

# BIOACCUMULATION POTENTIAL OF SURFACTANTS: A REVIEW

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## 1 INTRODUCTION

Surfactants are a chemical group for which it is difficult to obtain reliable partitioning ( $\log P_{ow}$ ) or bioconcentration factor (BCF) data for inclusion in current models used in performing environmental risk assessments. The difficulties revolve largely around the intrinsic property of surface-active substances to adsorb to surfaces and to accumulate at phase interfaces. Despite the apparent limitations of surrogate analytical approaches to estimation of bioaccumulation potential for a surfactant, regulatory authorities have, with few exceptions, insisted on the submission of  $\log P_{ow}$  data for surfactants for the purposes of environmental risk assessments (OSPAR HOCNF 1995). The alternative approaches – experimental determination of a BCF, or derivation of a  $\log P_{ow}$  using quantitative structure-activity relationships (QSARs) – would appear to be equally unreliable for surfactants.

A wide range of surfactants is used offshore, for a number of different purposes, although the quantities of each class of surfactant used are difficult to estimate. It is considered that the most important environmental issues in relation to surfactant use/discharge offshore are whether the surfactants pose a risk as a result of direct toxicity in the aqueous environment, or whether biodegradation, bioaccumulation and biomagnification of surfactants poses a greater risk to the marine environment.

EOSCA commissioned a review to collate and assess currently available data on bioaccumulation potential of surfactants ( $\log P_{ow}$  and BCF) in order to address a number of issues. This paper gives a brief summary of the salient points of this review.

## 2 ENVIRONMENTAL ISSUES

All major surfactant groups (anionic, cationic, nonionic and amphoteric) are currently used to some extent by the offshore oil industry (see Table 1).

<b>SURFACTANT CATEGORY</b>	<b>TYPE</b>	<b>USED IN PRODUCTS OF TYPE*</b>	<b>CURRENTLY IN USE IN NORTH SEA</b>
Alkyl aryl sulfonates	Anionic	EB, CI	Yes
Alkyl sulfates	Anionic	AF	Yes
Alkyl ethoxylate sulfates	Anionic	AF	Yes
Phosphate esters	Anionic	CI	Yes
Quaternary ammonium compounds	Cationic	CI, BC	Yes
Fatty amine salts	Cationic	CI	Yes
Fatty acid amides	Cationic	EB	Yes
Imidazolines	Cationic	CI	Yes
Alkyl phenol ethoxylates	Non-ionic	CI, BC, EB	No
Alkyl poly glycosides	Non-ionic	CI	Yes
Ethoxylate-Propoxylate polymers	Non-ionic	EB	Yes
Fatty alcohol ethoxylates	Non-ionic	BC, CI, EB	Yes
Betaines	Amphoteric	CI	Yes

\*Key: **AF**, antifoam; **BC**, biocide; **CI**, corrosion inhibitor; **EB**, emulsion breaker

**Table 1. Summary classification of currently used/discharged oilfield surfactants and their general applications in the North Sea.**

Nonionic surfactants are the most widely used, with perhaps the greatest concern focusing on bioaccumulation potential of alkylphenolethoxylates, for some of which there is tentative evidence of weak endocrine disruption activity. Interest in the bioaccumulation of surfactants has increased over recent years due to the large quantities of these materials manufactured and the relatively high proportion discharged to the environment. In environmental terms, surfactants possess properties that mean that their fate and behaviour in an aqueous environment will differ from that predicted for non-surface-active chemicals. In particular, they all have a combined lipophilic/hydrophilic structure which gives them a tendency to collect at aqueous/organic-phase boundaries, and they will form micelles in water when present above critical levels (CMC). Most surfactants are susceptible to biodegradation, metabolism and other breakdown reactions that may lead to metabolites with significantly different chemical properties.

