

## EFFECT OF NUTRIENT DYNAMICS ON ORGANIC CONTAMINANT FATE IN RIVERS: A MICROCOSM STUDY

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### INTRODUCTION

Despite the fact that conventional pollutants such as nutrients can have considerable effects on the fate of organic contaminants in rivers, little attention has been given to couple these two water quality problems in traditional river water quality modelling. Nutrient enrichment in aquatic ecosystems can regulate microbial growth, and can enhance organic contaminant degradation. Such beneficial effect is possible however only when none of the growth substrates is limiting microbial growth e.g. dissolved oxygen (as electron acceptor, in aerobic degradation), and nitrogen or phosphorus sources (Venosa et al., 2002).

Recently a new conceptual integrated exposure model that takes into account the effect of nutrient dynamics on the fate of organic contaminants in rivers was developed (Deksissa and Vanrollegheem, 2003). To validate this model an experimental study related to the interaction of these two main water quality problems is needed.

The goal of this study is to experimentally investigate the effect of nutrient dynamics on the fate of organic contaminants in rivers so that data can be used to validate the integrated exposure model. Using an artificial river (microcosm study) and the chemical substance Linear Alkylbenzene Sulphonate (LAS), an active ingredient of detergents, the effect of different factors such as extra nutrient load (ammonia nitrogen and soluble readily biodegradable organic substrates, aeration and attached microbial biomass (biofilm) on the (only aerobic) degradation of LAS was examined.

### MATERIAL AND METHODS

#### River system selection and design

An artificial river was constructed as a cascade of 5 U-shaped gutters, each of 2 m length. The total river length and volume are 10 m and 37 l respectively. The flow rate was selected based on the half-life of an organic contaminant e.g. for LAS 1-3 h can be applied. To get the average hydraulic retention time of 3 h, the flow rate was then adjusted to  $0.2 \text{ l min}^{-1}$ . The synthetic river water was prepared from a Sequential Batch Reactor (SBR) effluent that is diluted with softened tap water. The inflow and dilution rate were controlled by a LabView<sup>®</sup> programme.

### Analytical methods

Samples were taken at distances of 0.5, 2, 4, 6, 8 and 10 m and analysed for total (unfiltered) LAS concentration in the bulk water using a non-specific Azure A analytical method (de Tonkelaar and Bergshoef, 1969) knowing that there is no other type of anionic surfactants except LAS in the river system. Samples of the same location were analysed for the other water quality variables: Dissolved Oxygen (DO) and pH (with standard DO and pH electrodes respectively); soluble Chemical Oxygen Demand (COD), NH<sub>4</sub>-N and NO<sub>3</sub>-N (with Dr. Lange kits) and temperature. Furthermore, the microbial biomass, both in suspension and in the benthic sediment, was determined based on measuring the dry weight (24 h at 100 °C) of a known volume of water samples.

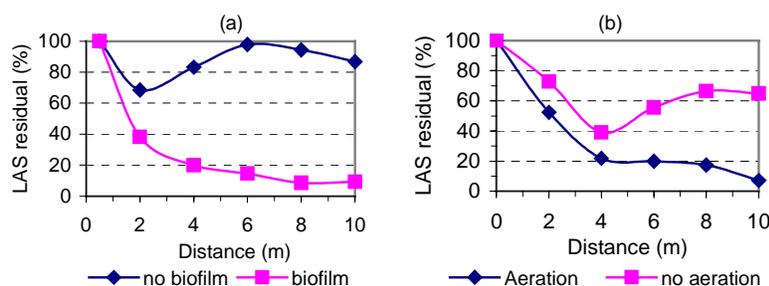
### RESULT AND DISCUSSION

A series of experiments was conducted to investigate the effect of biofilm, aeration, and external substrate load (ammonia nitrogen and COD) on the fate of LAS in the artificial river.

In the absence of biofilm there was no significant LAS removal. When biofilm had grown a significant ( $p < 0.05$ ) rapid degradation of LAS was observed (see Figure 1(a)). This is due to the fact that (1) there is a higher microbial density in biofilm than in suspension, and (2) the attached microbial biomass is continuously exposed to the contaminant and gets a longer contact time allowing it to adapt and degrade the contaminant faster than suspended bacteria. In another words 3 hours of hydraulic retention time is too short to result in a significant degradation when the concentration of suspended microbial biomass is very low. This indicates the importance of incorporating biofilm kinetics in the organic contaminant fate modelling in rivers, particularly in shallow rivers.

The effect of aeration and LAS accumulation was also tested and the result is indicated in Figure 1 (b). Regardless of the DO concentration ( $> 4 \text{ mg l}^{-1}$ ) in the bulk water, accumulation of LAS in the river stretch was observed. This is due to the low DO concentration ( $< 0.4 \text{ mg l}^{-1}$ ) in the biofilm, where degradation predominantly should take place. This suggests that aeration can limit LAS degradation in rivers.

