2.69 0.002 - 2.00 0.0002 - 0.51
Spiked amount of AE	$C_{10}EO_8$ $C_{12}EO_8$ $C_{14}EO_8$	6.19±0.42	0.13 - 89	0.019 - 1.65 0.002 - 1.06 0.0002 - 0.21
Added amount of sediment	$C_{10}EO_8$ $C_{12}EO_8$ $C_{14}EO_8$	0.16 - 7.97	3.60±0.04 3.29±0.03 3.43±0.03	0.028 - 0.090 0.002 - 0.080 0.0002 - 0.044

Mathematical model for competition

A mathematical model was formulated to simulate competition effects of AE in sediment suspensions. It is based on the assumptions of a simple dual-mode model (DMM) as in eq 1, with a single term for a nonlinear sorption phase, and a single term for a linear sorption phase. A mass balance equation of analyte 1 in the sorption test is given in eq 3:

$$N_{1,tot}/V = C_{1,aq,tot} = C_{1,aq} + C_{1,ad} \cdot m/V + C_{1,ab} \cdot m/V \qquad (3)$$

where $N_{1,tot}$ represents the total amount (in mol) of compound 1 in the system, V (in L) is the total volume of the aqueous phase and m (in kg) the mass of the sediment phase. $C_{1,aq}$ is the freely dissolved concentration of compound 1 at equilibrium, $C_{1,ad}$ is the concentration of compound 1 adsorbed to the sediment (mol/kg), $C_{1,ab}$ is the concentration of compound 1 absorbed to the sediment (mol/kg). Combining the dual-mode model for homologue mixtures (eq 2) with the mass balance equation (eq 3), and using W_s to denote the ratio m/V results in:

$$\begin{aligned} C_{1,aq\text{-}tot} &= C_{1,aq} + \left(\frac{C_{S,max} \cdot b_1 \cdot C_{1,aq}}{1 + b_1 \cdot C_{1,aq} + \sum_{i=2}^{n} b_i \cdot C_{i,aq}} \right) \cdot W_s + \left(K_{p,1} \cdot C_{1,aq} \right) \cdot W_s \\ &= C_{1,aq} \cdot \left[1 + \left(\frac{C_{S,max} \cdot b_1}{1 + b_1 \cdot C_{1,aq} + \sum_{i=2}^{n} b_i \cdot C_{1,aq}} \right) \cdot W_s + K_{p,1} \cdot W_s \right] \end{aligned} \qquad (4)$$

The parameters b_1, $C_{S,max}$ and $K_{p,1}$ are obtained from the isotherms of analyte 1 fitted by the dual-mode model (*6,7*). It was assumed that the AE homologues present in a test system can only compete for binding sites at the adsorption phase of the sediment, represented by the Langmuir term in eq 4, and that $C_{S,max}$ is constant for all homologues.

For a binary AE mixture of compounds 1 and 2 (and assuming that $C_{S,max}$ is equal for 1 and 2), the mass balances for compounds 1 and 2 are thus as follows:

$$C_{1,aq,tot} = C_{1,aq} + C_{1,ad} \; W_s + C_{1,ad} \; W_s = C_{1,aq} \left(1 + \left(\frac{b_1 \cdot C_{S,max}}{1 + b_1 \cdot C_{1,aq} + b_2 \cdot C_{2,aq}} \right) W_s + K_{p,1} \cdot W_s \right) \qquad (5a)$$

$$C_{2,aq,tot} = C_{2,aq} + C_{2,ad} \; W_s + C_{2,ad} \; W_s = C_{2,aq} \left(1 + \left(\frac{b_2 \cdot C_{S,max}}{1 + b_1 \cdot C_{1,aq} + b_2 \cdot C_{2,aq}} \right) W_s + K_{p,2} \cdot W_s \right) \qquad (5b)$$

For the NFF sediment, an average $C_{S,max}$ of 0.6 mmol/kg was observed for different AE homologues (*6*), and this value was used in all model simulations. The model, using equations (5a) and (5b), was written and run in the software package Berkeley Madonna (www.berkeleymadonna.com). The script of the model and the general parameter values for this model can be found in the Appendix for binary and ternary mixtures. To simulate the effect of a variable amount of sediment in the test system (W_s) on the sorption of the ternary mixture, a variation of the script was used, presented along with the parameter values in section B of the Appendix.

RESULTS AND DISCUSSION

The effect of a homologue with stronger adsorption affinity on sorption isotherms in binary mixtures

Figure 1 shows the sorption data of the two series on kaolinite, together with the series for $C_{12}EO_8$ without $C_{14}EO_{14}$ from ref (*6*). The maximum adsorption capacity ($C_{S,max}$) of kaolinite for $C_{12}EO_8$, estimated from the single solute sorption data from ref (*6*), is 1.0±0.1 mmol/kg. With increasing sorbed concentration of $C_{14}EO_{14}$, from 0.93±0.083 mmol/kg in the first series to 2.1±0.13 mmol/kg in the second series, the sorption of $C_{12}EO_8$ at the lower concentrations is clearly reduced, and the sorption isotherm of $C_{12}EO_8$ to the kaolinite shifts towards a single linear isotherm. Apparently, while most adsorption sites are blocked, the adsorbed amount of $C_{14}EO_{14}$ forms a secondary sorption phase for which $C_{12}EO_8$ has a constant affinity. At high concentrations of $C_{12}EO_8$ the data in the mixture coincide with the data for the individual isotherm of $C_{12}EO_8$. The same phenomena were observed for the binary mixture tested with the sediment, as presented in Figure 2. The distinctly nonlinear isotherm of $C_{14}EO_6$, as observed in the experiment with the individual compound, shifts again to a linear isotherm, when $C_{14}EO_{14}$ is present at concentrations (2.3 mmol/kg) above the maximum adsorption capacity ($C_{S,max}$) of the sediment (0.26 mmol/kg, in ref (*6*)).

Previous studies showed that the adsorption affinity of AE homologues increases with the length of the alkyl chains and number of ethoxylate units (*6,7*). The binary AE mixture studies demonstrate for both clay and sediment that the presence of a homologue with a much stronger adsorption affinity, $C_{14}EO_{14}$, can block all adsorption sites for the weaker adsorbing AE homologues, $C_{12}EO_8$ and $C_{14}EO_6$. These observations strongly suggests that adsorption is the dominant sorption process in sediment for the lower concentration range of the isotherm for $C_{14}EO_6$. Although the role of sorption into the organic matter in the sediment can not be ruled out, we assume that the remaining linear process (with a constant affinity coefficient) is related to sorption to the adsorbed layer of $C_{14}EO_{14}$, as observed for the binary mixture on kaolinite clay. A more detailed discussion of these phenomena of bilayer formation is given in the accompanying paper (*6*).

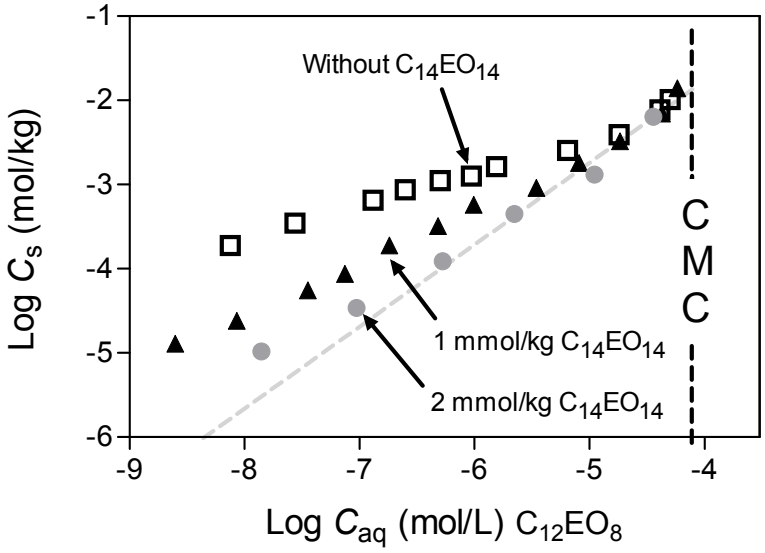

Figure 1. Sorption data of $C_{12}EO_8$ on kaolinite in seawater as a single solute (□), from ref (*6*), in the presence of 1 mmol/kg (▲) and 2 mmol/kg (●) $C_{14}EO_{14}$. The dashed line indicates the predicted linear isotherm based on K_p (*6*). CMC is the critical micelle concentration for $C_{12}EO_8$ in a single solute solution in seawater (*17*).

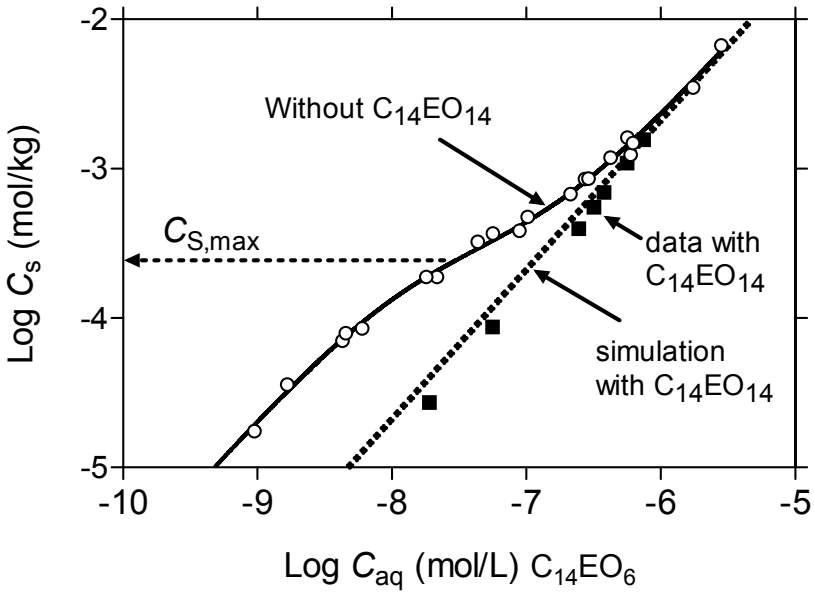

Figure 2. Sorption data for $C_{14}EO_6$ on marine NFF sediment for test systems with 2.3 mmol/kg $C_{14}EO_{14}$ (■). The curved line is the DMM isotherm fitted to the single solute sorption data for $C_{14}EO_6$ (○) from ref (*6*). The dotted line shows the simulated isotherm of $C_{14}EO_6$ in the binary mixture under similar test conditions, using the mathematical model based on eq 2.

When eq 1 is applied to the sorption data of $C_{12}EO_8$ to kaolinite, K_p values of 177, 187 and 146 L/kg are obtained for the data without, with 1 mmol $C_{14}EO_{14}$/kg, and with 2 mmol $C_{14}EO_{14}$/kg, respectively. From these K_p values for kaolinite, which is free of organic matter, it is possible to estimate the affinity constant of an AE homologue for an AE monolayer ($K_{p,mono}$). The fraction of the AE monolayer per kg bulk dry weight (f_{mono}) is the sorption phase for this process and. Following eq 1, the maximum adsorbed monolayer is similar to $C_{S,max}$. $C_{S,max}$ for $C_{12}EO_8$, tested as a single chemical, on kaolinite is 1.05 mmol/kg (*6*), or 564 mg/kg, therefore f_{mono} is 0.000564. $K_{p,mono}$ is obtained by dividing K_p by f_{mono}, resulting in a Log $K_{p,mono}$ of 5.5±0.1 for $C_{12}EO_8$. Accordingly, the binary test with sediment indicates a Log $K_{p,mono}$ of 7.2 for $C_{14}EO_6$, if sorption to organic matter is considered negligible. Log $K_{p,mono}$ seems to be an interesting property of AE, but requires accurate values for $C_{S,max}$, and a better understanding of the bilayer formation process, which is outside the scope of this study.

The effect of varying concentrations of co-solutes on sorption isotherms of individual homologues in ternary mixtures

In the binary AE mixtures described above, and the sorption tests with PAH mixtures by Zhao *et al*. (*15*), the cosolute(s) were always present at constant, relatively high concentrations. In our study, several series of sorption experiments were also performed with equimolar stocks of three AE homologues which only varied in alkyl chain length; $C_{10}EO_8$, $C_{12}EO_8$, $C_{14}EO_8$. For these three AE, the single solute sorption coefficients (K_{ad} and K_p) on the same batch of marine sediment are known and are presented in ref (*7*). Three series were tested with a different amount of sediment in each series, and these sorption data are presented in Figure 3. In a fourth test series with the ternary mixture, presented in Figure 4, a constant amount of AE was added to the test vials, whereas the amount of sediment per vial was increased. Also plotted in these figures are the dual-mode isotherms from the single solute sorption experiments reported previously (*6,7*), and the simulations from the mathematical model, which are discussed further on in the text.

