Anaerobic Biodegradation of Linear Alkylbenzenes

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Abstract

Linear alkylbenzenes (LAB) are commonly found in the environment due to their use as a precursor in the manufacture of linear alkylbenzene sulphonate (LAS) detergents, in which they remain as trace contaminants. Other uses include insulating oils in buried electricity transmission cables, from where they may enter soil and groundwater in the event of damage to the cable sheath or joints. They are readily biodegraded under aerobic conditions but may be released into anoxic environments where they can persist for some time. Laboratory experiments show that LAB can be degraded under nitrate-reducing conditions, and isomeric analysis of the remaining LAB is good indicator of the degree of degradation. Work is continuing to identify changes in microbial diversity using denaturing gradient gel electrophoresis of rDNA polymerase chain reaction (PCR) products.

Oil-filled cables

Most high tension electricity transmission is via overhead lines suspended from pylons. This is an efficient and cost-effective solution. Where overhead lines are not appropriate, transmission may be via buried cables. Approximately 600 km of underground electricity cable is in use in England and Wales, at potentials of 275 and 400 kV. The majority of these cables (Fig. 1) are oil-insulated in many cases the insulating oil is a mixture of synthetic linear alkylbenzenes (Fig. 2).
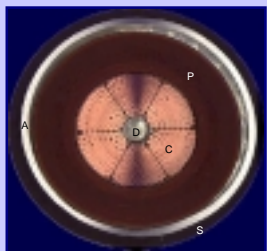

Figure 1. Section of oil-filled cable. The cable consists of a shaped copper conductor (C) with a central oil duct (D). The conductor is wrapped with paper tape (P) which is impregnated with cable oil. An aluminium casing (A) provides mechanical strength and an outer polythene sheath (S) prevents the ingress of water. Image courtesy National Grid Company plc.

The cables are occasionally subject to mechanical damage and failure of the joints between sections. This can result in the release of LAB into the surrounding soil and groundwater. Most of the oil is removed when the soil is excavated to allow the cable to be repaired, but residual oil may remain.

LAB is a light, non-aqueous phase liquid and so will partition at the water table where conditions are likely to be anaerobic. It is known to degrade rapidly in aerobic conditions but it is considered to be persistent in anaerobic sediments.

Aqueous cultures of microorganisms from a contaminated soil with LAB as the sole carbon and energy source indicate that it may be degraded under nitrate-reducing conditions

Measuring biodegradation

Gas chromatography – mass spectrometry is a sensitive method for both identification and quantifying hydrocarbons. Individual homologues of LAB, extracted by shaking in hexane, were separated and quantified by reference to an internal standard ($1C_{12}$ LAB – a terminal isomer, not present in the synthetic mixture).

External isomers, where the phenyl group is towards one end of the alkane chain, are more readily degraded than internal isomers under aerobic conditions. Cultures were incubated with a variety of terminal electron acceptors to investigate whether this was true under different redox conditions (Figs. 3 & 4).

A commonly used indicator of biodegradation of LAB is the ratio of internal to external isomers of nC_{12} LAB. This can be calculated from the peak areas obtained from GC-MS (Eq. 1)
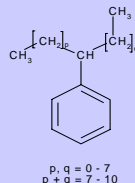

p, q = 0 - 7
p + q = 7 - 10

Figure 2. Generalized structure of LAB in cable oil.

Figure 3. Typical GC of fresh LAB cable oil. Annotated with alkyl chain length and position of phenyl group.

$$I:E = \frac{6C_{12}+5C_{12}}{4C_{12}+3C_{12}+2C_{12}}$$

Equation 1. Definition of I:E isomeric ratio (Naming convention nCm, where n = position of benzene ring; m = length of alkyl chain).
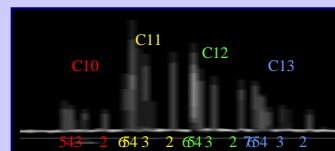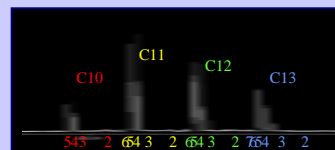

Figure 4. GC of LAB cable oil exposed to nitrate as a TEA (after 13 weeks).

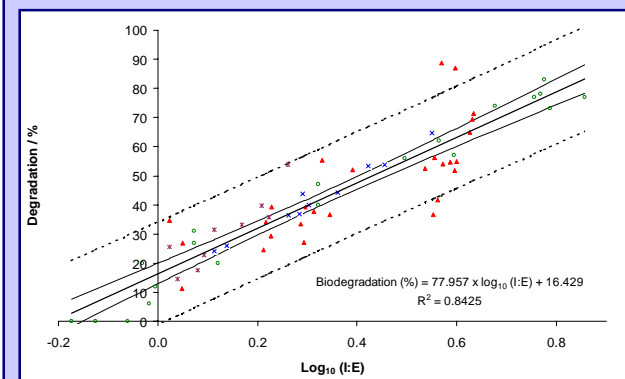Biodegradation (%) = 77.957 x log$_{10}$ (I:E) + 16.429
R^2 = 0.8425

Figure 5. Plot of % biodegradation of LAB vs. $\log_{10}$ internal:external (I:E) nC_{12} LAB isomer ratio with linear regression (heavy) line, 95% confidence (light) and 95% prediction intervals (broken lines). Data points are from individual bottles: aerobic (◊), anaerobic containing multiple TEAs (•) or nitrate alone (▲) and aerobic data from Takada & Ishiwatari (×). Thanks to Hiroshige Takada for providing raw data.

I:E ratio indicates biodegradation

Plots of % biodegradation against I:E ratio for a variety of conditions are not statistically different (p < 0.05) from each other, or from published aerobic data (Takada & Ishiwatari, 1990 *Environ. Sci. Technol.* **24**, 86-91).

The data are combined to give a common regression line (Fig. 5) that may be used to indicate the degree of biodegradation in contaminated sites where neither the original concentration, nor the redox history are known.