Oscillations in soil bacterial redox reactions

A. C. Fowler[1,2], H. F. Winstanley[1], M. J. McGuinness[3], and L. B. Cribbin[1]

[1]MACSI, University of Limerick, Limerick, Ireland
[2]OCIAM, University of Oxford, Oxford, UK
[3]Victoria University of Wellington, Wellington, New Zealand

October 15, 2013

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.

Keywords: Heterotrophs, fermenters, oscillations, contaminant plumes.

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$_2$O' by oxygen,

$$\text{`CH}_2\text{O'} + \text{O}_2 \xrightarrow{r} \text{H}_2\text{O} + \text{CO}_2, \tag{1.1}$$
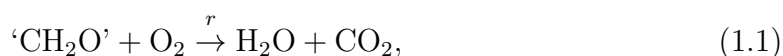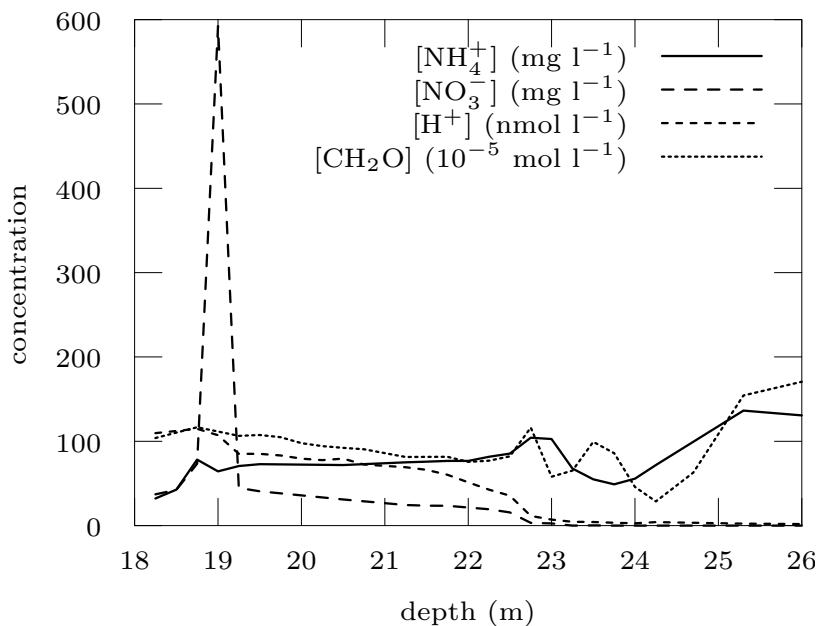
Figure 1: Borehole data from Rexco borehole 102. Contaminant concentrations are shown as a function of depth in the hole.

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

$$r = r_0 X \frac{[O_2]}{K + [O_2]} \frac{[`CH_2O']}{K_c + [`CH_2O']},$$

(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 metres 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 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 figure 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 figure 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 figure 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 popula-

tions 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 (Chappelle 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 ($Mn_{(aq)}^{2+}$ product) makes it difficult to ascertain the nature of the oscillations in ammonium concentration. However, for the oscillation in organic C we can straightforwardly hypothesise 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 figure 1.

Early work on competing microbial populations (Aris and Humphrey 1977, Hsu
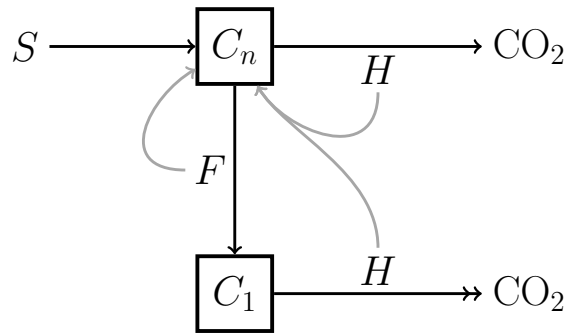
Figure 2: A schematic representation of our model. Complex carbon C_n is broken down by fermenters F to more simple carbon C_1. Both forms can be consumed by the respiring heterotrophs H, but the simpler carbon is favoured. Cell death of F and H provides a source of complex carbon in addition to the external source S.