The SPME duplicates varied within 10%, allowing precise measurements of the freely dissolved concentrations. Especially for $C_{10}EO_8$, which has a relatively low sorption affinity, the amount of AE sorbed to the sediment was often less than 30% of the total amount in the system. Therefore, concentrations measured in the sediment extracts were used for all samples, instead of calculating sorbed concentrations from aqueous concentrations and the assumption of a closed mass balance. For those cases where more than 30% of the total amount of an AE was sorbed, the average difference between measured and mass balance calculated sorbed concentrations was 3(±10)%. Still, the data from the series with less than 20 mg wet sediment per vial, including the series with 0.26 g dw/L, should be considered as indicative only. The reason is that the exact amount of sediment sampled for extraction with methanol could not always be determined accurately. For example, freeze drying the remaining wet sediment after removal of the supernatant often left crusts of salt (up to 5 mg) behind in the vials. As much as possible,

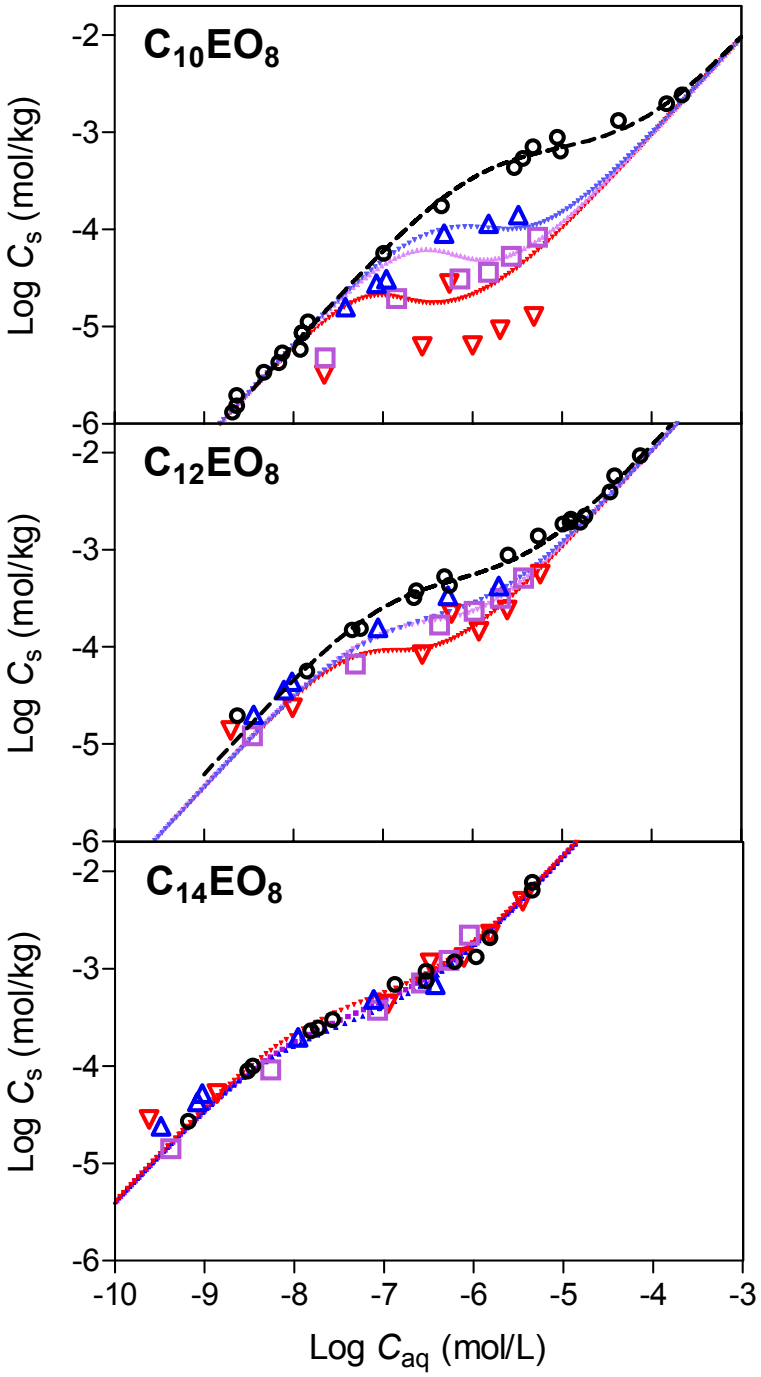

Figure 3. Sorption data for equimolar mixtures of $C_{10}EO_8$, $C_{12}EO_8$ and $C_{14}EO_8$ spiked to sediment-seawater systems with marine NFF sediment. Single solute sorption data (○) and isotherms (dashed lines) are from ref (*7*). The symbols (△, □ and ▽) refer to sorption data from separate test series in which the systems contained 6.2, 1.3 g/L and 0.26 g/L gram sediment per liter seawater, respectively. The dotted lines are simulated isotherms in the ternary mixture under similar test conditions using the mathematical model based on eq 2.

the dry sediment phase was transferred to separate vials, but often a small sediment fraction remained in the test vial. The data in Figure 4 includes two vials in which the amount of dry sediment was less than 20 mg.

Figures 3 and 4 clearly show that the two cosolutes with a weaker adsorption affinity did not influence the sorption isotherm of $C_{14}EO_8$. The sorption data of $C_{12}EO_8$, and even more so for $C_{10}EO_8$, however, strongly deviate from the single solute sorption data. As observed in the binary mixture, the stronger adsorbing homologue, $C_{14}EO_8$, is apparently a stronger competitor for adsorption sites than weaker adsorbing homologues. The deviations between the isotherms for single compounds and mixtures are highest for the systems with the lowest amount of sediment in the systems.

The varying solid concentrations used to obtain the data presented in Figure 4 resulted in a varying ratio of the aqueous concentrations of the three AE homologues. The total concentration of sorbed AE for the vial with the highest amount of sediment is 0.056 mmol/kg, which is about a factor 10 below the average $C_{S,max}$ for AE on this sediment (*6*). The sorption data at these concentrations still follow the isotherm for the individual homologues. With decreasing amount of sediment, the total AE sorbed concentrations increase up to 0.48 mmol/kg, close to the $C_{S,max}$ of this sediment. At these levels, $C_{12}EO_8$ and $C_{10}EO_8$ are displaced by $C_{14}EO_8$ at increasing total sorbed concentrations, resulting in reduced sorbed concentrations while the dissolved concentrations still increase.

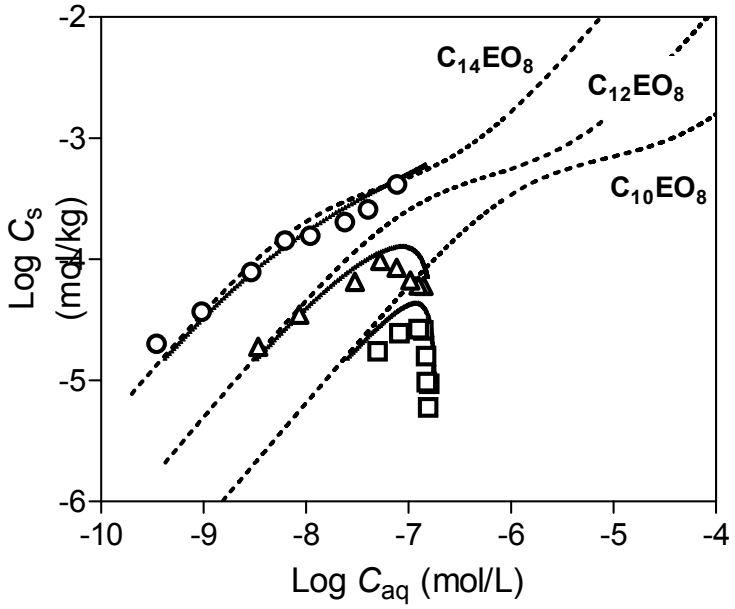

Figure 4. Sorption data for a ternary mixture of $C_{10}EO_8$,(□), $C_{12}EO_8$ (Δ) and $C_{14}EO_8$ (○) spiked to sediment-seawater systems with a varying amount of marine NFF sediment. Amounts of sediment decrease from data point to data point from left to right. The dashed lines represent the dual-mode model isotherms of the individual homologues, according to ref (*7*). The thick black lines are simulations of the sorbed and dissolved concentrations of the AE homologues using the mathematical model based on eq 2, varying the solids concentration from 0.01-100 g/L for systems with the same amount of AE as used in the tests.

Modeling competition effects based on the dual-mode model parameters for individual homologues

The strength of the dual-mode model, with an adsorption coefficient (K_{ad}) and a linear sorption coefficient (K_p), is that it also enables to model the competition effects. The competition model as formulated in eq 2, has been applied to the three data sets in Figure 2, 3 and 4. It should be emphasized that the only input parameters in the model predictions are measured data for $C_{S,max}$, b and K_p (see equations 2, 5a and 5b) of the individual homologues (*6*), and the amount of the added AE homologues and sediment. We could only model the data from the binary experiment with sediment and the two ternary mixtures. The data for the experiment with clay, cannot be modeled because the sorption parameters for $C_{14}EO_{14}$ are not known.

The observed linear isotherm for $C_{14}EO_6$, with sediment, when sorbed $C_{14}EO_{14}$ concentrations were above the $C_{S,max}$, is also predicted by the model simulation, presented as the dotted red line in Figure 2. The model is also applicable to the experiments with ternary mixtures. The simulations closely overlap with most sorption data of the mixtures presented in Figures 3 and 4. Deviations of the model from the data are most apparent for $C_{10}EO_8$ in the ternary mixture with the lowest solids concentration, but this is at least partially due to uncertainties in the measurements, as described above.

The simulations and the sorption data itself show that competitive sorption will only result in deviations from single solute isotherms when total adsorbed AE concentrations reach ~10% of the maximum adsorption capacity. The model further shows that whether or not the concentration of an AE in the sediment is reduced by competition with another AE, depends on the concentrations as well as adsorption affinities of the two AE. Related to the second linear sorption process, it is further clear that the sorption affinity of an AE in both experiments with individual isomers or in mixtures, can not become lower than K_p. The data and simulations also show that the effect of the solids concentration observed in this study is solely the effect of the varying composition of the mixture in the aqueous phase.

Implications of competitive sorption effects

As shown above, the presence of cosolutes can strongly affect the isotherms of individual compounds, when (i) mixtures of chemicals are used which compete for the same adsorption sites, and (ii) the adsorption sites become saturated. For several industrial and technological applications, saturation of surfaces by nonionic surfactants is required, and here competitive sorption should be taken into consideration as an important process. The dual-mode model with extended for competition of cosolutes, that has been applied in this study, is a useful tool to predict competition effects. It only requires compound specific affinity parameters.

Since all industrial and household products with AE are complex mixtures, sediment contaminated with AE will also contain complex mixtures. The composition of such mixtures will be altered due to a wide variety of processes during treatment and transport

(*18*). It can be questioned, however, whether competitive sorption effects are really an important issue for the bioavailability of AE in contaminated field sediments. The highest range of total AE concentrations measured in AE contaminated sediments is in the order of 2 mg/kg (*4,5*), which is orders of magnitude below the $C_{S,max}$ of 100-1000 mg/kg that have been observed for a small set of marine sediments and AE homologues. On the other hand, contamination with other compounds which also adsorb to the same sites, such as poly(ethylene) glycols (PEG's) (*19,20*), may contribute to the saturation of adsorption sites. PEG's are also one of the first degradation products of linear and short branched AE (*21*), and they may thus be abundant in sewage treatment effluents. The environmental concentrations of PEG's unfortunately are not well studied.

For environmental studies with AE focusing at relatively high concentrations, such as sorption studies and sediment toxicity tests, competitive sorption will clearly be an issue. Many of the ethoxylated surfactants that have been studied in sorption tests and toxicity tests, especially alkylphenol ethoxylates, are complex mixtures of tens of different homologues (*9,11,22-25*). In a test with a single AE homologue, the sediment sorbed concentrations that are required to induce toxic aqueous concentrations, are in the range of the maximum adsorption capacity (*26*). The sediment-water distribution coefficients of individual homologues in toxicity tests with complex AE mixtures will thus most likely depend on the concentrations of the cosolutes. Ignoring these effects will lead to outcomes that are difficult to interpret. For many compounds in complex mixtures, the bioavailability will probably be significantly higher compared to single solute tests due to competition effects. Similar phenomena may occur in sorption studies that are performed at relative high concentrations. Modeling these competition effects, as is done in this study, is very useful for the prediction of changes in the composition and concentrations of AE in both sediment and the aqueous phase.

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APPENDIX

Scripts for Berkeley Madonna software applying the dual-mode competition model for binary and ternary mixtures, including a script with the solids concentration as the variable parameter.

Section A. Models with varying amounts of AE in the test systems

Binary mixture $C_{14}EO_6$ and $C_{14}EO_{14}$

Figure 2
Compound X= increasing $C_{14}EO_6$
Compound E= constant high conc of $C_{14}EO_{14}$

```
Ws = kg sediment per L seawater
Xtot = total amount of X in test system
Xf = freely dissolved concentration of X
CsX = sorbed concentration of X
bx and KpX are DMM sorption parameters of X

logXtot0=-9
logXtotf=-2
dmin=1.e-9
dmax=1.
dout=0.05

Csmax=0.00045
Ws=0.00259
bx=3.36e+07
be=8.9e+07
KpX=2085
KpE=467
Etot=1.3e-5

rX=Xf
CsX=(Xf*bx*Csmax/(1+be*Ef+bx*Xf))+Xf*KpX
rE=Ef
CsE=(Ef*be*Csmax/(1+be*Ef+bx*Xf))+Ef*KpE

Xtot=10.00**logXtot
GUESS Xf=Xtot/10000.
GUESS Ef=Etot/10000.
ROOTS Xf=Xf*(1+Ws*bx*Csmax/
          (1.0+be*Ef+bx*Xf)+KpX*Ws)-Xtot
ROOTS Ef=Ef*(1+Ws*be*Csmax/
          (1.0+be*Ef+bx*Xf)+KpE*Ws)-Etot
LIMIT Xf >=0.
LIMIT Xf<=Xtot
LIMIT Ef>=0.
LIMIT Ef<=Etot
```

Ternary mixture $C_{10}EO_8$, $C_{12}EO_8$, $C_{14}EO_8$

Figure 3
Compound X= increasing C14EO8
Compound E= increasing C12EO8
Compound F= increasing C10EO8

```
Ws = kg sediment per L seawater
Xtot = total amount of X in test system
Xf = freely dissolved concentration of X
CsX = sorbed concentration of X
bx and KpX are DMM sorption parameters of X

logXtot0=-9
logXtotf=-2
dmin=1.e-9
dmax=1.
dout=0.02

KadX=38194
KadE=3540
KadF=644
Csmax=0.00058
Ws=0.000157
bx=7.39e+07
be=9.37e+06
bf=1.25e+06
KpX=1264
KpE=115
KpF=9.01
Etot=1.008*Xtot
Ftot=1.165*Xtot

rX=Xf
CsX=(Xf*bx*Csmax/(1+be*Ef+bx*Xf+bf*Ff))+Xf*KpX
rE=Ef
CsE=(Ef*be*Csmax/(1+be*Ef+bx*Xf+bf*Ff))+Ef*KpE
rF=Ff
CsF=(Ff*bf*Csmax/(1+be*Ef+bx*Xf+bf*Ff))+Ff*KpF

Xtot=10.00**logXtot
GUESS Xf=Xtot/10000.
GUESS Ef=Etot/10000.
GUESS Ff=Ftot/1000.
ROOTS Xf=Xf*(1+Ws*bx*Csmax/
          (1.0+be*Ef+bx*Xf+bf*Ff)+KpX*Ws)-Xtot
ROOTS Ef=Ef*(1+Ws*be*Csmax/
          (1.0+be*Ef+bx*Xf+bf*Ff)+KpE*Ws)-Etot
ROOTS Ff=Ff*(1+Ws*bf*Csmax/
          (1.0+be*Ef+bx*Xf+bf*Ff)+KpF*Ws)-Ftot
LIMIT Xf >=0.
LIMIT Xf<=Xtot
LIMIT Ef>=0.
LIMIT Ef<=Etot
LIMIT Ff >=0.
LIMIT Ff<=Ftot
```

