

## **RECENT ADVANCES IN DATING AND TRACING GROUNDWATER ABSTRACTS**

### **TRACER TESTS, GEOMORPHIC ZONES AND KARSTIC CIRCULATION IN THE BERKSHIRE CHALK**

L Maurice<sup>1</sup>, T Atkinson<sup>1</sup>, J Barker<sup>1</sup>, J Bloomfield<sup>2</sup>, A Farrant<sup>3</sup>, A Williams<sup>2</sup>

<sup>1</sup>University College, London

<sup>2</sup>British Geological Survey, Wallingford

<sup>3</sup>British Geological Survey, Keyworth

Field survey of surface karst features in the Chalk catchments of the Pang and Lambourn rivers in southern England demonstrates the importance of overlying and adjacent Palaeogene strata in the development of karst features and reveals three distinctive geomorphological zones. Zone 1 comprises areas where the Chalk is overlain by Palaeogene deposits and is characterised by a high density of karst features including many active stream sinks. In Zone 2 the Palaeogene has been recently removed and the Chalk is overlain by Clay-with-Flints. There are frequent karst dolines in Zone 2 but no active stream sinks. Zone 3 is the area furthest away from the Palaeogene margin where the Chalk is exposed at the surface, and here there is very little evidence of surface karst, apart from the extensive network of dry valleys that characterises much of the Chalk outcrop.

In Zone 1 Chalk karst areas in the Pang and elsewhere in the UK, tracer testing has demonstrated groundwater flow velocities comparable to those observed in highly karstic aquifers. Tracer testing was undertaken from several stream sinks located in Zone 1 in the Pang and Lambourn catchments to enable further characterisation of the karst conduit networks and to investigate contaminant attenuation mechanisms. Tracer test results from the Pang and Lambourn will be presented and the nature of groundwater flow in Zone 1 Chalk karst will be considered.

### **TRACER TESTS AT DIFFERENT SCALES IN EAST ANGLIAN CHALK - WHAT IS THE RIGHT MODEL FOR CONTAMINANT TRANSPORT?**

T Atkinson, University College, Department of Earth Sciences, London

There are two alternative conceptual models for the behaviour of tracers and contaminants in the Chalk aquifer. The choice of which model to assume has practical importance when predicting the behaviour of contaminants in contexts such as risk assessment and source protection for drinking waters. On one hand, short-term dilution of a tracer during transport may be dominated by classical hydrodynamic dispersion, arising from irregularities of flow within individual fractures, and from the presence of multiple pathways through a 3-D fracture network, each pathway having its own characteristic advective transit time. This model is expressed mathematically by solutions of the advection-dispersion equation. On the other hand, tracer dilution may be dominated by migration of solutes between moving water in fractures and static water in the pore-space of blocks bounded by these fractures. The simplest mathematical expressions of this Double Porosity model involve no classical hydrodynamic dispersion at all, with pure piston-flow advection in the fissures, and diffusion between fissures and matrix acting as the sole mechanism for dilution.

Equations for both models can be cast in terms of characteristic times. For any tracer experiment the breakthrough curve is usually a graph of concentration against time at a fixed location some distance downflow of the injection. For both models the transit time from injection to sampling location is a fundamental parameter. Advection-dispersion can be expressed in terms of a dispersion time which is related to the aquifer dispersivity, whereas for double porosity the controlling parameter is the characteristic diffusion time for fissures or tcf. Dispersivity and tcf can each be regarded as properties of the aquifer.

The consequences of using an incorrect or insufficient model to describe real tracer transport will be illustrated using an experiment in a 14 km long reach of the River Severn in which advection-dispersion is due to turbulence and the changes of velocity over the cross-section. Because this experiment was in an accessible channel, the tracer cloud could be sampled at several stations along its course, and its evolution recorded. The advection-dispersion model was unable to describe the

evolution of the cloud unless its principle parameter (analogous to dispersivity in an aquifer) was allowed to increase with distance travelled. There was no physical justification for this. A better explanation was that the important process of dead-zone storage of tracer was neglected in the simple advection-dispersion model. A hybrid model incorporating dead-zones proved capable of describing the whole tracer cloud evolution accurately with invariant parameters. At distances more than ~3 km from the injection, a model with no advection-dispersion, only dead zones, was as good as or better than the hybrid one, suggesting that dead-zone storage was the dominant mechanism once tracer had travelled this far.

