

# Reactive Multicomponent Transport Modelling of Contaminated Aquifers: Natural Attenuation of a Petroleum Hydrocarbon Plume Under Sulphate-Reducing Conditions

Henning Prommer (h.prommer@ed.ac.uk)<sup>1</sup>, Katherine J. Woolhouse (katherinew@flow.civ.ed.ac.uk)<sup>1</sup>,  
D. Andrew Barry (a.barry@ed.ac.uk)<sup>1</sup> & Gregory B. Davis (greg.davis@per.clw.csiro.au)<sup>2</sup>

<sup>1</sup> CLARRC, School of Civil and Env. Engineering, The University of Edinburgh, EH9 3JN, UK

<sup>2</sup> CSIRO Land and Water, Private Bag, PO Wembley, WA 6014, Australia

Over many decades, growing industrial production and utilisation of energy and materials were accompanied by an increasing flux of hazardous organic and inorganic chemicals to groundwater. It is now well recognised that naturally occurring soil micro-organisms have the capability to metabolise a wide range of hazardous organic chemicals and to remove contaminants from groundwater without human intervention. This process is known as natural attenuation (NA). Under a wide range of hydrogeochemical conditions, monitored natural attenuation (MNA) has been shown to be a cost-effective remediation method for managing the risk of contaminant plumes. Because of the relatively long time scales involved, risk assessments involving MNA rely heavily on modelling to predict expected remediation outcomes. In comparison to traditional groundwater and soil remediation methods such as pump-and-treat, which by construction involve a limited number of dominating processes, NA requires a much more detailed understanding to quantify the interactions between organic contaminants, the inorganic aquifer geochemistry and the microbiological environment. That being the case, inorganic chemicals involved in the degradation reactions serve as geochemical markers to provide supporting evidence for the occurrence of NA and its performance. However, the use of these geochemical tracers/markers is complicated by the fact that the chemical species utilised or produced during biodegradation undergo further secondary reactions such as complexation or dissolution/precipitation of minerals. Furthermore, although numerical modelling has become a popular tool for the assessment and analysis of NA, the reactive processes included are typically confined to the primary biodegradation reactions, i.e. the oxidation of one or more organic compounds coupled to the reduction of one or more electron acceptors.

During this study, a three-dimensional numerical model accounting for (i) hydrological transport, (ii) inorganic aqueous/sediment chemistry and (iii) the biodegradation rate-determining microbial activity during kinetically controlled biodegradation of organic chemicals in groundwater has been developed. The model couples, via operator-splitting (OS),

advective-dispersive transport of organic and inorganic solutes, solved by MT3DMS (Zheng and Wang, 1998), and the geochemical package PHREEQC-2 (Parkhurst and Appelo, 2000). Immobile non-aqueous phase liquids (NAPL's), the appropriate dissolved organic compounds and bacterial groups as well as their reaction kinetics, such as (multicomponent) NAPL-dissolution and biodegradation, were included/incorporated into the framework provided by the PHREEQC-2 module. Hydrological transport is carried out for organic compounds and for total aqueous component concentrations of inorganic solutes. The (local) redox-state is modelled by transporting chemicals/components in different redox states separately.

The model was applied to a field case in the Metropolitan area of Perth/Western Australia, where a plume of hydrocarbon compounds, originating from a leaking underground storage tank located at a service station, undergoes NA under anaerobic conditions. Concentration of organic compounds and inorganic chemicals were observed for several years by a detailed monitoring network (Davis et al., 1999). The model is shown to be capable of reproducing quantitatively the observed removal (mineralisation) of toluene, ethylbenzene and xylene and can mimic the resulting response of the inorganic aquifer geochemistry. Most importantly, the model approach allowed a detailed study of the role of groundwater-sediment interactions such as the dissolution of iron(III) minerals and the precipitation of iron sulphide and pyrite. Both field investigations and modelling suggest that sulphate, rather than iron(III), is clearly the principle source of oxidation capacity for the organic contaminants.

Davis GB, Barber C, Power TR, Thierrin J, Patterson BM, Rayner JL & Wu Q, *J. Contam. Hydrol.*, **36(3-4)**, 265-290, (1999).

Parkhurst DL & Appelo CAJ, *US Geol. Survey Water-Resources Investigations Report 99-4259*, (2000).

Zheng C & Wang PP, *Technical Report, US Army Corps of Engineers Waterways Experiment Station*, (1998).