The quantities of each class of surfactant used are difficult to estimate. As an approximation, anionic surfactants are the most important, representing 60-70% of surfactants currently in use. Non-ionic compounds constitute around 30% but their use is increasing, while cationic and amphoteric products make up the smallest proportion. Currently adopted approaches to hazard assessment and risk management of chemicals, including surfactants, used and discharged offshore in the North Sea are based on a harmonised scheme of testing and evaluation (Harmonised Offshore Chemical Notification Format, OSPAR HOCNF 1995; and CHARM). The octanol-water partition coefficient ( $\log P_{ow}$ ) has been defined as a central parameter in the risk assessment of offshore chemicals, being used to estimate predicted environmental concentration (PEC) through its use in partitioning calculations (CHARM), but the evidence is not convincing enough to support the view that it is a key parameter, especially for surfactants or complex mixtures. There are a lot of experimental data which indicate that it is often useless in this respect for

oilfield chemicals, and that indeed there is no single partition coefficient for many chemicals (i.e., their partitioning behaviour depends on various factors such as salinity, pH and temperature). Log  $P_{ow}$  demonstrably does *not* determine environmental fate, although it is used for this purpose.

If log  $P_{ow}$  is not considered to be satisfactory for bioaccumulation prediction, then it is not only unsatisfactory for sediment partitioning estimation, but it is *a priori* unsatisfactory for estimating the amount released in produced water. Surfactants are important, and often significant (in terms of quantity) components of production chemicals, and using current approaches, log  $P_{ow}$  is clearly an unsatisfactory parameter as a basis for hazard and risk assessment of surfactants and/or highly hydrophobic chemicals. The current (mandatory) test methods adopted in the HOCNF (OECD 117 HPLC method or OECD 107 Shake Flask method) are inherently unsuitable for the determination of a log  $P_{ow}$  for surface-active chemicals, not least because of the tendency for surfactant molecules to accumulate at phase interfaces or form emulsions, thereby giving spurious and unreliable results. Despite these obvious limitations, regulatory authorities have based environmental hazard and risk assessment of surfactants on log  $P_{ow}$  data obtained from these tests (HOCNF). In reality the existing OECD 117 HPLC method is being misused by being applied to formulations of "unknown" content, and in particular the estimation of a weighted-average log  $P_{ow}$  for anything other than a group of homologues cannot be construed as scientifically valid. Intended changes to the present requirements of the HOCNF (Summary Record SEBA 2000) propose that log  $P_{ow}$  determinations for surfactants should be abandoned in favour of a sediment-water partitioning coefficient ( $K_{oc}$ ), and that default values should be used for fraction released to water and for bioconcentration factor (BCF). This should be regarded as only a temporary measure, until industry and regulatory authorities have explored other approaches or looked at ways of improving current methodology, particularly focusing on some of the large-volume surfactants currently in use.

A factor that has been largely overlooked in the environmental assessment of surfactants, apart from the intrinsic toxicity of the surfactant, is that of the potential synergistic effects on migration, dispersion, bioavailability, etc. of otherwise low-toxicity chemical compounds in a formulation. The current HOCNF guidelines accept that surfactants may increase the bioavailability of other substances in preparations, and suggest that a bioconcentration test may be required in such cases. However, it is difficult to justify a "black box" regulatory approach that relies on a single and often arbitrary measurement. Any assessment of bioaccumulation potential should, realistically, take into account as much information as possible on the chemistry, metabolism, degradability and potential breakdown products of the chemical. With oilfield chemicals, this can be difficult, since they are often quite complex mixtures and their chemistry is often very poorly described.

Default fraction released values estimated from available log  $P_{ow}$  data and adopted in CHARM evaluations are viewed as extremely conservative, as exemplified by the often significant disagreement (up to an order of magnitude or more) between adopted values and those determined by field validation studies on various surfactants Table 2.