There is possibly an analogy between this experience and the well-known phenomenon in aquifers that dispersivity apparently increases with distance travelled by a tracer. Perhaps in the Chalk aquifer we are using models that neglect an important process, namely diffusion in a double porosity medium. This notion can be tested by comparing tracer tests at different scales. The example will be given of a convergent radial flow forced gradient test which was used to determine dispersivity and also tcf on a 200 m scale for a site at South Farm, near Thetford, East Anglia. The applicability of the advection-dispersion and double porosity models was assessed for each in turn by applying the values of the South Farm parameters to three natural-gradient tracer tests at much larger scales - 1600 - 3000 m. The actual attenuation of tracers was extremely high, so only times and concentrations of the peaks of the breakthrough curves could be determined from the natural-gradient field data. The advection dispersion model performed noticeably worse than double porosity, in simulating these peak concentrations using the parameters derived from South Farm. Double porosity parameters derived at the local scale can potentially be used to make successful predictions of tracer behaviour over the much larger scales found in pollutant plumes. Advection-dispersion produces predictions which overestimate peak concentrations by up to several orders of magnitude, depending on assumptions made.

In applied hydrogeology, advection-dispersion is by far the more commonly used model. The conclusion which may be tentatively drawn from this study is that double porosity would be a more realistic single-concept model to employ in many situations."

## **RADON IN CHALK SPRINGS – COMPARISON BETWEEN THE RIVER PANG AND RIVER LAMBOURN CATCHMENTS, BERKSHIRE**

Simon Quinn

University College London, Department of Earth Sciences, London

Measurements of radon activity have been made in Chalk spring and groundwaters in the River Pang and Lambourn catchments on a regular basis during the past year. This work forms part of an ongoing LOCAR (NERC) investigation into the potential for radon gas to be used as a natural groundwater tracer in a double porosity aquifer system, such as the Chalk. From the results analyzed so far it is apparent that there are distinct spatial and temporal differences in radon activity at the selected sampling locations. Historically such variation has been regarded as primarily a function of groundwater velocity (Andrews and Wood, 1972). However in recent years work of others (Atkinson et al, 2001; Spizzico, 2005) indicate that rock type, fracture type and fracture frequency, as well as the surrounding soils are among the other geological factors that may affect the radon content of groundwater. The results will be used to highlight the differences in geological setting of the two catchments and to illustrate how radon might provide an indicator of the flow characteristics at any particular spring.

Andrews and Wood, 1972. Mechanism of radon release in rock matrices and entry into groundwaters. Transactions of the Institution of Mining and Metallurgy, B81 198-209.

Atkinson et al, 2001. Radon: An indicator of solute transport in double-porosity aquifers. Seiler, K. P and Wohnlich, S. XXXI International Association of Hydrogeologists congress. Munich, Federal Republic of Germany. Sept. 10-14, 2001. New Approaches Characterizing Groundwater Flow 1, 441-445. 2001. Netherlands.

Spizzico, 2005. Radium and radon content in the carbonate-rock aquifer of the southern Italian region of Apulia. Hydrogeology Journal, 13 (3): 493-505.

## **RADON AS A HYDROGEOLOGICAL TRACER IN GROUNDWATER-SURFACE WATER INTERACTIONS; TEMPORAL AND SPATIAL VARIATIONS**

Neil Mullinger, Nigel Crook, Jackie Pates and Andrew Binley

Department of Environmental Science, Lancaster University, Lancaster, LA1 4YQ

An understanding of groundwater – surface water interactions is of great importance for sustainable water resources management. Greater knowledge of the processes that maintain river flows will allow us to meet human demands made on water supplies for drinking, sanitation and industrial purposes whilst balancing ecological and recreational needs. Radon is a radioactive noble gas that occurs naturally in aquifer materials as a decay product of radium. Diffusion of radon in to pore spaces and fractures of an aquifer makes it available for solution in groundwater. In the saturated zone water will acquire a radon signature depending on the composition of the aquifer material. Surface waters have generally low radon concentrations, hence in areas of groundwater-river interaction increased river radon concentrations may be observed. Here we report on the temporal and spatial variations in radon concentrations in lowland chalk catchments of the Pang and Lambourn rivers in south-east England. In-stream and borehole radon sampling was conducted at three monthly intervals, in conjunction with flow monitoring and water chemistry (metals, CO<sub>2</sub>, temperature and conductivity), over a two year period. From these data we aim to evaluate the use of radon as a natural hydrogeological tracer for water exchange in the hyporheic zone.

## **THE USE OF CHLOROFLUOROCARBONS AS EARLY INDICATORS OF LANDFILL LEACHATE CONTAMINATION IN UK GROUNDWATER**

Paul Hardwick<sup>1</sup>, Giorgio Martinelli<sup>2</sup>, John Gunn<sup>3</sup>, Martin Lovelock<sup>1</sup>, Daren Gooddy<sup>4</sup>

<sup>1</sup>Principal Hydrogeologist Arley Consulting Company Limited

<sup>2</sup>Principal Hydrogeologist White Young Green Environment

<sup>3</sup>Director Limestone Research Group University of Huddersfield

<sup>4</sup>Senior Hydrogeochemist British Geological Survey Wallingford

Chlorofluorocarbons are frequently found in leachate and gas samples from UK landfills. Recent investigations at landfill sites on the Chalk in Hampshire, the Millstone Grit in West Yorkshire and the Dinantian Limestone in the Derbyshire Peak District indicate that CFC-11 and CFC-12 may provide an early indication of leachate contamination of groundwater pathways and receptor springs many years before the significant breakthrough of conservative contaminants such as chloride.