Section B. Models with varying amounts of sediment (W_s) in the test systems

Ternary mixture $C_{10}EO_8$, $C_{12}EO_8$, $C_{14}EO_8$

Figure 4

```
X = kg sediment per L seawater (Ws)
Compound D = C14EO8
Compound E = C12EO8
Compound F = C10EO8

Dtot = total amount of D in test system
Df = freely dissolved concentration of D
CsD = sorbed concentration of D
bd and KpD are DMM sorption parameters

logX0 =-5
logXf =-2
dmin =1.e-9
dmax =1.
dout =0.02
KadD =38194
KadE =4841
KadF =644
Csmax =0.000517
bd =7.39e+07
be =9.37e+06
bf =1.25e+06
KpD =1264
KpE =115
KpF =9.01
Dtot =1.53e-7
Etot =1.008*Dtot
Ftot =1.165*Dtot

rD =Df
CsD =(Df*bd*Csmax/(1+be*Ef+bd*Df+bf*Ff))+Df*KpD
rE =Ef
CsE =(Ef*be*Csmax/(1+be*Ef+bd*Df+bf*Ff))+Ef*KpE
rF =Ff
CsF =(Ff*bf*Csmax/(1+be*Ef+bd*Df+bf*Ff))+Ff*KpF

X= 10.00**logX
GUESS Df =Dtot/10000.
GUESS Ef =Etot/10000.
GUESS Ff =Ftot/1000.
ROOTS Df =Df*(1+X*bd*Csmax/
          (1.0+be*Ef+bd*Df+bf*Ff)+KpD*X)-Dtot
ROOTS Ef =Ef*(1+X*be*Csmax/
          (1.0+be*Ef+bd*Df+bf*Ff)+KpE*X)-Etot
ROOTS Ff =Ff*(1+X*bf*Csmax/
          (1.0+be*Ef+bd*Df+bf*Ff)+KpF*X)-Ftot
LIMIT Df >=0.
LIMIT Df<=Dtot
LIMIT Ef>=0.
LIMIT Ef<=Etot
LIMIT Ff >=0.
LIMIT Ff<=Ftot
```

Chapter 8

Sediment Toxicity of a Rapidly Biodegrading Nonionic Surfactant: Comparing the Equilibrium Partitioning Approach with Measurements in Pore Water

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Sediment Toxicity of a Rapidly Biodegrading Nonionic Surfactant: Comparing the Equilibrium Partitioning Approach with Measurements in Pore Water

ABSTRACT

Freely dissolved concentrations were measured for a model alcohol ethoxylate (AE) homologue in marine sediment toxicity tests. The amphipod *Corophium volutator* was exposed to equilibrated test systems with and without a layer of spiked sediment. In accordance with the equilibrium partitioning theory (EqP), the concentration of $C_{12}EO_8$ in pore water of the sediment layer that caused 50% mortality (LC50) was in the same range as LC50 values observed for organisms exposed to the AE in seawater only. Effect concentrations in pore water, calculated from a sorption coefficient, were also close to observed toxic concentrations in water only tests. In the sediment systems, AE concentrations in the pore water remained constant up to 15 days, while AE in the water overlying the sediment decreased to less than 1% of initial concentrations within 6 days due to biodegradation. Organisms exposed to sediment systems, that were already at disequilibrium at the start of a toxicity test, readily survived exposure to pore water dissolved concentrations above the LC50. Whereas the aqueous phase clearly drives toxicity of AE for *C. volutator*, these results indicate that the actual route of exposure for this benthic species is more related to overlying water rather than only via pore water.

INTRODUCTION

For most sediment associated organic contaminants, the risk for benthic organisms is often assessed by the equilibrium-partitioning (EqP) approach (*1-3*). In the EqP approach, the concentration of a contaminant that has accumulated in biota is in equilibrium with the freely dissolved concentration. Furthermore, it assumes that the distribution of the contaminant between the aqueous phase and the sediment phase is in an equilibrated state. Sediment quality criteria can therefore be derived from aqueous effect concentrations and sediment-water distribution coefficients (K_d). The 'classical' EqP approach assumes that sorption to organic matter dominates the affinity of organic contaminants for sediment. The K_d is then derived by multiplying the fraction of organic carbon (f_{oc}) in the sediment with organic carbon-water partition coefficients (K_{oc}). Applying the EqP approach to accurately assess the risk of contaminated sediment becomes more difficult when these conditions are not met.

Alcohol ethoxylates (AEs), a commercially important group of nonionic surfactants with a basic narcotic mode of toxic action (*4*), have been detected in coastal sediments at several locations which are probably contaminated by rivers carrying sewage discharges and effluents that have received no, or only limited, treatment (*5,6*). Commercial AE consist of a wide variety of homologue structures, which further complicates the risk assessment of AEs in the environment. At least some of the basic assumptions behind EqP do not apply for this complex group of nonionic surfactants. First of all, sorption studies with AEs indicate that sorption to the organic matter in sediment often plays only a minor role in the total sorption affinity (*7-10*), and that the affinity to sorb to sediment is dominated by adsorption to mineral surfaces. For many AE homologues, the K_{oc} in the EqP approach is thus an irrelevant parameter. The sorption processes are not yet clearly understood, and extrapolations from existing sorption data will therefore still include considerable uncertainty (*10,11*).

Secondly, under both aerobic and anaerobic conditions, AEs are rapidly biodegraded (*12-14*), a characteristic that makes these chemicals very attractive for adequate treatment. As a result, fully equilibrated situations are not likely to occur and the impacted systems are probably dynamic. The concentrations of AE in a sediment phase, and residence time of these chemicals, will be a constantly shifting balance between desorption, biodegradation processes and fresh input. Within fish, and likely most biota, AEs are rapidly biotransformed (*15,16*). This could further disturb the dependency of the internal concentration on the aqueous phase, because the intake of contaminant via sediment phase may become more important in such a nonequilibrated system.

In this study, we investigated to what extent the EqP describes the toxicity of a single AE homologue ($C_{12}EO_8$) in a standardized sediment-seawater test system. The sorption isotherm for this homologue was recently presented for the same sediment as used in this study (*10*). The amphipod *Corophium volutator*, commonly used in bioassays with contaminated sediments, was used as benthic test organism. The first objective was to obtain accurate measurements of AE in the pore water phase in the test systems used in

the sediment toxicity assay. For this purpose, the solid phase microextraction (SPME) method was used, a diffusion based extraction technique with polymer coated glass fibers which measures freely dissolved AE in marine samples (*17*). Measurements of pore water dissolved concentrations of AE in the sediment toxicity test were performed with sediment samples equilibrated with the SPME fiber outside the test system ("*ex situ*"). To test the validity of this procedure, the *ex situ* measurements of the pore water were compared with SPME measurements in the sediment layer itself ("*in situ*").

The second objective was to test the validity of the EqP approach by a comparison of effect concentrations measured in a water only toxicity test with those measured in the pore water of a sediment toxicity test. The effect concentrations in the sediment system were based on SPME measured concentrations in the pore water, and these were compared with predicted effect concentrations in pore water based on a sorption isotherm (*10*).

As a third objective, the effect of a disequilibrium state of the sediment-water test system on toxicity was studied. As discussed in detail by Schwarzenbach *et al*. (*18*), an analysis of a system where the overlying water is no longer in equilibrium with the pore water phase could give more detailed insight in the route of exposure for benthic organisms. In a separate series, vials with spiked sediment were kept several days under normal test conditions before introducing the test organisms, thereby allowing for a period of microbial degradation. To follow the distribution of the chemical in the test systems, the concentrations of AE in overlying water and pore water were carefully analyzed during the test period.

To our best knowledge, toxicity data of AE on marine organisms is very limited and standardized sediment toxicity tests have not been performed with AE or other nonionic surfactants. Toxicity data for commercial mixtures of AE, with both varying alkyl chains and ethoxylate units, to freshwater organisms are relatively abundant (*19-21*). Each AE homologue in these mixtures, however, has a specific sorption affinity, bioaccumulation factor, and likely also degradation and biotransformation rate. Therefore, sediment toxicity tests with mixtures are often difficult to interpret. This study aimed at gaining a detailed insight in the exposure concentration in a well controlled marine sediment toxicity test for a single AE homologue.

EXPERIMENTAL SECTION

Chemicals and SPME fibers

Octaethylene glycol monododecylether ($C_{12}EO_8$, purity >98% TLC) was purchased from Fluka (Buchs, Switzerland). The methanol was HPLC-quality (99.9%, Labscan, Dublin, Ireland). The 37% formaldehyde solution was free of methanol (Sigma-Aldrich, Steinheim, Germany). The SPME fibers consisted of glass fibers with an internal diameter of 108 µm and a 34.5-µm polyacrylate coating (coating volume 15.4 µL per meter fiber), and were obtained via Polymicro Technologies (Phoenix, AZ).

Sediment, seawater, and test organisms

The marine sediment used in the toxicity tests was sampled with box cores at a remote North Sea location (North of the Frisian Front (54 ^{o}N, 4.5 ^{o}E), The Netherlands) and was stored wet as received for a year at 4 ^{o}C. The organic carbon content (0.27%) and other properties of this sediment had been determined in a previous study (*10*). Sediment from below the first cm was taken for the experiments, and homogenized after removing large debris. Filtered natural seawater was obtained from an inlet near the mouth of the Dutch Eastern Scheldt estuary at high tide, and stored at 4 ^{o}C. Test organisms, 5-10 mm *Corophium volutator*, were collected with a 0.5 mm sieve from a mudflat in the Eastern Scheldt, a commonly used reference location and collection site. The organisms were kept and transported on sediment that was passed through the sieve. Before the start of the tests, animals were sieved out of the sediment and kept in filtered seawater for at least 4 h, in order to lose most of their gut content.

Spiking the seawater and sediment

The water only exposure was performed in 250 mL erlenmeyer flasks. Methanol stock solutions of $C_{12}EO_8$ were added after which the methanol was evaporated off. Erlenmeyer flasks were filled with seawater, closed off with aluminum foil and shaken on a 2D shaker for two days. These test systems were then kept for another five days at 4 ^{o}C.

Erlenmeyer flasks of 500 mL were used as test systems for the exposure series with spiked sediment. The spiking procedure aimed at achieving a homogenous contaminant distribution and grain size distribution in the sediment layer, and at avoiding biodegradation of the alcohol ethoxylate before the start of the test. First, methanol stock solution was added and all methanol was evaporated. Then ~200 g (155±2 g dw) of wet sediment was mixed with 25 mL seawater in these vials, creating a smooth sediment slurry which kept a homogenous grain size distribution during and after shaking. The test erlenmeyer flasks were capped with aluminum foil and kept at 4 ^{o}C to minimize biodegradation. To desorb all surfactant from the glass and mix it into the sediment slurry, the test systems were shaken for two days. After this, erlenmeyer flasks were carefully

filled up with seawater. These systems were kept for another seven days at 4 °C to equilibrate the chemical in the test systems.

Pore water dissolved AE in sediment: grab samples versus *in situ* measurement

The concentration of $C_{12}EO_8$ in the pore water can be determined via SPME fibers exposed in the sediment layer, which we will refer to as "*in situ*". This, however, requires that fibers reach equilibrium under static conditions, which does not allow direct measurements at all time points. Therefore, sediment was sampled during the sediment toxicity test, and SPME fibers were equilibrated "*ex situ*" to the pore water of these samples. During this equilibration period, biodegradation of $C_{12}EO_8$ was prevented by adding formaldehyde. The *ex situ* analysis, however, will overestimate the actual dissolved concentration of $C_{12}EO_8$ in the sediment layer if biodegradation in the pore water is faster than desorption from the sediment phase. The validity of the *ex situ* analysis of pore water was therefore compared with *in situ* analysis in a separate experiment.

In this experiment, the uptake kinetics for statically positioned *in situ* fibers were studied to determine when equilibrium was reached in the fiber. Five 500 mL erlenmeyer flasks with a 3 cm sediment layer spiked at 1400±12 mg/kg were prepared as described above. Two vials were shaken with 25 mL formaldehyde solution, instead of 25 mL seawater, to serve as sterilized controls. To facilitate positioning and sampling of fibers in the sediment layer, a metal wire was fixed perpendicular to the fiber via a 3.6 mm lead sinker that was clamped to the end of a fiber. With the wire sticking out of the sediment layer, eight 20 mm SPME fibers were placed simultaneously in the sediment layer of the test systems, after 3 h acclimatization at 16 °C. During the next 3 days, duplicate fibers were sampled, the first two after 3 h and then daily. After carefully removing the lead sinkers, fibers were wiped clean and desorbed in methanol. This was repeated for three more sets of SPME constructs, thereby obtaining four *in situ* SPME uptake curves in 15 days. At the start of the experiment and the end of each series of *in situ* measurements, duplicate sediment samples were taken for the *ex situ* pore water analysis. Using 1 mL polypropylene pipette tips, sediment cores were taken from the sediment layer and transferred into 7 mL glass vials (Supelco, Bellefonte, PA), which contained 0.1 mL formaldehyde. The vials were filled up with clean seawater, and a 20 mm SPME fiber was added and equilibrated for 3 days on a shaking device. Duplicate samples were also taken from the overlying water (OW), just before sediment cores were taken, as described below.

Toxicity test with spiked seawater only

In order to avoid a decrease in exposure concentrations due to sorption to food particles, the seawater exposed organisms were not fed. International guidelines for acute toxicity testing with amphipods recommend an exposure period of ten days (*22-24*). Ten days without food and sediment would probably induce too much stress and therefore the

toxicity tests in this study were terminated after six days. In a six day range finding pilot (data not shown), it was observed that the dissolved concentrations showed a significant decrease after three days under standard test conditions (16 °C, 16/8 h light-dark regime and gentle aeration). Therefore, the test solutions were renewed every two days in the toxicity test.

To reduce stress due to bright light conditions and the absence of sediment, two small pieces of wrinkled aluminum foil (~6 cm^2) were added to the seawater exposures as a refuge for the organisms. Most amphipods were observed to be resting calmly underneath the foil, instead of swimming around most of the time as was observed in vials without foil. No significant reductions of the aqueous surfactant concentrations were observed due to the presence of the foil.

The test organisms were added 4 h after transfer from 4 °C to standard test conditions. Five test concentrations between 0.4 and 10 mg/L were prepared in duplicate, with 15 test organisms per vial and two pieces of aluminum foil. Dissolved oxygen was always higher than 70% of saturation throughout the tests. At the end of the exposure periods, the organisms were transferred to clean water, and considered dead when they did not respond to repeated agitation during several minutes. Information on survival obtained at day 2 and 4, during transfer to new exposure vials, was considered only as indicative, because sometimes organisms that were initially immobile showed signs of life after further observation.

The concentration of AE in the seawater exposures was determined for all vials just before adding test organisms to the vials, just before transferring them to the new exposure vials, and at the end of the test. Borosilicate (Wheaton, Millville, NJ) vials (2 mL) were filled up with sampled solution, together with 50 µL formaldehyde to prevent biodegradation. A 10 mm SPME fiber was equilibrated to these solutions for three days, and analyzed as described below.

