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.

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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 CH₂O by oxygen,

\[
\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{CO}_2
\]

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

\[
r = r_0 X \left( \frac{[\text{O}_2]}{K + [\text{O}_2]} \right) \left( \frac{[\text{CH}_2\text{O}]}{K_c + [\text{CH}_2\text{O}]} \right)
\]

where \([\text{O}_2] \) and \([\text{CH}_2\text{O}] \) 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 Resco 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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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 CH₂O and ammonium NH₄⁺. 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 H₂) 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 O₂ {aerobic} and NO₃⁻, NO₂⁻ (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 (Mn⁴⁺, 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
well documented, for example in *Saccharomyces cerevisiae* (Borzan et al., 1977; Chen et al., 1990; Patnaik, 2003), and a variety of mathematical models have been developed for these (e.g., Skishko and Kol'tsova, 2006). While oscillations can occur in single species bacterial metabolism, they have also been reported in systems of competing microbial populations; Lenas et al. (1998) and Gaki et al. (2009) report oscillations in a competitive system in which substrate inhibition is included via a sigmoidal non-Monod growth rate. Recently, Khatri et al. (2012) have provided a model for competing microbial populations which is based (their equations 1 and 2) on a classic model of substrate/biomass interaction, whose relatives arise in many different fields (Goldbeter, 1996; Fowler, 2013; Anderson and May, 1981; Huppert et al., 2005; Omta et al., 2013), and their extension of the model to completing populations (their equation 22) is similar in shape to the model we propose below, although having different feedbacks; particularly, their model gives stable steady solutions, which are then forced stochastically to produce oscillations.

The basis of the model we consider here is indicated in Fig. 2. We denote the heterotroph population by \( H \) [mg COD l\(^{-1}\)], and the fermenter population as \( F \) [mg COD l\(^{-1}\)]. Both populations feed off carbon, which we specify in two different forms, \( C_n \) [mg COD l\(^{-1}\)] and \( C_1 \) [mg COD l\(^{-1}\)], the subscript indicating the complexity of the molecules: \( C_n \) represents the complex form, and \( C_1 \) the simpler form. In our model the respiring heterotrophs can use both forms of carbon, but prefer the simpler form. On the other hand, the fermenters use only the complex carbon, but break it down to the simpler form. Because of this, the fermenters facilitate growth of the heterotrophs, by providing them with an easier food source. However, the use by the heterotrophs of the complex carbon removes the food source for the fermenters. Thus, we appear to have a classic activator–inhibitor system: \( F \) activates \( H \), while \( H \) inhibits \( F \). On this basis, we can expect oscillations to occur; and, when a diffusive term is added, we can expect the formation of travelling waves, although we do not pursue the issue of spatial oscillations here.

A mathematical model to describe these interactions is given by

\[
\begin{align*}
H &= \frac{r_n C_n H}{C_n + K_n} + \frac{r_1 C_1 H}{C_1 + K_1} - d_H H, \\
F &= \frac{r_C C_F F}{C_n + K_F} - d_F F, \\
\dot{C}_n &= \frac{r_n C_n F}{Y_{nf}(C_n + K_n)} - \frac{r_n C_n H}{Y_{nh}(C_n + K_n)} + S + \zeta(d_H H + d_F F), \\
\dot{C}_1 &= \frac{r_n C_n F}{Y_{f1}(C_n + K_n)} - \frac{r_1 C_1 H}{Y_{f1}(C_1 + K_1)}.
\end{align*}
\]

(2.1)

The model is built using simple Monod uptake terms with Monod coefficients \( K_n, K_1 \) and \( K_F \) [mg COD l\(^{-1}\)], suitable yield coefficients \( Y_n, Y_1, Y_{nf} \) and \( Y_{f1} [-] \), and assuming linear death rates \( d_H, d_F \) [d \(^{-1}\)] for the bacteria. For simplicity we assume that TEAs are not rate-limiting, and consider the reaction rates \( r_n, r_1 \) [d \(^{-1}\)] to include the TEA-dependent term of (1.2) as an approximately constant multiplicative factor. The complex carbon is supplied at a rate \( S \) [mg COD l\(^{-1}\) d\(^{-1}\)] with an additional source term from organic material released on bacterial death (with a conversion ratio \( \zeta \)).