Type of surfactant	Default fraction released	Fraction released in field validation studies
Primary amines (cationic type C>12)	0.1 (10%)	0.038 (3.8 %) <sup>1)</sup>
Quaternary amines	1.0 (100%)	
Ethoxylate-Propoxylate (Eo-Po) Block polymer demulsifier	0.4 (40%)	
Imidazolines	0.1 (10%)	0.01 (1.0 %) <sup>2)</sup>
Amines	0.1 (10%)	
Phosphate esters (anionic type C>13)	0.1 (10%)	0.002 (0.2 %) <sup>1)</sup>
Other	1.0 (100%)	

<sup>1)</sup> TNO: Fokema et al. (1998)

<sup>2)</sup> Statoil: Sæten et al. (1999)

**Table 2 Default values (from Thatcher et al. 1999) and results from field validation studies for the fraction released of surface-active production chemicals**

The list of default fraction released values, i.e. chemical discharge factors established in CHARM table some surfactant categories should be expanded to include all the relevant surfactant categories/classes included in this review. There are doubts that it is practical to relate such default values to the water-cut. Measured values are “real”, but can only be related to the particular operation at the time of the measurement, since the process is unlikely ever to be in equilibrium. Factors determined this way may thus be a valid tool for documentation, but the results may be inappropriate for modelling over the lifetime of a field. Site-specific environmental risk assessment should preferably be based on experimentally determined discharge factors obtained from mass-balance studies (e.g. Sæten et al. 1999; Bakke et al. 2000). If the circumstances upon which the site-specific discharge factors have been determined are studied in detail, it could be judged whether the same figures could be applied under other conditions (expert judgement).

### 3 RELIABILITY OF EXISTING DATA

Physico-chemical properties of a substance, such as solubility, Pow and sorption properties, are parameters that can be used early in an evaluation process to assess its likely fate and to determine the environmental compartments into which it will partition. An octanol-water partition coefficient can be used to predict BCF, and in many cases molecular structure has been used to estimate Pow, using so-called 'fragment contribution' methods. These fragment methods do not, however, take into account the branching positions on the molecule, and may therefore not give a true representation of bioaccumulation potential. For some molecules there are significant differences between the results obtained using different calculation methods, and as the complexity of the surfactant molecule increases the reliability of the methods decreases. The development of QSARs to predict partition coefficients has been a useful approach to reducing the need for extensive live animal or surrogate testing, but such approaches require extensive validation before they can be adopted and used with any degree of confidence. The available data indicate that the use of QSARs to estimate log Pow for some classes of surfactant are not reliable. Not least, the development of QSARs depends on valid data on which to develop the relationship. For surfactants, the reliability of existing Pow data is questionable. The OECD 117 HPLC method, for example, adopts a QSAR approach to the estimation of a

log  $P_{ow}$  for a substance, but for surfactants there are insufficient established log  $P_{ow}$  values for specific surfactant molecules to enable a valid calibration of the system.

Experimentally derived log  $P_{ow}$  values were found for a small number of surfactants (Tolls et al. 1995). However, the formation of emulsions must be regarded as a serious problem when determining octanol-water partition coefficients for surfactants, and for ionic surfactants the use of current techniques will most likely yield distribution ratios rather than partition coefficients. For this reason,  $P_{ow}$  cannot be regarded as characterizing the partitioning of ionic surfactants, and current data obtained using OECD 107 or 117 tests cannot be viewed as valid. The majority of surfactant log  $P_{ow}$  data have been derived by calculation, many using equations based on the fragment contribution methods of Leo and Hansch (1979). Calculation methods are based on the theoretical fragmentation of the molecule into suitable substructures for which reliable log  $P_{ow}$  values are known. The log  $P_{ow}$  is obtained by summing these fragment values and applying correction factors for bonding, branching etc. However, the validity of calculated values must be questioned since the reliability of the various calculation methods decreases as the complexity of the molecule increases, and interpretations may often be subjective.

