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INCORPORATION OF BIOFILM ACTIVITY IN RIVER BIODEGRADATION MODELING: A CASE STUDY FOR LINEAR ALKYLBENZENE SULPHONATE (LAS)*

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Abstract—A mathematical model was constructed which considers both biofilm and suspended biomass activity in relation to the biodegradation of individual chemicals in rivers. To calibrate this model for the surfactant LAS (linear alkylbenzene sulphonate), experimental data were obtained in a lab-scale artificial river system, which allowed to collect accurate and reproducible river biodegradation data next to the required river characteristics. Biofilm processes were shown to be by far the most significant removal mechanism of LAS in the considered system which had a high surface area to volume ratio. The biodegradation model could be fitted to the data using realistic parameter values. Subsequently, the model was corroborated by comparing its predictions to a field study in the Red Beck, a small Yorkshire river. Only easy to collect or default data were used as model parameters. The predicted LAS first-order removal rate coefficient (without any calibration using the field data) was 0.25 h^{-1}, which is less than 20% slower than removal measured in the field. © 2000 Elsevier Science Ltd. All rights reserved

Key words—artificial river, biodegradation, biofilm, fate model, river, LAS

NOMENCLATURE

$a_{biofilm}$	biofilm surface area per volume of water (m^2/m^3)
A/V	surface area to volume ratio (m^2/m^3)
COD	chemical oxygen demand (g/m^3)
D	chemical diffusion coefficient in water (m^2/h)
D_e	chemical diffusion coefficient in biofilm (m^2/h)
HRT	hydraulic residence time (h)
k_{biodeg}	first-order biodegradation rate coefficient (total) (h^{-1})
$k_{biodeg}^{biofilm}$	first-order biodegradation rate coefficient in biofilm (h^{-1})
k_{biodeg}^{bulk}	first-order biodegradation rate coefficient in "bulk water" (h^{-1})
K_b	biomass level independent first-order biodegradation constant ($[g_{dwt}/m^3]^{-1}\ h^{-1}$)
L	stagnant water film thickness (m)
LAS	linear alkylbenzene sulphonate
L_f	biofilm thickness (m)
SS	(active) suspended solids (g_{dwt}/m^3)
SSA	specific surface area (m^2/m^3)
X_f	biofilm density (g_{dwt}/m^3)

INTRODUCTION

Current environmental exposure assessment techniques in European Union chemical legislation make use of generic "multimedia" chemical fate models (EEC, 1994). In these models the environment is represented in a very simplified way, by using one completely mixed "box" for each medium (water, soil, air, etc.). Hence, they do not incorporate spatial variability, and their results are generally not realistic. The GREAT-ER project (geography-referenced regional exposure assessment tool for european rivers) aims to refine aquatic exposure assessments, by modeling the fate pathway of "down-the-drain" chemicals from the household to the river, and by applying specific river fate models to predict concentrations downstream of pollution sources (Feijtel *et al.*, 1997). Typically, the latter assume removal kinetics are first-order with respect to chemical concentration.

LAS was used as the main test chemical within the GREAT-ER project. It is a major surfactant which is used worldwide at high volumes in household detergents, and may constitute more than 1% of the BOD in domestic sewage. In different field studies a wide range of LAS removal rate coeffi-

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cients in rivers has been observed (between 0.006 and 1.71 h^{-1}) (e.g. Hennes and Rapaport, 1989; Amano *et al.*, 1991; Schöberl *et al.*, 1994; Takada *et al.*, 1994; Schröder, 1995; Grob, 1996; Fox *et al.*, submitted for publication). Takada *et al.* (1994) showed a major influence of the presence of biomass (especially biofilms) on the removal rate coefficient. Biofilms have the highest relative importance in small rivers, as these have a higher surface area to volume ratio.

To improve the accuracy of chemical fate modeling in rivers, it is desirable to estimate chemical removal kinetics for different river types. However, for practical feasibility of the approach, such estimation should not require large amounts of detailed river-specific data. In the case of LAS, biodegradation is the predominant process which will determine removal. In this paper, a simple mathematical model is presented which estimates the rate of LAS biodegradation in rivers as a function of biomass presence — both biofilm and suspended microorganisms. The presence of biofilms was linked with the surface area available for attached growth. The model was calibrated using experimental data collected in a laboratory scale artificial river system. Corroboration was done by comparing the model to a field study for LAS.

