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Effect of sediment properties on the sorption of C_{12}-2-LAS in marine and estuarine sediments

Ángeles Rico-Rico [a,*], Ali Temara [b], Thilo Behrends [c], Joop L.M. Hermens [a]

[a] Institute for Risk Assessment Sciences, Utrecht University, Yalelaan 2, 3508 TD Utrecht, The Netherlands
[b] The Procter & Gamble Company, Central Product Safety, Temselaan 100, 1853 Strombeek-Bever, Belgium
[c] Department of Earth Sciences-Geochemistry, Faculty of Geosciences, Utrecht University, 3508 TA Utrecht, The Netherlands

Sorption of C_{12}-2-LAS to marine sediments mainly depends on both clay and organic carbon content. The importance of each parameter varies with the surfactant concentration.

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ABSTRACT

Linear alkylbenzene sulfonates (LAS) are anionic high production volume surfactants used in the manufacture of cleaning products. Here, we have studied the effect of the characteristics of marine and estuarine sediments on the sorption of LAS. Sorption experiments were performed with single sediment materials (pure clays and sea sand), with sediments treated to reduce their organic carbon content, and with field marine and estuarine sediments. C_{12}-2-LAS was used as a model compound. Sorption to the clays montmorillonite and kaolinite resulted in non-linear isotherms very similar for both clays. When reducing the organic content, sorption coefficients decreased proportionally to the fraction removed in fine grain sediments but this was not the case for the sandy sediment. The correlation of the sediment characteristics with the sorption coefficients at different surfactant concentrations showed that at concentrations below 10 µg C_{12}-2-LAS/L, the clay content correlated better with sorption, while the organic fraction became more significant at higher concentrations.

1. Introduction

Linear alkylbenzene sulfonates (LAS) are high production volume surfactants commonly used in the formulation of industrial and domestic cleaning products. Commercial LAS consist of a mixture of several isomers with an alkyl chain length of 10–13 carbon atoms, and a benzene-sulfonate group at the para position, attached to the carbon chain. The average number of carbon atoms in the alkyl chain of commercial LAS is 11.7–11.8 (Sanderson et al., 2006).

LAS reach the marine environment by urban and industrial wastewater effluents and can be detected mainly in the sediment, due to their affinity to sorb to the particulate material (Knepper et al., 2003). Monitoring studies have reported concentrations up to 238 mg/kg of LAS in coastal areas in the Northeast and South of Spain close to wastewater effluents (primary or no wastewater treatment at all) (Gonzalez et al., 2004; Petrovic et al., 2002). The sorption of the various LAS homologues and isomers in sediments will likely drive its bioavailability to the endofauna.

The sorption of a compound to sediment depends on the physico-chemical properties of the chemical, the water composition and the sediment characteristics. A number of authors have reported on the effects of the test system (salinity, temperature, etc) or the sediment matrix characteristics (organic carbon content, particle size, metal oxides, etc) on sorption, but a mechanistic model for the sorption of LAS is not yet available. LAS sorption increases with the number of methyl groups in the alkyl chain and with the position of the phenyl group (Hand and Williams, 1987; Westall et al., 1999) likely because the strength of van der Waals interactions increases with an increase in the chain length. Isomers with the phenyl position closer to the end of the alkyl chain have more available surface for van der Waals forces (Hand and Williams, 1987) leading to higher sorption affinities. An increase in sorption with the salinity was observed in marine sediments (Rubio et al., 1996), and with the increase in H^+ concentration in riverine sediments (Di Toro et al., 1990; Westall et al., 1999).

Several studies have shown that LAS sorption to sediments and soils is correlated with the organic carbon or the clay content (Doi et al., 2002; Fytianos et al., 1998; Matthijs and De Henau, 1985; Westall et al., 1999). Considering that organic carbon and clay contents are usually well related to each other in sediments, it is not clear yet which of these two components control LAS sorption. Sorption of LAS to soil and sediment has also been related to aluminium oxides content (Kristiansen et al., 2003; Matthijs and De Henau, 1985; Westall et al., 1999), or the concentration of iron

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* Corresponding author. Tel.: +31 30 253 5018; fax: +31 30 253 5077.
E-mail address: a.ricorico@uu.nl (Á. Rico-Rico).

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oxides (Kristiansen et al., 2003). Amorphous iron oxides showed a higher sorption affinity than crystalline iron oxides due to the larger surface area of the first one (Kristiansen et al., 2003). In summary, sorption of LAS to sediment has been related to both non-specific (van der Waals) and specific (polar) interactions and this is not surprising because the LAS molecule has both a non-polar and polar functionality.

