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Behaviour of Linear Alkylbenzene Sulfonate (LAS) in Soil Infiltration and Groundwater**

Als Komponenten von Konsumgütern können Waschmittelchemikalien, wie z.B. LAS, in oberflächennahe Bodenschichten und ins Grundwasser eingebracht werden. In den USA z. B. gelangen annähernd 30% des in Wasch- und Reinigungsmitteln verwendeten LAS in häusliche oder Kleinstkläranlagen. Der Ablauf dieser Kläranlagen fließt direkt in ein unterirdisches Drainagesystem, hier findet hauptsächlich der Abbau statt. Im Vergleich zu städtischen Kläranlagen können die Abläufe dieser häuslichen Anlagen höhere Konzentrationen an LAS und anderen Waschmittelchemikalien enthalten. Es ist daher wichtig, den Verbleib und das Abbauverhalten dieser Chemikalien, die in den Boden und in das Grundwasser gelangen, zu untersuchen. Vier wichtige Prozesse kontrollieren das Verhalten und den Transport dieser Chemikalien im Grundwasser und in oberflächennahen Böden: Advektion, Dispersion, Sorption und biologischer Abbau. Die drei erstgenannten Prozesse können die relative Konzentration einer Substanz oder ihre Verteilung (räumlich und zeitlich) in einem bestimmten unterirdischen Kompartiment beeinflussen, sie können jedoch zu keiner Änderung der Gesamtmasse führen, dieses kann nur mit dem letztgenannten Prozeß, dem biologischen Abbau, erreicht werden. Forschungsarbeiten haben nun gezeigt, daß unterirdische oberflächennahe Umweltkompartimente signifikante Mengen an heterotrophen Mikroorganismen enthalten, die in der Lage sind, Waschmittelchemikalien (einschließlich LAS) biologisch abzubauen. In diesem Beitrag werden einige Ergebnisse einer größeren Studie präsentiert. Die Studie beinhaltete Untersuchungen und Feldstudien, bei denen verschiedenartige LAS-Expositionen meßtechnisch verfolgt wurden.

As components of consumer products, detergent chemicals like LAS have the potential to be distributed broadly to subsurface and surface soil environments and ground water. In the United States for example, approximately 25 to 30% of the LAS used in laundry and cleaning products is disposed of to home or "on-site" wastewater treatment systems. The effluents from these systems are directly discharged to subsurface soil drainage systems, where the majority of treatment occurs. Relative to effluents from municipal wastewater treatment systems, effluents from onsite systems may contain higher concentrations of LAS and other detergent chemicals. It is important, therefore, to characterize the fate of chemicals in these effluents once they are released to soil and adjoining ground water compartments. Four major processes control the fate and transport of chemicals in ground water/subsurface soil environments. These are advection, dispersion, sorption and biodegradation. The first three of these processes can change the relative concentration of a material or its distribution (both spatially and temporally) in a particular subsurface compartment. They cannot, however, lead to true removal and a decrease in overall mass. Only the last process, biodegradation, results in an actual decrease in chemical mass as well as environmental concentration. This process is key, therefore, in removing LAS and other detergent chemicals from subsurface environments. Research in our laboratories has shown that subsurface environments contain significant quantities of heterotrophic microorganisms which are capable of biodegrading a range of detergent chemicals, including LAS. This paper outlines some of the results of a comprehensive research program to characterize the fate of LAS in near-surface and subsurface soils and ground water. The program included both laboratory and field components, and was designed to determine the fate of LAS over a range of exposure conditions.

1 Introduction

Ground water may be defined as subsurface water that occurs beneath the water table in fully-saturated soils, rocks or other geologic formations called aquifers [1]. Ground water is a vast natural resource, comprising approximately 20% of the water found in or on the earth's land masses. On a global basis, it is estimated that the volume of ground water is more than 50 times the annual flow of surface water [2]. Ground water is an important natural resource in the United States, comprising an estimated 95% of all the fresh water reserves

of this country. Approximately 50% of the U.S. population relies on ground water as their primary source of drinking water. This includes most major U.S. cities (75%) and virtually all (95%) of the rural population [3]. Ground water is also a major part of the freshwater resources available in the European community, supplying on average over 60% of the drinking water used in EC Member States [4].