The existing BCF data set for surfactants is relatively small, with the majority of data relating to anionic surfactants, particularly LAS. Some data is available for cationic and nonionic surfactants, but no data were found for amphoteric surfactants. The usefulness of the data is limited by the lack of a unified approach to experimental determination of a BCF. Measurement of a BCF for a surfactant is an alternative to estimation of  $P_{ow}$ , but this approach can also be problematic. There is often significant variability in BCFs determined for the same surfactant with different species, and also for the same surfactant tested on the same species (e.g. Tolls et al. 1994). In addition, the vast majority of studies have been carried out on freshwater species. As indicated by Tolls et. al. (1995), much of the available data can only be used tentatively since it has been derived from experiments using radiolabelled compounds. Very few such studies can differentiate between parent compounds and metabolites or other breakdown products. Because of this limitation, many reported BCFs are probably significant overestimates. In general, BCFs for surfactants are reported as being comparatively low, and are generally below the conventional criteria for concern (i.e. log  $P_{ow}$  value of 3 - 4).

#### 4 RELEVANCE OF log $P_{ow}$ /BCF TO SURFACTANTS

In principle, partition coefficients are not relevant to surfactants since they do not partition between immiscible solvents such as octanol and water, but will tend to accumulate at the phase interface or form emulsions at high concentrations. The question should really be 'how relevant are existing (or potentially new) techniques to assessing the passage of surfactants across a biological membrane?', or 'how likely is it that a surfactant molecule will cross a biological membrane?'. In view of the surface-active properties of this class of chemicals, this consideration naturally leads on to the question of whether discharge of surfactants poses a risk as a result of *direct toxicity* in the marine environment, or whether *biotransformation*, *bioaccumulation* and/or *biomagnification* of surfactants constitute a greater risk.

In the longer term, the exposure of organisms to surfactants in the marine environment will be dependent on the fate and behaviour of this class of chemicals when discharged. In

general terms, surfactants may be removed from the marine environment by mechanisms such as volatilisation, abiotic degradation, adsorption to particles, microbial degradation or uptake by marine organisms, factors that are applicable for any type of chemical. Volatilisation is not likely to be a significant factor because of the relatively high aqueous solubility and low/negligible vapour pressures of most surfactants. Surfactants are likely to adsorb to sediments, although sorption of surfactants on marine sediments has received little attention. Generally speaking, sorption behaviour of surfactants on marine sediments is consistent with observed characteristics in freshwater sediments, although other factors such as salinity, organic carbon content, temperature and pH may be important.

The studies and data reviewed in this report indicate that the majority of surfactants are susceptible to biodegradation, both aerobic and anaerobic. Compared to freshwater studies, there is a limited data set of biodegradation values for surfactants in the marine environment. The majority of studies on the environmental fate and behaviour of surfactants in the marine environment have been carried out on LAS and other anionic surfactants. The general conclusion must be that surfactants are not likely to be persistent in the marine environment, although there is an observed trend of slower rates of biodegradation in marine compared to freshwater environments. For this reason a safety factor is applied in CHARM when only freshwater data are available. Therefore, while sediment sorption processes are undoubtedly of significance in reducing water column exposure concentrations of surfactants in aqueous environments, the most important process controlling the environmental fate of surfactants in the marine environment is undoubtedly biodegradation. Sorption will result in a redistribution of surfactants from water to sediments, while biodegradation results in a net loss of chemical from environmental compartments. However, with regard to environmental exposures, the primary consideration when reviewing biodegradation characteristics of surfactants, or any chemical for that matter, is that it is not the extent of biodegradation over an arbitrary time period that is important, but rather the rate of biodegradation compared to residence time in an environmental compartment that will ultimately determine exposure. Environmental exposure will vary, depending on solution strength, application method and rate, the degree of dilution and dispersion, and meteorological conditions. Subsequent biodegradation of surfactants will affect exposure concentration and duration, although the toxicity of surfactant metabolites is an issue on which no studies were found. Lewis (1991) notes that although comprehensive data on effect and exposure exists for LAS, comparable information is not available for other surfactants, especially in the marine environment. Consequently, existing risk assessments should be considered to be of limited validity since they are based on extrapolated data and may be inapplicable to all marine species and all surfactant classes without extensive validation.