As described later, the external source \( S \) may stand in for a supply due to either advection or diffusion in the contaminant plume, or for production by hydrolysis of organic carbon, and is a suitable model for an experimental system in a chemostat. We also assume that the system is well-mixed and ignore any dependence of uptake and growth on other chemical and physical conditions or microbial populations.

We scale these equations by balancing terms on the right-hand side, together with an assumption that the \( r_1 \) growth term for \( H \) is larger than the \( r_n \) term, and that the yield coefficients \( Y_i \) are \( O(1) \). This leads to the definitions

\[
\begin{align*}
H &= \frac{S}{d_H}; \quad F = \frac{S}{d_F}, \quad C_1 = \frac{K_1 d_H}{r_1}, \quad C_n = \frac{K_n d_F}{r_1 \zeta},
\end{align*}
\]

(2.2)

and we choose (for reasons that will emerge below) the time scale

\[
t \sim t_0 = \frac{K_F}{\sqrt{S}}[d]
\]

(2.3)

The resulting dimensionless model takes the form

\[
\begin{align*}
\dot{e} &= \frac{sf}{1 + \beta s} - e, \\
\dot{f} &= \frac{sf}{1 + \beta s} - f, \\
\dot{s} &= \frac{sf}{1 + \beta s} - \frac{\delta s}{Y_{nf}(1 + \gamma s)} - \zeta(h + f), \\
\dot{c} &= \frac{sf}{1 + \beta s} - \frac{hc}{Y_{f1}(1 + \alpha c)}.
\end{align*}
\]

(2.4)

where the dimensionless parameters are defined by

\[
\begin{align*}
\alpha &= \frac{d_H}{t_0}; \quad \beta = \frac{d_F}{t_0}; \quad \gamma = \frac{r_1 K_n d_F}{K_F r_1 d_H}; \quad \delta = \frac{r_1 K_n d_F}{r_1 K_n d_H},
\end{align*}
\]

(2.5)

Typical assumed values of the constants of the model, and the resulting values of the dimensionless parameters, are given in Table 1. Generally, we expect that the bacterial decay time scales \( d_H^{-1} \) and \( d_F^{-1} \) will be comparable, and, we suppose, much less than the nutrient uptake time scale \( t_0 \), so that \( \lambda \sim 1, \epsilon \ll 1 \), and if the \( K_S \) and \( r_S \) are comparable, then \( \mu \sim \delta \sim 1 \). The bulk of the parameters are taken from Langergraber et al. (2009). An issue arises concerning the choice of the supply term \( S \) in Langergraber et al.’s model. In their description of wastewater treatment by constructed wetlands, \( C_n \) is itself formed through bacterially enabled hydrolysis of biodegradable organic matter, and this description may not be consistent with the situation which concerns us, a contaminant plume in which the contaminating carbon source is delivered by groundwater flow, and is much less concentrated. In seeking a value for \( S \), we suppose that the source term represents the supply by horizontal advection and vertical diffusion, that is,

\[
S \sim -u \frac{\partial C_n}{\partial x} + D \frac{\partial^2 C_n}{\partial z^2}
\]

(2.6)

where \( u \) is the horizontal groundwater velocity, \( D \) is the transverse dispersion coefficient, and \( x \) and \( z \) are the horizontal and vertical coordinates. We can thus define a convective time scale \( t_c \) and a diffusive time scale \( t_D \) via

\[
t_c \sim \frac{x}{u}; \quad t_D \sim \frac{z^2}{D}
\]