The understanding of the key parameters that characterize the bioavailability of chemicals in marine sediments is still limited. To our knowledge, few studies have been performed on the sorption of LAS in marine sediments (Fytianos et al., 1998; Rubio et al., 1996), and these studies were focused on the effect of aqueous chemistry rather than sorbent characteristics. Sorption studies with riverine sediments are a helpful first approach but do obviously not consider the specifics of seawater composition. Seawater composition is characterized by a high salt content and a relatively constant pH. Sorption coefficients for LAS in seawater media are often higher than in the freshwater environment (Knepper et al., 2003). Higher concentrations of divalent cations, especially Ca^{2+}, will affect the solubility of LAS in the seawater as well as the intensity of its sorption to the marine sediments. The effect of Ca^{2+} on the sorption of anionic surfactants has already been investigated in studies where the ion concentration was changed (Jones-Hughes and Turner, 2005; Westall et al., 1999). The increase in sorption was explained by a decrease in the negative charge of the sediment particles due to the adsorption of Ca^{2+} to the particle surface that consequently favours electrostatic interactions.

The objective of this work is to determine which characteristics of marine sediments influence the sorption of LAS. Besides the testing of field marine and estuarine sediments, this work presents for the first time the contribution of individual sediment constituents under seawater conditions. For this purpose, sorption experiments with pure clays, sea sand, sediments, and sediments treated to reduce their organic carbon fraction, were performed with the model compound 2-*n*-(*p*-sulfophenyl)dodecane (C_{12}-2-LAS). Next, several field sediments were characterized in terms of organic carbon, clay content, specific surface area and iron and aluminium oxides. Sediment characteristics were then correlated with the distribution coefficients at different surfactant concentrations in order to understand the main denominators that affect the sorption in the complex sediment matrix.

2. Materials and methods

2.1. Chemicals

C_{12}-2-LAS (97.4% purity) was synthesized in our laboratory by Dr. J.Tolls. Surfactant stocks were made in analytical methanol obtained from Lab-Scan (Dublin, Ireland). Artificial Seawater GP2 medium ($pH = 8.3$) (Environmental Protection Agency, 2002) was made from deionized water prepared with Millipore Milli-Q purification system (resistivity of circa 18 MΩ cm) by adding the salts NaCl, Na_2SO_4, KCl, $Na_2B_4O_7 \cdot 10H_2O$, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$, $SrCl_2 \cdot 6H_2O$ and $NaHCO_3$ (all from Merck, Darmstadt, Germany) and KBr and KCl salts (Fluka, Buchs, Switzerland). NaN_3 (10 mM; Merck, Darmstad, Germany) was used as a biocide to avoid biodegradation during the experiments. NaOCl and HCl used for the reduction of the organic fraction were obtained from Fluka (Buchs, Switzerland) and Merck (Darmstad, Germany), respectively.

2.2. Collection and characterization of the sediments and materials properties

Marine and estuarine sediments were collected from the North Sea "Friese Front" area (North Sea 1, 2, 3) and the Eastern Scheldt estuary (Oesterput) in The Netherlands and from four different locations in the Southwest of Spain (La Antilla and Espigón areas in Huelva, Cádiz and San Fernando in the Bay of Cádiz). Freshwater sediment from the Drontermeer Lake (The Netherlands) was only used for the study of the effect of the organic carbon content on the sorption of LAS to sediments and was supplied by Aquasense (Grontmij, The Netherlands). Sediments were sieved (500 μm mesh) and stored at 4 °C until their use. The background concentrations of LAS in all areas were relatively low (<0.2 mg LAS/kg). Sea sand purified by acid and calcined was obtained from Merck (Darmstadt, Germany). Standard kaolinite (K Ga-1) obtained from Washington County (Georgia, USA) and Ca-montmorillonite (SAz-1) from Apache County (Arizona, USA) was kindly provided by the Geochemistry group of the Department of Earth Sciences at Utrecht University. Both clays were first equilibrated in artificial seawater to avoid differences in the composition of the ions in the media during the sorption experiments. The equilibration was performed as follows: 5 g of clay was suspended in 20 mL of seawater and sonicated in two steps of 30 min. The samples were then centrifuged at 3000 rpm and the supernatant was carefully removed. The clay samples were homogenized and stored at 4 °C until their use.

Physico-chemical characteristics of the sediments and materials were determined according to standard procedures (Van Reeuwijk, 2002) at the Integrated Laboratory of the Faculty of Geosciences/TNO at Utrecht University, except for the Drontermeer Lake sediment that was characterized by Analytico Milieu B.V. (Barneveld, The Netherlands).

2.3. Removal of the organic fraction of the sediments

Two of the marine sediments (Cádiz and San Fernando) and the Drontermeer Lake sediment were treated to remove the organic fraction, following an adapted methodology with sodium hypochlorite as described by Mikutta et al. (2005) and Kaiser and Guggenberger (2003). Briefly, sediment samples of ca. 1 g (d.w.) were mixed with 45 mL of a solution of 1 M NaOCl adjusted to pH 8.0 with concentrated HCl. The suspension was shaken over 6 h, followed by a centrifugation at 3000 rpm during 30 min, and the supernatant was then discarded. The treatment was repeated five times and samples were subsequently washed with deionized water and left to dry in air. The organic fraction before and after this treatment was measured by loss of ignition at 500 °C. With the use of the NaOCl method, the effects of the treatment on the original matrix are minimized since the whole procedure is performed at room temperature and the natural pH of the marine sediments is not affected. Other traditional methods using H_2O_2 or Na_2SO_8 need prolonged heating (>40 °C), causing the transformation of poorly crystalline minerals into more crystalline forms and consequently reducing the surface area of the sediment materials (Siregar et al., 2005), ultimately affecting sorption characteristics.