Although ground water is important in supplying large quantities of fresh water to the general public and to industry, relatively little research has been conducted to determine the fate of synthetic organic chemicals in ground water/subsurface soil (GWSS) systems. In general, four major processes control the fate and transport of chemicals in GWSS environments. These include advection, dispersion, sorption and biodegradation. The first three of these processes can

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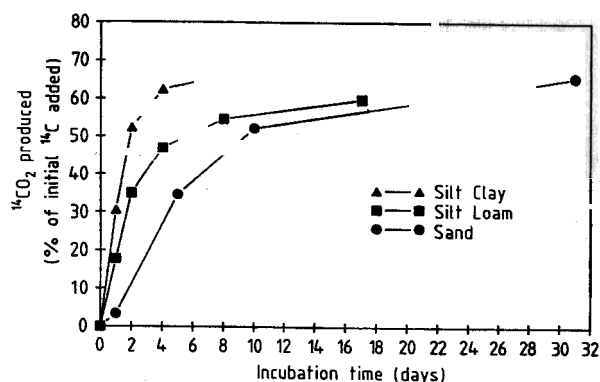


Fig. 2. Kinetics of biodegradation of LAS in surface soils as a function of soil type

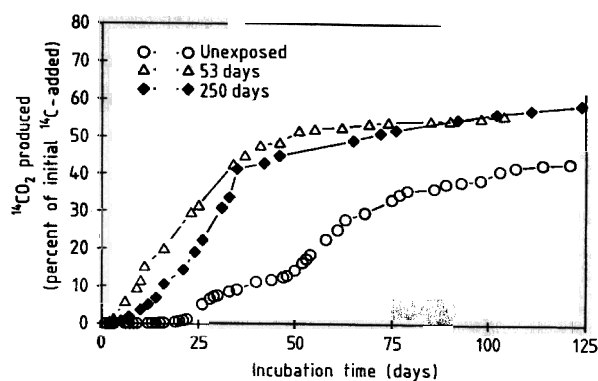


Fig. 3. Kinetics of biodegradation of LAS in subsurface soil samples exposed to LAS (0.2 µg/g) for various periods of time

3 Results and Discussion

3.1 Surface Soils

Typical results of time-course studies to characterize the kinetics of mineralization of LAS in different soil types is shown in Figure 2. All biodegradation studies were conducted in batch microcosms, using soil samples with no known exposure to detergent chemicals. The specific data shown are for a C13 homolog, tested at an initial concentration of 0.05 µg/g. Similar results, however, were obtained for other pure-chainlength homologs.

As Figure 2 indicates, the rate and extent of degradation was generally unaffected by soil type. Cumulative values for ¹⁴CO₂ production reached fairly high values (60 to 70%), and were consistent across the range of soils tested. Degradation proceeded without a noticeable lag phase, indicating that soil microbial communities were already adapted to the biodegradation of LAS. Biodegradation half-lives for LAS were relatively constant and showed little variation as a function of soil type (Table 1). Half-life values ranged from about 1 to 5 days, averaging about 2 days in the majority of samples tested. The half-lives measured for LAS in our studies were comparable to values measured for a naturally-occurring fatty acid (stearic acid) and in the range of values reported for

LAS degradation in the literature (Table 2). In general, therefore, biodegradation proved to be an effective removal mechanism for LAS in surface soil environments.

3.2 Subsurface Soil Microcosms

The results of time-course studies to determine the rate and extent of LAS degradation in subsurface soil microcosms exposed to LAS for various periods of time are shown in Figure 3. A porous sand with no prior history of exposure to detergent chemicals was collected from the unsaturated zone of an unconfined aquifer (~8 m) and approximately 1 kg was exposed to a mixture of unlabeled LAS homologs (0.2 µg/g) typical of that used in commercial formulations (average chainlength C12). At days 0, 53 and 250, subsamples (10 g) were taken and dosed with ¹⁴C-labeled LAS (0.8 µg/g) to follow cumulative ¹⁴CO₂ production as a function of time. The radiolabel data presented are for a C12 mixture typical of that used in commercial formulations. The data for the C12 material, however, are consistent with results obtained in a number of other microcosm studies where a range of pure chainlength homologs (C10-C14) were tested.

As shown in Figure 3, prior exposure to trace levels of LAS decreased the lag time prior to the onset of biodegradation and increased the biodegradation rate. Degradation in the exposed microcosms followed first-order kinetics, with biodegradation half-lives in the range of 20 days for both of the pre-exposure periods (53, 250 days). Degradation rates in the unexposed microcosms were more variable than the exposed microcosms and did not demonstrate a consistent kinetic pattern. Degradation lag phases were also longer in the unexposed microcosms than in the pre-exposed microcosms and mineralization efficiencies were somewhat lower. In general, the results of subsurface soil microcosm studies indicate that prior exposure to trace levels of LAS (0.2 µg/g) leads to the development of a biodegradation response which is significantly improved relative to unexposed microcosms. This response is maintained for extended periods of time (> 250 days) without additional inputs of LAS.