(2.7)
Table 1

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Typical value</th>
<th>Equivalent (a)</th>
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<td>$h_B$</td>
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<td>$d_t$</td>
<td>0.2 d$^{-1}$</td>
<td>$h_I$</td>
</tr>
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<td>$K_0$</td>
<td>2 mgCOD l$^{-1}$</td>
<td>$h_C$</td>
</tr>
<tr>
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<td>$h_{SR}$</td>
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<tr>
<td>$r_f$</td>
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<td>$\mu_{FR}$</td>
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<tr>
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<td>$\mu_B$</td>
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<tr>
<td>$S$</td>
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<td>$\eta$</td>
</tr>
<tr>
<td>$t_0$</td>
<td>0.71 \times 10^6 d</td>
<td>$\theta$</td>
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<td>$Y_{f1}$</td>
</tr>
<tr>
<td>$Y_t$</td>
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<td>$Y_{f2}$</td>
</tr>
<tr>
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</tr>
<tr>
<td>$Y_{H}$</td>
<td>18</td>
<td>$1$</td>
</tr>
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</table>

(a) The value for $S$ is determined as described in the text. We might alternatively use a value based on Langergraber et al. (2009) of $S \approx 60$ mgCOD l$^{-1}$ d$^{-1}$, using an estimate $H = 30$ mgCOD l$^{-1}$ from Henze et al. (1999). As discussed in the text, we do not consider this appropriate in the case of a contaminant plume.

For a field site with downstream distance from contaminant source of $x = 300$ m, say, and groundwater velocity $u = 10$ m y$^{-1}$, we have $t_c \approx 10^4$ d, while for a grain size of $d_p \approx 10^{-4}$ m, we have $u_d \approx 0.3 \times 10^{-10}$ m$^2$ s$^{-1}$, which is less than the diffusion coefficient, so we can take $D \approx 10^{-9}$ m$^2$ s$^{-1}$, and thus $t_D \approx 3 \times 10^5$ d, choosing $z \approx 5$ m. Since $t_c < t_D$, we estimate $S \approx C_n/t_c$, and using (2.2), this suggests we choose

$$S \approx \frac{K_f d_p}{Y_f t_c}$$

and this gives the value in Table 1.

2.1. Steady state and stability

The activator–inhibitor nature of the model lies in the following observation. Assuming $\delta > 0$, then increasing $h$ causes loss of $s$ in (2.4)$_3$, and thus lower production of $f$ in (2.4)$_2$: $h$ inhibits $f$. On the other hand, increased $f$ produces larger $c$ in (2.4)$_4$, and thus larger $h$ in (2.4)$_1$, so that $f$ can activate $h$. To examine whether this mechanism can produce instability, we begin by studying the simpler situation in which the Monod constants and cell material recycling are put to zero, i. e., $\alpha = \beta = \gamma = \zeta = 0$. In this case, the model is simply

$$\varepsilon \delta h = \delta s + h(c - 1),$$

$$\varepsilon f = (s - 1)f,$$

$$\dot{s} = \frac{s}{Y_f} - \delta h,$$

$$\dot{c} = \mu \frac{[s]}{Y_f} + \frac{h c}{Y_f}.$$  

(2.9)

Now firstly note that if $\delta = 0$ (i.e., $r_n = 0$), the $(f, s)$ system uncouples from the $(h, c)$ system. In this case, the $(f, s)$ sub-system is

$$\dot{s} = (s - 1)f,$$

$$\dot{c} = \frac{s}{Y_f}.$$  

(2.10)

and can be easily studied in the phase plane. Alternatively (cf. Fowler (2013)), we write

$$f = Y_{f1}e^{\theta},$$

whence

$$s = 1 + \varepsilon \dot{\theta},$$

and $\theta$ satisfies the nonlinear oscillator equation

$$\dot{\theta} + \varepsilon \theta - 1 = -\varepsilon \theta e^{\phi},$$

(2.13)

whose steady solution $\theta = 0$ is stable. If, as we surmise, $\varepsilon \ll 1$, then (2.13) describes a weakly damped oscillator in the potential well

$$V(\theta) = e^{\phi} - \theta.$$  

(2.14)