Current scientific understanding of the toxic effects of surfactants is based mainly on laboratory experiments for a few freshwater species. As a result, extrapolation of existing laboratory data to the marine environment is difficult. As a general observation, most surfactants appear to be less toxic in the environment than would be inferred from laboratory tests (Lewis 1990). Current awareness of surfactant toxicity to aquatic organisms, and apparent trends in toxicity in relation to different surfactant classes should be viewed with caution and broad generalisations avoided as the range of species tested and the number of different surfactants involved is limited. A taxonomic cross-comparison of the surfactant toxicity data in this review highlights the difficulties in identifying trends in surfactant toxicity. For acute toxicity studies with anionic surfactants the algae and fish species tested appear to be most sensitive, with the molluscs showing an intermediate sensitivity and crustaceans being the least sensitive. However, larval stages of crustacean

species appear to show significantly higher sensitivity to this class of surfactant than adults.

Surfactants generally seem to impact on higher aquatic organisms via their respiratory structures. In invertebrates such as crustaceans these may be simple external gills or areas of specialised cells on the body surface. In higher organisms such as fish the respiratory structures (gills) consist of epithelial membranes that may be extensively folded to provide large surface areas for gaseous exchanges. Destabilisation of these epithelial membranes, as may occur when exposed to surfactants, results in changes in membrane permeability, cellular lysis, and impairment of cellular respiration. In lower organisms, in which exchange of respiratory gases is via mechanisms of simple diffusion across membrane surfaces, surfactant toxicity appears to result from an initial disruption of normal membrane function followed by physical disruption of the cellular membrane. As might be expected, charged surfactants (anionic and cationic) appear to have a greater denaturing effect than neutral surfactants. Cationic surfactants also appear to be the most toxic to both freshwater and marine species of algae, invertebrates and fish.

Although only a limited range of surfactants has been investigated for aquatic toxicity, a few studies have illustrated a difference in toxicity between surfactant classes. Lewis (1990) noted that the toxicity of different surfactants on the same algal test species might vary over four orders of magnitude. Charged surfactants (anionic and cationic) have been reported to have a greater denaturing effect than neutral chemicals, and cationic surfactants are generally considered to be most toxic to both freshwater and marine algae, invertebrates and fish (Ukeles 1965; Lewis 1991). It is possible that existing HOCNF data includes reference to toxicity of various oilfield surfactants to marine organisms, and if made available, these could usefully supplement the comparatively limited marine data available in the public domain. However, the current emphasis on toxicity testing of complete preparations will mean that few such studies will be relevant.

Surfactant toxicity has also been found to vary between homologues within a given surfactant type and may also depend on chemical structure. Increasing the length of the alkyl chain can modify toxicity of LAS, and toxicity of nonionic ethoxylated surfactants depends on the length of the ethoxylate chain (Lewis 1991 and references therein). In some cases, toxicity may be predicted from the ethylene oxide molar ratio, with a ratio of 15 or less being associated with the most toxic surfactants and ratios of 30-50 being consistent with observations of low toxicity (Scott Hall et al. 1989). This observation applied both for a given series of homologues and across various surfactant types.