2.4. Determination of the sorption coefficients

Experiments were performed at a density of sediment of 0.1 g (d.w.) in 20 mL seawater solution containing 10 mM NaN_3. Scintillation vials (20 mL) (Perkin Elmer, Boston, MA, USA) were used. For the sorption experiments with sea sand, 2 g of sand was used because of the low depletion from the aqueous phase by this material. C_{12}-2-LAS was spiked from a stock made in methanol, while keeping the amount of solvent in the sediment suspension below 1% of the total volume of the system. C_{12}-2-LAS aqueous concentration ranged from 0.02 to 2 mg/L, which are well below the Critical Micelle Concentration (105 mg/L; Smith, 1997). The system was left to equilibrate on a rolling device for 24 h at room temperature (20 ± 1 °C). Preliminary tests demonstrated that equilibrium was reached within this time period. The amount of NaN_3 added was adequate to suppress microbial degradation during the experiment. After equilibration, phases were separated by centrifugation (3000 rpm, 30 min) and analyzed (see below). The mass balance was tested for several concentrations and resulted 96.9 (±8.4)% showing that sorption to the walls of the used scintillation vials was negligible.

In most cases, the distribution coefficient (K_d) was calculated from the measured aqueous and sediment concentrations. For the rest of the samples, C_{12}-2-LAS concentration in the sediment was estimated from the decrease in the concentration of the aqueous phase assuming a 100% mass balance.

2.5. Sample treatment and chemical analyses

The clean up procedure of the water samples was performed by Solid Phase Extraction (SPE) using octadecyl reversed-phase silica (C18) columns (Supelclean™ ENVI™-18, 0.5 g, Supelco, Bellforte, PA, USA), using a similar procedure as developed and tested by Rubio et al. (1996). The columns were preconditioned with 4 mL of analytical methanol, followed by 5 mL of Millipore water. Next, the whole sample (ca. 20 mL) was transferred and the column was then rinsed with 15 mL of Millipore water. Eight millilitres of methanol were used to elude the C_{12}-2-LAS from the column.

Freeze-dried sediment samples (ca. 0.1 g d.w.) were extracted with 10 mL of methanol in an ultrasonic bath in two steps of 1 and 2 h. The methanol aliquots were collected in 20 mL scintillation vials and evaporated under a nitrogen gas flow. The dry extracts were then redissolved in 20 mL of Millipore water, and purified by SPE treatment as for water samples.

All samples were analyzed by Flow Injection Analysis (FIA) on a LC–MS/MS system, API 3000 triple quadruple analyzer (MDS Sciex-Applied Biosystems, Foster City, CA, USA). The interface was a Turbo ion Spray source used in the negative mode, the source temperature was 450 °C and the source gas flow was 7–8 L/min. Injection volume of the samples was 20 μL and the flow rate was 0.12 mL/min. C_{12}-2-LAS was measured by screening the molecular ion $[M - H]^-$ 325.20 *m*/*z* and the daughter ion 183 *m*/*z*.

In order to avoid the effects of the matrix components on the detection and quantification of C_{12}-2-LAS, a standard addition method was applied. Detection limit

Table 1
Characteristics of the sediments and materials.

Sediment	Al *d* (g/Kg)	Al *o* (g/kg)	Al *p* (g/kg)	Fe *d* (g/kg)	Fe *o* (g/kg)	Fe *p* (g/kg)	OC %	Clay %	SSA (m^2/g)
Marine or estuarine sediments									
Oesterput	0.19	0.26	0.19	3.52	3.74	1.11	1.38	6.99	46.02
Cádiz	0.07	0.04	0.06	0.45	0.11	n.d.	0.06	0.25	5.41
La Antilla	0.67	0.43	0.80	6.29	2.16	1.14	0.84	8.85	60.22
San Fernando	0.19	0.26	0.56	1.44	1.25	0.78	1.24	5.08	67.72
Espigón	1.87	1.66	0.32	16.12	9.87	1.60	0.99	11.90	75.55
North Sea 1	0.19	0.15	0.23	2.87	1.44	0.19	0.28	0.98	18.62
North Sea 2	0.20	0.22	0.15	3.28	2.17	0.10	0.27	1.21	18.83
North Sea 3	0.23	0.27	0.19	3.58	2.87	0.14	0.54	1.19	25.25
Lake sediment									
Drontermeer	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	9.52	15.00	82.00
Specific materials									
Kaolinite	0.34	0.27	0.28	0.51	0.23	n.d.	n.d.	n.a.	24.16
Montmorillonite	0.85	0.88	0.77	4.04	0.78	0.51	n.d.	n.a.	535.05
Sand	0.04	0.01	0.03	0.01	n.d.	n.d.	n.d	n.a.	2.60

n.d: Not detected; n.a: not analyzed.
d, *o* and *p* are the dithionite, oxalate and pyrophosphate extractions for aluminium and iron, respectively. OC% is the organic carbon fraction of the sediments and SSA is the specific surface area.