Toxicity test with a spiked layer of sediment

A range finding test, with nominal concentrations between 169 and 1332 mg/kg, showed that concentrations in pore water in the sediment exposures remained constant during 6 days (data not shown). Therefore, the animals in the sediment toxicity test were left in the same vial during the test. Six concentrations were prepared in triplicate, ranging between 619±2 and 3110±17 mg/kg, and 15 organisms (5-10 mm) were used per test system. Three extra test systems with sediment were prepared at nominal concentrations of 620, 860 and 1072 mg/kg, in which 20 individuals were exposed for 10 days, in line with standard guidelines. Gentle aeration via glass pipettes kept dissolved oxygen in the overlying water above 70%. Concentrations in overlying water (OW) were measured daily, in a similar way as in the water only test. Sediment cores were sampled at days 0, 2, 4 and 6 and analyzed with SPME as described above. After six days, the sediments from the test systems were sieved over 500 µm and surviving individuals counted.

A second sediment toxicity test series was prepared, with four concentrations in triplicate (nominal range 1101±2 – 3140±85 mg/kg). The 10 organisms added per vial in this series, however, were added after leaving the test systems for 6 days under normal test conditions, to allow for an initial period in which biodegradation processes could be induced. Sediment cores and OW samples were taken every three days.

Chemical analysis

All equilibrated SPME fibers and those from the kinetic study were wiped clean with a wet tissue, and AE was desorbed in 0.6 mL of methanol and stored at -20 °C until analysis. The SPME extracts were analyzed by LC-MS as described previously (*17*), and freely dissolved concentrations were calculated using the experimentally derived fiber-water partition coefficient (log K_{fw}) of 2.58 (*10*).

Data analysis

To determine whether the concentrations within and between replicates differed significantly, independent t-tests ($p<0.05$) were performed. The duplicate and triplicate exposure concentrations were pooled to obtain average exposure concentrations during the whole exposure period and these concentrations were used to calculate the concentrations which induced 50% mortality (LC50). For the sediment toxicity tests, nominal sediment concentrations and average measured pore water concentrations were used. The survival relative to the average control survival in each vial ($f(x)$) was calculated, and a two-parameter logistic curve was fitted to the data:

$$f(x) = \frac{1}{1+\exp(b(x \cdot e))} \qquad (1)$$

where x is the logarithm of the average aqueous concentration (mg/L) for the replicates, b a parameter for the relative slope at the LC50 level, and e the log LC50 value. The obtained parameters were used to calculate 10% effect concentrations (LC10), with $f(x)$ in eq 1 is equal to 0.9.

RESULTS AND DISCUSSION

Concentrations of AE in sediment pore water: grab samples versus *in situ* measurement

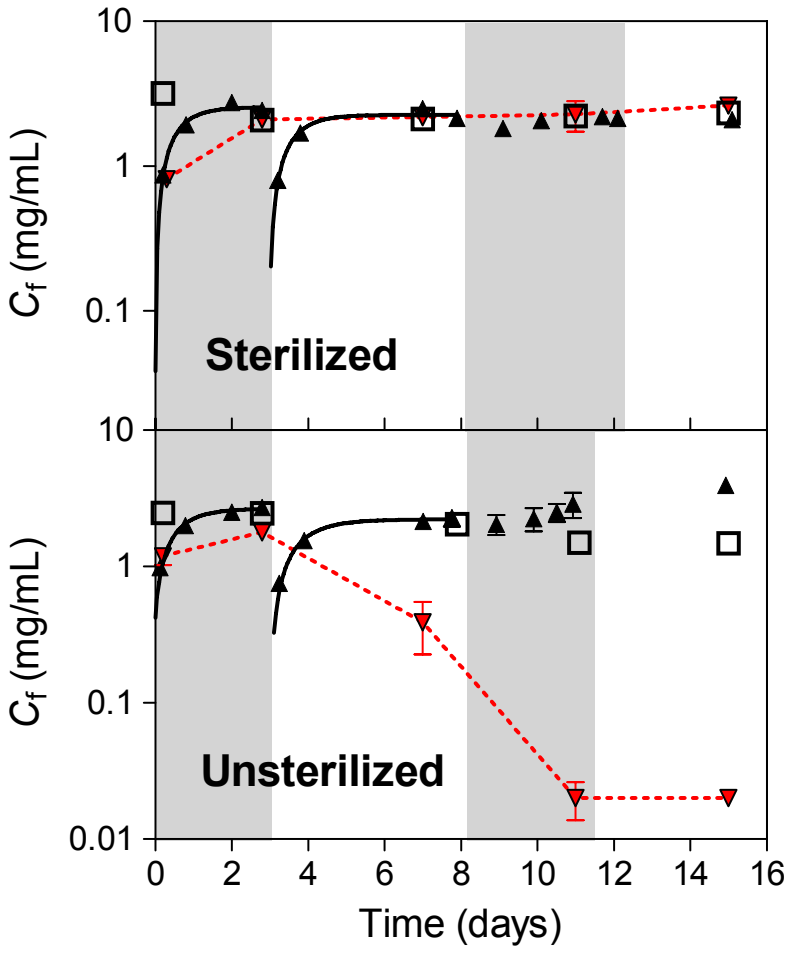

Figure 1. SPME concentrations in samples from sediment toxicity test systems with 25 mL formaldehyde (Sterilized, upper panel) and without formaldehyde (Unsterilized, lower panel). "*In situ*" static exposure of SPME fibers in the sediment layer, sampled and exposed between day 0-3 (grey area), day 3-8 (white), day 8-11 (grey) and day 11-15 (white) are indicated by (▲±SD). The solid lines in the first two exposure periods are fitted curves following a one compartment, first order kinetic model. "*Ex situ*" exposure of SPME equilibrated to sediment cores (□,±SD), and SPME measurements of the overlying water (▼±SD) were performed in a similar way as in the toxicity tests. Connecting dotted lines are presented as visual guidance only.

In test systems without test organisms, the concentration of AE desorbed from sediment cores (*ex situ*) were compared with SPME fibers exposed in the sediment layer itself (*in situ*). Figure 1 shows the concentrations in SPME fibers exposed in the two sterilized controls and the results from the three vials without formaldehyde. The concentrations in the SPME fiber exposed *in situ* clearly increase between 3 and 24 h, and equilibrium is

reached the second day. The data from vials with and without formaldehyde show that the equilibrium concentrations in SPME fibers exposed *in situ* are similar to measurements with sediment cores. The concentrations in the pore water in the sterilized controls were also comparable with those in the vials without formaldehyde. Apparently, the effect of biodegradation on the pore water dissolved AE is negligible. *Ex situ* measurement of the pore water is thus representative for the actual pore water concentration in the sediment layer. At the tested concentration of 1400 mg/kg in this marine sediment, results from the sediment cores show that the pore water dissolved concentrations after 15 days under normal test conditions were still within 50% of the initial concentrations.

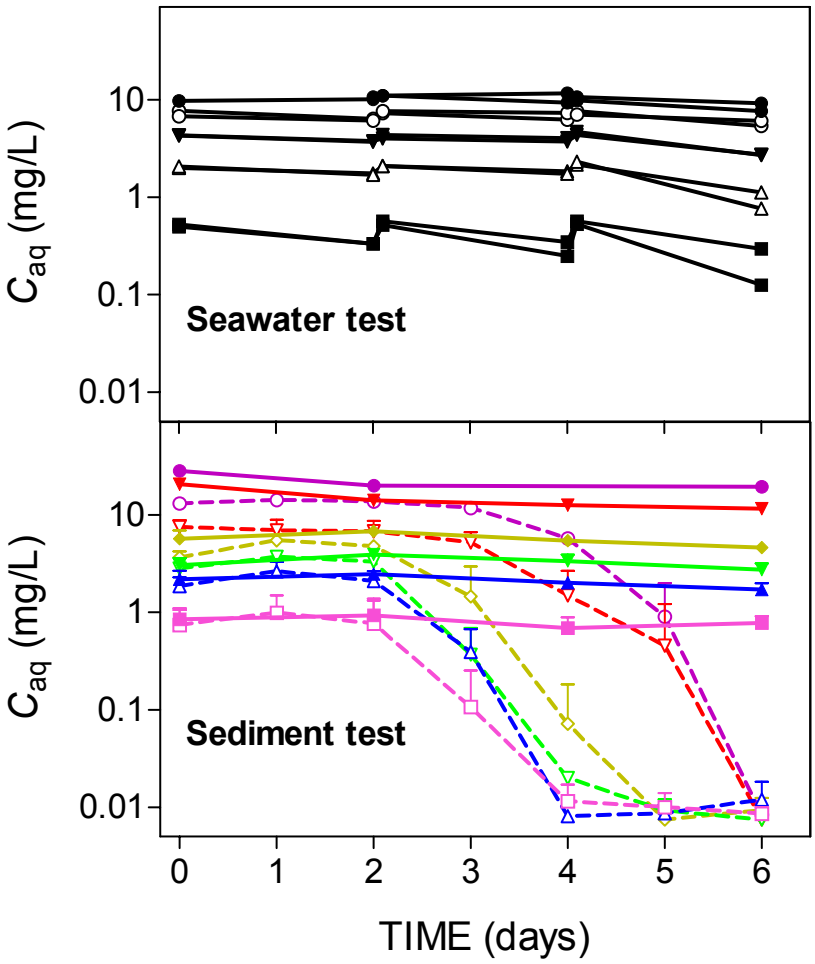

Figure 2. Aqueous concentrations in seawater toxicity test (upper panel) and in the sediment toxicity test (lower panel). Duplicate exposure concentrations are plotted for seawater toxicity test. All connecting lines are presented as visual guidance only. Vertical lines show standard deviations of triplicate measurements in sediment toxicity test. Concentrations in the pore water of the sediment toxicity test are plotted as closed symbols connected by solid lines, data from the overlying water (OW) are plotted as open symbols connected by dashed lines. OW and PW samples from each exposure concentration have the same color and type of symbol.

The concentration of $C_{12}EO_8$ in the overlying water (OW) samples from the first time point, three h after transfer from 4 °C to standard test conditions, are lower than those after 3 days (Figure 1). Apparently, the concentration in the OW equilibrated rather slowly to the increased temperature. In the sterilized controls the concentration in the OW remained constant during 15 days and was not significantly different from the AE concentration measured in the pore water. In vials without formaldehyde, resembling conditions in the toxicity tests, concentrations in the OW decreased to below 1% of the initial concentrations between day 6 - 11. Although samples were not analyzed for possible degradation products of AE, the data with formaldehyde strongly suggests that decreasing concentrations are the result of microbial degradation.

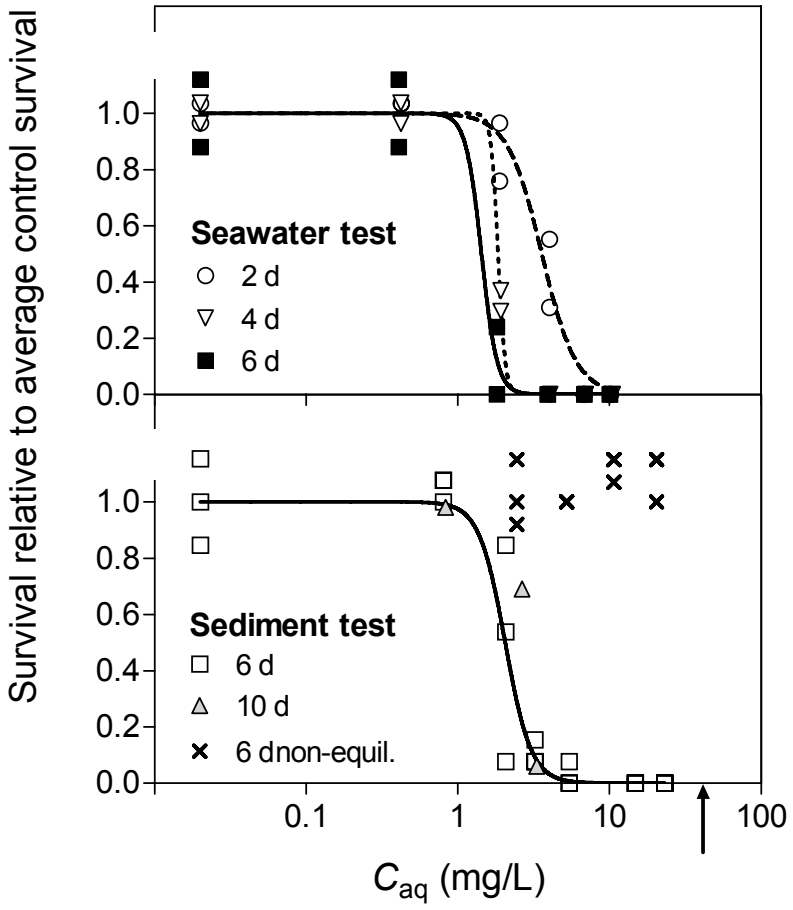

Figure 3. Survival in each test system, relative to the average control survival, plotted against aqueous concentration for the 6 day seawater toxicity test (upper panel) and against pore water dissolved concentration for the 6 day sediment toxicity test (lower panel). Survival scored in the seawater toxicity test after 2 and 4 days are indicative only, as discussed in the text. Grey triangles are toxicity data for organisms exposed to spiked sediment during 10 days. Data from the 6 day sediment toxicity test under nonequilibrium conditions, by allowing for biodegradation during an initial period at normal test conditions before introducing organisms, are indicated by (**x**). Data points at the lowest concentrations are controls. The arrow indicates the critical micelle concentration for $C_{12}EO_8$ in seawater (*17*).

Table 1. Effect Concentrations of $C_{12}EO_8$ for the Seawater and Sediment Toxicity Test Series, and a Comparison with the Calculated 50% Effect Concentration (LC50) Based on the Equilibrium Partitioning Approach (EqP).

