

Short Note

ON THE ORIGIN OF ALKYL BENZENES IN GEOCHEMICAL SAMPLES

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(Received November 19, 1984; accepted December 20, 1984)

In 1978, Stuermer and Harvey reported the isolation of a series of  $C_{10}$ – $C_{14}$  alkyl-substituted benzenes after high-pressure hydrogenation and ether cleavage reactions on a Sargasso Sea fulvic acid. Mass spectra of the multiple homologues indicated that the phenyl group was substituted on every possible secondary position of the alkyl chain. The presence of this series of compounds in the reaction products was interpreted as evidence that the basic structural units had been part of the original fulvic acid and that the severe reactions employed had cleaved them out of the main structure. More recently, Harvey et al. (1983) used this observation in partial support of a proposed marine fulvic acid structure resulting from the oxidative cross-linking of polyunsaturated lipids. There now appears to be a more likely origin for these particular alkyl benzenes isolated from a marine fulvic acid reaction mixture; we believe they are the  $C_{10}$ – $C_{14}$  linear alkyl benzenes (LAB) which are the precursors in the commercial production of linear alkyl benzene sulfonate (LAS) surfactants widely used in detergents. We present this evidence now so as to avoid a similar situation of a decade ago with the phthalate plasticizers which were reported by many workers to be widely distributed natural products (Mathur, 1974; Mayer et al., 1972).

Crisp et al. (1979) isolated several isomeric  $C_{10}$ – $C_{13}$  secondary phenyl-alkanes from particulates captured in sediment traps deployed in San Pedro Basin, California. They noted the relationship of these hydrocarbons to anionic surfactants of the LAS type. Ishiwatari et al. (1983) and Eganhouse et al. (1982, 1983) have described in detail the presence of  $C_{10}$ – $C_{14}$  LAB in Tokyo Bay sediments, and waste effluents, commercial detergents and San Pedro Basin sediments, respectively. Their occurrence in the above samples is believed to result from incomplete sulfonation of LAB during LAS

production with subsequent association and dispersal into the environment with the detergents.

Recently, in the Delft Group, Klok et al. (1984) and Van Graas et al. (unpublished results) have encountered the LAB in Namibian Shelf sediments and in Cretaceous black shales. On the basis of the narrow chain lengths found ( $C_{10}$ – $C_{12}$ ), contamination by synthetic detergents was deemed likely. Reexamination of the mass spectra of the LAB reported by Stuermer and Harvey (1978) show that they are identical with those published by Ishiwatari et al. (1983). Both Stuermer and Harvey (1978) and Van Graas (unpublished) determined that these compounds were not introduced during the isolation and chemical workup. We conclude that the LAB were already present in the geochemical samples as contaminants and indicate their widespread distribution in the environment. Finally, we suggest that when  $C_{10}$ – $C_{14}$  LAB are found in geochemical samples that they be attributed to contamination rather than to a natural source.

#### REFERENCES

- Crisp, P.T., Brenner, S., Venkatesan, M.L., Ruth E. and Kaplan, I.R., 1979. Organic chemical characterization of sediment-trap particulates from San Nicolas, Santa Barbara, Santa Monica and San Pedro Basins, California. *Geochim. Cosmochim. Acta*, 43: 1791–1801.
- Eganhouse, R.P. and Kaplan, I.R., 1982. Extractable organic matter in municipal wastewaters. 2. Hydrocarbons: molecular characterization. *Environ. Sci. Technol.*, 16: 541–551.
- Eganhouse, R.P., Blumfield, D.L. and Kaplan, I.R., 1983. Long-chain alkylbenzenes as molecular tracers of domestic wastes in the marine environment. *Environ. Sci. Technol.*, 17: 523–530.
- Harvey, G.R., Boran, D.A., Chesal, L.A. and Tokar, J.M., 1983. The structure of marine fulvic and humic acids. *Mar. Chem.*, 12: 119–132.
- Ishiwatari, R., Takada, H., Yun, S.J. and Matsumoto, E., 1983. Alkylbenzene pollution of Tokyo Bay sediments. *Nature (London)*, 301: 599–600.
- Klok, J., Baas, M., Cox, H.C., De Leeuw, J.W., Rijpstra, W.I.C. and Schenck, P.A., 1984. Qualitative and quantitative characterization of the total organic matter in a recent marine sediment, II. In: P.A. Schenck, J.W. De Leeuw and G.W.M. Lijmbach (Editors), *Advances in Organic Geochemistry, 1983*. Pergamon, Oxford, in press.
- Mathur, S.P., 1974. Phthalate esters in the environment: pollutants or natural products? *J. Environ. Qual.*, 3: 189.
- Mayer, F.L., Jr., Stalling, D.L. and Johnson, J.L., 1972. Phthalate esters as environmental contaminants. *Nature (London)*, 238: 411.
- Stuermer, D.H. and Harvey, G.R., 1978. Structural studies on marine humus: a new reduction sequence for carbon skeleton determination. *Mar. Chem.*, 6: 55–70.