In reviewing the potential of surfactants to bioaccumulate, a general association of increasing alkyl chain length (i.e., increasing hydrophobicity) with an increase in BCF was noted (Tolls et al. 1997, 2000) for LAS compounds and isomers, and alcohol ethoxylate components. Conversely, increasing the length of the hydrophilic section of a surfactant molecule (i.e., decreasing overall hydrophobicity) results in a reduction in BCF (reviewed in Staples et al. 1998). Tolls et al. (2000) also found increased uptake rates and BCFs for alcohol ethoxylate surfactants when hydrophobicity was increased. These apparent steric influences on surfactant toxicity and BCF appear to be consistent, and may offer a means of predicting likely toxic effects of surfactants on marine organisms through a consideration of steric factors. A more thorough evaluation of existing data may be useful, particularly if combined with further investigative studies, to establish and validate some general principles describing the relationship between surfactant chemistry

(molecular/steric factors) and toxicity/BCF. If modifications to the molecular structure of surfactants can result in predictable influences on bioaccumulation and toxicity to aqueous organisms, then environmental effects of new formulations could be predicted at an early stage in product development.

A tendency for surfactant molecules to be retained on epithelial surfaces, rather than to cross cellular/epithelial membranes (uptake) and hence bioaccumulate, may be a possible explanation for the longer-chain/lower-toxicity observations. Surfactant molecules residing (bound) on an epithelial membrane surface may be expected to disrupt membrane integrity (permeability/fluidity), and interact with mucus (a charged, fibrous glycoprotein-carbohydrate matrix). Studies of the effects of sodium lauryl sulphate (SLS) and LAS at concentrations of 100 mg l<sup>-1</sup> showed that the integrity of the upper layers of the epithelium of fish gills was severely disrupted, resulting in severe water imbalance. However, the test concentrations used are several orders of magnitude greater than would be expected in the environment. At low concentrations (e.g. 6 µg l<sup>-1</sup> of SLS) some effects are reversible, indicating temporary binding to specific sites (Stagg et al. 1981). The number of binding sites on epithelial or cellular membranes is usually limited, resulting, for example, in transmembrane transport mechanisms that display saturation kinetics. If a critical number of (surfactant) molecules must occupy the available binding (transport) sites in order for lethal poisoning to occur, then surfactants that can more easily cross the membrane and bioaccumulate (as indicated by a higher BCF) are less likely to exhibit acute toxic effects. In general, BCFs for surfactants are reported as being comparatively low, and are generally below the conventional level for concern (i.e. log  $P_{ow}$  value of 3 - 4). Although considerable evidence of surfactant bioaccumulation has been collected and published, lower lethal toxicity associated with an increased BCF would argue in favour of the contention that it is not surfactant bioaccumulation *per se* which is of concern, but direct toxicity.

Biotransformation and biomagnification are processes that may occur once a chemical has entered an organism (bioaccumulated). Evidence for biotransformation of surfactants in aquatic organisms is scant, and limited to radiolabel studies. For the few surfactants investigated (e.g., C<sub>14</sub>EO<sub>8</sub>: Tolls and Sjim 1999; C<sub>12</sub>-LAS and C<sub>13</sub>-LAS: Tolls et al. 1997), biotransformation was deduced to be the dominant factor in the elimination of these surfactants from the test organisms.

In order for biomagnification of a chemical to take place the compound must be stable in the environment for significant periods of time. Compounds which (bio)degrade relatively rapidly or which are readily metabolised (biotransformed) will not be biomagnified within the food chain. While the bioaccumulation of a chemical can still present a problem where exposure levels and uptake rates are sufficiently high in relation to depuration and metabolism rates, a high bioaccumulation potential does not automatically imply the potential for biomagnification. Indeed, for some chemicals, which are readily taken up by organisms near the bottom of the food chain, a capacity for metabolism is more likely in successively higher trophic levels. In some cases, calculated BCF values for surfactants in higher aquatic organisms (fish) were found to be 30-3000 times lower than values for algae (Ahel et al. 1993). The available information indicates that most commonly used surfactants do not have the properties required to exhibit biomagnification, i.e., they have a tendency to be rapidly degraded and metabolised and are not highly hydrophobic.