	Seawater only test			Spiked sediment test		EqP approach: via sorption coefficient [a]	
	day 2 [b]	day 4 [b,c]	day 6 [c]	measured in pore water	nominal in sediment	Based on LC50 for C_{aq} (pw)	Based on LC50 for C_s (nom)
	C_{aq} (mg/L)	C_{aq} (mg/L)	C_{aq} (mg/L)	C_{aq} (pw) (mg/L)	C_s (nom) (mg/kg)	C_s (mg/kg)	C_{aq} (pw) (mg/L)
Log LC50	0.55	0.27	0.16	0.31	2.9		
s.e. [c]	0.030	-	-	0.028	0.009		
Hill slope	-3.8	-19	-8.4	-5.1	-12		
LC50	3.6	1.8	1.4	2.1	870	490	5.3
LC10 [d] / NOEC [e]	2.0 [d]	0.42 [e]	0.41 [e]	1.3 [d]	720 [d]		

C_{aq} is the aqueous concentration, C_{aq} (pw) is the pore water dissolved concentration and C_s the concentration of AE sorbed to the sediment phase; [a] calculated with the dual mode sorption model reported for the same sediment in ref (*10*); [b] indicative only because immobile organisms sometimes appeared to be alive; [c] s.e. = standard error values of Log LC50, no accurate confidence limits could be calculated for days 4 and 6 because of insufficient data in the region with partial mortality; [d] calculated from the best fitting model parameters (Log LC50 and Hill slope). [e] lowest test concentration for which survival did not significantly differ from controls.

Toxicity of $C_{12}EO_8$ dissolved in seawater

The equilibrated 10 mm SPME contained a negligible amount (2.3%) of the total amount of $C_{12}EO_8$ in the aqueous samples, and allowed for accurate measurements down to 10 µg/L. Figure 2 shows that the aqueous concentrations in the seawater toxicity test decreased during 2 days, but was relatively constant during the 6 day exposure because freshly prepared test solutions were used every two days. The average aqueous concentrations were not significantly different for the duplicates exposure vials ($p>0.05$). Within two days, the concentrations decrease more for the lower than for the higher test concentrations. Assuming, for the sake of simplicity, linear degradation in time, the relative standard deviation (RSD) for the average concentration over six days was 36% for the lowest exposure concentration, and 11% for the highest exposure concentration.

Figure 3 shows the survival relative to the control survival for each vial plotted against the average exposure concentration. Average control survival was 83% in the water only test. The parameters of the logistic curve and calculated effect concentrations are summarized in Table 1. Because toxicity data for day 4 and 6 do not contain sufficient

partial mortality, the confidence limits for the LC50 and slope are high, and, therefore, the lowest no observed effect concentration is given instead of LC10. At the highest concentrations, the organisms were already immobile within one hour. Still, the LC50 decreased between day 2 and 4. The LC50 was relatively constant between day 4 and 6. The six day LC50 value of 1.4 mg $C_{12}EO_8$/L for the marine amphipod *Corophium volutator* corresponds well with the predicted two day EC50 (50% induced immobility) of 1.6 mg/L for the freshwater cladoceran *Daphnia magna*, using the quantitative structure–activity relationship that Wong *et al*. (*25*) derived from tests with nine commercial AE mixtures.

Toxicity of $C_{12}EO_8$ spiked to sediment

Figure 2 shows the concentrations of $C_{12}EO_8$ in the pore water (PW) of the sediment toxicity test and the daily measurements in the OW. Similar to observations without test organisms, the pore water dissolved concentrations in the sediment toxicity test remained fairly constant during the 6 day test period. The overall average difference between the initial PW concentrations and those at the end was 21±20% (n = 18). The concentrations of $C_{12}EO_8$ in the OW at the start of the test were 92% to 57% of the AE concentrations in the pore water for the lowest and highest test concentration, respectively, indicating that the systems were relatively well equilibrated. Based on the nominal sediment sorbed concentrations, the concentrations in the aqueous phase of the sediment exposure system were slightly lower (factor 1.1 - 2.3) than predicted by the sorption isotherm for $C_{12}EO_8$ and the same sediment (*10*), as presented in Figure S1 of the Appendix.

Whereas concentrations in the OW were comparable to the pore water during the first days, concentrations in the OW also strongly decreased during the exposure period. It was expected that the bioturbation of the amphipods would cause an increased flux of the compound into the overlying water via the increased amount of suspended solids, as observed for sediment spiked with fluoranthene (*26,27*). Compared to the systems without test organisms, biodegradation in the presence of *Corophium volutator* is even faster, after 2-3 days for the lower concentrations, and after 4-5 days for the highest concentrations. This suggests that bioturbation increases the microbial activity in the overlying water, which counteracts the increased flux into the OW from suspended solids. Initial inhibition of microbial activity at the highest test concentrations may explain the longer lag phase before degradation starts, but this can also be related to the absence of bioturbation due to narcotic effects on the amphipods. The gradual increase in OW concentrations after transfer from 4 to 16 ^{o}C, also visible in Figure 2, already suggested that the desorption flux from the sediment and diffusion rate in the OW are relatively slow. In combination with biodegradation, a large concentration gradient is formed between the pore water and overlying water after three days exposure. Biodegradation likely also occurs in the sediment layer, even at anoxic conditions (*12,13*), but, on the micro-scale of sediment pores, desorption fluxes are apparently sufficiently rapid to compensate.

Average control survival was 87% in the sediment toxicity test. In the three highest sediment exposure concentrations, many test organisms lay immobile on the sediment surface within the first hour. Because the animals rapidly constructed burrows at the other test concentrations, it is not known in which time period most mortality occurred. The overlying water in the highest concentrations was also clear, while that in the lowest two was as turbid as in the controls, indicating normal activity. Based on concentrations in the pore water, the six day LC50 in the sediment exposure was 2.1 mg/L (95% c.i. 1.8-2.4 mg/L), see Table 1. Exposure to the spiked sediment for ten days did not show increased toxicity compared to the six day series (Figure 3). Tolls *et al*. (*16*) showed that bioaccumulation of the AE homologue $C_{13}EO_8$ in fish reaches steady state within one day, so the exposure period of six days, with three days high OW concentrations, can be considered sufficient to induce acute effects of the accumulated chemical.

Based on the nominal sediment concentrations, the LC50 for this marine sediment for $C_{12}EO_8$ is calculated to be 860 mg/kg (95% c.i. 816 - 913 mg/kg). Sediment sorbed concentrations were not measured in the test, but there are no indications that actual concentration are different from nominal concentrations. The stability of the pore water dissolved concentrations during the toxicity tests imply that the sediment sorbed concentrations also remain constant throughout the tests. The similarity between data from vials with and without formaldehyde showed biodegradation was negligible during the equilibration period at 4 ^{o}C. In addition, the initial depletion of the sediment phase by partitioning to the aqueous phase is less than 2.4 %, so biodegradation of dissolved AE will not readily decrease the 97.6% of sorbed AE.

Comparison of observed sediment toxicity with EqP predictions

The pore water based LC50 from the sediment toxicity test is 1.5 times higher than the LC50 obtained from seawater exposed test organisms (Table 1). This difference in LC50 is within the common variation in toxicity data for this species (*28*). In accordance with the EqP approach, it can be concluded that it is indeed the aqueous phase that drives toxicity of this nonionic surfactant for a benthic organism.

In the EqP approach, sediment-water distribution coefficients are used to derive effect concentrations in the sediment based on aquatic toxicity data, and accordingly estimate the risk of contaminated sediment. The measured aqueous concentrations plotted against nominal sediment concentrations are close to the nonlinear sorption isotherm from ref (*10*) (Figure S1). The sorption isotherm, obtained at a considerably lower sediment to water ratio compared to the pore water in the sediment layer, can be used to derive a good estimate of the effect concentration in an equilibrated layer of sediment. Predictions based on the measured pore water LC50 are within a factor two (Table 1). Based on nominal sediment concentrations the predicted pore water LC50 is within a factor 2.6 (because of the nonlinearity of the sorption isotherm). As mentioned above, such differences are within the normal variation in toxicity data. Application of the EqP approach and extrapolations of the pore water LC50 values to AE homologues and other

sediments should be valid in conformity with aqueous risk assessment. The dependency of AE sorption coefficients and sediment properties is still not sufficiently understood and requires an improved understanding of the sorption mechanisms (*10*). Accurate risk assessment based on sorption data is therefore limited to those sediments and AE homologues for which sorption isotherms have been established.

The effect of disequilibrium on toxicity of spiked sediment

In conformance with EqP, the results from the toxicity tests show that the aqueous phase drives toxicity of sediment spiked with AE. Although fairly well equilibrated during the first few days, the strong concentration gradient between pore water and overlying water at the end of the toxicity test resulted in a clear, nonequilibrated test system. When sorption coefficients are used in EqP, predicted hazardous concentrations in such a disequilibrated system will only be accurate when pore water is the dominating route of exposure to benthic test species. Because of its burrowing behavior and active bioturbation, overlying water has been suggested as an important route of exposure for *C. volutator* (*29*).

The importance of pore water as a route of exposure for *C. volutator* was tested in a separate toxicity test series. As presented in Figure S2 in theAppendix, after the first six days at 16 ^{o}C without organisms, prior to the introduction of test organisms, the concentrations in the OW were already strongly decreased. The pore water dissolved concentrations, however, ranged between the water only LC50 values and more than ten times above the LC50 (2.4 and 20.5 mg/L), respectively. The organisms added to these test systems rapidly dug into the sediment and displayed normal activity during exposure. Besides the SPME measurements, the heavy foaming that occurred when sieving the animals out of the sediment, clearly indicated that the surfactant was abundantly present in the test systems at the end of the test. The survival in the delayed toxicity test, however, was not different from the control survival, and in all vials higher than 80% (Figure 3).

EqP clearly overestimated the risk for this test species in this test system. The actual exposure concentrations for *C. volutator* must have been much lower than the toxic pore water dissolved concentrations. Because of their burrowing behavior and active filtering of overlying water through their burrows, the organisms will, at least periodically, be exposed to a mixture of pore water and, mainly, overlying water. In a similar set-up with *C. volutator* exposed to polycyclic aromatic hydrocarbons (PAH), Kraaij *et al.* (*29*) observed a reduction in the internal PAH concentrations in *C. volutator* during time, while the bioavailable fraction in the pore water was not altered. Although no data on the OW were reported, reduced concentrations in the OW were considered the most likely cause for the observations in that study.

Since many other benthic species actively filter oxygen rich overlying water via burrows or siphons, actual exposure concentrations in disequilibrated laboratory and natural systems are likely far more complex than predicted via EqP (*26,27*). In this study, the disequilibrium results from rapid biodegradation in the overlying water.

Nonequilibrium situations will also occur for compounds with very slow desorption and diffusion from the sediment into the overlying water, for example when the overlying water has not been equilibrated sufficiently with the sediment phase, or is regularly refreshed, as done in long term bioassays (*30*). Environmental systems where relatively clean water regularly overflows contaminated sediment, e.g. in tidal systems, or incidental spills in relatively clean sediment, are large scale examples of nonequilibrated field situations. In such cases, the EqP approach will not correctly estimate the toxicity to those sediment organisms that will mainly equilibrate with the contaminant concentration in the overlying water instead of the pore water in the sediment.

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APPENDIX

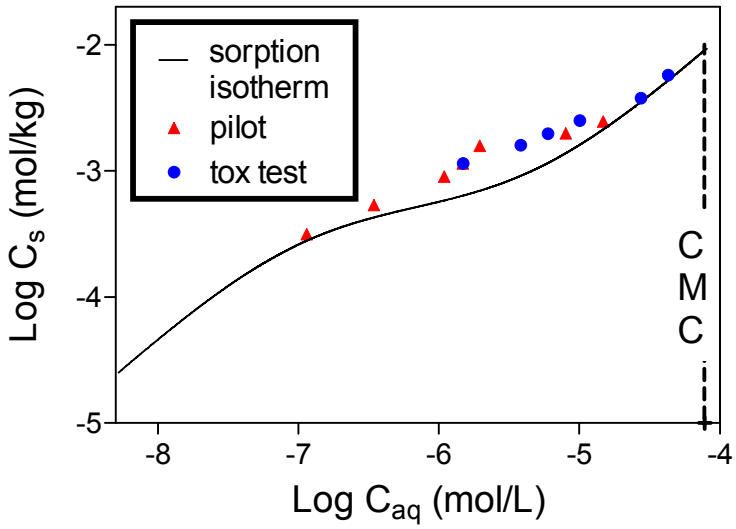

Figure S1. Nominal sediment concentrations of $C_{12}EO_8$ in the sediment toxicity tests plotted against average SPME measured concentrations in the pore water for triplicate vials (range finding pilot ▲, sediment toxicity test ●). The dual mode model sorption isotherm for $C_{12}EO_8$ (solid line) are from refs (*10*). CMC is the critical micelle concentration in seawater (*17*).

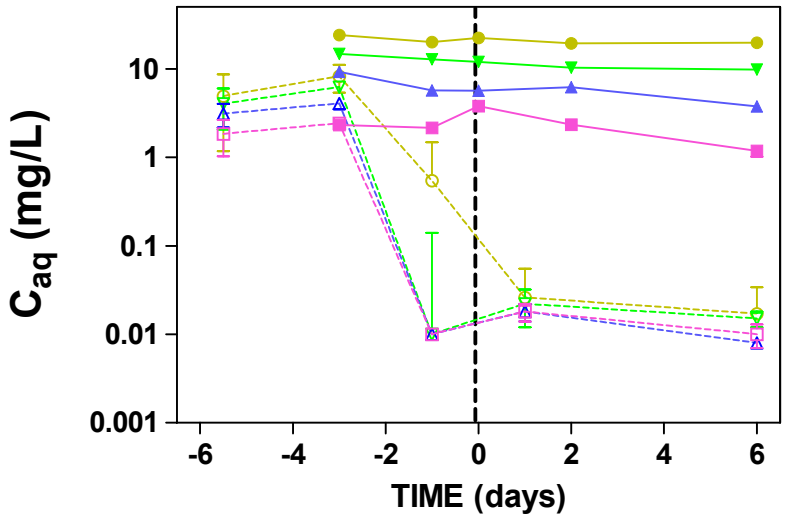

Figure S2. Concentration profile of $C_{12}EO_8$ in the overlying water (symbols connected by dashed lines) and pore water (connected by solid lines) in the sediment toxicity test with a system in disequilibrium. The vertical dashed line indicates the point in time where test organisms started the 6 day exposure period. The connecting lines are presented only as visual guidance. The low concentrations in overlying water are set to a detection limit of 10 µg/L when AE was below the lowest concentrations of the calibration curve or not detected at all.

Chapter 9

Summary and General Discussion

SUMMARY

The main focus of this thesis is to provide an improved scientific basis for the risk assessment of alcohol ethoxylates (AE) in marine sediment. The studies in this thesis focus on one of the basic assumptions that underlie the equilibrium partitioning theory (EqP), i.e. that understanding the freely dissolved concentration is a prerequisite for sediment risk assessment. In Chapters 2 and 3, a method with a polyacrylate Solid Phase Microextraction (SPME) fiber is validated as a passive sampling tool for the analysis of the freely dissolved concentrations for individual AE and linear alkylbenzene sulfonates (LAS). Chapters 5, 6 and 7 investigate how the dissolved concentration depends on the concentration of AE sorbed to marine sediment. The toxicity tests in Chapter 8 show that, in accordance with the EqP, the freely dissolved AE concentration at which toxic effects occur is similar for organisms that are either exposed to spiked seawater only or to a layer of spiked marine sediment.

