Calibration and Reliability in Groundwater Modelling: From Uncertainty to Decision Making
(Proceedings of ModelCARE'2005, The Hague, The Netherlands, June 2005). IAHS Publ. 304, 2006.

Influence of modelling concepts and approaches on the results of field scale reactive transport modelling

SASCHA E. OSWALD[1], **IAN A. WATSON**[2], **ROGER S. CROUCH**[2] **& STEVEN A. BANWART**[2]

1 *Hydrogeology Department, Centre for Environmental Research UFZ Leipzig-Halle, Permoserstrasse 15,D-04318 Germany*
sascha.oswald@ufz.de

2 *Groundwater Protection and Restoration Group, Department of Civil and Structural Engineering, University of Sheffield, Mappin Street, Sheffield S1 3JD, UK*

Abstract The mass removal of an organic contaminant in an aquifer by microbial biodegradation has been the focus of a field case study of natural attenuation. By detailed numerical modelling we looked at the importance of field-scale Terminal Electron Accepting Processes (TEAP) based on results from previous laboratory experiments. A main aim was to study the dependence of results not only on parameter values, but also on the different concepts and approaches that the modelling was based upon. To be able to investigate this uncertainty in the results, we first had to build up the numerical and computational capability to perform a series of runs with models based on different approaches, including the most complex and thus demanding ones. Therefore, we applied parallel computing and automatic grid adaptation for a relatively comprehensive set of chemical species. Some of the conceptual changes had a large effect on the results; for example, the biodegradation concept. Some had only a minor influence, at least for this field site plume; for example, the permeability heterogeneities.

Keywords biodegradation concept; conceptual approach; groundwater; natural attenuation; numerical simulation; parameter sensitivity; three-dimensional

INTRODUCTION

The natural attenuation (NA) processes for field site contaminant plumes may be investigated at field sites, where the actual field circumstances are present. Numerical modelling is a useful tool that can increase the understanding of the complex and diverse processes affecting NA, by also including and transferring insight from laboratory experiments.

The current study used a fully kinetic two-step biodegradation concept together with iron and manganese mineral dissolution and surface complexation of ferrous iron, to model NA at a field site. This constitutes a complex biogeochemical process concept relative to most current modelling studies (cf. Brun & Engesgaard, 2002). Furthermore, as a consequence of experimental field and laboratory results, hydrogen as an intermediate is taken into account explicitly, as well as acetate, the latter as a product due to inhibition of its further degradation. Thus this work aims to demonstrate the benefit of applying a detailed concept for description of the biodegradation processes to the field site (*biogeochemistry concept*), and looks particularly at the influence of other conceptual changes including two-dimensional (2-D) *vs* 3-D modelling (*dimensionality*), source heterogeneity (*source uncertainty*), and aquifer permeability heterogeneity (*hydrogeology*). Furthermore, this has been accompanied by a numerical study of the accuracy of an adaptive meshing approach (*numerics*).

METHODS

Based on the interpretation of laboratory experiments (Watson *et al.*, 2003) a kinetic rate expression was used to model the degradation of the substrate phenol (C_6H_6O), with concentration S, via the specific terminal electron acceptor (TEA), as has been implemented formerly by Mayer *et al.* (2002) for NA modelling:

$$r_S = \frac{\mathrm{d}S}{\mathrm{d}t} = -k_{\max}\ X\ \frac{S}{(K_{M\_S}+S)}\,\frac{TEA}{(K_{M\_TEA}+TEA)}\,\frac{K_I}{(K_I+I)} \tag{1}$$

where r_S is the rate of consumption of substrate S by this TEAP (mol L^{-1} s^{-1}); $k_{\max}$ is the maximum substrate utilization rate (s^{-1}); X is the biomass concentration; K_{M_S} is the Monod half saturation constant with respect to substrate S (mol L^{-1}); K_{M_TEA} is the Monod half saturation constant with respect to the specific TEA (mol L^{-1}); I is the concentration of an inhibiting substance; K_I is the inhibition constant (mol L^{-1}); and all concentrations are in mol L^{-1}.

