Reaction front formation in contaminant plumes

Laura B. Cribbin [a], Henry F. Winstanley [a,*], Sarah L. Mitchell [a],
Andrew C. Fowler [a,b], Graham C. Sander [b,c]

[a] *MACSI, University of Limerick, Limerick, Ireland*
[b] *OCIAM, University of Oxford, Oxford, UK*
[c] *School of Civil and Building Engineering, Loughborough University, Loughborough, UK*

ABSTRACT

The formation of successive fronts in contaminated groundwater plumes by subsoil bacterial action is a commonly accepted feature of their propagation, but it is not obviously clear from a mathematical standpoint quite how such fronts are formed or propagate. In this paper we show that these can be explained by combining classical reaction–diffusion theory involving just two reactants (oxidant and reductant), and a secondary reaction in which a reactant on one side of such a front is (re-)formed on the other side of the front via diffusion of its product across the front. We give approximate asymptotic solutions for the reactant profiles, and the propagation rate of the front.

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1. Introduction

The motivation for modelling and simulating groundwater contaminant transport and degradation is clear and compelling. Groundwater contaminants from both historical and current human activity are ubiquitous in the developed and developing world. Human and environmental risks arise wherever these contaminants enter surface waters or abstraction wells. Site data is limited to spatially sparse datasets; data gathering costs are significant and remedial intervention costs are high and generally prohibitive. Hence quantitative predictions of contaminant concentrations are of great importance in assessing necessary actions. However, there are limitations on the accuracy and reliability of predictive models: the heterogeneity of natural media introduces uncertainties, and though the physico-chemical processes are relatively well understood, knowledge of microbial processes and rates is limited.

Microbially-mediated reactions are the dominant process in degradation of many groundwater contaminants. In particular, a wide range of common organic (e.g. petrochemicals, solvents, coal tars) and inorganic (e.g. ammonia) groundwater contaminants are degraded by respirative microbiota, whose respiration is effectively an overall redox reaction between these contaminants as electron donors and a terminal electron acceptor (TEA) sourced from the local environment. The availability of TEAs and thermodynamic viability of TEA-donor redox couples depends on spatial location and chemical environment, but a typical range can include dissolved oxygen, nitrate, manganese (IV) and iron (III) minerals, sulphate, and carbon dioxide (in approximate order of oxidant strength).

The paradigm of redox zonation due to microbially mediated reactions in groundwater and aquatic sediments is well-engrained in the literature (cf. Chapelle, 2001; Christensen et al., 2000; Froelich et al., 1979). In its barest form, the principle is that microbes exploiting higher energy yield reactions will tend to outcompete others and dominate the local electron flux (i.e. overall reaction rate). As a result, a spatial sequence of more-or-less distinct zones forms in which each zone is dominated by
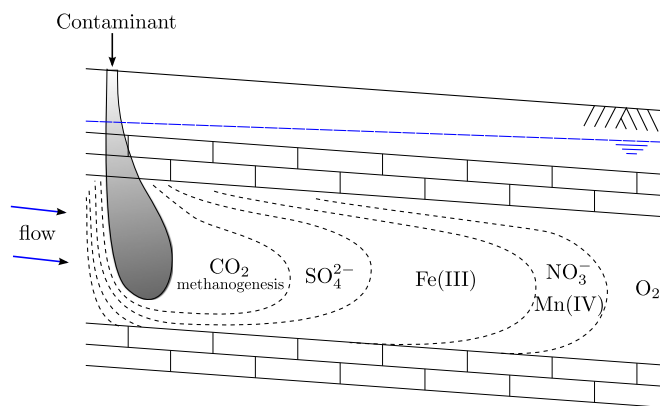
Fig. 1. Schematic propagation of a contaminant plume, and the zones where the successive terminal electron acceptors operate, separated by a sequence of reaction fronts.

a specific TEA process until that TEA is depleted, and the next zone is dominated by the next most reactive available TEA in sequence, as depicted in Fig. 1. Relative to the redox zone width, the transitions between redox zones often appear to occur over relatively short distances of order 1 m or less in contaminant plumes suggesting that at the field scale they may be thought of as reaction fronts.