Furthermore aeration is not only providing oxygen for the aerobic biodegradation but also induces turbulence/mixing. It breaks structured plug flow, produces fast oxygen transfer from the overlying water to the biofilm, provides uniform distribution of the contaminant and nutrients including oxygen in the bulk water, prevents localized high levels of organic contaminant and nutrient concentrations, and thereby enhances organic contaminant degradation. Thus, the turbulence or flow velocity of the river can play a significant role in the fate of pollutants in rivers.

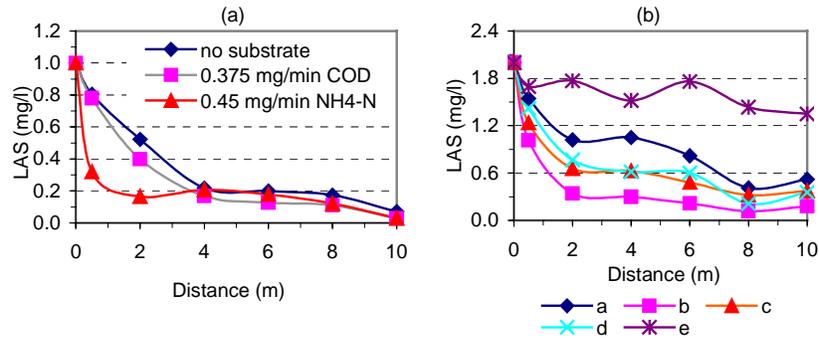


**Figure 1.** LAS concentration profile (a) in the presence and absence of biofilm and (b) with and without aerating the river stretches

A preliminary experiment was conducted to investigate whether ammonia nitrogen or soluble COD limits the LAS degradation in rivers. Two series of batch experiments were conducted: first  $0.375 \text{ mg min}^{-1}$  readily biodegradable COD (acetate), and then  $0.45 \text{ mg min}^{-1} \text{ NH}_4\text{-N}$  were added for 6 hours consecutively. After each batch experiment, the LAS concentration profile was monitored, and the results are compared with the data of no external substrate load (see Figure 2 (a)). An external  $\text{NH}_4\text{-N}$  load resulted in more rapid LAS degradation (immediate uptake) than COD. The measured  $\text{NH}_4\text{-N}$  concentration in the river stretches prior to the external load was indeed very low ( $< 0.05 \text{ mg l}^{-1} \text{ NH}_4\text{-N}$ ). However, the concentration of  $\text{NO}_3\text{-N}$ , which can also be potentially utilized as a nitrogen source, was high ( $> 5 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$  in the bulk water). This indicates that  $\text{NH}_4\text{-N}$  rather than the total inorganic nitrogen limits the LAS degradation. This is an interesting finding and can deserve more study.

For the sensitivity of LAS degradation to the presence of ammonia nitrogen, the following possible reason can be given. Heterotrophic bacteria can use nitrate as a nitrogen source in aerobic conditions, but ammonia is preferred. Addition of excess ammonia nitrogen therefore induces aerobic growth and therefore degradation, whereas addition of excess nitrate nitrogen supports anoxic degradation (Rihn *et al.*, 1997). The latter is however not relevant to the LAS degradation that only occurs aerobically. It was also suggested that LAS can be degraded after an initial monooxygenation by ammonia oxidizers, heterotrophic organisms will then catalyze the further reactions (Schleheck *et al.*, 2000). This indicates that the concentration of ammonium nitrogen can limit the LAS degradation regardless of high total inorganic nitrogen concentrations in the bulk water.

Furthermore, the effect of COD load on the LAS degradation was investigated. Using  $0.45 \text{ mg min}^{-1} \text{ NH}_4\text{-N}$  load, five series of experiments based on COD load: (a) 0, (b)  $0.0125$ , (c)  $0.0375$ , (d)  $0.375$  and (e)  $0.375 \text{ mg min}^{-1}$  COD combined with no aeration were conducted (see Figure 2 (b)). The results show that the lowest external COD load (a) resulted in the most rapid LAS degradation, whereas, the highest COD load



**Figure 2.** Effect of external  $\text{NH}_4\text{-N}$  and COD load on the LAS degradation: (a) ammonia nitrogen (b) COD

(d) had less effect due to its negative effect on the DO in the river stretches. High COD loaded waters in combination with an absence of aeration (e) results in accumulation of LAS in the river stretch.

## CONCLUSIONS

Based on the results obtained during this study one can conclude that including biofilm kinetics in the organic contaminant fate model in rivers, especially in shallow rivers, is very important. Besides, both in nutrient rich or poor rivers, the variation of the external nutrient load can affect the fate of an organic contaminant, and thus including limitations (oxygen, nitrogen and phosphorus) in the organic contaminant degradation models is necessary. The sensitivity of LAS degradation to the ammonia nitrogen is an interesting finding and may induce further research to investigate the mechanism.

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