The 2-D model with a uniform flow field represents a vertical section along the groundwater flow from the centre of the source located at the Four Ashes site (Thornton *et al.*, 2001), as presented in Watson *et al.* (2005b), including simulation parameters. The model has 24 species and eight kinetic reactions (aerobic degradation, denitrification, two fermentation reactions, manganese reduction, iron reduction, sulphate reduction, methanogenesis) plus additional equilibrium reactions (iron surface complexation, pyrite precipitation, pH reaction, aqueous complexes). Phenol is the primary organic contaminant, and the phenol source is spatially variable in the vertical direction and changes in time, giving a more realistic plume morphology. A two-step reaction process is implemented to simulate the fermentation of phenol to intermediate species, hydrogen and acetate, followed by the further consumption of hydrogen by respiration reactions. The fate of microbially produced ferrous iron can also be simulated because it can be present in the mobile aqueous phase or the immobile minerals or surface complexes (see Watson *et al.* (2005b) for discussion). This 2-D model constitutes the reference simulation, against which the results of alternative concepts were compared. For 2-D, a stochastic permeability field, varying by about an order of magnitude, was implemented as an alternative approach.

In addition, 3-D models have been simulated using the same eight kinetic reactions, but including only 11 species; equilibrium chemical species were omitted for simplicity since the 3-D problem is more demanding in terms of size than 2-D. The domain has the same height and length as the 2-D one, but now is 90 m wide. For the 3-D set-up another conceptual alternative was studied, i.e. a stochastically spatially varying source instead of a deterministically defined one.

Since often NA modelling of field site plumes is limited by the available computational power, it was decided to develop software capabilities for parallel processing and automatic grid adaptation, including automatic grid refinement and coarsening. Therefore, a module for reactive transport modelling of NA processes was developed on the basis of the UG toolbox (Bastian *et al.*, 1997). The quantification of the advantages and disadvantages of the numerical methods used here has been reported in Watson *et al.* (2005a). As hardware components a small, eight processor Beowulf cluster of Linux PCs was set up, and occasionally a 512 processor Linux cluster could be accessed too.

RESULTS

For brevity we concentrate here on the aspects of 3-D modelling and only summarize the results regarding the other conceptual aspects.

Two-dimensional homogeneous model and parameter sensitivity

Figure 1 shows selected results for a reference case, a 2-D homogeneous model, with a locally adapted mesh. Grid adaptation parameters were set to obtain results comparable to simulations on a fine uniform mesh (cf. Table 3; Watson *et al.*, 2005a). The advancing phenol plume consumes TEAs in and around the plume area, i.e. oxygen and nitrate at the plume fringes, but also iron and manganese minerals, mainly in the plume core. The 2-D results are also discussed in Watson *et al.* (2005b).