approached 1 μg/L for all measurements. Quantification was done using the software Analyst 1.4.1 (AB/MDS Sciex Instruments).

2.6. Data analyses

Experimental sorption data were fitted to the Freundlich isotherm:

$$\log C_s = \log K_f + n\log C_a \quad (1)$$

where C_s (mg/kg) and C_a (mg/L) are the concentrations of the surfactant in the sediment and in the aqueous phase at equilibrium, respectively. K_f (L/kg) is the Freundlich constant and n provides information about the linearity of the isotherm. Freundlich isotherms were fitted using GraphPad Prism version 4.00 for Windows (GraphPad Software, San Diego, CA, USA). Ordinary least square (OLS) regression was performed to relate the single sediment characteristics to the sorption coefficients. Principal component analysis (PCA) was used in order to group the different sediment characteristics. OLS and PCA were performed using Scan software Version 1.1 (Minitab, Coventry, UK).

3. Results and discussion

3.1. Sediment characteristics

A list of sediment characteristics is given in Table 1 and Fig. 1 represents the PCA score and loading plot for all the marine and estuarine sediments and their characteristics. This plot shows that the sediments collected from the North Sea and from Cádiz have relatively similar properties. These sediments show similarities in extractable metal composition (iron and aluminium), clay content and specific surface area. They furthermore contain low organic carbon content. On the other hand, the marine and estuarine sediments from Oesterput, La Antilla and San Fernando are similar regarding organic carbon, clay content and specific surface area, although their extractable aluminium and iron are relatively different. The Espigón sediment is clearly different from the other sediments and this is probably due to the very high clay and iron and aluminium contents of this sediment.

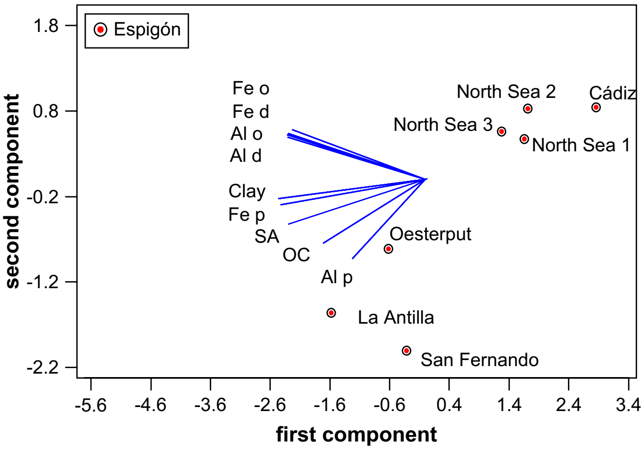

Fig. 1. Principal component biplot for all the marine and estuarine sediment characteristics. Al *p* and Fe *p* are the pyrophosphate extractions for aluminium and iron, Al *o* and Fe *o* the oxalate extractions and Al *d* and Fe *d* the dithionite extractions. OC is the organic carbon content and SA is the specific surface area.

The correlation between the characteristics is shown in Table 2. The correlation matrix shows that most of aluminium and iron extracted fractions are related to the clay content of the sediment. Oxalate and dithionite extraction processes (Al *o*, Al *d* and Fe *o*, Fe *d* in Tables 1 and 2) are supposed to extract predominately Al and Fe oxy(hydr-)oxides. Iron and aluminium oxides occur attached to clay minerals as a consequence of clay mineral weathering. Organic carbon and clay contents, which are the main fractions usually associated to LAS sorption to sediments (Hand and Williams, 1987; Westall et al., 1999), are correlated by an R^2 of 0.54. Specific surface area is significantly correlated with both organic carbon and clay contents. This correlation between the sediment properties is one of the main problems to differentiate the contribution of each sediment parameter to the sorption of LAS to the entire sediment matrix. In this study, the contribution of key parameters (e.g., OC, SA) was experimentally investigated using materials with different surface area or by experimentally removing organic carbon from selected sediments.

