

**Natural attenuation : the major biodegradation reactions, modelling at the plume scale and in situ measurements**

O. Atteia, M. Franceschi and A. Dupuy  
EGID, Université de Bordeaux 3

Natural attenuation processes, and particularly intrinsic biodegradation, are complex as they involve bacteria, chemical reactants and transport of these species. Many laboratory experiments showed that biodegradation rates of BTEX, phenols or even chlorinated solvents, may be fast, i.e. half lives of hours or days, under optimal conditions (Wiedmeier *et al.* 1999). At contrary, much slower degradation rates were found in field studies, and these degradation rates seemed to be limited by the flux of redox reactants (Borden *et al.* 1995). Despite this knowledge, modelling approaches often rely on first order kinetic degradation rates fitted on field results. In this paper we try to detail the influence of different types of modelling options on the resulting concentrations at various places of the plume. Beside we suggest different measuring strategies needed to extract the maximum of information from an existing plume.

Numerous tools do exist presently in the field of biodegradation modelling. Originating from transport approaches augmented with retardation and simple first order degradation, they evolved to complete biogeochemical models including reactions in the liquid phase, bacteria development, dissolution, exchange, kinetics and gas phases. As said above, owing to the laboratory and field results we may only use the models able to really take into account the transport of electron donors (ED) or acceptors (EA).

In this context, the most difficult phenomena to model is the "preference" of bacteria for one compound instead of another. One example is toluene compared to benzene, both compounds have similar forming Gibbs free energy but benzene, contrary to toluene, is scarcely degraded under anaerobic conditions. To take this process into account one must use kinetics with specific reactants and thus make a choice which can have dubious consequences on the plume development. The importance of such options taken during the modelling processes are analysed through various examples. This leads us to propose a new method to model plume development which rely on superimposed analytical solutions and thus allows a fast review of the influence of different modelling strategies.

A close analysis of the simulations shows that fast degradation of compounds at places where EA flux is sufficient conduct to very steep concentration gradients at plume borders. This is why a particular characterisation effort must be devoted to the plume borders. A complementary technique of characterisation of such fast reaction at the plume borders is proposed; it is mainly constituted of in situ respirometric measurements, but allows to get the details of the consumed EA. The measuring system has been tested in the laboratory within a 200 l barrel full of saturated sand, isolated from ambient air. The experiments showed that under optimal conditions, i.e. when oxygen was not limiting, the kinetic of BTEX degradation was fast, with a half-life close to 1 h. In the absence of oxygen almost no degradation occurred. The few experiments done in the field showed that local degradation rates could be measured down to approximately one mg/L of organics converted to CO<sub>2</sub> in one day.

Literature

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- Wiedmeier T.H., Rifai H.S., Newell C.J. Wilson J.T. (1999) : Natural attenuation of fuels and chlorinated solvents in the subsurface. Wiley and sons.