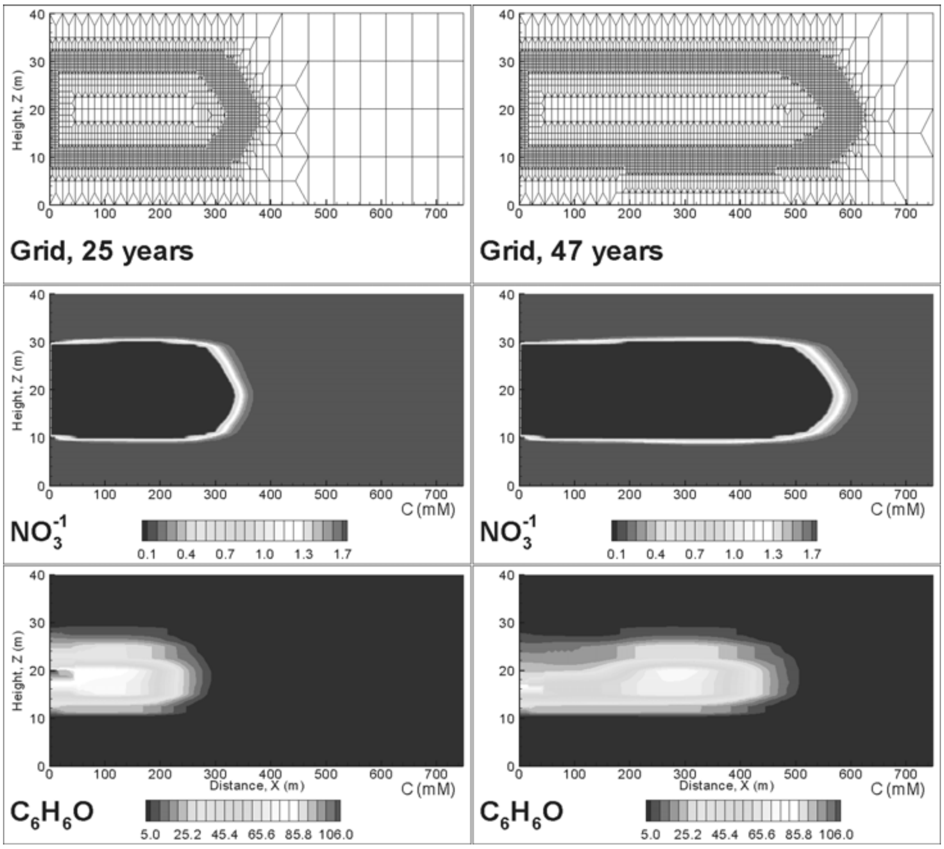

Fig. 1 Two-dimensional results for nitrate (NO_3^{-1}) and phenol (C_6H_6O) at 25 and 47 years, simulated with an adaptively refined and coarsened mesh.

The heterogeneous flow field, based on what was known as possible permeability variations of the Triassic sandstone aquifer at the site, creates some additional variability of the plume shapes, but does not significantly change the mass turnover.

Comparison with earlier simulation runs (Mayer *et al.*, 2001) performed before the more detailed biodegradation concept has been developed by additional laboratory studies, showed that the conceptual improvement, especially the iron surface complexation and the two-step biodegradation kinetics (Oswald *et al.*, 2004; Watson *et al.*, 2005b), had a significant effect on the phenol mass removal (cf. Table 2).

Many of the parameters were taken from literature values, but some calibration to detailed field observations was necessary. Sensitivity of these parameters was studied by re-running the homogeneous 2-D model with each parameter first doubled and then halved. Since a total of 46 simulations were necessary, they were run on a relatively coarse grid, level 3, which had been observed to give, in a much shorter time, results not too dissimilar to more refined simulations in terms of concentrations and mass turnover, which was sufficient to reveal which parameters were most sensitive.

Table 1 shows selected results giving typical patterns which emerged from the sensitivity study. In general the results are most sensitive to changes in the k_{max} parameter and less sensitive to other parameters such as K_M or K_I. The most sensitive parameter for the whole model is the k_{max} rate parameter for fermentation of phenol to hydrogen, for which parameter doubling approximately doubles the reacted mass of most species. Most of the parameters shown relate to plume core reactions, and have little effect on nitrate which reacts at the fringe. The mass of nitrate reacted is insensitive to denitrification reaction parameters, k_{max} and K_M, but is sensitive to transverse dispersivity, α_{TV}, and to a lesser extent longitudinal dispersivity. This shows that the fringe reactions are limited by dispersive mixing and not by the reaction rates, i.e. fringe reactants react immediately after dispersive mixing. This is true even on the coarse grid which includes more numerical dispersion than more highly refined grids. Overall, the plume core processes are controlled by the fermentation rate, while the fringe processes are controlled by dispersive mixing processes.

Table 1 Parameter sensitivity study of two-dimensional homogeneous case, showing selected typical results for relative changes in reacted masses for doubling of parameter values.

Parameter	Reaction	Phenol	NO_3^-	H_2	FeII	MnII	SO_4^{2-}	CH_4
k_{max}	Fermentation	1.61	0.98	2.43	1.91	1.91	2.06	2.12
k_{max}	Fe(III) red'n	1.00	1.00	0.58	1.28	0.64	0.76	0.78
k_{max}	CH4 prod'n	1.00	1.00	0.84	0.91	0.92	0.78	1.49
k_{max}	SO_4^{2-} red'n	1.00	1.00	0.89	0.94	0.94	1.72	0.84
K_{M_SO4}	SO_4^{2-} red'n	1.00	1.00	1.04	1.02	1.02	0.75	1.07
K_{M_H2}	SO_4^{2-} red'n	1.00	1.00	1.07	1.03	1.03	0.56	1.11
K_{I_phenol}	All TEAPs	1.00	1.00	0.76	1.00	1.00	1.00	0.99
k_{max}	NO_3^- red'n	1.01	1.00	1.00	1.00	1.00	1.01	1.01
K_{M_NO3}	NO_3^- red'n	1.00	1.00	1.00	1.00	1.00	1.01	0.99
α_{TV}	-	1.05	1.14	1.01	1.00	1.00	1.01	1.00

All 23 parameters were doubled. red'n – reduction; prod'n – production. Numbers are total reacted mass of species in moles normalized to the reacted mass given by the base case. For the original parameter values see (Watson *et al.*, 2005b). All simulations were done on a level 3 uniform grid, to save time. Halving the parameters typically gave a similar magnitude of change, but in the opposite direction from doubling.