3.2. Sorption of C_{12}-2-LAS to sea sand and clays

The parameters (K_f and n) of the Freundlich isotherms for sorption of C_{12}-2-LAS to the natural sediments, the clays montmorillonite and kaolinite and the purified sea sand are shown in Table 3. Sorption of C_{12}-2-LAS to pure sand was two orders of magnitude lower than to marine sediments collected from the field at the test concentration range. It is therefore expected that the freely dissolved – hence bioavailable fraction – of LAS in sand would be up to two orders of magnitude higher than in field marine sediments. As a consequence, the bioavailability of LAS in toxicity tests run with organisms exposed in acid-washed sand (Moreno-Garrido et al., 2003) is expected to be significantly different from

Table 2
Correlation matrix (R^2) between the sediment properties for the marine and estuarine sediments.

	Al *d* (g/Kg)	Al *o* (g/kg)	Al *p* (g/kg)	Fe *d* (g/kg)	Fe *o* (g/kg)	Fe *p* (g/kg)	OC %	Clay %	SSA (m^2/g)
Al *d* (g/kg)	1.00	0.98	0.07	0.97	0.84	0.57	0.09	0.65	0.45
Al *o* (g/kg)		1.00	0.03	0.96	0.91	0.57	0.13	0.63	0.46
Al *p* (g/kg)			1.00	0.04	0.00	0.30	0.23	0.33	0.50
Fe *d* (g/kg)				1.00	0.91	0.56	0.10	0.64	0.40
Fe *o* (g/kg)					1.00	0.54	0.18	0.57	0.37
Fe *p* (g/kg)						1.00	0.65	0.98	0.84
OC %							1.00	0.54	0.70
Clay %								1.00	0.82
SA (m^2/g)									1.00

the one in field sediments, and natural field sediment is therefore recommended.

Hand and Williams (1987) reported that sorption of LAS to sediments decreased for sediments with a higher sand content. This is not unexpected because a high sand content is also typically related to a low content of the most reactive constituents for LAS in sediments, organic carbon and clay contents. Comparable K_d values to those obtained here have been reported (0.43–0.89 L/kg) for soils with organic matter contents lower than 0.01% (Doi et al., 2002).

The sorption of C_{12}-2-LAS isotherms to kaolinite and montmorillonite are represented in Fig. 2. These two types of clays, typically present in sediments and soils, were chosen for their different structure and properties.

Kaolinite belongs to the 1:1 sheet silicates with a layer of tetrahedral silica connected to a layer of octahedral aluminate. The surface charge of kaolinite is predominately controlled by charge determining reactions of surface groups, in particular acid/base reactions of the aluminol and silanol groups. At seawater pH, both types of surfaces are expected to carry a net negative charge (Tertre et al., 2006). Montmorillonite is a 2:1 silicate, which carries, in contrast to kaolinite, a permanent negative layer charge. The expandable layers of montmorillonite confer a considerably larger specific surface area (535 m^2/g) respect to kaolinite (24 m^2/g). The layer charge is caused by isomorphic substitution of Al^{3+} by divalent cations and Si^{4+} by Al^{3+}. The surface charge of montmorillonite depends only to a minor extent on protonation and deprotonation of surface sites due to the negative layer charge and adsorption of negatively charged ions onto the montmorillonite surface is typically electrostatically unfavorable.

Sorption of LAS to these two clays in seawater showed non-linear isotherms (see Table 3) with *n* values of 0.55 and 0.58 for kaolinite and montmorillonite, respectively. The Freundlich coefficients were very similar for these two clay types. The similarity of the isotherms suggests that C_{12}-2-LAS only sorbs to the surface of the clays and it do not reach the interlayer spaces of montmorillonite. These results may facilitate the prediction of LAS sorption to natural sediments, where more than one type of clay is present. Specific clay characterization is likely not necessary and information about the total clay fraction is likely sufficient. A recent study of the sorption of LAS to two types of montmorillonite (calcium and sodium montmorillonite) (Yang et al., 2007) has confirmed that LAS were not present in the interlayer space. Matthijs and De Henau (1985) reported a non-linear isotherm ($n = 0.5$) and a relatively low Freundlich sorption coefficient (log $K_f = 1.3$) for the sorption of an LAS mixture to kaolinite. A study of the sorption of LAS to kaolinite using a 0.01 M $KHCO_3$ solution showed a sorption coefficient for C_{12}-LAS (mixture of isomers) of ~35 (log $K_f = 1.5$) when traces of organic matter were removed (House and Farr, 1989). The higher sorption coefficient obtained here can be due to the higher electrolyte concentration in seawater. Unfavorable electrostatic interactions between LAS and the clay minerals are diminished at high ionic strength and, in particular, adsorption of bivalent cations onto the clay surface may positively influence sorption of LAS.

