

## What's New in Groundwater? & NGWA Darcy Lecture

### Contaminant transport in the Chalk: field investigations and modelling of dual-porosity behaviour at Tilmanstone

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The Chalk aquifer at Tilmanstone in south-east Kent, contaminated by coalfield brine from disposal lagoons operating throughout much of the 20<sup>th</sup> century, was the subject of the first published numerical model of regionally-extensive solute transport in a dual-porosity aquifer which properly incorporated diffusive exchange between mobile groundwater in fractures and immobile porewater (Bibby, 1981). Recent appraisals of the extent of groundwater contamination at Tilmanstone have shown however that Bibby's results significantly underestimate the diffusive retardation of contaminants in the aquifer. We have developed a revised conceptual model of solute transport in the Tilmanstone valley from i) tracer test investigations of fracture aperture and groundwater flow velocity, ii) characterisation of the aquifer hydraulic structure using geophysical logs and packer tests and updated Chalk stratigraphy, and iii) new determinations of porewater chloride content<sup>\*</sup>. The contamination has been re-modelled, using MT3D-DMS which incorporates diffusive exchange *via* a mass-transfer coefficient, and DP1D which incorporates Fickian diffusion. Results emphasise the significance of fracture density, groundwater flow and the history of the contamination source, and the imperative that porewater profiles should inform model development. Diagnosis of Chalk groundwater quality at sites of historical pollution, and prognosis of future trends, require determination of porewater chemical profiles and dual-porosity modelling.

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### The Role of Matrix Diffusion in BTEX and Fuel Oxygenate Attenuation in the Chalk

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A novel sampling strategy is described for the measurement of contaminant and electron acceptor concentrations in matrix and fracture waters from the Chalk aquifer. The technique is field based, and has been successfully employed at a site in S.E. England contaminated with BTEX and the fuel oxygenates MTBE and TAME. Solute concentrations in fracture waters are shown to be similar to those in the adjacent matrix, over a length scale of 1-2m. This degree of equilibrium allows matrix porewater solute concentrations to be estimated from the fracture water chemistry. At the study site this is accomplished via multilevel samplers (MLS), providing a convenient means of monitoring total dissolved pollutant concentrations in the aquifer. Profiles of solute concentration beneath the source and along the flowpath reveal progressive displacement of a residual source through migration of porewater benzene and oxygenates in the direction of groundwater flow. Stable isotope analysis of sulphate recovered from matrix porewater shows <sup>34</sup>S enrichment, consistent with bacterial sulphate reduction. This is good evidence that sulphate present in matrix porewater is being utilised for biodegradation, either through diffusive exchange with fracture waters, or in-situ reduction within the matrix.

The transport and natural attenuation of unleaded fuel containing BTEX and oxygenates (MTBE, TAME) is investigated in a UK chalk aquifer. The effects of dual porosity have been

assessed by comparing matrix and fracture water contaminant concentrations, using multilevel samplers in cored boreholes. Monitoring wells beneath the source area show NAPL dissolution products from the unsaturated zone flowing into a karstic horizon close to water table, where groundwater flow velocities are considerably increased. Below this horizon a seasonally low water table allows contaminants to accumulate in deeper, less transmissive, parts of the formation. In this zone BTEX oxidation by bacterial nitrate and sulphate reduction occurs, with the precipitation of iron sulphide in fractures. These processes effectively remove BTEX within 100m of the source. Carbon and sulphur isotope data for dissolved inorganic carbon and sulphate demonstrate the importance of sulphate reduction in BTEX degradation. Profiles of pore and fracture water solute concentrations are generally similar, indicating that the system is close to diffusive equilibrium. Porewater analyses confirm that the aquifer matrix is an important reservoir of both contaminants and oxidants for degradation, and that diffusion into the matrix is an important mechanism for contaminant attenuation at the site.

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### **Changes in Interfacial Tension of Chlorinated Solvents following flow through UK Soils and Shallow Aquifer Material**

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The interfacial tension (IFT) that arises at the interface between water and an immiscible organic liquid is a key parameter affecting the transport and subsequent fate of the organic liquid in water-saturated porous media. In this report, data are presented which show how contact between a range of soil types and chlorinated hydrocarbon solvent (CHS) dense non-aqueous phase liquids (DNAPLs) can affect DNAPL/water IFT values. The soils examined are indicative of UK soil types and shallow aquifer materials. The solvents investigated were tetrachloroethylene (PCE) and trichloroethylene (TCE). Lab grade, recovered field DNAPL and industrial waste chlorinated solvent mixtures were used. The data from batch and column experiments invariably revealed that water/DNAPL IFT values change following contact with unsaturated soils. In the majority of cases the IFT values increase following soil exposure. However after contact with an organic rich soil the IFT of the lab grade solvents decreased. The experimental evidence suggests that these reductions are linked to the removal of organic material from the soil and its subsequent incorporation into the solvent. IFT increases in the case of lab solvents are shown to be linked to the removal of stabilisers (added by the manufacturers to obviate degradation) which are removed by adsorption to soil mineral surfaces. Similarly it is conjectured that adsorption of surface active compounds from the industrial waste samples to soil surfaces is responsible for increases in the IFT in these samples. Finally it was observed that invading CHSs are capable of dissolving and subsequently mobilising *in-situ* soil contaminants. GC/MS analysis revealed these mobilised soil contaminants to be polyaromatic hydrocarbons and phthalate esters.