NEW BIODEGRADATION MODEL

Model formulation

Biodegradation by suspended organisms (''bulk water'' phase) and by biofilms was taken into account. The ''bulk water'' and biofilm processes were considered to be independent, and to both follow first-order kinetics in chemical concentration. The total biodegradation rate coefficient can be obtained by summing both rate coefficients:

$$k_{\text{biodeg}} = k_{\text{biodeg}}^{\text{bulk}} + k_{\text{biodeg}}^{\text{biofilm}} \tag{1}$$

The first-order biodegradation rate coefficient in ''bulk water'' was calculated from the ''active'' SS (suspended solids) level and the chemical biodegradation constant K_b. This K_b, which is independent of the biomass level, can for example be derived from standard activated sludge test results by dividing the measured first-order biodegradation rate coefficient by the biomass concentration.

$$k_{\text{biodeg}}^{\text{bulk}} = K_b SS \tag{2}$$

The biofilm biodegradation model (including diffusion) was taken from a trickling filter fate model developed by Melcer *et al.* (1995).

$$k_{\text{biodeg}}^{\text{biofilm}} = a_{\text{biofilm}} \frac{D}{L} \frac{D_e r_1 \tanh(r_1 L_f)}{D_e r_1 \tanh(r_1 L_f) + D/L}$$
$$r_1 = \sqrt{\frac{X_f K_b}{D_e}} \quad D_e = 0.8D \tag{3}$$

The biofilm surface area a_{biofilm} is proportional to the area available for growth. Due to the irregular morphology (cf. mountains and valleys), the biofilm/water interfacial area is typically larger than the carrier surface itself (e.g. Lazarova and Manem, 1995). In this paper, a correction factor of 2 was assumed.

MATERIALS AND METHODS

Artificial river system selection and design

As many river and biofilm characteristics cannot be (accurately) measured or are nonhomogeneous in the field, artificial river experiments were preferred. The artificial river was constructed as a cascade of 5 U-shaped gutters, each of 2 m length (Fig. 1). Its total volume was 36 L. To obtain an HRT (hydraulic residence time) of ~3 h, the flow was set to 0.2 L/min. This HRT was chosen to correspond with the first-order half-life (= time needed to achieve 50% removal) of LAS in small rivers, as measured for the Red Beck (Fox *et al.*, submitted for publication). Two air diffusers were placed in each gutter for oxygenation and to counteract sedimentation. To ensure a relatively constant and known composition, synthetic river water was used. To obtain easily measurable LAS levels which were on the other hand not unrealistically high (in the order of 1–2 mg/L), this was prepared as a 50/50 mixture of a laboratory scale trickling filter's effluent with tap water. The COD concentration in the river water was in the order of 40 mg/L. The trickling filter's influent was a synthetic sewage containing LAS, based on Boeije *et al.* (1998). As the trickling filter was operated under steady state conditions, and its influent loading and composition were constant, the short-term variability in the river water composition (i.e. in the time-frame of the river's HRT) was negligible. The experiments were conducted at room temperature (20°C).

In the artificial river, biofilm could develop on the edges of the gutters, and on biofilter carrier material which was put into the gutters to mimic bed material or vegetation present in natural rivers. The polypropylene carrier material had the shape of a truncated cone (average diameter = ~ 5 cm, height = ~ 4 cm) with several fins to increase the SSA (specific surface area). The total edges surface area was ~1.5 m^2 and the surface area to volume ratio (A/V) was 42 m^2/m^3. The total surface of the biofilter carrier material (30 pieces per gutter), with an SSA of 220 m^2/m^3, was ~3.4 m^2 (A/V = 94 m^2/m^3).

Hydraulic characterization

Before the biological experiments were started, a hydraulic characterization was performed by means of a NaCl tracer test. The flow was fixed at 0.2 L/min. The mean HRT after stretches 1 through 5 was respectively 44, 78, 114, 149 and 189 min.