In conclusion, no evidence has been found to support concern with respect to the biomagnification of surfactants, although it is noted that most of the research effort has been devoted to a relatively small number of surfactant types. Bioconcentration factors in the aqueous phase are generally below the level of concern, and (for some nonionic surfactants at least) can be quantitatively related to the length of the hydrophobic and hydrophilic components. There is also evidence that overall molecular size may place constraints on biological uptake. The studies examined raise no concerns with respect to long-term retention of accumulated surfactant material in tissue, and indeed they present considerable evidence that many surfactants are metabolised. The fate of metabolites has not been thoroughly studied, however, and there is consequently a degree of uncertainty as to the fate and longer-term effects of some hydrophobic components (such as some alkylphenols) following partial metabolism.

## 5 ALTERNATIVE ANALYTICAL APPROACHES

In respect of the potential developments in analytical techniques the following questions should be addressed:

- Are the new methods likely to offer a better alternative to the existing ones?
- How practical and relevant are these new techniques to surfactants?
- Are surrogates to live animal testing reliable?
- Are the new methods suitable for standard tests?

Surfactant behaviour cannot be related to partitioning between two disparate liquid phases because of their inherent tendency to collect at phase interfaces or to form emulsions (micelles), placing the existing methods of estimating BCF in doubt. The lack of a widely-applicable, robust and simple method to assess bioaccumulation potential and sediment/water partitioning of surfactants has hindered the establishment of a rational and hence meaningful evaluation of the environmental hazards and risks that surfactants may pose. Surrogates to live animal testing are always preferable, and it is likely that the recently introduced MEEKC technique will provide a more valid result in the form of a pseudo-log  $P_{ow}$ . The technique has been used to investigate octanol-water partitioning of a wide range of organic compounds giving a good correlation with HPLC-generated values for simple organic molecules (Smith and Vinjamoori 1995). Salimi-Moosavi and Cassidy (1996) used the technique to separate long-chain surfactants and have further investigated the potential of the technique for surfactant applications. The newly developed techniques of MEEKC use the properties of surfactants to great effect in the analytical process. Currently in reverse-phase HPLC there is a tendency for irreversible adsorption of some compounds. This is not the case with MEEKC. It is a fact that products are often presented for testing as a mixture of substances, for which no useful (in analytical terms) information on the formulation is provided. There is therefore little possibility to apply a "correct" analytical technique. The MEEKC approach seems to offer a broader scope for a wider range of compounds even if a series of different conditions needs to be used on a formulation.

The indications from the literature are that the MEEKC technique would be very suitable as a standard method. It also seems feasible that the equipment could be used to determine log  $P_{ows}$  of ordinary compounds, and there are references citing the use of diode array

detection. While capillary electrophoresis is not as widely used as HPLC, there are at least two commercial models available at comparable cost to a HPLC system. Test costs are therefore likely to be similar to those for current log  $P_{ow}$  analysis.

The suitability of SPMDs as an alternative surrogate technique to live animal testing for estimation of BCFs for surfactants needs to be more closely investigated. Although a good relationship between BCFs for PAHs obtained using SPMDs and live animal tests on blue mussels, *Mytilus edulis*, (Røe et al. 1998), the intrinsic properties of surfactants may pose problems when interpreting data from the use of such devices. The justification for using SPMD is based on uptake and BCF for lipophilic chemicals, and the whole question centres on whether lipophilic descriptors are valid for surfactants – this seems illogical. The use of an SPMD requires analysis of the solvent inside the device – if surfactants sit on or in the semi-permeable membrane, there might possibly be very little material present in the solvent phase inside. BCF tests are considered to be prohibitively expensive, but the main cost element is the chemical analysis, not the ‘biological’ component. If it is necessary to analyse both the water and the content of the SPMD, then the cost of the work will not be very different from the cost of a BCF, and the primary advantage would be that a SPMD might equilibrate faster than an experimental animal. In BCF tests, actual uptake and depuration rates are measured, and the resulting estimate takes account both of passive depuration and metabolic transformation. SPMDs will model only passive processes.