Table 3
Freundlich parameters (log K_f and *n*) for C_{12}-2-LAS with all the tested sediments and materials.

	n	log K_f	R^2	n^a
Marine or estuarine sediment				
Oesterput	0.87 ± 0.04	2.72 ± 0.06	0.96	29
Cádiz	0.83 ± 0.05	2.06 ± 0.05	0,92	28
La Antilla	0.66 ± 0.02	2.50 ± 0.04	0.97	24
San Fernando	0.75 ± 0.04	2.58 ± 0.05	0.92	37
Espigón	0.61 ± 0.04	2.30 ± 0.06	0.89	33
North Sea 1	0.78 ± 0.04	2.07 ± 0.06	0.94	24
North Sea 2	0.73 ± 0.04	2.09 ± 0.05	0.92	26
North Sea 3	0.80 ± 0.05	2.24 ± 0.06	0.96	14
Lake sediment				
Drontermeer	0.91 ± 0.05	3.55 ± 0.09	0.96	15
Specific materials				
Kaolinite	0.55 ± 0.03	1.91 ± 0.04	0.96	11
Montmorillonite	0.58 ± 0.03	1.95 ± 0.03	0.98	9
Sand	1.23 ± 0.17	0.05 ± 0.10	0.85	12

[a] Total number of samples used for the isotherm.

3.3. *Effect of the removal of the organic carbon content on the sorption of C_{12}-2-LAS to sediments*

Removal of organic matter from the sediments by the NaOCl treatment was incomplete and the organic matter content was reduced by 77%, 60% and 81% compared with the initial values in the samples from Cádiz, San Fernando and Drontermeer,

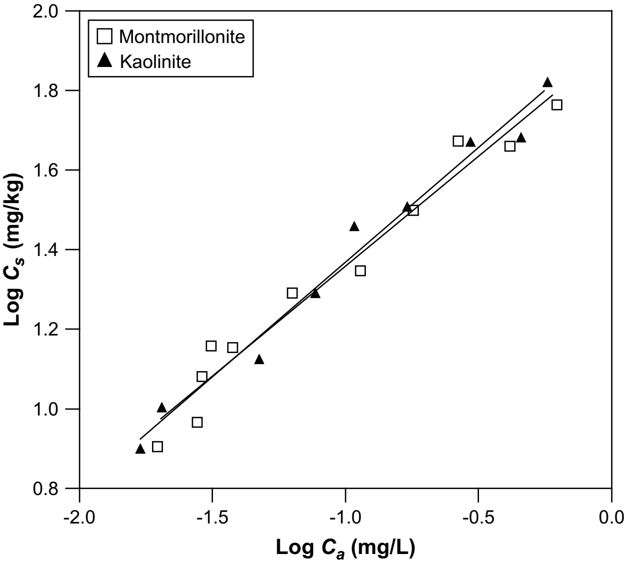

Fig. 2. Freundlich isotherms for sorption of C_{12}-2-LAS to montmorillonite (□) and kaolinite (▲) clays.

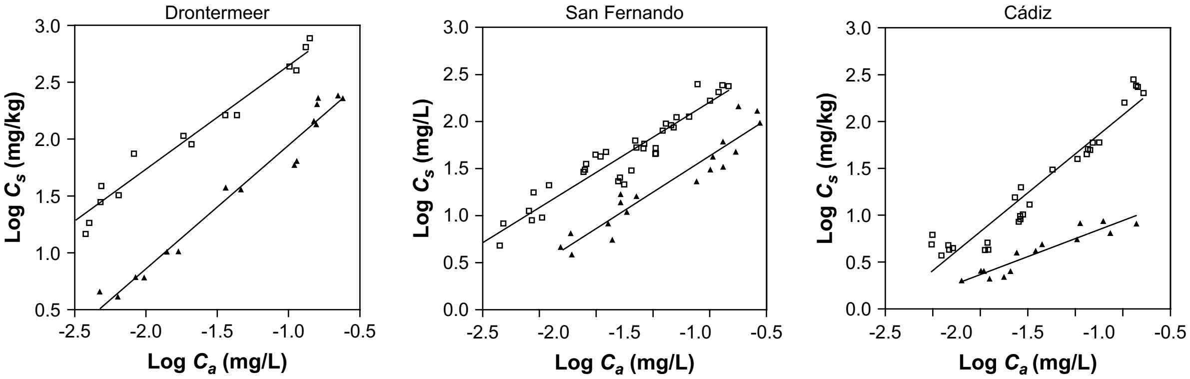

Fig. 3. Freundlich isotherms for the natural (□) and NaOCl treated sediments (▲) for the three selected sediments.

respectively. Results for the sorption of C_{12}-2-LAS on the three natural and NaOCl treated sediments are shown in Fig. 3. In the case of the Cádiz sediment (initial organic carbon content of 0.06%), LAS sorption substantially decreased upon reducing the organic fraction. A possible explanation for this observation is that the small fraction of organic matter of the natural sediment was covering the sand grains before the NaOCl treatment, enhancing the sorption of C_{12}-2-LAS to the sediment, while after the reduction of the organic content, sorption was not enhanced by any of the rest of the constituents from the sediment (mainly sand).