Application of SPME for surfactants

The partition coefficient to the polymer coating of the SPME fibers (K_{fw}) relates the concentration of AE in the fiber, which is measured, to the freely dissolved concentration of AE, which is what we want to know. Chapter 2 shows that the partition coefficients of AE to the polymer coating of the SPME fibers (K_{fw}) can be applied to a variety of test systems in seawater. K_{fw} values are about a factor three lower in freshwater than in seawater (Chapter 4). Although the set of compounds could still be somewhat extended to cover a broader range of chain lengths, Chapter 6 shows that a strong relationship exists between the partition coefficient and the molecular structure (alkyl chain length and number of ethoxylate units). With this relationship, K_{fw} values can be calculated for any AE homologue and SPME can be used to determine the freely dissolved concentrations in samples with complex AE mixtures. Chapter 5 shows that the SPME method is also very suitable for measuring sorption coefficients in sediment suspensions.

Chapter 3 shows that the SPME method is also a helpful analytical tool for the negatively charged surfactant LAS. It took a lot of effort (i) to understand the influence of the conditioning of the polyacrylate SPME coating on the uptake kinetics, and (ii), to select the best conditioning treatment. Using the optimized SPME method, the concentration of individual LAS structures in SPME fibers is linearly related to the dissolved aqueous concentration. The K_{fw} value increases with the alkyl chain length of the specific LAS structures. The linear sorption isotherms between SPME and the aqueous phase provide a first indication that the negatively charged organics really absorb into the polymer phase. Additional tests are required to validate the applicability of SPME for the analysis of LAS in field samples, where LAS occurs in complex mixtures of different homologues and isomers.

Risk assessment of contaminated sediment strongly depends on the octanol-water partition coefficient (K_{ow}), because this parameters is often used as an indicator of the hydrophobicity of organic compounds. However, experimental K_{ow} data for AE are not available. The partition coefficient to the polyacrylate SPME fibers is also related to the

hydrophobicity of organic compounds, and Chapter 4 discusses if the experimental K_{fw} values for AE could replace K_{ow} as hydrophobicity parameters in risk assessment. SPME partition coefficients were collected from the literature and a few new data were generated experimentally. The polyacrylate K_{fw} values are within a factor 10 of K_{ow} values for all 70 chemicals in the data set. The chemical domain, however, does not include the ethoxylated surfactants. The K_{fw} - K_{ow} relationship should therefore not be extrapolated directly to AE.

A polyparameter linear free energy relationship (pp-LFER) approach would allow for a detailed comparison between K_{fw} and K_{ow} values. Pp-LFER models explain the partition coefficient of organic compounds between two bulk phases via the molecular interactions between the compound and the bulk phases. The pp-LFER model for the octanol-water system is based K_{ow} values for more than 600 chemicals. From the data set of K_{fw} values in Chapter 4, a pp-LFER model for water-polyacrylate systems is established. A comparison of the pp-LFER models shows that there are both similarities, but also differences in the properties of octanol and polyacrylate. A full comparison of the two phases will only be possible if the dataset is extended to cover a broader variety in structures and descriptor space.

Sorption behavior of AE

Sorption isotherms of AE with more than 3 EO units to marine sediments are clearly nonlinear. While in most cases a Freundlich model is applied to fit the nonlinear sorption data, the sorption was much better described via a dual-mode model with two sorption phases. A nonlinear adsorption term, with a maximum capacity, can account for sorption to clay minerals. It was postulated in Chapter 5 that the linear sorption term in the dual-mode model is related to absorption to organic matter. These model assumptions from Chapter 5 are partly refined in Chapters 6 and 7. The additional sorption data for the other alcohol ethoxylates and mixtures confirm that the nonlinear Langmuir term is related to adsorption to the mineral surface area of the sediment. The results presented in Chapters 6 and 7 demonstrate that the linear sorption term in the dual-mode model is not related to sorption to the organic matter, but to sorption to surfactant aggregates on the mineral surfaces. A comparison with sorption data to three pure clay minerals demonstrate that the nonlinear sorption isotherm of a single AE compound to marine sediment can be explained solely by sorption to the clay mineral surface area. Alcohol ethoxylates are the first nonionic organic chemicals for which the influence of clay minerals on sorption in natural sediment has been demonstrated to be so dominant.

Another consequence of the dual-mode sorption model is that if the total sorbed AE concentration is in the range of the maximum adsorption capacity, the AE in a mixture will compete for the adsorption sites. Chapter 7 demonstrates that the sorption isotherms of individual compounds can indeed be strongly affected by the presence of competing AE in the solution. An extension of the dual-mode model with competition effects accurately simulated the sorption of both binary and ternary mixtures of AEs.

The results of Chapters 5-7 show that the application of a more mechanistic based model may give insights into sorption mechanisms and, at the same time, is more powerful for estimating sorption in real field situations where the concentrations are often rather low and where always complex mixtures are present.

Sediment toxicity tests with AE

The equilibrium partitioning theory (EqP) assumes that the sediment toxicity of a chemical is determined by the freely dissolved concentration in the sediment. The application of the EqP to assess the risk of toxicants in a sediment requires that the system (sediment, water and biota) is in equilibrium. In Chapter 8, the importance of both the freely dissolved concentration and the required equilibrium are demonstrated. The results of sediment toxicity tests with a single AE homologue are compared to results of a water only exposure. In both systems, the freely dissolved concentration are determined via SPME. In accordance with the equilibrium partitioning theory, the toxicity to the benthic amphipod *Corophium volutator* is the same when the effect concentrations in both test systems are based on the freely dissolved concentrations. Furthermore, the sorption coefficient obtained in Chapter 5 accurately predicts the adverse effect concentrations in the aqueous phase of the sediment systems.

While concentrations in the pore water of the sediment phase remain constant throughout the tests, the concentrations in the water overlying the sediment strongly decrease 2-3 days after the start of the toxicity tests. Because most of the toxic effects occur during the first days, when the systems are still well equilibrated, this did not affect the outcome of the toxicity test. In a separate test, however, the amphipods were exposed to a system that was not in equilibrium and where the concentration in the overlying water was decreased significantly. In these nonequilibrated systems, amphipods easily survive concentrations in the pore water far above toxic concentrations. Apparently, the amphipods live in close contact with the water overlying the sediment phase, and their actual exposure concentrations are therefore much lower than the concentrations in the pore water. The risk for the amphipods in nonequilibrated test systems will therefore be overestimated if only sorption coefficients are applied. On the other hand, sediment toxicity in a standard laboratory bioassays can easily be underestimated if the test system is not in equilibrium. *C. volutator* is therefore not a suitable test organism for bioassays and sediment toxicity tests if the test systems are not sufficiently equilibrated and actual exposure concentrations are not measured.

GENERAL DISCUSSION

The aim of this final chapter is to discuss the field relevance of the findings presented in this thesis, because none of the chapters include field validation data.
The discussion will focus on the following aspects:
- detection limits of the methods used in the laboratory studies.
- the relevance of laboratory tests for extrapolation to the highly dynamic and much more complex situation in the actual coastal environment.
- the applicability of sorption models to predict concentrations in sediment and pore water under field conditions, including the behavior of mixtures.
- the relevance of free concentrations of surfactants in toxicity testing.

At the end of the discussion, a short outlook is presented on the applicability of SPME for other types of surfactants, including some preliminary work for a cationic surfactant. Another question that is raised is whether there are other parameters besides free concentrations that are better indicators of the risk of surfactants in sediment.

Field relevance of data presented in this thesis

Detection limits

The lowest sediment sorbed concentrations that have been determined via SPME in the sorption experiments in this thesis, are in the range of 1-10 mg/kg. The detection limits of the SPME method strongly depends on the AE structure, because the affinity for the SPME fiber decreases for AE with longer ethoxylate chains, while the adsorption to clay increases with more EO units. Because of these two trends, the SPME method could not be used to obtain sorption data below 200 mg/kg for $C_{14}EO_{14}$.

A major shortcoming of the currently available monitoring data on AE in literature is that in most cases, only total concentrations of AE are presented. Only the study by Dyer *et al*. (*4*) gives data for individual AE concentrations in sediment downstream of sewage treatment plant (STP) discharges. Only AE with EO chains of 2 or less units were detected downstream of an activated sludge type STP. The sediment (f_{oc} 0.009, 89% sand) hundred meters downstream a trickling filter type STP also contained concentrations of AE with longer EO chains above their detection limits. Still, individual AE with more than 2 EO units were not present at concentrations above 0.010 mg/kg dry weight.

The marine location with the highest concentration of surfactants reported in literature had a total AE concentration of 10 mg/kg (*5*). These data are from a site 20 m from the discharge outlet in a channel in open connection with the sea that until 2002 received untreated sewage. In other coastal sediments, total AE concentrations were reported up to 1.3 mg/kg (*5,7*). Although these studies did measure individual AE compounds or groups of alkyl homologues, these concentrations are not reported. Estimates of individual AE compounds will surely be less than 10% to the total AE concentration, so readily below 0.1 mg/kg.

These field concentrations are far lower (a factor 100-1000) than the lowest range of sediment concentrations in the sorption tests presented in this thesis. Still, the lowest experimental concentrations presented in this thesis are, to our best knowledge, below all currently reported values in the literature, even from studies that applied radiolabelled material (*8*). Using radiolabelled material, for which detection limits with AE can be achieved of 0.3 µg/L in the final sample (P&G, personal communication), in combination with the SPME method, will not increase the sensitivity much compared to the LC-MS method used in this study (detection limit of ~10 pg in the injected sample). The SPME system can be scaled-up, though, e.g. using longer fibers, using a thicker fiber coating or desorbing in smaller solvent volumes of the solvent.

Field concentrations versus toxic concentrations

The sediment toxicity test in Chapter 8 showed that the toxic effect concentrations of a single homologue are not very different for the marine mud shrimp *Corophium volutator* and the fresh water *Daphnia magna*. Effect concentrations for these organisms are very similar if they are expressed based on the dissolved concentration in the aqueous phase. Therefore, it is interesting to see how the detection limit of the SPME fiber method relates to concentrations at which adverse effects of AE occur. The fiber-water partition coefficient (K_{fw}) determines the detection limit in the aqueous phase and, as shown in Chapters 2 and 6, K_{fw} increases with alkyl chain length (#C) and decreases with ethoxylate chain length (#EO), according to:

$$\text{Log } K_{fw} \text{ (sea water)} = 0.520 \cdot \#C - 0.264 \cdot \#EO - 1.56$$

Effect concentrations (EC_{50}) of AE to aquatic organisms are also related to these two molecular parameters. Wong *et al*. (*3*), for example, report the following equation for immobilization of daphnids after 48 h (using average chain lengths of AE mixtures):

$$\text{Log } EC_{50} = -0.38 \cdot \#C + 0.1 \cdot \#EO - 1.77 \qquad (EC_{50} \text{ in mol/L}, n = 9, r^2 = 0.96)$$

A common technical AE mixture in commercial products has alkyl chain lengths of C_{10}-C_{18}, with 1-20 EO units. For simplicity, it can be assumed that AE with more than 14 EO units will not pose a risk, due to the combination of a strong sorption to the clay mineral fraction in sediments and low toxicity due to the relatively low "hydrophobicity". The K_{fw} equation can be used to estimate the lowest possible aqueous concentrations that can be measured via the SPME method for several compounds in an AE mixture (LC-MS detection limit of 20 pg per injection). The application of the equations show that for $C_{10}EO_2$ and $C_{10}EO_{14}$, SPME detection limits are a factor of 1100 and 40, respectively, below acutely toxic concentrations (EC_{50}) for daphnids. For $C_{14}EO_2$ and $C_{14}EO_{14}$ these factors are 5000 and 150, respectively, while for $C_{18}EO_2$ and $C_{18}EO_{14}$ then factors are 20000 and 580, respectively. In summary, for the most important AE homologues, SPME can detect individual AE structures at concentrations of 40-20000 times below the predicted toxic

effect concentrations. Whether this is useful for the complex AE mixtures that can be present in the field, depends on the characteristics of the AE mixture in the sediment. In a toxic unit (TU) concept (see Introduction Chapter Figure 5), dissolved concentrations of each AE structure can be added up as fractions of their effect concentrations to determine the sum of toxic units (Σ_{TU}). Whereas the SPME method will most likely not be able to detect all individual AE in field sediments, the SPME method could be used to demonstrate that the dissolved AE present in a contaminated sediment is *not* able to reach a Σ_{TU} in the range of 0.1-1.

It does not seem likely that a Σ_{TU} unit close to 1 will occur for the other reported AE concentrations in sediment impacted by the effluent of normally functioning sewage treatment plants. Chapter 8 showed that the toxic concentrations of a single AE structure ($C_{12}EO_8$) in the sediment phase are in the order of 500-1000 mg/kg. These effect concentrations are much higher than the total AE concentrations determined in field sediments. Still, because of the complexity of the AE mixtures and different properties of the sediment in the toxicity test as compared to those in the field, sorption models should provide further evidence on the risk of AE in the field sediments.

Test conditions versus field conditions

Considering the rapid degradation potential of AE, it still seems strange that AE have been detected in coastal environments at all. Several process likely play important roles here. First of all, there is always a continuous input of low levels of AE via discharges Moreover, branched AE show slower degradation rates in aerobic conditions (*10*), while they are poorly broken down anaerobically (*11*). The AE mixture in field sediments that are relatively far away from point discharges may thus be enriched with branched structures. Data on different isomer structures of the individual AE in field sediments is not available. Furthermore, as shown by Knaebel *et al*. (*12*), the sorbent phases in soil or sediment, such as clay minerals, sand and organic matter, influence the extent and rate of biodegradation. In that study, AE was preadsorbed to varying substrates before it was added to a clean test soil (at 70% of its water holding capacity). Compared to the controls, where dissolved AE was added, the initial mineralisation was slower for the preadsorbed AE. Furthermore, the mineralisation (in produced $^{14}CO_2$) for AE preadsorbed to montmorillonite (a swelling clay mineral) leveled of at 30% after 10 days, whereas in the control 55% was mineralized. This suggests that AEs in field sediment may be sorbed mainly to specific sediment phases that have slower desorption rates, especially at locations that are far away from discharge locations.