A weakness of the OECD 117 method is that it does not always provide a reliable indication of the *quantity* of each component present – in fact, in some instances the peaks detected represent only trace components or solvents and active ingredients are not registered at all. Surfactants submitted for testing may often be complex mixtures, rather than pure compounds, and the analytical costs associated with alternative surrogate techniques may be multiplied accordingly. When adopting alternative approaches, it might be better to focus initially on a selected range of widely used ‘generic’ individual surfactant compounds, and use the resulting data as a form of range-finding exercise. In any case, the ‘success’ of the studies will depend critically on the precision of the chemical assays that are developed – even using the SPMD it will be necessary to analyse for individual compounds both in the internal solvent and in the exposure medium. The SPMD method seems to simply represent a technical improvement of the OECD 107 shake-flask method, but would still be subject to the same constraints when applied to surfactants, although the formation of emulsions would be avoided. For all its shortcomings, a practical advantage of the OECD 117 method is that it is possible to ‘analyse’ mixtures, without the need for compound-specific analytical methods (and without in most instances knowing which compounds are represented by the chromatography peaks).

Current developments in SPMD technology involve fairly large-scale test systems that would impose unacceptably high costs on current testing requirements, and in many cases practical restraints on a general widespread adoption of the method. There is obviously a need for ‘laboratory scale’ systems providing low-cost integrated methods suitable for use at realistic environmental concentrations. Small SPMDs suitable for laboratory use are under development, but their suitability for use with surfactants or other highly hydrophobic chemicals is currently unknown. However, in any program designed to develop an alternative surrogate technique for estimating surfactant BCFs, a sufficiently large number of chemicals will need to be examined in order to derive an independent QSAR. In view of the likely cost restraints, it is almost inevitable that there will be greater reliance on existing data. A thorough review of the literature with a view to defining

exactly what (in terms of reliability and precision) could be achieved from existing data is therefore desirable. This review provides a sound basis on which to further develop this approach. Such an assessment can then be compared with estimates of what could be achieved from an acceptable (in terms of time and cost) experimental programme, and an assessment made as to whether such a programme would actually offer real, quantifiable benefit in terms of the quality of the QSAR. Pragmatically, there is no advantage in having a more thoroughly validated data set if it does not result in a tangible improvement in precision and reliability.

The main stumbling block to further development of the QSAR approach to BCF estimation is the substantial effort and cost that would be associated with establishing experimental BCF values with which to compare surrogate measures. A unified (harmonised) approach to BCF testing in live animals is currently lacking, reflected by the uncertainty of the reliability of existing BCF values. The time and cost of developing appropriate extraction and analytical methods for a suitably large number of surfactants would be high; before starting, it would be essential to set targets for recovery and precision, so that it would be possible to judge when sufficient work had been done to deliver a reliable and useable method. There would be no point in correlating an experimental measure with a surrogate measure if the confidence limits on the former were as high as  $\pm 100\%$ . Setting such performance parameters should be an integral part of any such project.

## 6 GENERAL CONCLUSIONS:

1. There is limited ecotoxicological data for surfactants in the marine environment.
2. BCFs for surfactants in the aqueous phase are generally below the level for concern. Many reported concentration factors are probably overestimates.
3. BCFs derived from current QSARs based on log Pow data for surfactants are not reliable.
4. Existing data does not indicate a specific generic problem with aquatic toxicity or persistence.
5. There is no evidence to support concerns with respect to biomagnification of surfactants.
6. There is no evidence to support concerns with respect to long-term retention of bioaccumulated surfactants.
7. Two surrogate partitioning techniques which may be usefully explored as alternative approaches to determining partition coefficients for surfactants are:
  - MEEKC (MicroEmulsion ElectroKinetic Chromatography)
  - SPMD (SemiPermeable Membrane Devices)

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