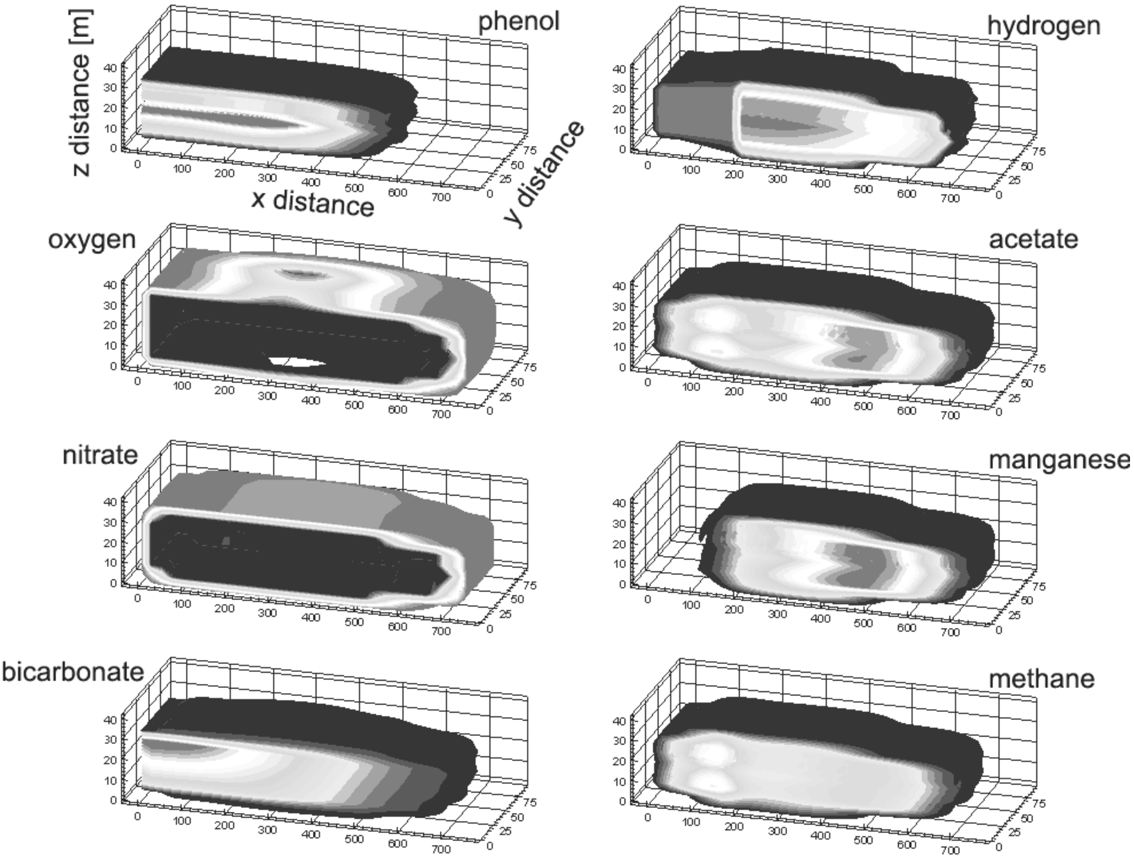

Fig. 2 Three-dimensional results at 47 years, cut at the plume centre along the flow direction to show concentrations inside. Concentrations are plotted with the same shade coding as in Fig. 1, each between zero and maximum concentration of the given species.

Table 2 Mass balance comparison after 47 years between models with different conceptual approaches.

		2-D with homogeneous flow field	3-D with deterministic source [a]	3-D with stochastic source [a]	3-D (Mayer *et al.*, 2001) with former degr. concept [b]
Total mass degraded (mol phenol)		1.47×10^3	1.18×10^5	1.18×10^5	1.30×10^5
Total mass degraded per m plume width (mol phenol)		1.47×10^3	1.82×10^3	1.82×10^3	1.00×10^3
Total mass degraded relative to total added (wt. %)		4.2	5.3	5.0	2.2
Balance of carbon in products (% of mol C degraded)	TIC	41.5	45.0	45.2	97.3
	Acetate	56.1	53.0	52.8	0
	CH_4	2.4	2.0	2.0	2.7
Relative contribution of each TEA to total degradation (%)	O_2	4.1	5.0	5.0	6.5
	NO_3^-	28.9	31.3	31.5	47.5
	MnO_2	13.7	13.8	13.7	5.6
	FeOOH	30.7	30.8	30.7	4.9
	SO_4^{2-}	8.2	6.9	6.9	19.3
	CH_4	14.4	12.2	12.2	16.2
Degradation at fringe (%)		33.0	36.3	36.5	54.0
Degradation in core (%)		67.0	63.7	63.5	46.0