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* (Borzani *et al.* 1977, Chen *et al.* 1990, Patnaik 2003), and a variety of mathematical models have been developed for these (e. g., Skichko 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 figure 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

$$
\begin{aligned}
\dot{H} &= \frac{r_n C_n H}{C_n + K_n} + \frac{r_1 C_1 H}{C_1 + K_1} - d_H H, \\
\dot{F} &= \frac{r_F C_n F}{C_n + K_F} - d_F F, \\
\dot{C}_n &= -\frac{r_F C_n F}{Y_{Fn}(C_n + K_F)} - \frac{r_n C_n H}{Y_n(C_n + K_n)} + S + \theta(d_h H + d_F F), \\
\dot{C}_1 &= \frac{r_F C_n F}{Y_{F1}(C_n + K_F)} - \frac{r_1 C_1 H}{Y_1(C_1 + K_1)}.
\end{aligned}
\tag{2.1}
$$

The model is built using simple Monod uptake terms with Monod coefficients K_n, K_1 and K_F [mg$_{\text{COD}}$l^{-1}], suitable yield coefficients Y_n, Y_1, Y_{Fn} and Y_{F1} [$-$], and assuming linear death rates d_H, d_F [d^{-1}] for the bacteria. For simplicity we assume TEAs are not rate-limiting, and consider the reaction rates r_1, r_n [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$_{\text{COD}}$l^{-1}d^{-1}] with an additional source term from organic material released on bacterial death (with a conversion ratio θ). 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 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

$$
H = \frac{S}{d_H} h, \quad F = \frac{S}{d_F} f, \quad C_1 = \frac{K_1 d_H}{r_1} c, \quad C_n = \frac{K_F d_F}{r_F} s,
\tag{2.2}
$$

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

$$
t \sim t_0 = \sqrt{\frac{K_F}{r_F S}}. \qquad [\text{d}]
\tag{2.3}
$$

The resulting dimensionless model takes the form

$$
\begin{aligned}
\varepsilon \lambda \dot{h} &= \frac{\delta h s}{1 + \gamma s} + \frac{hc}{1 + \alpha c} - h, \\
\varepsilon \dot{f} &= \left[\frac{sf}{1 + \beta s} - f \right], \\
\dot{s} &= \varepsilon \left[1 - \frac{sf}{Y_{Fn}(1 + \beta s)} - \frac{\delta h s}{Y_n(1 + \gamma s)} + \theta(h + f) \right], \\
\dot{c} &= \varepsilon \mu \left[\frac{sf}{Y_{F1}(1 + \beta s)} - \frac{hc}{Y_1(1 + \alpha c)} \right],
\end{aligned}
\tag{2.4}
$$

Symbol	Typical value	Equivalent[a]
d_F	0.02 d^{-1}	b_{FB}
d_H	0.2 d^{-1}	b_H
K_n	2 mg$_{COD}$ l^{-1}	K_{SF}
K_1	4 mg$_{COD}$ l^{-1}	K_{SA}
K_F	28 mg$_{COD}$ l^{-1}	K_{SFB}
r_n	2.4 d^{-1}	$\mu_H \eta_g$
r_1	2.4 d^{-1}	$\mu_H \eta_g$
r_F	1.5 d^{-1}	μ_{FB}
S	0.37×10^{-4} mg$_{COD}$ l^{-1} d^{-1}	
t_0	0.71×10^3 d	
Y_n	0.63	Y_H
Y_1	0.63	Y_H
Y_{Fn}	0.053	Y_{FB}
Y_{F1}	18	$\frac{1}{Y_{FB}} - 1$
α	0.08	
β	0.013	
γ	0.18	
δ	2.2	
ε	0.07	
θ	≤ 1	
λ	0.1	
μ	1.1	

Table 1: Values of the constants and parameters at 10°C, based on Langergraber *et al.* (2009) equivalents marked [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 $S = k_h H = 60$ mg$_{COD}$ l^{-1} d^{-1}, using an estimate $H \sim 30$ mg$_{COD}$ 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.