During the biological experiments, the tracer test was not repeated. Instead, the HRTs during each individual measurement were derived from the tracer test HRTs. A correction was conducted for the actual measured flow rate (which was not always exactly 0.2 L/min), and for the volume reduction due to the presence of carrier material and biofilm (assuming that 1 cm^3 of biofilm or carrier material reduces the water volume by an equal amount). For these simplified corrections, the river's mixing characteristics were assumed to be similar under the different experimental conditions.

Measurements

LAS was measured at 4 distances (0, 2, 5 and 10 m). The samples were not filtered, hence LAS associated with

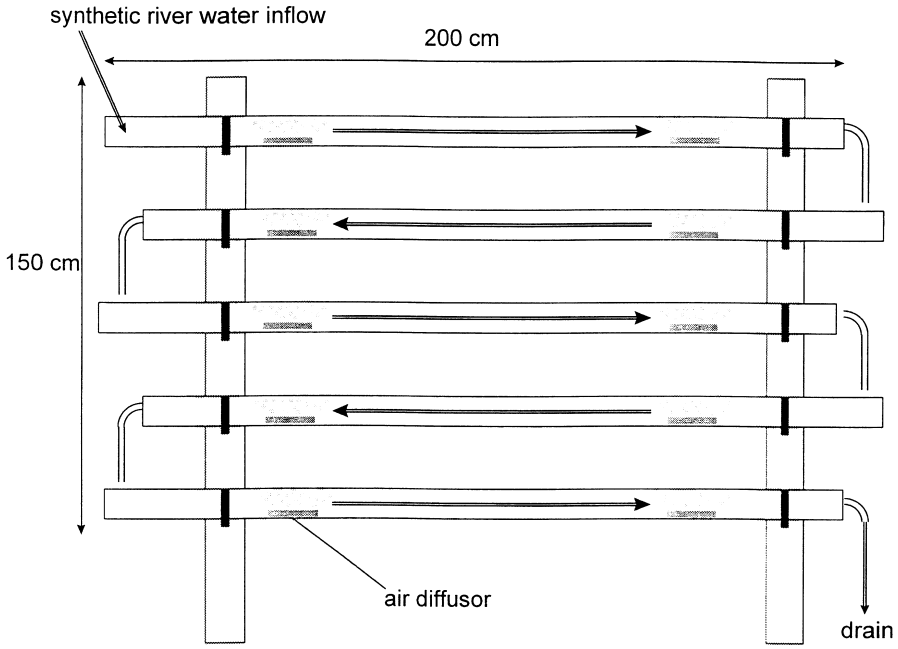

Fig. 1. Artificial river design.

solids was included in the analysis. No anionic surfactants other than LAS were present, hence the aspecific Azure-A analytical method could be used reliably (Den Tonkelaar and Bergshoeff, 1969). Three experimental series were conducted: (1) no biofilm present (i.e. only suspended biomass, originating from the trickling filter's effluent), (2) suspended biomass and biofilm on the gutters' edges and (3) suspended biomass and biofilm on the edges and on carrier material. The biofilm thickness on the carrier material was estimated from its wet (leaked out) mass; the biofilm thickness on the gutter's edges could not be accurately determined.

Relative LAS removal profiles were obtained by expressing the concentrations as fraction LAS remaining. ANOVA (analysis of variance) was used to check whether any significant removal had taken place, by comparison of relative LAS levels at the 4 different measurement locations (SPSS software, version 7.5, SPSS Inc.). First-order removal rate coefficients were obtained by linear regression between the natural logarithms of the relative LAS levels and the HRTs for each experiment (imposing a zero-intercept).

RESULTS

Artificial river experiments

LAS removal was assumed to be completely due to biodegradation. LAS is nonvolatile; sorption to solids and subsequent sedimentation were assumed to be negligible because of the low suspended solids levels and the intensive aeration. The mean initial LAS level for each experimental series varied between 1.2 and 2.5 mg/L. The variation in the river's influent (due to variation in the trickling filter's performance or sewage composition) was too slow (time-frame: days) to have any effect on the removal experiments (time-frame: hours). The artificial river SS (suspended solids) were on average 20 mg/L (with large variations of the measurements: 5–35 mg/L). The river water's pH was neutral. Dissolved oxygen levels were always high (>4 mg/L).