Isotherms for the natural and treated Drontermeer sediment are both relatively close to linearity with *n* of 1.08 and 0.91 for the untreated and treated sediments, respectively. This suggests that hydrophobic interactions are probably the driving force of LAS sorption in these samples. This is not strange considering that the organic carbon content of this sediment is still relatively high after the NaOCl treatment (from 9.5% down to 1.8%). The observed decrease of the K_f coefficient between the treated and the untreated Drontermeer sediment is proportional to the difference in the organic fraction. K_f (considering $n \approx 1$) decreased by 70% when reducing the organic content of the sediment by 81%. A proportional decrease in sorption was also observed for the San Fernando sediment, with K_f of 380 and 105 L/kg for the treated and untreated sediments, respectively (72% decrease in K_f value for 60% decrease in organic carbon content). The fact that K_f changed proportionally to the organic carbon reduction in Drontermeer and San Fernando sediments clearly shows the importance of the organic carbon content in the sorption process.

3.4. Sorption of C_{12}-2-LAS to estuarine and marine sediments

The Freundlich parameters of the isotherms for C_{12}-2-LAS with all the selected marine and estuarine sediments are shown in Table 3. Isotherms are non-linear with $n < 1$ in all cases, suggesting that other kinds of interactions than only hydrophobic interactions occur. Sorption isotherms did not show the same degree of non-linearity and the Freundlich parameter *n* varied from 0.61 to 0.87. In the case of Oesterput, San Fernando, La Antilla and Espigón sediments, which are the sediments with the highest organic carbon and clay contents, *n* value tends to be lower when the clay content increases. Although some trends can be observed for the rest of the sediments, it is not easy to relate the Freundlich parameter *n* with the organic carbon or clay content. The highest K_f values were observed for the Oesterput and San Fernando sediments, which are also the sediments with the highest organic carbon content. However, this tendency was not observed for the rest of the sediments, confirming the multivariate nature of sorption of LAS in marine sediments. Because the distribution coefficient (K_d) is not a constant, correlations between K_d values and sediment properties were investigated at several aqueous concentrations of LAS varying from 0.001 to 0.5 mg/L. Distribution coefficients were estimated using the Freundlich parameters from Table 3. The correlation coefficients (R^2) between the distribution coefficients at different aqueous concentrations and each single sediment characteristic are given in Table 4. In general, organic carbon, clay, specific surface area and some extractable metals (aluminium and iron pyrophosphate extractions, Al *p* and Fe *p*) correlate well with C_{12}-2-LAS sorption to sediments. However, these correlations depend on the surfactant concentration. Far better correlations with the iron, clay fraction and specific surface area are observed ($R^2 > 0.8$) for concentrations below 0.01 mg/L, while K_d values correlate much better with the organic carbon content at higher concentrations. This trend is graphically shown in Fig. 4, where correlation coefficients for the relationships of K_d versus the organic carbon content and clay fraction are given as a function of the aqueous concentration.

In the coastal environment, the expected range of LAS concentrations (all isomers and homologues) downstream of a wastewater plant with secondary or with no treatment is <1–10 μg/L, or 10–1000 μg/L, respectively (Temara et al., 2001). The organic carbon content has therefore significant effects on the sorption of LAS (and its bioavailability) in coastal sediments receiving untreated wastewater. It is also in these sites that the organic carbon content is high (Petrovic et al., 2002). In contrast, the clay and the iron

Table 4
Correlation coefficients (R^2) between the individual sediment characteristics and the K_d at different aqueous concentrations for all the tested marine and estuarine sediments.

	Al *d* (g/kg)	Al *o* (g/kg)	Al *p* (g/kg)	Fe *d* (g/kg)	Fe *o* (g/kg)	Fe *p* (g/kg)	OC %	Clay %	SSA (m^2/g)
K_d 0.001 mg/L	0.55	0.50	0.62	0.48	0.34	0.80	0.45	0.85	0.90
K_d 0.005 mg/L	0.39	0.37	0.64	0.33	0.25	0.81	0.62	0.82	0.95
K_d 0.01 mg/L	0.30	0.30	0.63	0.26	0.21	0.80	0.71	0.79	0.94
K_d 0.05 mg/L	0.12	0.13	0.50	0.10	0.11	0.69	0.88	0.63	0.83
K_d 0.10 mg/L	0.06	0.07	0.41	0.05	0.07	0.61	0.92	0.53	0.73
K_d 0.25 mg/L	0.01	0.02	0.29	0.01	0.03	0.49	0.92	0.40	0.57
K_d 0.5 mg/L	0.00	0.00	0.20	0.00	0.02	0.40	0.89	0.31	0.45

K_d values were calculated from the Freundlich isotherm for every sediment using the parameters listed in Table 3.