where the dimensionless parameters are defined by

$$\alpha = \frac{d_H}{r_1}, \quad \beta = \frac{d_F}{r_F}, \quad \gamma = \frac{K_F d_F}{K_n r_F}, \quad \delta = \frac{r_n K_F d_F}{r_F K_n d_H},$$

$$\varepsilon = \frac{1}{d_F t_0}, \quad \lambda = \frac{d_F}{d_H}, \quad \mu = \frac{r_1 K_F d_F}{r_F K_1 d_H}. \tag{2.5}$$

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 $\lambda \sim 1$, $\varepsilon \ll 1$, and if the K_is and r_is 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,

$$S \sim -u\frac{\partial C_n}{\partial x} + D\frac{\partial^2 C_n}{\partial z^2}, \tag{2.6}$$

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

$$t_c \sim \frac{x}{u}, \quad t_D \sim \frac{z^2}{D}. \tag{2.7}$$

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

$$S \sim \frac{K_F d_F}{r_F t_c}, \tag{2.8}$$

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., $\alpha = \beta = \gamma = \theta = 0$. In this case, the model is simply

$$\begin{aligned}
\varepsilon\lambda\dot{h} &= \delta hs + h(c-1), \\
\varepsilon\dot{f} &= (s-1)f, \\
\dot{s} &= \varepsilon\left[1 - \frac{sf}{Y_{Fn}} - \frac{\delta hs}{Y_n}\right], \\
\dot{c} &= \varepsilon\mu\left[\frac{sf}{Y_{F1}} - \frac{hc}{Y_1}\right].
\end{aligned} \tag{2.9}$$

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

$$\begin{aligned}
\varepsilon\dot{f} &= (s-1)f, \\
\dot{s} &= \varepsilon\left[1 - \frac{sf}{Y_{Fn}}\right],
\end{aligned} \tag{2.10}$$

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

$$f = Y_{Fn}e^\theta, \tag{2.11}$$

whence

$$s = 1 + \varepsilon\dot\theta, \tag{2.12}$$

and θ satisfies the nonlinear oscillator equation

$$\ddot\theta + e^\theta - 1 = -\varepsilon\dot\theta e^\theta, \tag{2.13}$$

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

$$V(\theta) = e^\theta - \theta. \tag{2.14}$$

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

$$\varepsilon\lambda\dot h = h(c - 1),$$
$$\dot c = \varepsilon\mu\left[\frac{Y_{Fn}}{Y_{F1}} - \frac{hc}{Y_1}\right]. \tag{2.15}$$

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

$$h = \frac{Y_{Fn}Y_1}{Y_{F1}}e^\phi, \quad c = 1 + \varepsilon\lambda\dot\phi, \tag{2.16}$$

we have

$$\ddot\phi + \frac{\mu Y_{Fn}}{\lambda Y_{F1}}\left[e^\phi - 1\right] = -\frac{\varepsilon\mu Y_{Fn}}{Y_{F1}}\dot\phi e^\phi, \tag{2.17}$$

with the same dynamics as θ, 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 δ is. We use the same definitions as above, namely

$$f = Y_{Fn}e^\theta, \quad h = \frac{Y_{Fn}Y_1}{Y_{F1}}e^\phi; \tag{2.18}$$

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

$$\ddot\theta + V_f(\theta, \phi) = -\varepsilon(e^\theta + \bar\delta e^\phi)\dot\theta,$$
$$\lambda\ddot\phi - \delta\ddot\theta + V_h(\theta, \phi) = \varepsilon\bar\mu\{(e^\theta + \delta e^\phi)\dot\theta - \lambda\dot\phi e^\phi\}, \tag{2.19}$$