No biofilm. The removal profile with only suspended biomass in the river (originating from the trickling filter's effluent) is shown in Fig. 2 (left). No significant removal was detected over the 3 -h period.

Biofilm on edges. The removal profile after one month of biofilm colonization on the gutters' edges is shown in Fig. 2 (center). No accurate measurements of biofilm thickness could be made. Significant LAS removal was observed. The calculated removal rate coefficient was 0.38 ($\pm$0.12) h^{-1} (mean $r^2 = 0.86$).

Biofilm on carriers and edges. Next, carrier material was entered into the river. The removal profile after one month of further biofilm growth is shown in Fig. 2 (right). The biofilm thickness on the carriers was measured to be $\sim$50 μm. LAS removal was significant. The removal rate coefficient was 0.71 ($\pm$0.17) h^{-1} (mean $r^2 = 0.86$).

Removal rate coefficients recorded in the three experimental series were compared by means of a Tukey test ($\alpha = 0.05$) (SPSS software, version 7.5, SPSS Inc.). This showed that LAS removal was significantly different in all three cases.

Biodegradation model calibration: artificial river

For the calibration based on the artificial river data, a further distinction was made between edge

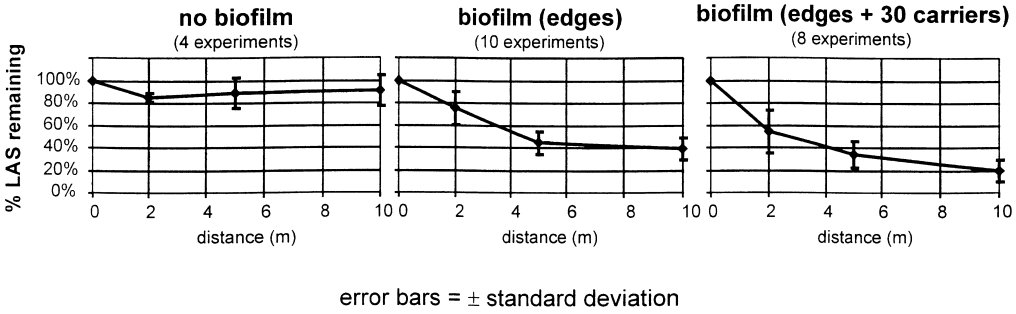

Fig. 2. Artificial river removal measurements for LAS.

and carriers biofilm, because a different biofilm thickness might have occurred. The calculation of biofilm surface was based on the gutters' geometry and on the surface area of the carriers. The system was modeled as a single stretch, hence homogeneous conditions (a.o. biofilm thickness) were assumed along the river.

Some parameters were taken from Melcer *et al.* (1995), as their actual value could not be determined within the scope of this work: i.e. $D = 0.2\ m^2/h$, $L = 100\ \mu m$, $X_f = 40{,}000\ g_{dwt}/m^3$. All river parameters were measured. The K_b of LAS, $0.001\ (g_{dwt}/m^3)^{-1}\ h^{-1}$, was calculated from the first-order rate coefficient used for LAS biodegradation by suspended biomass in activated sludge waste water treatment plants ($3\ h^{-1}$, with mixed liquor $SS = 3000\ g_{dwt}/m^3$) (Struijs *et al.*, 1991). The model was calibrated only by tuning the (active) thickness of the edge and the carrier biofilm. Calibration parameters, model predictions and corresponding measurements are given in Table 1.

For the "no biofilm" case no calibration was needed as all parameters were given. Next, the edge biofilm thickness was calibrated. The resulting value was fixed and used for the third case (edges + carriers), for which the carrier biofilm thickness was estimated.

Biodegradation model corroboration: Red Beck field study

The model was applied to the Red Beck, a small river in the Calder catchment (Yorkshire, UK), for which LAS removal measurements were available (Fox *et al.*, submitted for publication).

