Difference in the Composition of Linear Alkylbenzene Sulfonate Homologues in River Sediment and River Water

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Abstract

Linear alkylbenzene sulfonates (LAS) in the surface sediment and the river water of the Tama River were determined by combined gas liquid chromatography and mass spectrometry. The composition of LAS homologues in the river sediment was remarkably different from that in the river water; the proportions of C12 and C13 LAS in the sediment were higher than those in the water, while those of C10 and C11 LAS were lower. The ratio of the concentration of the LAS homologues in the sediment to that in the water increased exponentially with increasing the carbon number of the alkyl group.

1. Introduction

As the major components of commercial synthetic detergent, linear alkylbenzene sulfonates (LAS) have been widely used in Japan since 1968. Although LAS is relatively susceptible to degradation by microorganisms (SWISHER, 1963a, 1963b, GLEDHILL, 1974), the behaviour of LAS in the environment has still been a matter of considerable concern as an artificial pollutant. The determination of LAS in the aquatic environments has not been reported so far at the molecular level.

The present study describes the determination of LAS homologues in the sediment and the water of the Tama River by the GLC-MS method improved by the authors (HON-NAMI and HANYA, 1978), and reports a remarkable difference in the composition of LAS homologues between the river sediment and the river water.

2. Experimental

Sampling. Sampling locations are shown in Fig. 1. Three locations at the Tama River were selected to compare the compositions of LAS homologues in its surface sediment with those in the river water.

![Fig. 1. Sampling location at the Tama River.](image-url)
Composition of LAS Homologues in River

was centrifuged (3000 rpm, 30 min) to remove the interstitial water, and mixed with 100 ml of methanol in a homogenizer and stirred rigorously for 20 min. The extraction was repeated four times. The extracts were combined and evaporated to dryness under a reduced pressure. The residue containing LAS was dissolved in about 300 ml of hot, distilled water. LAS in the solution was determined by the same procedure as employed in the river water.

The individual components of LAS homologues were determined by mass fragmentography, which was run at the m/e value of the molecular ion of their methyl sulfonate derivatives. According to the recovery test by the addition of n-dodecylbenzene sulfonate (DBS) to the river sediments, more than 84% of the added DBS was recovered.

3. Results and Discussion

A typical gas chromatogram and mass fragmentograms of LAS in the river sediment (sampling location, Maruko) are shown in Fig. 2.

LAS concentrations in the river water and the sediment are listed in Table 1, which shows that the LAS concentrations in the sediments are 50 to 500 times as much as those in the river waters. Both in the water and the sediment at the estuary (Taishi) of the Tama River, the LAS concentrations were lower than those at other locations, which may be due to dilution by the bay water containing less than 0.014 ppm of LAS (Hon-Nami and Hanya, unpublished results).

Table 2 shows LAS compositions in the river water and the sediment. The percent composition of LAS homologues, C10, C11, C12 and C13 LAS was 13.3–26.8, 45.8–55.2, 18.2–30.4 and 0.0–9.2% in the water, and 0.0–2.5, 22.9–35.2, 39.3–48.3 and 16.4–34.4% in the sediment, respectively. The variation in the composition of LAS homologues among different sampling locations was found to be small both in the river water and the sediment, and a remarkable difference in the LAS composition was observed between the sediment and the water. The percent compositions

![Fig. 2. Gas chromatogram (A) and mass fragmentograms (B) of LAS as methyl sulfonate derivatives in sediment, using Shimadzu LKB-9000 instrument, 2 m x 3 mm L.D. glass column, silicon OV-1 substrate, temperature 230°C.](image-url)
of C₁₂ and C₁₃ LAS in the sediment were higher than those in the water, while that of C₁₁ LAS was lower. And it is noteworthy that C₁₀ LAS showed an extremely low in proportion in the sediments.

In order to estimate the difference in the behaviour among individual components of LAS homologues of migrating from the water to the sediment, ratios (K) of the concentration of individual LAS homologues in the sediment to that in the water was calculated, and the logarithms were of K plotted against the carbon number of the alkyl group (Fig. 3). Figure 3 shows that the ratio increased exponentially with increasing the carbon number of the alkyl group. The most probable explanation for this observation is that the longer the alkyl chain length, the more LAS adsorbed in the sediment. WAYMAN (1963) has reported that C₁₅ branch-type alkylbenzene sulfonate (TBS) was adsorbed more easily than C₁₂ TBS on the clays. Studies on the adsorption of LAS homologues on the sediment are under way.
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References