All figures based on global masses cumulatively reacted in 47 years unless stated otherwise
[a] plume width 65 m. [b] plume width 130 m

Three-dimensional homogeneous model with deterministic source

Simulations of the 3-D model, thus including the horizontal dispersive fringe, show a plume development very similar to the 2-D case (Fig. 2). Though the total mass of phenol degraded is much larger, the input of phenol is larger too due the lateral extension of the source, and the mass degraded per m width of the plume is only moderately larger (Table 2). In summary, the more realistic 3-D simulation gives a mass degradation increased by about 20% compared to a 2-D representation of the plume. But notably, there is no significant shift of the relative contribution, and thus importance, of the fringe and core processes; the majority of the degradation takes place in the core of the phenol plume (Table 2).

Three-dimensional model with variable source

Figure 3 illustrates the resulting plumes for a 3-D simulation with spatially variable phenol source with phenol and acetate as isosurfaces. A small amount of fingering of the plume is apparent in the simulations, which is not caused by the flow field, being uniform, but solely by the spatially variable phenol source. However, the effect on the mass balance and phenol removal is almost negligible.

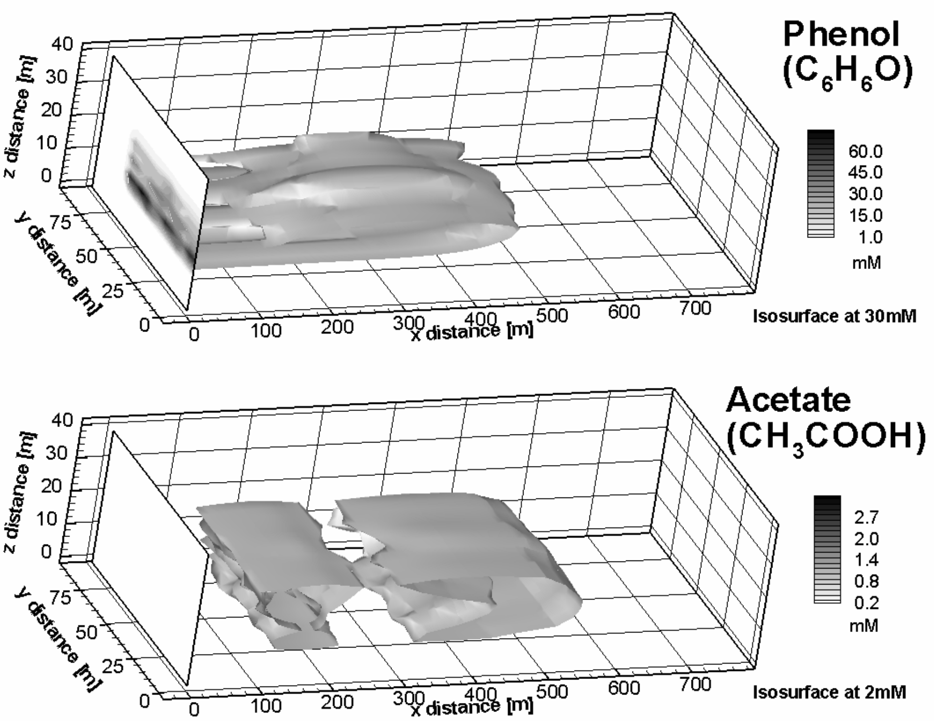

Fig. 3 Results of 3-D model showing contours on the variable source plane and the resulting fingering plume isosurfaces for phenolics and acetate after 47 years.

Numerical accuracy depending on grid refinement

A study on the grid refinement showed that automatic grid refinement can reduce the runtime with very limited changes in the mass balance, and also that a uniform grid level (level 5) with four times fewer nodes than the default (level 6) provides acceptable results, but that coarsening the grid further (level 4) then introduces more substantial deviations (Table 3).

Table 3 Results of parallel adaptive 2-D multi-species simulations given at 47 years.