Deterministic model calculations. The applied parameter values are shown in Table 2 (middle column). Except for the biodegradation rate coefficient, the same values as in the artificial river calibration were used. K_b was corrected for the lower temperature (9°C) by assuming that the biodegradation rate decreases by a factor 2 when the temperature is 10°C lower than under standard conditions (20°C). Similar corrections were e.g. used by Henze *et al.* (1995) and by Struijs (1996). The biofilm thickness was set to 100 μm (cf. calibrated edges biofilm thickness above). The river was split into 2 stretches: (1) Shibden Head (treatment plant) to Dam Head (1.3 km) and (2) Dam Head to Sunny Bank (3.5 km). The bed material consisted of pebbles, with an average depth of 15 cm. Its SSA was estimated to be $100\ m^2/m^3$ (by assuming spherical pebbles with 2 cm radius and 33% voids). From the river geometry and bed properties, it was possible to roughly estimate the surface available for biofilm growth, both on the river's "edges" (area per length = width + 2 × depth) and on the pebbles (area per length = width × bed depth × SSA). For section (1) this was respectively $0.3\ m^2$ and $23\ m^2$ per m, for section (2) it was $0.45\ m^2$ and $46\ m^2$ per m. The total surface area per unit of volume (A/V) was $100\ m^2/m^3$ in section (1) and $70\ m^2/m^3$ in section (2). The LAS concentrations in the Red Beck were

Table 1. Model calibration using the artificial river measurements

	Edges	Edges + 30 carriers/stretch
Calibration parameters		
$L_f^{\text{edge biofilm}}$ (μm)	106	106[a]
$L_f^{\text{carriers biofilm}}$ (μm)	–	44
Model predictions of LAS removal kinetics		
$k_{biodeg}^{\text{edge biofilm}}$ (h^{-1})	0.363	0.363
$k_{biodeg}^{\text{carriers biofilm}}$ (h^{-1})	–	0.332
k_{biodeg}^{bulk} (h^{-1})	0.020	0.020
k_{biodeg} (h^{-1})	0.383	0.715
Measured LAS removal kinetics		
k_{biodeg} (h^{-1})	0.382	0.711

[a]Edges biofilm thickness taken as such from the "Edges" calibration case.

Table 2. Model corroboration for the Red Beck: overview of parameters

	Deterministic value	Uncertainty distribution[a]
Parameters of which the value was accurately known		
HRT (h)	1.45[b] 3.6[c]	none
Parameters with limited uncertainty		
River width (m)	1.5[b] 3[c]	Normal distribution with a relative standard deviation of 10%
River depth (cm)	15[b] 22.5[c]	Normal distribution with a relative standard deviation of 10%
SS (mg/L)	16.5[b] 11.2[c]	Normal distribution with a relative standard deviation of 10%
X_f (g_{dwt}/m^3)	40,000	Normal distribution with a relative standard deviation of 10%
K_b (h^{-1} mg^{-1} L)	0.0005	Normal distribution with a relative standard deviation of 10%
Parameters with high uncertainty		
River bed depth (cm)	15	U(10,20)
River bed SSA (m^2/m^3)	100	U(50,150)
$a_{biofilm}$	2	U(1,3)
D (m^2/h)	0.2	U(0.04,1)
L (μm)	100	U(50,150)
L_f (μm)	100	U(50,150)

[a]U(min,max) = uniform distribution.
[b]In stretch (1) from Shibden Head (treatment plant) to Dam Head.
[c]In stretch (2) from Dam Head to Sunny Bank.

a factor 2 to 3 lower than in the artificial river study which was used for model calibration. The flow in the Red Beck was 0.1 m^3/s.

Biodegradation model calculations were performed for both stretches, resulting in an LAS removal rate coefficient of 0.33 h^{-1} in (1) and 0.22 h^{-1} in (2). In both cases, 97.5% of the biodegradation was predicted to take place in biofilms. By relating the initial level in (1) with the most downstream level in (2), an "overall" removal rate coefficient of 0.25 h^{-1} was calculated.

In the Red Beck field study, an overall LAS removal rate coefficient of 0.31 h^{-1} was found. For section (2) only, this was 0.26 h^{-1}. This corresponds well with the predictions: the deterministic model underestimated the overall rate coefficient by $<20\%$ and the rate coefficient in section (2) by $<16\%$.