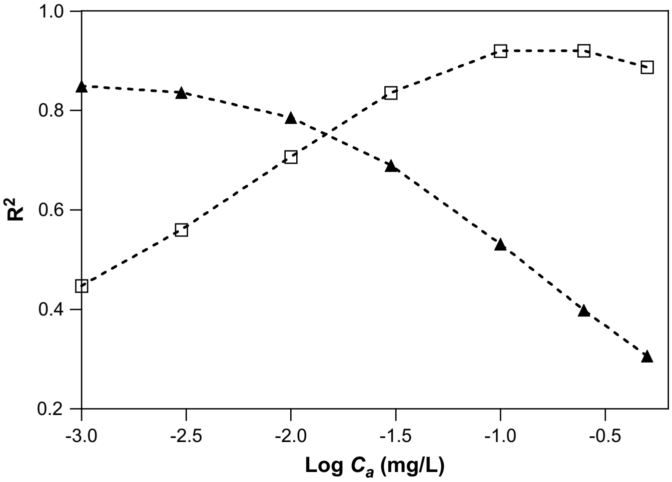

Fig. 4. Correlation coefficient (R^2) of the relation between sorption coefficients for all the marine and estuarine sediments and the organic carbon content (□), and the clay fraction (▲) at different aqueous concentrations. Sorption coefficients were calculated using the Freundlich parameters from Table 2.

pyrophosphate (Fe *p*) fractions are more important factors in marine/estuarine sediments of regions with appropriate (secondary) wastewater treatment.

The values of the Freundlich constant (log K_f) for C_{12}-2-LAS as measured for the eight natural marine sediments can be categorized into three groups that correspond to those identified by PCA of the physico-chemical characteristics of the sediment samples (Fig. 1), i.e., (1) Espigón (log $K_f = 2.3$; very high clay and metal content), (2) North Sea 1, 2, 3, and Cádiz (log $K_f = 2.1$–2.2, low organic carbon content), (3) Oesterput, La Antilla and San Fernando (log $K_f = 2.5$–2.7, high organic carbon and clay contents).

Good correlations between the organic fraction and sorption of LAS to sediment and soils have already been shown in several studies (Doi et al., 2002; Fytianos et al., 1998; Matthijs and De Henau, 1985; Westall et al., 1999). The sorption of LAS to natural sorbents can be related to hydrophobic interactions, and to specific chemical and electrostatic interactions of its functional ionic group. A recent study described the sorption of LAS and perfluoroalkyl surfactants in sediments based on the fraction of the organic matter that is accessible for the surfactant sorption (Higgins and Luthy, 2007). This model is based on electrostatic and hydrophobic interactions of surfactant molecules with the organic fraction of the sediments. However, organic carbon content is not always clearly related to the sorption of LAS to sediments. The relation of LAS sorption with the content of iron and aluminium oxides has often been observed for freshwater sediments and soils (Kristiansen et al., 2003; Ou et al., 1996; Westall et al., 1999). Interactions of LAS with these materials were explained by specific surface interactions. In a soil sorption study Kristiansen et al. (2003), LAS showed stronger affinity in the presence of amorphous oxides, likely due to their higher surface area. The sorption of LAS to the sediment constituents might furthermore be enhanced in the seawater media, because cations present in solution can adsorb to the particles surface, facilitating interactions with the functional sulfonate group. Besides, the high content of salts will also diminish the negative surface charge of the sediment, enhancing LAS absorption. Research with another anionic surfactant, sodium dodecyl sulfate (SDS), on estuarine sediments in freshwater and seawater media Jones-Hughes and Turner (2005) showed no differences between sorption of SDS in river water and seawater solutions using a sediment with a relatively high content in organic carbon (2%). However, after a treatment of this sediment to remove the organic fraction, a higher sorption was observed in seawater than in freshwater media. This phenomenon was explained by the reduction of the negative charge on the surface when removing the organic material, making it more favorable for electrostatic interactions in the case of seawater experiments.

4. Conclusions

The results obtained in this work provide relevant data for the understanding of the influence of single sediment materials on the sorption process of LAS to sediments. The challenge is to identify the range of the sediment properties that affect the sorption at the different surfactant concentrations. This study shows that at low concentrations (0.001–0.01 mg/L) C_{12}-2-LAS sorption was mainly dependent on iron and aluminium contents, and clay fraction, suggesting a relatively high importance of adsorption processes (interactions at the surface of the sediments). For higher concentrations (>0.01–0.05 mg/L) a better relation was observed with the organic carbon content, suggesting absorption in the organic fraction. Because concentrations in field sediments are relatively low in comparison with those used in the sorption studies, it is likely that particle size, clay and iron and aluminium oxide contents are more relevant for the predictions of LAS sorption to field marine and estuarine sediments than organic carbon content.

However, we must be prudent when selecting a dominant parameter to predict the sorption of LAS to sediments at environmental LAS concentrations. The work here performed was done for one model compound, while LAS in commercial mixtures are composed of molecules with different alkyl chains and phenyl positions. Furthermore, because water composition affects the sorption affinity of LAS to sediments, the salinity of the medium, together with the specific sediment constituents, may have an important contribution to the whole sorption process.

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