3.3 Laundromat Pond Studies

As part of our continuing efforts to characterize the biodegradation and fate of LAS in subsurface environments, we have been conducting field studies at a site in northern Wisconsin located near Summit Lake. The discharge of wastewater from a local laundromat operation into a natural depression has resulted in the formation of a permanent pond and wetland ecosystem (Figure 4). The soil substratum beneath the pond is a porous sand and in direct communication with

Table 1. Biodegradation Half-Lives for LAS in Surface Soils

Soil Type	Half-Life (days)	
	LAS	Stearic Acid
Loam	3.3	4.1
Silty Clay Loam	1.4	1.6
Silt Loam	2.2	3.8
	1.5	2.9
	1.7	2.0
	1.5	3.2
	1.7	3.3
Silty Clay	1.1	1.6
Sandy Loam	2.6	3.5
Sand	4.9	8.3
Compost	1.5	0.7
	3.1	0.5

Table 2. Half-Lives for Biodegradation of LAS in Soil Systems

Test Material	Half-Live (days)	References
¹⁴ C-LAS (ring)	10	[9]
¹⁴ C-LAS (ring)	11-18	[10]
¹⁴ C-LAS (ring)	8-27	[11]
¹⁴ C-LAS (ring)	21	[12]
¹⁴ C-LAS (ring)	5-25	[13]
¹² C-LAS		
¹² C-LAS	5	[14]
¹² C-LAS	7-22	[15]

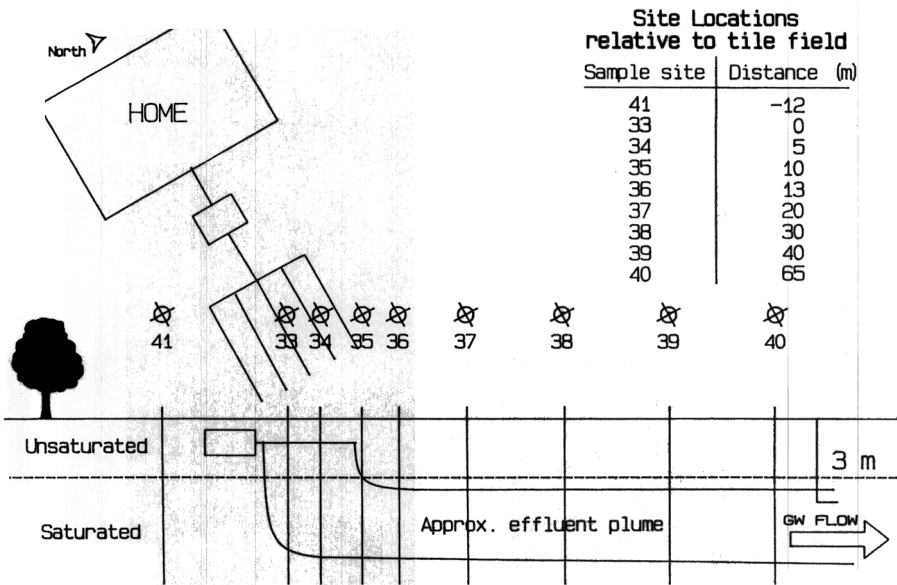


Fig. 7. Schematic diagram of the septic tank tile drainage field showing the location of sampling sites and the effluent plume

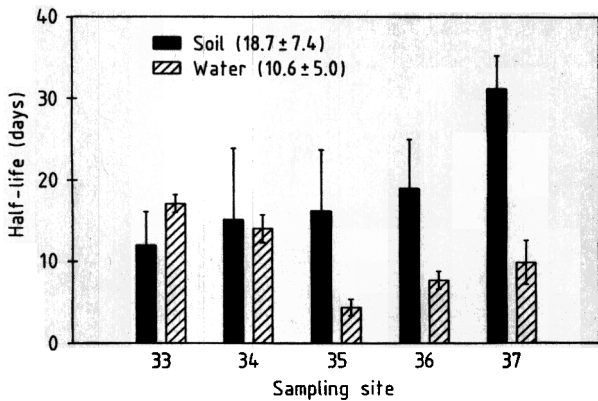


Fig. 8. Depth-averaged half-lives for biodegradation of LAS in subsurface soil and ground water. Error bars represent one standard deviation for samples collected at 0.3 to 1.0 m intervals over a depth of 5 m

indicates measured levels of LAS as a function of soil depth. Concentrations of LAS in the effluent plume decreased almost 3 orders of magnitude, from 10,000 $\mu\text{g/l}$ to 30 $\mu\text{g/l}$, over a horizontal distance of 10 m.