Uncertainty analysis. Next to the deterministic calculations, a stochastic simulation of the model was performed to capture the sensitivity of its predictions to parameter uncertainty (using Crystal Ball software, Decisioneering, Inc.). The uncertainty distributions assigned to each of the parameters are given in Table 2 (right column). The HRTs were accurately known, as they were obtained in a dye tracer study conducted simultaneously with the LAS sampling. Parameters with a low uncertainty were assigned a normal distribution with a relative standard deviation of 10%. Very uncertain parameters were described by a uniform distribution with a large range. A stochastic simulation (Monte Carlo method, 2500 iterations) resulted in a mean "overall" removal rate coefficient of 0.26 h^{-1} (5th percentile = 0.09 h^{-1} and 95th percentile = 0.53 h^{-1}). The resulting frequency distribution is shown in Fig. 4.

When compared to the value measured in the Red Beck, the mean rate coefficient resulting from the stochastic simulation had a similar accuracy as the result of the deterministic model calculation. The lower limit of the 90% confidence interval was a factor 3.5 lower than the measured rate, while the upper limit was a factor 1.7 higher.

DISCUSSION

Measurements

No significant removal took place in the absence of biofilm. Hence, suspended biodegradation half-lives were much higher than the HRT (3 h). The variation in SS levels had no measurable effect on LAS removal. In the presence of biofilm, significant removal was shown. This indicates that in small rivers with a high surface area to volume ratio, biodegradation by biofilms can be much more important than by suspended biomass. The observed absence of removal in the "no biofilm" case for LAS also indicates that biodegradation must have been the only significant removal process in the "with biofilm" cases.

Model calibration

It was possible to fit the biodegradation model to LAS removal measurements in the artificial river, using measured system information or realistic defaults as model parameters, and using an LAS biodegradation rate coefficient which was derived from activated sludge standard biodegradation test data. The calibrated active thickness of the edge biofilm (100 μm) is a plausible value, especially when taking into account that only the upper aerobic layer of the biofilm is active in LAS biodegradation (e.g. Jimenez *et al.*, 1991). Finally, the calibrated carrier biofilm thickness was very close to the (accurately) measured value of 50 μm. Note that the carriers were only introduced at a later stage of the experiments, hence less time was

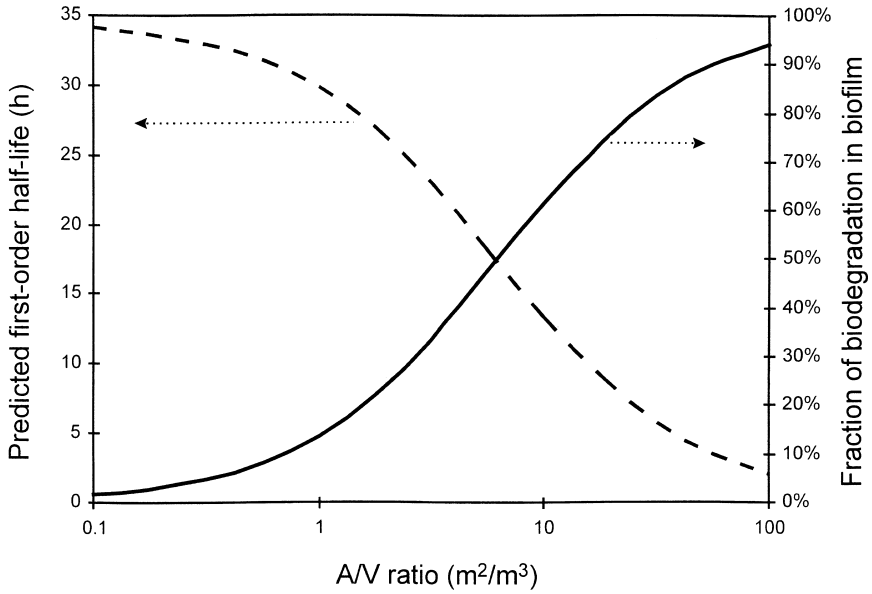

Fig. 3. Predicted removal rate coefficient (expressed as first-order half-life) as a function of surface area to volume (A/V) ratio.

available for biofilm growth compared to the edges.