where

$$V_f = e^\theta - 1 + \bar\delta e^\phi,$$
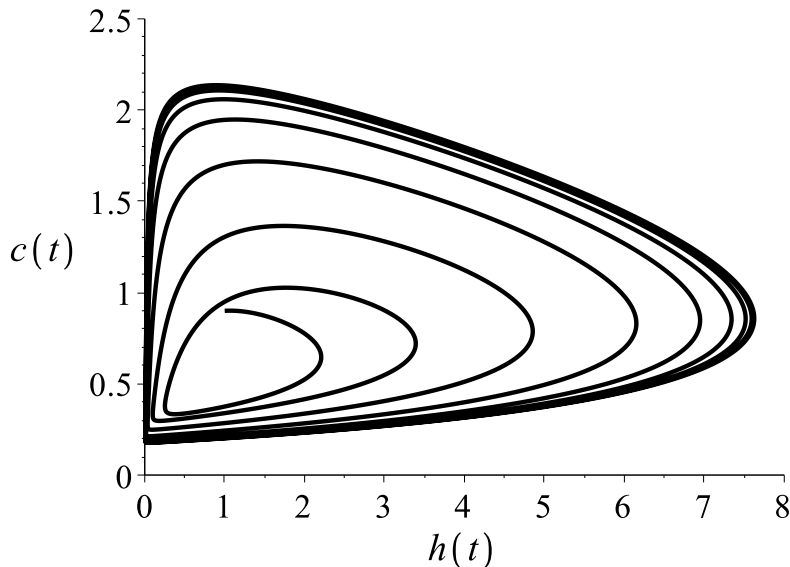$$V_h = \bar\mu\{(1 - \delta)e^\phi - e^\theta\}, \tag{2.20}$$

Figure 3: Oscillatory solution of (2.4) plotted in the (c, h) section of the phase plane. Parameter values are $\varepsilon = 0.3$, $\delta = 0.5$, $\mu = \lambda = Y_n = Y_1 = Y_{Fn} = Y_{F1} = 1$, $\alpha = \beta = \gamma = 0.1$, $\theta = 1$.

and

$$\bar{\delta} = \frac{\delta Y_{Fn} Y_1}{Y_{F1} Y_n}, \quad \bar{\mu} = \frac{\mu Y_{Fn}}{Y_{F1}}. \tag{2.21}$$

For small ε, assuming $\lambda, \bar{\mu}, \bar{\delta} \sim 1$, 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. Figure 3 shows a phase portrait of a relaxational solution in which c and h oscillate in a spiky fashion; figure 4 shows the corresponding time series. The oscillatory behaviour is retained for $\theta > 0$, and for $\theta = 0.5$, for example, oscillations are similar. At $\theta = 1$, h in figure 4 is similar but c is period-doubled, suggesting a more exotic dynamical behaviour. This is achieved by lowering ε: for example, with $\varepsilon = 0.07$ and $\theta = 1$, the solutions are oscillatory but apparently chaotic.

3 Conclusions

Motivated by data from a single borehole into an ammonium-contaminated plume which shows clear sign of oscillations in the ammonium and organic carbon profiles, we have explored the possibility that such oscillations are due to competitive interaction between two classes of bacteria, heterotrophs and fermenters, which interact in a manner similar to activator–inhibitor systems. It is well-known in reaction-diffusion systems that when the reaction kinetics are oscillatory, the presence of diffusion can cause the existence of periodic travelling waves (e. g., Fowler 2011, pp. 41 ff.), and so our purpose here has been to demonstrate that such oscillations can occur in realistic
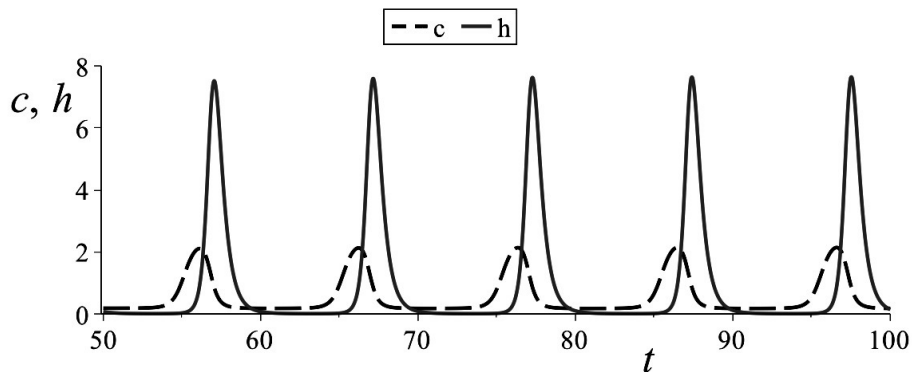
Figure 4: Time series of c and h corresponding to the trajectory in figure 3.