4 Removal of LAS due to Biodegradation

Figure 10 is a generic diagram which indicates the relative effectiveness of biodegradation as a removal mechanism for LAS in surface and subsurface soils and ground water. Plotted are concentrations of LAS remaining as a function of time for three different half-life values: 2 days, 10 days and 20 days. The 2, 10 and 20 day half-life values were chosen to be consistent with the values reported in this paper for surface soils, ground water and subsurface soils, respectively. It should be noted, however, that these half-lives are fairly typical of values we have measured in a number of different studies, and also agree well with values reported in the literature (see Table 2).

Due to the first-order or exponential character of LAS biodegradation, initial decreases in LAS concentrations occur quite rapidly with time. Greater than 90% removal occurs within a period of about 1 to 10 weeks, depending on the half-life value. Greater than 99% removal occurs within 2 to 20 weeks. These removal rates are clearly significant from an environmental exposure standpoint, since extended periods of time (months to years) are available in soil and ground

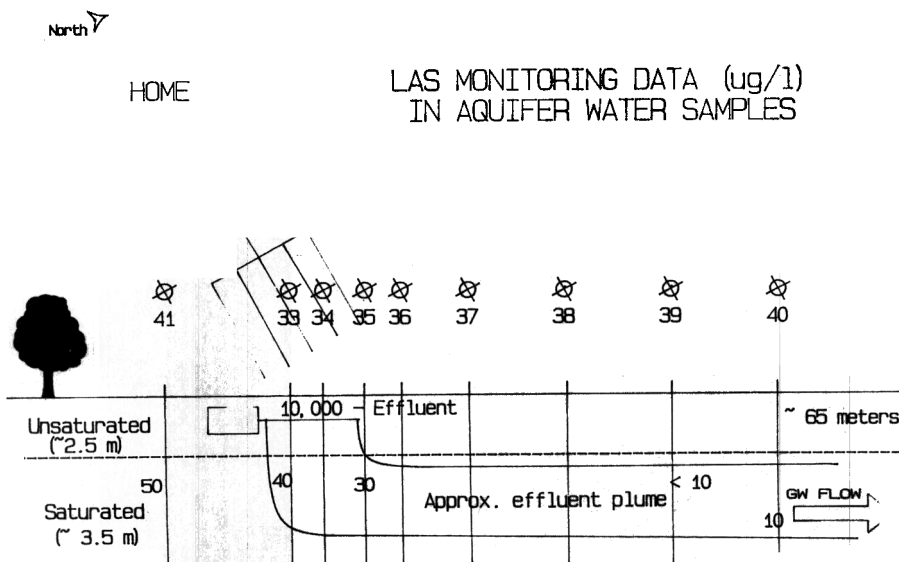


Fig. 9. Concentrations of LAS in the effluent plume as a function of distance from the septic tank discharge point

water environments for biodegradation to occur. Depending on the time-frames and biodegradation half-lives involved, LAS exposure concentrations can be reduced many orders of magnitude from their initial levels. Biodegradation, therefore, plays a major role in preventing the accumulation of LAS in soil and ground water environments.

5 Conclusions

A comprehensive research program has been conducted to characterize the fate of LAS in soil and ground water environments. Based on the results of this program, which included both laboratory and field components, the following conclusions can be drawn:

1. The benzene ring of LAS undergoes rapid mineralization in a variety of different surface and subsurface soils and ground water, with average biodegradation half-lives in the range of 2 to 20 days.
2. The biodegradation half-lives measured for LAS in both laboratory microcosm and field studies agree well with each other and with values reported in the literature.
3. Biodegradation is an important environmental removal mechanism for LAS which will limit its accumulation in soil and ground water compartments.

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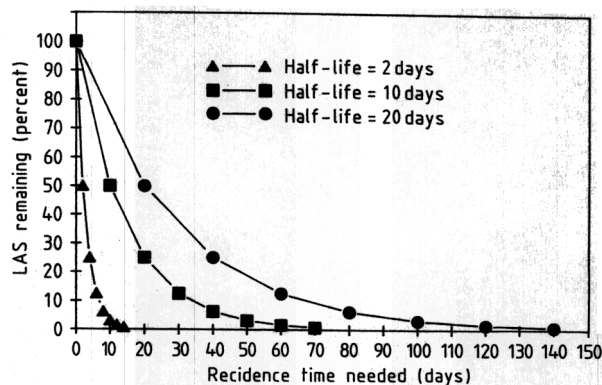


Fig. 10. Removal of LAS as a function of biodegradation half-life and the time available for biodegradation to occur

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