Model corroboration

The predicted biodegradation of LAS in the Red Beck corresponds well with measured removal, even with many model parameters being rough estimates or default values. However, to allow a more general applicability, further validation for other situations and testing of the applied assumptions and defaults are required. As many parameters used in the model prediction were rough estimations, it would be speculative to draw any conclusions from the model's underestimation of the removal rate coefficient. A tentative explanation may be given by the fact that, next to biodegradation, also sorption/sedimentation took place in the Red Beck. This hypothesis is supported by the SS levels which decreased downstream, and by the fact that 10–25% of the measured LAS was associated with solids (Fox *et al.*, submitted). Finally, in the field study no separation was made between suspended and biofilm biodegradation. Hence, it could not be tested whether the model correctly assesses the importance of both processes.

The results of a stochastic simulation, in which the uncertainty of all model parameters was captured, indicate that there is a relatively large uncertainty around the predicted removal rate. However, this has to be seen in the context of the much larger uncertainty which exists if river biodegradation rate coefficients have to be derived from literature data.

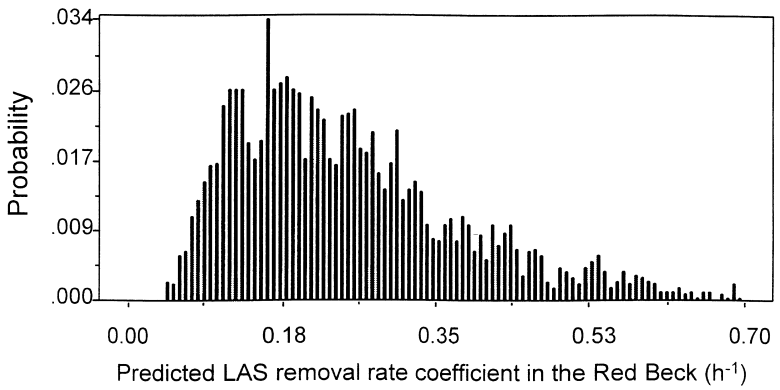

Fig. 4. Histogram of the predicted LAS removal rate coefficient in the Red Beck, resulting from a stochastic simulation capturing parameter uncertainty.

In the literature, a factor 285 can be found between the lowest and highest reported rate coefficient for LAS removal in rivers, compared to the factor 6 found here between the lowest and highest value in the 90% confidence interval of the model predictions.

The presented biodegradation modeling concept was also compared with measurements in the Emscher River (Germany) by Løkkegaard Bjerre *et al*. (1998). Based on the A/V ratio reported for this river (1 m^2/m^3), the model predicts that the biofilm accounts for 14% of the total biodegradation activity (Fig. 3). This prediction corresponds well with the microbial activity measurements reported by Løkkegaard Bjerre *et al*. (1998).

CONCLUSIONS

In the presented artificial river experiments, biodegradation was found to be the only significant removal process of LAS. In this specific case, measurable biodegradation only occurred when biofilm was present. The biodegradation rate was proportional to the amount of biofilm in the system.

A new biodegradation modeling concept, considering microbial activity both in biofilm and in bulk water, was presented. This model could be calibrated using the experimental data obtained in the artificial river experiments. Using this calibration, the model was able to predict the removal of LAS which was measured in the Red Beck field study (Fox *et al*., submitted for publication) within 20%. The accuracy was more than satisfactory within the GREAT-ER approach, where a final accuracy of a factor < 5 is aimed for (Feijtel *et al*., 1997). Hence, it can be concluded that the model was successfully corroborated for the fate prediction of LAS in the specific case of the Red Beck. Moreover, the model allowed to significantly reduce the uncertainty around the LAS removal rate coefficient compared to the wide range found in the literature.

It is recommended that a further corroboration of the presented modeling approach be conducted, especially based on other detailed field study data. The range of validity of the model and its assumptions needs to be extended to other chemical substances and to other types of rivers.

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