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Oscillations in soil bacterial redox reactions

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HIGHLIGHTS

- We report carbon and ammonium spatial oscillations in soils.
- We associate these with activator–inhibitor type microbial ecosystem dynamics in soils.
- A competitive heterotroph-fermenter system exhibits boom-and-bust oscillations.
- The oscillations are relaxational in conditions of starvation.
- We expect that spatial diffusion will cause travelling waves which explain the observations.

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ABSTRACT

Spatial oscillations in soil contaminant concentration profiles are sometimes observed, but rarely commented on, or are attributed to noisy data. In this paper we consider a possible mechanism for the occurrence of oscillatory reactant profiles within contaminant plumes. The bioremediative reactions which occur are effected by bacteria, whose rôle is normally conceived of as being passive. Here we argue that competition, for example between heterotrophic and fermentative bacteria, can occur in the form of an activator–inhibitor system, thus promoting oscillations. We describe a simple model for the competition between two such microbial populations, and we show that in normal oligotrophic groundwater conditions, oscillatory behaviour is easily obtained. When such competition occurs in a dispersive porous medium, travelling waves can be generated, which provide a possible explanation for the observed soil column oscillations.

1. Introduction

Measurements of soil mineral and contaminant concentrations are commonly interpreted in terms of a sequence of redox reactions effected by a succession of terminal electron acceptors, in the progressive order oxygen, nitrate, manganese, and so on (Chapelle, 2001). These reactions, typified by the degradation of generic organic carbon substrates CH_2O by oxygen,

$$CH_2O+O_2\xrightarrow{r}H_2O+CO_2, \tag{1.1}$$

are enabled by microbial reactions, and the reaction rate r is typically described by a multiplicative Monod term of the form (for (1.1))

$$r=r_0X\left(\frac{[O_2]}{K+[O_2]}\right)\left(\frac{[CH_2O]}{K_c+[CH_2O]}\right), \tag{1.2}$$

where $[O_2]$ and $[CH_2O]$ are the concentrations of oxygen and organic carbon, respectively, and X represents microbial biomass. Typically, computational models for the evolution of contaminated groundwater plumes seek to understand the succession of reaction fronts in soil columns (Chapelle, 2001, p. 294) by means of reaction-diffusion models in which the microbial biomass is not considered to vary (e.g., Hunter et al., 1998). Despite this, the growth of microbial populations depends on nutrient uptake, and different microbial communities actively compete with each other (e.g., Lovley and Klug, 1986). In particular, the principle of competitive exclusion allows different microbial communities to dominate in different strata (Chapelle, 2001, pp. 177 ff.). In this paper we explore another possibility which arises from microbial population interaction, and that is the occurrence of spatial oscillations in soil column concentrations.

The Rexco site in Mansfield was home to a coal carbonisation plant which spilled ammoniacal liquor into the surrounding soil in the mid-twentieth century. An estimated 70,000 tonnes of this liquor was disposed into a settling lagoon between 1956 and 1969. The active spillage was eventually stopped a year later. Since then, a sandstone unsaturated zone of depth around 20 m has been an ongoing source of groundwater contamination. The contamination consists of ammonium, nitrate and phenols. A large field investigation took place between 1994 and 1997 to study the natural

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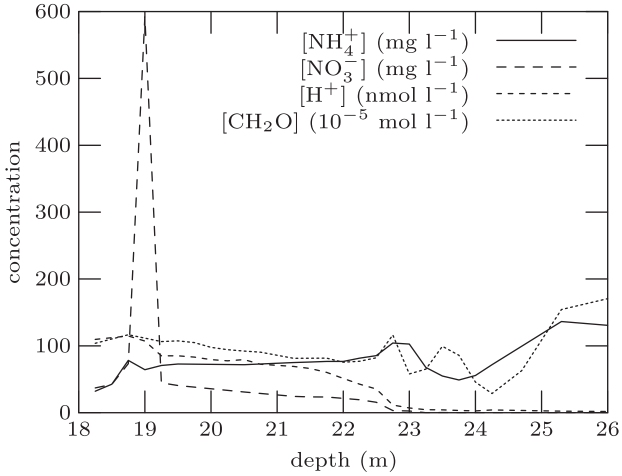

Fig. 1. Borehole data from Rexco borehole 102. Contaminant concentrations are shown as a function of depth in the hole.

attenuation of the contamination (Broholm et al., 1998; Jones et al., 1998, 1999). As part of the investigation, groundwater and soil samples were taken from a series of boreholes and the minerals in the aquifer were characterised. The results from one particular borehole, namely BH102, are shown in Fig. 1. Data for each contaminant was recorded along 25 cm intervals beginning 18 m underground at the top of the saturated zone. The borehole thus shows a vertical section through the contaminant plume.