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### **Investigation of the nitrogen isotope chemistry of an urban aquifer: a case study of the Nottingham Sherwood sandstone, UK**

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Recently in the UK, there has been renewed interest in the potential use of groundwater in urban environments as a public supply, although there are concerns for the source and concentration of nitrate contamination. In this study, the  $\delta^{15}\text{N-NO}_3^-$  signature of groundwater has been utilised for the source identification of nitrate. However, the signature alone does not unambiguously identify the sources of nitrogen atoms, since the isotopic enrichment of  $^{15}\text{N}$  in nitrate can result from isotopic fractionation processes such as denitrification.

To overcome the disadvantage of the above approach,  $\delta^{18}\text{O-NO}_3^-$  is increasingly used as a new tool for determining nitrate reactions. This study provides the first example of the dual-isotope approach (that is the application of both  $\delta^{15}\text{N-NO}_3^-$  and  $\delta^{18}\text{O-NO}_3^-$ ) in an urban environment as applied to the Sherwood sandstone aquifer beneath Nottingham. The nitrogen and oxygen isotope data were found to be effective in identifying nitrification and denitrification at two hydrogeologically contrasting sites: Old Basford – a recharge area; and The Meadows – a discharge area, with flow restricted by a fault.

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### **Investigating rising nitrate concentrations in groundwater in the Eden Valley, Cumbria.**

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Nitrate concentrations in groundwater from the Permo-Triassic aquifer of the Eden Valley are spatially variable, ranging from less than 4 mg/l to in excess of 100 mg/l (as  $\text{NO}_3$ ). A significant number of boreholes exhibit rising trends in nitrate concentration approaching or exceeding the CEC Directive 80/778 Maximum Admissible Concentration (MAC) of 50 mg/l. The main source of the nitrate is almost certainly the nitrogen applied to grassland, both as slurry and as inorganic fertilisers.

The variability in groundwater nitrate concentrations is thought to be due in part to land use, particularly where low yielding boreholes derive their water from a limited/localised area, and in part due to the variability in travel times of the flow paths from the soil to the water table and then to the borehole. This variability is a function of surficial geology, depth to water table, depth of borehole and drift thickness amongst other factors.

The considerable depth to water table (at least in some areas of the Eden Valley) is likely to impose a significant delay in the arrival of high nitrate infiltration at the watertable. This delay within the unsaturated zone could be many years or even decades. Thus groundwater nitrate concentrations are likely to increase in the short term whatever restrictions on land-use activities at the surface are imposed.

It is surprising, given the considerable storage within the saturated zone of the aquifer and the slow groundwater movement, that some relatively deep boreholes pump groundwater with

nitrate concentrations in excess of 20 mg<sup>l</sup><sup>-1</sup>. Simple numerical modelling suggests that the fraction of modern water pumped is sensitive to the presence of fissures and the location of “drift-free windows” relative to the abstraction borehole. For some scenarios, using realistic drift geometries and aquifer hydraulic parameters, within 15 years since pumping started, more than 60% of the water pumped could be ‘recent’ (that is derived from infiltration that reached the water table since pumping started).

These models were used to assess how sensitive ‘the percentage of modern water pumped’ is to a few key aquifer scenarios and the models were not used to predict future pumped nitrate concentrations.

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### **Improved characterization of heterogeneous near surface materials by two-dimensional joint inversion of seismic and DC resistivity data**

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Accurate non-invasive physical characterization of the subsoil is a difficult task and may only be accomplished by proper combination of independent geophysical techniques. However, field data from multiple combinations of techniques are typically inverted separately and this limits model resolution to a large extent. This lack of resolution often leads to incompatible geophysical models that equally satisfy their respective data. We have developed a robust scheme for simultaneous 2D inversion of seismic travel times and DC apparent resistivity data. Using an illustrative field example from collocated DC resistivity and seismic refraction experiments over a fractured crystalline rock-mass covered by heterogeneous sediments, we compare the results from conventional separate 2D inversions and those obtained using our 2D joint inversion scheme. The joint inversion models show interesting features not revealed by the conventional separate inversion results.