descriptions of bacterial interactions. Indeed, we did not have to look hard. The simplest model and choice of parameters produced robust oscillations. We thus consider that bacterial oscillation caused by competitive interaction is a possible mechanism to produce oscillation in soil chemical species. We should emphasise that the oscillations appear in conditions of sparse supply, i.e., the supply term S in (2.1) is small. This has the critical effect of making the parameter ε in (2.4) small, so that the damping terms are small. In laboratory experiments, nutrient supply is typically much larger, and we might expect large values of ε, and thus strong damping towards a steady state.

The present work opens the door for further studies which we hope to progress. The first such question is whether the kinetics explored here will lead to spatial oscillations in the advective-diffusive context of a contaminant plume. Preliminary work (Cribbin 2013) suggests that this is the case. This is slightly less obvious that one might expect, since the oscillations we have found rely on the supply term S, somewhat analogously to the glycolitic oscillators studied by Goldbeter (1996), though we surmise that the diffusive or advective flux can play the rôle of this term. However, it may be that more sophisticated modelling 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 figures 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

$$E = \tfrac{1}{2}\dot{\theta}^2 + e^{\theta} - \theta, \tag{3.1}$$

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.

11

The second feature is that the spikes are reminiscent of the nitrate spike in figure 1, and this raises the possibility that a single spike could occur through a similar kinetics, except that the system is excitable rather than oscillatorily unstable, as for example in the Fitzhugh-Nagumo equations. In this case, the unrepeated nitrate spike may result from aerobic ammonia oxidation at the limit of the oxic zone, though it is notable that NH_4^+ 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.

Acknowledgements

References

Anderson, R. M. and R. M. May 1981 The population dynamics of microparasites and their invertebrate hosts. Phil. Trans. R. Soc. Lond. B**291**, 451–524.

Aris, R. and A. E. Humphrey 1977 Dynamics of a chemostat in which two organisms compete for a common substrate. Biotechnol. Bioengng. **19**, 1,375–1,386.

Borzani, W., R. E. Gregori and M. L. R. Vairo 1977 Some observations on oscillatory changes in the growth rate of *Saccharomyces cerevisiae* in aerobic continuous undisturbed culture. Biotechnol. Bioengng. **19**, 1,363–1,374.

Broholm, M. M., I. Jones, D. Torstensson, and E. Arvin 1998 Groundwater contamination from a coal carbonization plant. In: Contaminated land and groundwater, future directions, eds. D. N. Lerner and N. R. G. Walton. Geological Society, London. Engineering Geology Special Publications **14** (1), 159–165.

Chapelle, F. H. 2001 Groundwater Microbiology and Geochemistry. Wiley, 2nd edition.

Chen, C.-I, K. A. McDonald and L. Bisson 1990 Oscillatory behavior of *Saccharomyces cerevisiae* in continuous culture: 1. Effects of pH and nitrogen levels. Biotechnol. Bioengng. **36**, 19–27.

Cribbin, L. B. 2013 Soil bacterial processes and dynamics. Ph. D. thesis, University of Limerick.

Fowler, A. C. 2011 Mathematical geoscience. Springer-Verlag, London.

Fowler, A. C. 2013 Note on a paper by Omta *et al.* on sawtooth oscillations. SEMA Journal **62**, 1–13.

Fredrickson, A. G. and G. Stephanopoulos 1981 Microbial competition. Science **213**, 972–979.

Froelich, P. N., G. P. Klinkhammer, M. L. Bender, N. A. Luedtke, G. R. Heath, D. Cullen, P. Dauphin, D. Hammond, B. Hartman and V. Maynard 1979 Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochimica et Cosmochimica Acta **43** (7), 1,075–1,090.

Gaki, A., A. Theodorou, D. V. Vayenas and S. Pavlou 2009 Complex dynamics of microbial competition in the gradostat. J. Biotechnol. **139**, 38–46.

Goldbeter, A. 1996 Biochemical oscillations and cellular rhythms. C. U. P., Cambridge.