This simple conceptual model focussing on TEA processes tacitly assumes that the dominant electron donors have relatively constant concentrations across the redox zones, whether occurring as the primary contaminant, or as simpler species resulting from microbial fermentation, such as hydrogen and acetate. Interestingly, this conflicts with what one might expect based on standard mathematical models of reaction fronts. Generally, when two diffusible reagents are supplied from opposite sides of a domain and the reaction rate is fast relative to transport, the solution is a reaction front with a distinct reaction zone flanked by diffusion-dominated zones in which negligible reaction occurs. Crucially, both reagents are 'taken out' by the front so that their concentrations are asymptotically small on the side away from their supply, and the reaction is effectively confined to the narrow reaction zone where both reagents are present (e. g., Gálfi and Rácz, 1988; Hagan et al., 1985). The position of the reaction front reflects the reaction stoichiometry and rate of supply of each reagent (Nambi et al., 2003).

The aim of the current paper is to reconcile the transition between successive redox zones in a contaminant plume with standard mathematical modelling of reaction fronts. We do this by building a simplified model of just the dominant reactions in a single such transition in order to illustrate the mathematical structure. The extension to multiple transitions is then largely a straightforward exercise.

A number of other papers have addressed the issue of modelling reaction fronts. Gálfi and Rácz (1988) (see also Chu et al., 2005) effectively solved the reaction front dynamics of the reaction $A + B \rightarrow C$ at large times; their work was partly motivated by the phenomenon of Liesegang rings, which were modelled in detail by Keller and Rubinow (1981) and Feeney et al. (1983). Taitelbaum et al. (1992) studied a two-component reaction–diffusion front, focussing interest on the rate of movement of the reaction front. Their analysis was valid for early times, and was later elaborated by Koza and Taitelbaum (1996). Sinder and Pelleg (1999) extended these results to the

case of a reversible reaction. Our present interest, however, is in the large time limit where the reactions are fast, and the results of Gálfi and Rácz (1988) are the most relevant.

Consideration of reaction fronts in contaminant plumes has been a focus of a number of papers. Gutierrez-Neri et al. (2009) considered fringe and core degradation, but assumed an instantaneous reaction between electron acceptor and electron donor at the fringe. A number of papers consider a simple two species reaction (between for example CH_2O and O_2) with associated growth of biomass, and give various analytic and numerical approximations to the propagation of the front (Cirpka, 2010; Keijzer et al., 1998); some study the front propagation as that of a travelling wave (Keijzer et al., 1999), where the front can be oscillatory (Murray, 2002; Oya and Valocchi, 1997); and a number of researchers prove mathematical results (Beck et al., 2006; Ai, 2007; Xin and Hyman, 2000). Other studies using numerical solutions of similar kinetic formulations include those of Abrams and Loague (2000a,b), Wang and Van Cappellen (1996), MacQuarrie and Sudicky (2001), Thullner et al. (2005), and Rolle et al. (2008).

Our approach is very different in aim and scope both to the more analytic papers referred to above, where the dynamics of the simplest (two species plus biomass) model is studied, and also to the standard approach of using a numerical simulation package to solve a highly detailed reactive transport system. Many good examples of such packages exist (such as PHREEQC, PHAST, HYDRUS 2D/3D, MIN3P, ORCHESTRA), each with its particular approach and emphasis. The typical complexity of the underlying models (and hence parameterisation) of these packages provides ease of application in diverse settings, but often contrasts with the treatment of biotic reaction rates and microbial population interactions due to the inherent uncertainties and site specificity in these. And yet, the redox zonation paradigm hinges on the emergence of a dominant metabolic type through population competition, so for our purposes a greatly simplified model appears warranted and can have the benefit of providing greater mechanistic insight. For simplicity we base our study on the one-dimensional kinetic model of Hunter et al. (1998), whose numerical solutions provide indication of front formation.

The resolution to the apparent conflict between the reaction front paradigm and the persistence of the primary electron donor across the front lies in the presence of secondary