Application of the sorption models proposed in this thesis

Extrapolating the models

In this thesis, the AE structures in sorption experiments varied from $C_{10}EO_8$ to $C_{14}EO_8$ and $C_{12}EO_3$ to $C_{14}EO_{14}$ (Chapter 6). The data in both Chapter 6 and 7 strongly suggest that the nonlinear sorption isotherms can be explained by two separate sorption processes; an adsorption process on mineral surface area following a Langmuir relation and a linear sorption process in which dissolved molecules interact with surfactant aggregates adsorbed on the mineral phase. Two separate models are presented where the sorption coefficients K_{ad} and K_p are related to the alkyl chain length and number of ethoxylates. However, the models should be further improved by additional testing before they can be applied in risk assessment. Extrapolating the results from these linear alcohol ethoxylates to other ethoxylates is also tempting, but this will require further investigations with other AEs, such as branched AE and nonylphenolethoxylates (NPEO), alkylether sulfates, or cationic amine ethoxylates.

The sorption data for the two clay minerals show that the variation between sorption isotherms on different substrates can, for a large extent (within a factor of about 5), be explained by the specific surface area. The surfaces of the different clay mineral phases that can be present in a sediment differ widely, varying from the interlayer between clay sheets (e.g. for bentonite), sheets with external surfaces of aluminum hydroxide as well as silicon oxide (kaolinite), or a relatively large negative surface charge (e.g. illite). The presented models may be further improved by incorporating this more detailed information in the sorption.

The dual-mode sorption model is much more informative for the risk assessment of AE in sediment, than the currently used Freundlich isotherms (*8,13,14*), or linearized sorption coefficients based on organic carbon corrections (*4,15*). Although the dual-mode model does not incorporate all detailed processes, the dominating sorption processes are covered. Furthermore, the dual-mode model assumes a linear sorption at concentrations readily below the maximum adsorption capacity of the sediment. Although it is not yet possible to confirm this by measuring at such concentrations, it will clearly be a benefit for risk assessors if these adsorption coefficients can be related to molecular structure of the AEs as well as to a single sediment property, i.e. specific surface area and a first attempt has been made in this thesis.

Additional testing to improve models

The sorption of different AE structures to a single marine sediment was explained by sorption to the mineral surface area of this sediment. The reasons for this included (i) the overlap of a sediment sorption isotherm of one compound with sorption data for two pure clays, both at the high and low concentration range, (ii) the increasing sorption coefficient at low concentrations for longer ethoxylate chains, (iii) the linear sorption isotherm of a single homologue to clay or sediment on which a much stronger adsorbing homologue was

present at concentrations above the maximum adsorption capacity. However, the relationships of the sorption parameters K_{ad} and K_p with the molecular structure of AEs (Chapter 6) are determined for a single marine sediment. It would be better if these sorption parameters are first established on a model clay mineral, to obtain a set of standard values which then can be extrapolated to other sediments.

The bentonite clay is a very important industrial sorption phase, but the sorption to the interlayer complicates the adsorption process. It does contribute to the maximum adsorption capacity but probably does not contribute to bilayer formation. Kaolinite clay is much used in sorption studies, but has two different types of surfaces (silicon oxide and aluminum hydroxide), in combination with a large contribution of the 'edges' of the sheets to the surface area. The clay mineral illite does not expand, and only has silicon oxide surfaces, and therefore may be a suitable model clay mineral to study the adsorption parameters for AE.

The sorption data in Chapters 6 and 7 suggest that bilayer formation is a linear process with a constant affinity coefficient (K_p). The relationship obtained from the sorption data on the marine NFF sediment shows that K_p increases with alkyl chain length and decreases slightly with increasing numbers of ethoxylates. The data obtained from the binary mixtures with $C_{14}EO_{14}$ seem to give a much more reliable affinity coefficient. It is interesting to study these 'bilayer-affinities' in more detail. As long as the contribution of sorption to organic matter is negligible, it forms the lower limit of the nonlinear sorption isotherms. This may even be the case for the majority of the marine sediments, where the surface area is closely related to the organic matter content. For freshwater sediments this relationship is less evident, and the sorption coefficient to organic matter is therefore likely more important than for marine sediments.

Free concentrations

Free concentrations in toxicity tests

Most marine and freshwater sediments are anoxic below the first centimeters or millimeters. The organisms inhabiting the sediment therefore often build tubes and actively pump oxygen rich overlying water through these burrows. Other organisms actively filtrate food particles from the overlying water and thereby expose their tissues to contaminants present in the overlying water. As long as the concentration in the overlying water is in equilibrium with the sediment sorbed concentrations, the prediction of the risk via sorption coefficients should work well. However, when bioassays or sediment toxicity tests are performed with nonequilibrated systems, the behavior of the organism can strongly influence the outcome. Chapter 8 shows for the nonequilibrated test systems that the actual exposure concentrations for the test organism were different from the pore water concentrations.

The above phenomenon clearly shows that the outcome of bioassays with contaminated field sediments should be carefully interpreted, to avoid that sediments are

wrongfully interpreted as safe. Ideally, the systems should be tested for equilibrium between pore water and overlying water. Also information should be available on the route of exposure of commonly used test organisms. As shown in Chapter 8, tests performed with a nonequilibrated system can also supply information about the actual route of exposure of benthic organisms.

Sampling of free concentrations

Chapter 5 showed that the AE concentrations in the aqueous phase of sediment suspensions, obtained via centrifugation, were similar as the SPME derived aqueous concentration. For these ethoxylates and this marine sediment, an overestimation of the freely dissolved concentration, due to the presence of nonseparable matter in the aqueous phase, was apparently negligible. A potential overestimation of the freely dissolved concentration will become more apparent for AE with a stronger affinity for phases that are difficult to separate by centrifugation. For ethoxylates, this could include long alkyl chains with short EO chains sorbing to organic matter, and AE with long ethoxylate chains sorbing to the very fine clay fraction.

There are other ways to sample pore water, e.g. via syringes at several depths of the sediment layer, or via separation with membranes (dialysis tubing). The results with the SPME in Chapter 8 showed that the 'readily desorbed concentration' obtained with small sediment samples could be used to analyze the pore water dissolved AE concentration. The main advantage of this method is that SPME, or other passive samplers, do not have to be equilibrated *in situ* (i.e. in the sediment layer). Depending on the type of AE compounds, *in situ* equilibration may take relatively long because the kinetics for a static system are slower than for an agitated system (if diffusion in the aqueous phase is the rate limiting factor).

Preliminary work with octylphenol ethoxylates showed that SPME could facilitate sorption studies with such nonionic surfactants as well, but it requires that the method is calibrated with better defined standards than the ethoxylate mixtures that are presently available. As shown in Chapter 3, the SPME method can also be applied for negatively charged surfactants. This technique has recently been applied in sorption studies and toxicity tests with LAS (A. Rico, unpublished data). The application of SPME would also be strongly beneficial for cationic surfactants, which carry a positive charge. The strong interaction with negatively charged surfaces is very interesting for risk assessment of contaminated sediments, since most clay minerals carry a negative charge. The affinity of cationics for negatively charged surfaces also makes experimental testing complicated because the cationics are well known to sorb to glassware, teflon and column packing materials used for analytical purposes. Sorption experiments with cationics would benefit from a sampling tool like SPME if it could be used to determine freely dissolved concentrations. The validation of an SPME method for catinoics, however, strongly depends on the possibility of direct analysis of the aqueous concentration because such a direct analysis is needed to derive the SPME calibration curves. In 2006, OASIS® WCX became

available as a new type of solid phase extraction (SPE) material that was especially well suited for strong bases. Using these columns, several small pilot studies could be performed with SPME in solutions with a single cationic surfactant. The results are discussed as the final part of this thesis, providing preliminary data which could be used in further studies with surfactants.

SPME pilots with cationic surfactant

Tests were performed with a monoquat (C_n-$N^+(CH_3)_3$) with n = 16 carbon atoms (IV-16), as summarized in the method box below. Based on the experience gained with the negatively charged LAS (Chapter 3), only thermally conditioned polyacrylate fibers were used for cationic organics. After selecting the optimal analytical conditions, the uptake kinetics were studied first to determine when equilibrium is reached (Figure 1). After that, the linearity of the sorption isotherm was checked at equilibrium over a broad concentration range. As for the nonionic and anionic surfactants, we hoped to achieve linear sorption isotherms, which would suggest a partitioning process with a single affinity coefficient. The data for the cationics show that the SPME concentration increases with aqueous concentrations. The sorption isotherms obtained so far, however, are nonlinear (Figure 2). Additional testing should clarify the robustness of the (non) linearity of the SPME method for of cationics.

SPME method for IV-16:

- Aqueous phase: Extraction slightly adapted from OASIS-WCX SPE guidance document (ref (*16*)). In short, conditioning with 3 mL methanol and 3 mL water, then 2 mL test solution. Flushed with 3 mL water (25 mM phosphate buffer, pH 7), 3 mL clean water (to remove salts), and 3 mL methanol. Eluted with 3 mL 84:14:2 acetonitril/water/formic acid (v/v/v) with 5 mM NH_4HCO_2, which included flushing of the 5 mL pipet tip. Pilot experiments indicated full recovery of the compound.
- SPME fibers: Thermally conditioned 7-µm and 35-µm polyacrylate, IV-16 was extracted from the SPME with the (84:14:2) solution.
- Analysis after Phenomenex Luna C_{18} column by LC-MS/MS using ($284.5^+/60.0^+$), isocratic at 85:15 acetonitril/water with 5mM NH_4HCO_2.

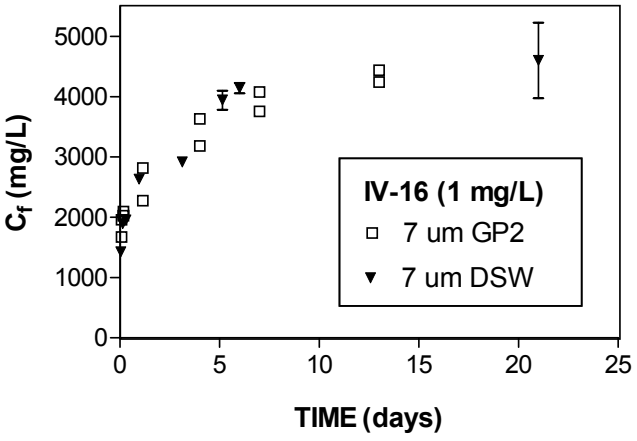

Figure 1. Uptake kinetics of IV-16 in conditioned 7-µm PA fibers from 1 mg/L are comparable for solutions in sea water (GP2) and fresh water (DSW). A rapid increase was observed between the blank and the first time point, followed by a slow increase, and equilibrium seems to be reached during the second week (agitated on the "Rock and Roller" device). No data yet for 35-µm PA fibers.

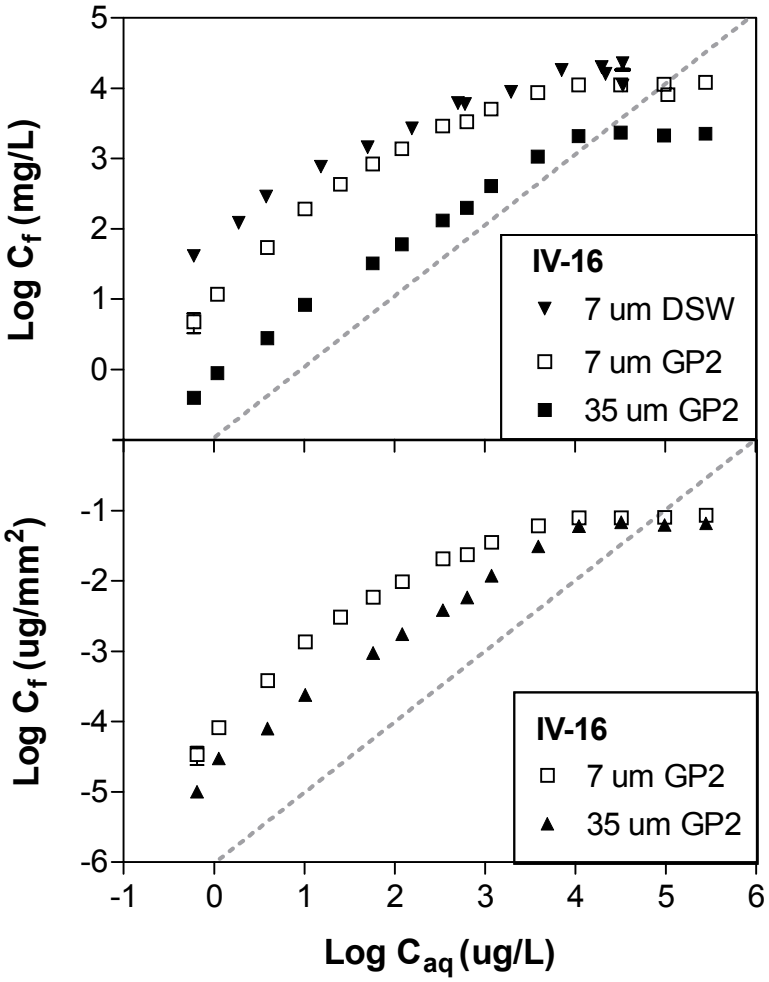

Figure 2. Sorption isotherms of IV-16 in conditioned polyacrylate SPME fibers from artificial seawater (GP2) and standard fresh water (DSW). The concentration in the fiber in the top graph is expressed per volume polyacrylate, and in the lower graph per unit area of the polymer's exterior surface. The dotted line indicates linearity.

Salinity has a small influence on the sorption isotherm of IV16 for 7-µm PA fibers.

The exterior surface areas for 7-µm and 35-µm PA were similar, while 7-µm PA had a five times lower volume. Even with C_f expressed per unit surface area, sorption affinity to 7-µm PA was higher. The 35-µm PA, however, showed better linearity than the 7-µm PA.

At seawater concentrations above 10 mg/L, SPME concentrations show no further increase. Whether this is due to saturation on the polymer phase or reaching CMC (~300 mg/L in pure water) is not yet clear.

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SAMENVATTING IN HET NEDERLANDS

In dit proefschrift is onderzoek gedaan naar oppervlakte-aktieve stoffen. Het belangrijkste kenmerk van oppervlakte-aktieve stoffen is dat een deel van het molecuul graag in water oplost (hydrofiel), terwijl een ander deel van het molecuul slecht in water oplost (hydrofoob), maar wel graag in een vettige omgeving zit. Deze stoffen zijn o.a. de belangrijkste componenten in veel schoonmaakproducten, zoals wasmiddel, shampoo's etc. Het overgrote deel van deze stoffen wordt dus via de riolering afgevoerd, en de concentraties in het rioolwater zijn in het algemeen zeer hoog. In rioolwaterzuiveringsinstallaties kunnen de concentraties van de meeste oppervlakte-aktieve stoffen met meer dan 95% worden gereduceerd voordat het afvalwater weer in het milieu wordt geloosd. In de kanalen, meren, rivieren en (uiteindelijk) de zee worden deze concentraties van dit soort stoffen verder gereduceerd door verdunning en afbraak door organismen. Een van de meest gebruikte "niet-ionogene" oppervlakte-aktieve stoffen in Europa, een groep stoffen genaamd alcohol ethoxylaten (AEs), staat bekend als makkelijk bio-afbreekbaar. Echter, in metingen aan de zeebodem langs de kusten van bijvoorbeeld Spanje worden deze stoffen toch aangetroffen, waarschijnlijk door onvoldoende functioneren van rioolwaterzuivering en een continue aanvoer via rivieren en andere punten waar deze stoffen in het milieu terecht komen.