Uni.	Rfn.	Crs.	Final nodes	Efficiency: Linear iterations	Runtime (h)	Global mass: Phenol (mols)	O_2 (mols)	NO_3^{2-} (mols)	FeII (mols)
6	–	–	16705	15895	55.3	100.0%	100.0%	100.0%	100.0%
–	6	–	8372	14694	36.0	100.0%	100.0%	100.0%	100.0%
–	6	5	5224	16500	28.3	100.2%	97.8%	97.9%	107.2%
–	6	4	4900	17004	28.3	100.4%	97.4%	97.6%	107.7%
5	–	–	4257	9598	9.5	100.4%	95.6%	96.7%	105.2%
–	5	–	2676	9587	7.6	100.4%	95.6%	96.7%	105.2%
4	–	–	1105	6086	2.2	101.4%	86.8%	93.6%	109.5%

Simulations were run on six processors of the Beowulf cluster. Uni. – maximum uniform level. Rfn. – most refined grid level. Crs. – lowest level grid coarsened to following refinement. Four adaptations were allowed each time step. Total Global Masses are normalized to the mass of the level 6 uniform results.

CONCLUSIONS

Enhanced numerical capabilities have been applied to facilitate comparison of modelling concepts for reactive transport and perform a realistic 3-D simulation. The biodegradation concept was shown to be the most important conceptual step-up, more important than extending a homogeneous model to one with a heterogeneous permeability field, or enlarging a 2-D to a 3-D model. Though this is a site-specific result, it indicates that the importance of improving the biodegradation concept should not be underestimated, even for already relatively sophisticated biodegradation concepts. This in turn also implies that there is a need for detailed laboratory data on biodegradation for close-to-field conditions, and that an effort in this direction may be more beneficial to capture the mass turnover than further characterizing the permeability heterogeneity of a weakly or moderately heterogeneous field site.

REFERENCES

Bastian, P., Birken, K., Johannsen, K., Lang, S., Eckstein, K., Neuss, N., Rentz-Reichert, H. & Wieners, C. (1997) UG - A flexible software toolbox for solving partial differential equations. *Comput. Visual. Sci.* **1**, 27–40.

Brun, A. & Engesgaard, P. (2002) Modelling of transport and biogeochemical processes in pollution plumes: literature review and model development. *J. Hydrol.* **256**, 211–227.

Mayer, K. U., Benner, S. G., Frind, E. O., Thornton, S. F. & Lerner, D. N. (2001) Reactive transport modeling of processes controlling the distribution and natural attenuation of phenolic compounds in a deep sandstone aquifer. *J. Contam. Hydrol.* **53**(3–4), 341–368.

Mayer, K. U., Frind, E. O. & Blowes, D. W. (2002) A numerical model for the investigation of reactive transport in variably saturated media using a generalized formulation for kinetically controlled reactions. *Water Resour. Res.* **38**(9), 1174, doi:10.1029/2001WR000862.

Oswald, S. E., Watson, I. A., Crouch, R. S. & Banwart, S. A. (2004) Applying a laboratory scale biodegradation concept to model field scale reactive transport with advanced numerical methods. In: *Bringing Groundwater Quality Research to the Watershed Scale* (ed. by Neil R. Thompson) (Proc. Int. Conf. GQ' 2004, July 2004, Waterloo, Canada), 517–524. IAHS Publ. 297. IAHS Press, Wallingford, UK.

Thornton, S. F., Quigley, S., Spence, M. J., Banwart, S. A., Bottrell, S. & Lerner, D. N. (2001) Processes controlling the distribution and natural attenuation of dissolved phenolic compounds in a deep sandstone aquifer. *J. Contam. Hydrol.* **53**(3–4), 233–267.

Watson, I. A., Oswald, S. E., Mayer, K. U., Wu, Y. & Banwart, S. A. (2003) Modeling kinetic processes controlling hydrogen and acetate concentrations in an aquifer-derived microcosm. *Environ. Sci. Technol.* **37**(17), 3910–3919.

Watson, I. A., Crouch, R. S., Bastian, P. & Oswald, S. E. (2005a) Advantages of using locally adaptive remeshing and parallel processing in modelling biodegradation in groundwater. *Adv. Water Resour.* **28**(11), 1143–1158, doi:10.1016/j.advwatres.2005.01.003.

Watson, I. A., Oswald, S. E., Banwart, S.A., Crouch, R. S. & Thornton, S. F. (2005b) Modelling the dynamics of fermentation and respiratory processes in a groundwater phenols plume interpreted from laboratory to field-scale. *Environ. Sci. Technol.* **39**(22), 8829–8839, doi:10.1021/es0507970.