Since $f \rightarrow Y_{f1}$ and $s \rightarrow 1$, the $(h, c)$ system is given after the $(f, s)$ transient by

$$\varepsilon \lambda h = h(c - 1),$$

$$\dot{c} = \mu \frac{[s]}{Y_f} + \frac{h c}{Y_f}.$$  

(2.15)

whose dynamics are entirely analogous to those of $(f, s)$. Specifically, with

$$h = \frac{Y_{f1}Y_f}{Y_{f1}},$$

$$c = 1 + \varepsilon \lambda \dot{\phi},$$

(2.16)

we have

$$\dot{\phi} - \mu \frac{[s]}{Y_{f1}Y_f} - 1 = -\varepsilon \mu Y_{f1} \phi e^\theta,$$

(2.17)

with the same dynamics as $\theta$, and on the same time scale if $\mu \sim 1$, $\lambda \sim 1$, $Y_k \sim 1$.

2.2. Cross coupling

Because in particular the solutions are weakly decaying oscillators, one wonders what the effect of the non-zero coupling term $\delta$ is. We use the same definitions as above, namely

$$f = Y_{f1}e^{\theta},$$

$$h = \frac{Y_{f1}Y_f}{Y_{f1}}e^{\phi};$$

(2.18)

then the system (2.9) is transformed to the coupled oscillator equations

$$\dot{\theta} + V_f(\theta, \phi) = -\varepsilon (e^{\phi} + \bar{\theta} e^{\phi}) \dot{\theta},$$

$$\lambda \dot{\phi} - 3\delta \dot{\theta} + V_h(\theta, \phi) = e^{\bar{\theta}}(e^{\phi} + \delta e^{\phi} \dot{\theta} - \lambda \phi e^{\phi}),$$

(2.19)

where

$$V_f = e^{\phi} - 1 + \bar{\theta} e^{\phi},$$

$$V_h = \bar{\theta}(1 - \delta) e^{\phi} - e^{\phi},$$

(2.20)

and

$$\vartheta = \delta Y_{f1}Y_f / Y_{f1}Y_f,$$

$$\bar{\theta} = \mu Y_{f1}.$$  

(2.21)

For small $\varepsilon$, assuming $\lambda$, $\bar{\theta}$, $\vartheta$ $\sim 1$, we expect the steady state to remain oscillatory under perturbations, but the cross coupling allows the possibility of instability, and indeed this is what we find. Fig. 3 shows a phase portrait of a relaxation solution in which $c$ and $h$ oscillate in a spiky fashion; Fig. 4 shows the corresponding time series. The oscillatory behaviour is retained for $\zeta > 0$, and for $\zeta = 0.5$, for example, oscillations are similar. At $\zeta = 1$, $h$ in Fig. 4 is similar but $c$ is period-doubled, suggesting a more exotic dynamical behaviour. This is achieved by lowering $\varepsilon$: for example, with $\varepsilon = 0.07$ and $\zeta = 1$, the solutions are oscillatory but apparently chaotic.
of the carbon supply along the lines of the model studied by Langergraber et al. (2009) will be warranted. This issue is deferred to further study.

Two other features of the solutions deserve study. The oscillations shown in Figs. 3 and 4 are relaxational in nature, and both bacteria and nutrient display pronounced spikes. In a similar study, Fowler (2013) found that the spikes are due to the (weakly damped) nonlinear oscillator in (2.13) having high values of the energy level

$$E = \frac{1}{2} \theta^2 + e^\theta - \theta,$$

(3.1)

and the solutions can be determined asymptotically for $E \gg 1$. This naturally leads to the conjecture that a similar limit explains the spiky oscillations here, but the question would then be why such high energy oscillators occur. The most obvious suggestion is that the two oscillators in (2.19) resonate, but the matter is opaque.

The second feature is that the spikes are reminiscent of the nitrate spike in Fig. 1, and this raises the possibility that a single spike could occur through a similar kinetics, except that the system is excitable rather than oscillatory unstable, as for example in the Fitzhugh–Nagumo equations. In this case, the unrepeatad nitrate spike may result from aerobic ammonia oxidation at the limit of the oxic zone, though it is notable that $NH_3$ is not entirely removed in the reaction as one might expect for a classical reaction front. As we said earlier, this spike might well be an outlier; but it might not. In any event it is a measured data point, and worth further consideration. Our philosophy is that what you see is what there is.

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