Henze, M., W. Gujer, T. Mino, T. Matsuo, M. C. Wentzel, G. v.R. Marais, M. C. M. Van Loosdrecht 1999 Activated sludge model No.2D, ASM2D. Water Science and Technology **39** (1), 165–182.

Hsu, S. B., S. Hubbell and P. Waltman 1977 A mathematical theory for single-nutrient competition in continuous cultures of micro-organisms. SIAM J. Appl. Math. **32**, 366–383.

Hunter, K. S., Y. Wang and P. van Cappellen 1998 Kinetic modeling of microbially-driven redox chemistry of subsurface environments: coupling transport, microbial metabolism and geochemistry. J. Hydrol. **209**, 53–80.

Huppert, A., B. Blasius, R. Olinky and L. Stone 2005 A model for seasonal phytoplankton blooms. J. Theor. Biol. **236**, 276–290.

Javanaud, C., V. Michotey, S. Guasco, N. Garcia, P. Anschutz, M. Canton and P. Bonin 2011 Anaerobic ammonium oxidation mediated by Mn-oxides: from sediment to strain level. Research in Microbiology **162** (9), 848–857.

Jones, I., R. M. Davison, and D. N. Lerner 1998 The importance of understanding groundwater flow history in assessing present-day groundwater contamination patterns: a case study. Geological Society, London, Engineering Geology Special Publications **14** (1), 137–148.

Jones, I., D. N. Lerner and O. P. Baines 1999 Multiport sock samplers: a lowcost technology for effective multilevel ground water sampling. Ground Water Monitoring and Remediation **19** (1), 134–142.

Khatri, B. S., A. Free and R. J. Allen 2012 Oscillating microbial dynamics driven by small populations, limited nutrient supply and high death rates. J. Theor. Biol. **314**, 120–129.

Langergraber, G., D. P. L. Rousseau, J. Garcia and J. Mena 2009 CWM1: a general model to describe biokinetic processes in subsurface flow constructed wetlands. Water Sci. Technol. **59**, 1,687–1,697.

Lenas, P., N. A. Thomopoulos, D. V. Vayenas and S. Pavlou 1998 Oscillations of two competing microbial populations in configurations of two interconnected chemostats. Math. Biosci. **148**, 43–63.

Lovley, D. R. and M. J. Klug 1986 Model for the distribution of sulfate reduction and methanogenesis in freshwater sediments. Geochim. Cosmochim. Acta **50**, 11–18.

Omta, A. W., G. A. K. van Voorn, R. E. M. Rickaby and M. J. Follows 2013 On the potential role of marine calcifiers in glacial-interlacial dynamics. Global Biogeochem. Cycles, in revision.

Patnaik, P. R. 2003 Oscillatory metabolism of *Saccharomyces cerevisiae*: an overview of mechanisms and models. Biotechnol. Adv. **21**, 183–192.

Skichko, A. S. and E. M. Kol'tsova 2006 Mathematical model for describing oscillations of bacterial biomass. Theor. Found. Chem. Engng. **40**, 503–513.

Smits, T. H. M., A. Hüttmann, D. N. Lerner and C. Holliger 2009 Detection and quantification of bacteria involved in aerobic and anaerobic ammonium oxidation in an ammonium-contaminated aquifer. Bioremed. J. **13**, 41–51.

Thullner, M., P. Regnier and P. Van Cappellen 2007 Modeling microbially induced carbon degradation in redox-stratified subsurface environments: concepts and open questions. Geomicrobiol. J. **24**, 139–155.

Watson, I. A., S. E. Oswald, K. U. Mayer, Y. Wu and S. A. Banwart 2003 Modeling kinetic processes controlling hydrogen and acetate concentrations in an aquifer-derived microcosm. Environ. Sci. Technol. **37**, 3,910–3,919.

Watson, I. A., S. E. Oswald, S. A. Banwart, R. S. Crouch and S. F. Thornton 2005 Modeling the dynamics of fermentation and respiratory processes in a groundwater plume of phenolic contaminants interpreted from laboratory- to field-scale. Environ. Sci. Technol. **39**, 8,829–8,839.