Vanuit milieuoogpunt is het interessant om te weten hoe de gemeten concentraties zich verhouden tot concentraties die schadelijk kunnen zijn flora en fauna. Bij nadere beschouwing blijkt het echter zeer ingewikkeld te zijn om dit nauwkeurig te bepalen. Dit type chemicaliën is om verschillende redenen relatief lastig te analyseren. Het beperkte aantal milieu-wetenschappelijke studies dat aan deze stoffen gewijd is, laat verder zien dat ze zich "anders gedragen" in het milieu dan de meeste andere schadelijke organische verbindingen zoals PCB's en PAK's. Hoe dit precies zit bleef in deze studies echter onduidelijk. Het is dus de vraag in welke mate risicomodellen, die zijn gebaseerd op de "klassieke" verontreinigende stoffen, ook toepasbaar zijn op oppervlakte-aktieve stoffen om maximaal toelaatbare concentraties te schatten. Een correcte risicobepaling van AEs in het mariene milieu op basis van de bestaande wetenschappelijke literatuur wordt verder bemoeilijkt doordat vrijwel alle studies gefocust zijn op het zoetwatermilieu. Over het milieugedrag van AEs onder mariene omstandigheden, en zeker in de zeebodem (marien sediment), is zo goed als niets bekend.

Het onderzoek in dit proefschrift probeert stap voor stap het risico van AEs in marien sediment beter te begrijpen. In de zeebodem zijn de stoffen deels gebonden (gesorbeerd) aan de sedimentdeeltjes, en deels opgelost in het water dat zich tussen het sediment bevindt, het poriewater. De verdeling tussen de sedimentgebonden concentratie (C_s) en de vrij-opgeloste concentratie (C_{aq}) wordt uitgedrukt door middel van de sorptie-coëfficiënt K_d:

$$K_d = \frac{C_s}{C_{aq}}$$

De sorptie-coëfficiënt K_d is afhankelijk van de molecuulstructuur van de AEs, en daarnaast van de eigenschappen van het sediment. Waar de klassieke verontreinigingen voornamelijk gebonden zijn aan de sedimentfractie die bestaat uit organisch materiaal (bijvoorbeeld verweerd bladmateriaal, bacteriën en algen), gaat dit niet op voor AEs. Het milieugedrag van AEs wijkt verder af van andere stoffen doordat de sedimentgebonden concentratie in veel gevallen niet lineair gerelateerd is aan de vrij-opgeloste concentratie. De sorptie-coëfficiënt is daardoor afhankelijk van de concentratie in het sediment.

Centraal uitgangspunt in dit proefschrift is de hypothese dat alleen de vrij-opgeloste concentratie van de stoffen het directe risico bepaalt voor organismen die in het sediment leven. De aan bodemdeeltjes gebonden stoffen kunnen namelijk niet direct celmembranen passeren. In vrijwel alle veldmetingen naar verontreinigingen in sediment en bodems wordt echter alleen de gebonden concentratie gemeten, en wordt de vrij-opgeloste concentratie hieruit berekend met behulp van de K_d. Het sorptiegedrag van AEs is dus een belangrijk gegeven voor de risicobepaling ervan in vervuild sediment. De AEs in commerciële producten zijn complexe technische mengsels van moleculen die onderling verschillen in de lengte van zowel het hydrofobe deel (alkylketen) als het hydrofiele deel (ethoxylaatketen). Om de interpretatie van de resultaten te vereenvoudigen is in dit proefschrift niet met de complexe mengsels gewerkt, maar zijn enkele pure stoffen gebruikt met bekende molecuulstructuren.

Het proefschrift is grofweg op te delen in 3 secties. **Hoofdstuk 2,3 en 4** behandelen voornamelijk verbeteringen aan technieken om oppervlakte-actieve stoffen eenvoudiger en nauwkeuriger te analyseren. In **hoofdstuk 5, 6 en 7 worden** verschillende aspecten van het sorptiegedrag van AEs besproken. **Hoofdstuk 8** legt de link tussen het sorptiegedrag van AEs, de vrij-opgeloste concentraties en de risico's voor organismen die in het sediment leven. Hoe de resultaten van de in het laboratorium uitgevoerde studies worden vertaald naar de situatie in het veld wordt mede in **hoofdstuk 9** verder besproken.

Hoofdstuk 2 beschrijft een analysemethode om de vrij-opgeloste concentratie van AEs mee te bepalen onder mariene omstandigheden. Het principe van de gebruikte solid-phase microextraction (SPME) techniek is dat alleen de vrij-opgeloste AE moleculen kunnen worden opgenomen in een dun polymeerlaagje (0.03 mm) dat is aangebracht om een paar centimeter glasvezel (fiber). De concentratie in de coating staat in vaste verhouding met de vrij-opgeloste concentratie. Uit de testen met een set van elf individuele AEs blijkt dat deze verhouding goed kan worden voorspeld aan de hand van de ketenlengte van het hydrofobe en het hydrofiele deel van de AEs. De concentratie AE in de SPME fibers is verder zeer eenvoudig te analyseren. De SPME methode is daardoor een zeer waardevolle techniek gebleken in het verdere onderzoek naar het milieugedrag van AEs. **Hoofdstuk 3** beschrijft een vergelijkbare studie naar de mogelijkheden van SPME voor een ander type veelgebruikte oppervlakte-aktieve stof, de lineaire alkylbenzeensulfonaten (LAS). Aanvankelijk leek het niet mogelijk om de SPME methode voor LAS te gebruiken op een vergelijkbare manier als met de AEs gelukt was. Toen eenmaal de werking van enkele subtiele processen was achterhaald, bleek de methode ook voor LAS zeer succesvol te

kunnen worden toegepast. Omdat de affiniteit van de AEs voor de fibers in hoofdstuk 2 goed te bepalen bleek, hoopten we hiermee een andere eigenschap van de AEs, de affiniteit voor octanol, te kunnen achterhalen. De affiniteit voor octanol is een belangrijke stofeigenschap in risicobeoordeling, maar voor AEs berusten de geschatte waarden tot nu toe slechts op grove aannames. In **hoofdstuk 4** zijn de moleculaire eigenschappen van een 70 chemische verbindingen gekoppeld aan de affiniteit van die stoffen voor de polymeercoating van SPME fibers. Aangezien eenzelfde koppeling tussen moleculaire eigenschappen en de affiniteit voor octanol reeds bestaat, is het mogelijk om de affiniteit voor octanol te vergelijke met de affiniteit voor SPME fibers. Toch bleek het voor AEs nog niet mogelijk de gewenste waarden te achterhalen door het ontbreken van de juiste gegevens over moleculaire eigenschappen.

Hoofdstuk 5 laat zien dat de ontwikkelde SPME techniek goed gebruikt kan worden om het sorptiegedrag van AEs te onderzoeken. In combinatie met een gevoelige detectietechniek (LC-MS) geven de metingen met SPME fibers zeer betrouwbare waardes bij relatief lage concentraties in vergelijking met vergelijkbare studies. De laagst geteste concentraties zijn echter nog altijd meer dan een factor 10 hoger dan de hoogste sediment concentraties die in het veld zijn gemeten. Net als in eerdere studies blijkt ook in dit hoofdstuk dat de sorptie-coëfficienten afhankelijk zijn van de testconcentraties. De experimentele data wordt echter goed beschreven door een sorptiemodel dat uitgaat van twee simpele processen. In **hoofdstukken 6 en 7** worden de twee bindingsprocessen nader onderzocht, en wordt de invloed van de molecuulstructuur en de sedimenteigenschappen op de bindingsprocessen beschreven. Binding van AEs aan het oppervlakte van kleideeltjes (adsorptie) blijkt het belangrijkste sorptieproces. Op basis van het minerale oppervlak blijkt het sorptiegedrag van één specifieke AE aan diverse mariene sedimenten en typen pure kleimineralen vrijwel gelijk te zijn. Het reeds aan het kleioppervlak geadsorbeerde “laagje” AE vormt een bindingsplek waar extra AE aan kan binden als tweede proces in het model. Bij de onderzochte AEs en de diverse geteste mariene sedimenten blijkt binding aan de fractie organisch materiaal verwaarloosbaar in vergelijking met deze twee processen.

De afhankelijkheid van de sorptie-coëfficiënt van de concentratie kan worden verklaard doordat bij een bepaalde concentratie de adsorptie-plaatsen op de kleideeltjes verzadigd raken. In hoofdstuk 7 wordt het sorptiemodel in enkele details aangepast om de sorptieprocessen in mengsels van meerdere AEs te beschrijven. Omdat het kleioppervlak verzadigd kan raken, zal er competitie zijn tussen de verschillende AEs in een mengsel om de laatste plaatsen te vullen. Het aangepaste sorptiemodel geeft een redelijke voorspelling voor het sorptiegedrag ten opzichte van de gemeten data voor mengsels van 2 en 3 stoffen.

De twee sorptieprocessen zijn redelijk goed gecorreleerd aan de molecuulstructuur van de individuele AEs. Het is hierdoor mogelijk om het sorptiegedrag goed te benaderen met gegevens over de molecuulstructuur van de AE verbindingen en het specifieke oppervlakte van het mariene sediment. Dit maakt het wellicht in de toekomst mogelijk om

een realistischere inschatting te maken van het sorptiegedrag van AEs in vergelijking met de huidige risicomodellen. Voor directe toepassing van de in dit proefschrift opgestelde modellen in risicobepalingen van vervuilde locaties in de natuur, dient er echter nog rekening gehouden te worden met een aanzienlijke onzekerheidsmarge.

De toxiciteitstesten in **hoofdstuk 8** bevestigen de hypothese dat de giftigheid van een specifieke AE in sediment voor slijkgarnaaltjes (*Corophium volutator*) geheel kan worden verklaard door de vrij-opgeloste concentratie. Met behulp van de SPME techniek kon de concentratie in het poriewater van een laag marien sediment nauwkeurig worden bepaald. De gemeten concentraties in de sedimentsystemen waren vergelijkbaar met de schattingen via de sorptie-coëfficiënt. Hoewel AE bekend staan als makkelijk afbreekbaar, bleven de concentraties in het poriewater constant gedurende de testen, waarschijnlijk door nalevering uit de sedimentgebonden fractie. De concentraties in het water boven de sedimentlaag, die aanvankelijk even hoog waren als die in het poriewater, namen echter tijdens de testen dag binnen enkele dagen af tot minder dan 1% van de uitgangsconcentratie als gevolg van afbraak door micro-organismen. Als slijkgarnaaltjes werden blootgesteld aan testsystemen waarin de concentratie AE in het water boven het sediment al was verlaagd, overleefden de testorganismen sedimentconcentraties die in de oorspronkelijke test nog zeer giftig bleken. Hieruit blijkt dat *Corophium volutator* sterk wordt beinvloed door de kwaliteit van het water boven het sediment. Het gebruik van dit testorganisme in bijvoorbeeld de beoordeling van verontreinigd slib zou daardoor mogelijk risico's kunnen onderschatten voor biota die sterker door poriewater worden beïnvloed.

Conclusie

Het sorptiegedrag van individuele AEs aan marien sediment is voor een groot deel opgehelderd, en kan met een simpel model redelijk beschreven worden. De invloed van de molecuulstructuur van AEs en sedimenteigenschappen op de twee bindingsprocessen zijn tot simpele vergelijkingen terug te brengen. In tegenstelling tot wat nu toe werd aangenomen is de binding van de meeste AEs aan organisch materiaal verwaarloosbaar. De vrij-opgeloste AE concentraties in het veld zijn te laag om met de gebruikte SPME techniek te meten, maar worden met behulp van het sorptiemodel beter benaderd dan tot nu toe mogelijk was. De in zeebodems gedetecteerde totale concentraties van AE zijn lager dan het testbereik van de sorptie-experimenten met individuele AEs in dit proefschrift. De AE concentratie in het sediment waarbij de overleving van slijkgarnaaltjes significant beïnvloed werd, ligt een factor 1000 hoger dan de hoogst bekende totaalconcentraties van AEs in zeebodems. Door de concentratie-afhankelijkheid van de sorptie-coëfficiënt is het verschil in vrij-opgeloste concentraties nog groter. De gemeten veldconcentraties lijken dus geen risico te vormen, maar nabij uitstroompunten van onbehandeld rioolwater kunnen hogere AE concentraties voorkomen. Toxiciteitstesten met AE mengsels in marien sediment kunnen verder uitsluitsel geven, maar deze zijn waarschijnlijk zeer lastig te interpreteren gezien de mogelijke competitieve sorptieprocessen, gecombineerd met de invloed van micro-organismen tijdens de testen en het specifieke gedrag van het gebruikte testorganisme.

CURRICULUM VITAE

Steven Droge was born in Alkmaar, The Netherlands, on 19 February 1978. After finishing high school (Petrus Canisius College Alkmaar) in 1996, he studied Biology at the University of Amsterdam (UvA). During the specialization phase (M.Sc.) his first research project focused on the use of a biomimetic tool (SPME) to study the effects of tetrachlorobenzene on midge larvae at the Department of Aquatic Ecology and Ecotoxicology (UvA). During a second research period in 2000 at the Dutch Institute for Inland Water Management and Waste Water Treatment (RIZA), he studied whether the SPME tool could be used to predict the bioaccumulation potential of industrial effluents. After his graduation in 2001 he worked for two months as a guest researcher at the UK Environment Agency in Waterlooville, UK, as an extension of his project at the RIZA. In 2002 and 2003 he worked as a research assistant at the Animal Ecology section of the Vrije Universiteit in Amsterdam on the toxicity of polycyclic aromatic compounds on two soil invertebrates. From 2004 to 2008 he worked at the Universiteit Utrecht on the PhD project entitled bioavailability of surfactants in marine sediments, which resulted in this dissertation. Since 2003 he has presented research at several European and North American conferences and received the Young Student's Best Poster Award at the Society of Environmental Toxicology and Chemistry meeting in Lille, France 2005. Presently he is studying the sorption of cationic organics in a post-doc position at the UFZ Leipzig, Germany.

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