As we explained above, the accepted wisdom concerning such plumes is that the contaminant is sequentially consumed by a sequence of terminal electron acceptors (TEAs), generally in the order oxygen, nitrate, manganese IV, iron III, sulphate and carbon dioxide. Thus a vertical borehole would expect to find a sequence of fronts in which first oxygen, then nitrate, and so on, are removed. It is this conceptual picture with which we wish to confront Fig. 1.

In more detail (Thullner et al., 2007), the breakdown of organic carbon takes place in stages, with hydrolysis producing sugars, then fermentative processes producing simpler carbon sources such as acetate, and it is these which are mostly accessed by the TEA processes.

There are a number of features in Fig. 1 of note. Oxygen was not monitored, but we assume that it was removed at a front at depth 19 m, where there is a notable nitrate spike. As the data was measured every 25 cm, it is quite conceivable that the nitrate spike is nothing more than an outlier; of interest, but not requiring detailed explanation.

However, our present concern is with an apparent second front at around 23 m depth, where both nitrate and acid (H^+) are removed. In such reaction fronts, we expect another reactant to be removed from the other side of the front, but none were monitored. The feature which concerns us here is the change in the profiles of both organic carbon CH_2O and ammonium NH_4^+. Exactly at the front, there is a transition to oscillatory profiles of both these reactants. The data is very clear to indicate this, and in addition the two reactants are out of phase. It is this oscillation which we seek to explain.

Such oscillations have been found elsewhere. For example, a later borehole study by Smits et al. (2009) at the same site found similar oscillations in both nitrate and nitrite at two different boreholes. In a laboratory microcosm study, Watson et al. (2003) found oscillatory behaviour both in the experimental data and also in the simulation model which they use to fit the data. A later application (Watson et al., 2005) to a field scale plume was inconclusive in this aspect, as the data was apparently not sampled at such fine spatial scale.

2. Mathematical model

Microbial populations generally present in the subsoil are metabolically very diverse. The standard picture is one of competitive exclusion between different populations leading to the dominance of one metabolic type in any location. The hierarchy of redox zonation is typically explained by the competitive advantage enjoyed by populations exploiting the most energetically favourable terminal electron acceptor available. As – or where – this TEA's supply is exhausted, the next most reactive TEA supplants it as the dominant metabolic TEA process (Chapelle, 2001; Froelich et al., 1979).

This paradigm paints a relatively static picture of the zonation in a contaminant plume once the native microbiota have acclimated and adapted to the contaminant and established the initial zonation through competition. A more nuanced view recognises that a range of subsidiary metabolic processes and population interactions can accompany the dominant TEA process at any (macroscopic) location. The subsurface microbial habitat is usually very diverse at smaller (Darcy- and pore-) scales due to heterogeneity both of the porous medium and groundwater flows. This allows for populations exploiting metabolic pathways other than the locally dominant TEA process to coexist, and expand if conditions become favourable. Similarly, some metabolic pathways can be split between different populations due to biochemical limitations or thermodynamic considerations. For example, complex or recalcitrant organic substrates can be more readily broken down by fermenters than by heterotrophic respirers. The heterotrophs can more efficiently combine respiration of the dominant TEA with the fermentation products (typically acetates and other simple organics, and H_2) than with the complex substrate. The richness of these interactions plausibly allows for a dynamic view of groundwater ecology which is underexplored.

In the case of the current site, use of ammonia as an electron donor is limited thermodynamically by the need for a relatively potent TEA. Ammonia oxidation using O_2 (aerobic) and NO_2^-, NO_3^- (anaerobic) as TEA are now well documented. There are also recent suggestions that some bacteria are able to use manganate (IV) as TEA in ammonia oxidation (Javanaud et al., 2011). A further sink for ammonia is uptake for growth, rather than for respiration, since nitrogen is a necessary nutrient to all organisms. The lack of data on nitrite or manganese ($Mn^{2+}_{(aq)}$ product) makes it difficult to ascertain the nature of the oscillations in ammonium concentration. However, for the oscillation in organic C we can straightforwardly hypothesis microbial interactions which permit oscillatory population dynamics. The particular value of the present borehole data is that it has sufficient spatial resolution to suggest that the concentration variation in the 23–25 m depth range is genuinely oscillatory rather than due to experimental noise. We use this simple example to illustrate the paradigm of oscillatory dynamics in the groundwater context. Similar types of population interactions may underlie the ammonium oscillations in this data, and indeed in a variety of borehole data in the literature which may previously have been dismissed as experimental noise.

Mathematical models of bacterial reactions in contaminant plumes normally assume a passive suite of bacterial populations, although it is well recognised that different populations can compete for resources, as do all populations. While it is not so easy for chemical reactions to oscillate, it is more common for competing populations to do so. The thesis we examine in this paper is whether a realistic description of competing bacterial populations can cause the oscillations which are seen in Fig. 1.

Early work on competing microbial populations (Aris and Humphrey, 1977; Hsu et al., 1977; Fredrickson and Stephanopoulos, 1981) focussed on competitive exclusion and the survival of a dominant population. Oscillations in single microbial cultures are