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### **Hydro-Mechanical Modelling of Fractured Rock in Performance Assessment of Deep Waste Disposal**

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Near-field studies of flow in discrete fracture networks (DFN) using stress/permeability relationships to gain upscaled parameter values to support far-field modelling employing a continuum approach have been undertaken to examine the importance of hydro-mechanical (HM) processes for the performance assessment of nuclear waste repositories. The HM-coupling of the near-field was performed with a combination approach using the 2D thermal-hydro-mechanical (THM) code UDEC incorporating the empirical Barton-Bandis model (UDEC-BB) and a fracture flow and transport code FRAC2D. Multiple realisations of DFN with a power-law fracture length distribution and different fracture densities were generated. Upscaled permeability tensors were evaluated, which were used in the regional continuum model. Particle tracking was used in the far-field studies to model travel time distributions

through the repository host rock. The continuum flow code FAT3D was used for the far-field studies. Three main upscaled scenarios were considered: (1) Hydraulic base case with constant hydraulic apertures, (2) HM base case with variable apertures according to the HM-coupling using the mean mechanical values and (3) 'Natural' HM case with the spatial variability of the M-properties in the rock mass. The results from the near- and far-field studies provide a valuable illustration of the relative importance of hydraulic fracture densities, mechanical properties and their spatial variability in the rock mass.

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### **Regional groundwater pollution by boron in the Bengal Basin, with implications for fluxes of barium and strontium to the Bay of Bengal.**

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Regional natural pollution by boron of aquifers in the Bengal Basin and Ingham County, Michigan, occurs by desorption of boron from mineral surfaces as saline waters are flushed from the aquifers by freshwater. Concentrations of boron in groundwater concentrations of 2.1 mg l<sup>-1</sup> in Bangladesh and 6.0 mg l<sup>-1</sup> in Ingham County, Michigan, both well above regulatory guideline values. Boron enrichment is driven by exchange reactions that also depletes calcium and magnesium in flushing freshwater and enriches sodium, thereby providing a false measure of salt-water intrusion. In deep Bangladesh aquifers, boron enrichment through exchange delineates a buried estuary marking a previous course of the Ganges and/or Brahmaputra River. Freshwater flushing of shallow coastal aquifers creates temporary storage of divalent cations by ion-exchange for later release during localised saline intrusion, a process that enriches coastal seawater in barium and one that has been confused with a mass groundwater flow to the Bay of Bengal, which we show does not significantly impact global budgets of freshwater inputs to the ocean

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### **2003 NGWA Darcy Lecturer**

Dr Richelle Allen-King,

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*Dr. Richelle Allen-King is an Associate Professor at Washington State University. She received her Ph.D. from the Department of Earth Sciences, University of Waterloo and B.A. from the Department of Chemistry at the University of California, San Diego. She has served on committees for the National Research Council and presently serves as a member of their Water Science and Technology Board. She also serves as an Associate Editor for the journals Ground Water and Water Resources Research. Her research focuses on the geochemical processes that control the fate and transport of contaminants in ground and surface waters.*

### **A Hydrogeochemist's Perspective on Organic Contaminant Transport in Groundwater**

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Sediment geochemical (and physical) heterogeneity can cause “nonideal” contaminant transport. The problem is framed by the contrasting transport behavior of perchloroethene (PCE) in two natural gradient field experiments conducted nearby one another in the well-studied Borden aquifer. The PCE retardation factor increased from ~3-6 with time/distance of travel in the Stanford-Waterloo experiment (conducted in the early '80s by others) while it was uniform and <2 in the subsequently conducted Emplaced Source experiment. Laboratory measurements show that contaminant sorption is nonlinear and competitive, indicating grain scale chemical heterogeneity. Retardation factor ( $R$ ) predictions of plume-scale behavior that account for solute and co-solute concentrations using the laboratory-derived sorption parameters are consistent with the behavior of both field plumes. This approach suggests that different  $R$  for the two plumes are a consequence of source conditions combined with nonlinear/competitive sorption effects. Further, identified lenses of relatively higher sorption coefficient may contribute to the apparently enhanced dispersion exhibited by the retarded, compared to the nonreactive, solutes.

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### **What's over the horizon? – An Environment Agency perspective on future research needs**

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In March, the Environment Agency's Board approved a new Science Strategy. This strategy will build on the Agency's reputation for Science, ensure that our policies and operational decisions continue to be based on sound science, and influence other organisations to join us in undertaking research that yields real environmental benefits.

In order to deliver this new Strategy, and to tighten the focus and management of the R&D programme, the existing National Centres (Groundwater & Contaminated Land, Ecotoxicology and Hazardous Substances, and Environmental Data and Surveillance) are being re-structured. A smaller number of larger, more strategic projects will be commissioned in future, and closer links with universities and other research institutes in the UK and internationally will be developed.

Key science areas for the Agency include:

- Impacts of climate change
- Assessment of aquatic ecosystem health
- Sensors, telemetry and remote sensing
- Diffuse pollution and chemical mixtures
- Social and economic responses to environmental and human health threats

We have also identified emerging areas in which new scientific expertise will be required:

- Pathogens in the environment
- Pharmaceuticals and Veterinary Medicines

- Molecular approaches to environmental assessment (genomics, proteomics, etc.)
- Innovative chemical and biochemical analysis techniques
- Novel data management systems
- Estuarine science

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