## **A RADIALLY CONVERGENT TRACER TEST IN THE BERKSHIRE CHALK**

A Williams<sup>1</sup>, S. A. Mathias<sup>2</sup> and A. P. Butler<sup>2</sup>.

<sup>1</sup>British Geological Survey Wallingford

<sup>2</sup>Imperial College, London

A radially convergent tracer test was performed at a LOCAR research site located in a Berkshire Chalk outcrop. The site is based around an 86m deep Environment Agency abstraction well and consists of three 100 m deep open observation wells and 3 double piezometers. Different fluorescent tracers were introduced to two of the open wells within 50 m of the abstraction well, which was pumping at ~ 6 Ml/d. Salt was added to the fluorescent tracer so that the way the tracer left the injection wells could be monitored by fluid electrical conductivity (FEC) logging. The concentration of tracer in the abstracted water was measured using a logging in-line fluorometer.

The two breakthrough curves (BTC) were apparently quite different. Tracer arrival times from the nearest and furthest injection boreholes were 15 and 4 minutes, respectively. Both BTCs exhibited late-time log-log slopes of approximately  $-3/2$ , consistent with the Fickian matrix-diffusion mechanism associated with dual-porosity aquifers. However, neither BTCs could be adequately simulated using an instantaneous source term. This is because the periods over which the tracers left the injection wells were comparable with the corresponding advective travel times to the pumping well. A revised method involving a time-dependent source term, derived from the FEC logs, was consequently developed. This has enabled a better understanding of both the flow regime at the site and the dynamics of this type of tracer test.

## **WHERE DOES ALL THE DISSOLVED ORGANIC MATTER GLOW?**

Andy Baker

School of Geography, Earth & Environmental Sciences, The University of Birmingham, Birmingham, B15 2TT

Dissolved organic matter has distinctive spectrophotometric properties. As well as strong absorption in ultra-violet light, much DOM has a strong intrinsic fluorescence. Recent advances in fluorescent spectrophotometry permit the rapid (<1 min), continuous, portable detection of fluorescent dissolved organic matter at sub ppb concentrations at a wide range of both excitation and emission wavelengths to produce an excitation-emission matrix. This typically covers a range of excitation and emission wavelengths from ~200 nm (short wavelength UV) through to ~ 500 nm (visible blue-green light), and can quantify and qualify fluorescence centres that are attributed to both high molecular weight groups such as humic and fulvic-like material, as well as microbially derived fluorescent proteins and fluorescent anthropogenic pollutants such as fluorescent whitening agents, naphthalene and endocrine disruptors. Recent investigations of dissolved organic matter intrinsic fluorescence help understand dissolved organic matter interferences with fluorescent dye traces. Examples will be given of recent case studies that include the use of intrinsic fluorescence (1) as a groundwater tracer of landfill leachates of different ages (2) to detect leachates associated with mass burial sites (3) to identify diffuse groundwater pollution inputs to surface streams.

## **PARTITIONING OF TRACER GASES BY N<sub>2</sub>-BUBBLES FROM EXCESS DENITRIFICATION IN RECHARGE AREAS: METHODS TO INTERPRET <sup>3</sup>H/<sup>3</sup>HE DATA**

Ate Visser<sup>1,2\*</sup>, Hans Peter Broers<sup>2</sup>, Marc F. P. Bierkens<sup>1,2</sup>

<sup>1</sup>Utrecht University, Faculty of Geosciences, P.O. box 80115, 3508 TA Utrecht, The Netherlands

<sup>2</sup>TNO – Netherlands Institute of Applied Geosciences, P.O. Box 80015, 3508 TA Utrecht, The Netherlands

The province of Brabant (The Netherlands) has a land use history of intensive livestock farming with heavy nitrate deposition since the 1970s. Denitrification in shallow pyrite containing layers (pyrite oxidation) in the unconsolidated Pleistocene sandy aquifer causes in-situ N<sub>2</sub>-bubble formation in recharge areas. This leads to partitioning of tracer gases between the aqueous and the gas phase present in the aquifer.

To interpret the measurement results of partitioned/degassed  $^3\text{H}/^3\text{He}$  (and CFC and  $\text{SF}_6$ ) samples, we present three methods with increasing complexity. The first gives the minimum and maximum groundwater age of a sample following the assumption that the partitioning of  $^3\text{He}$  took place either at the time of recharge or at the time of sampling. The second uses a total dissolved gas sensor to estimate the depth at which partitioning took place and from this the relative timing between recharge and sampling. The third method includes 1-D inverse modelling of tracer transport and denitrification, coupled with the partitioning process

### **STRONTIUM ISOTOPES AND NOBLE GAS “EXCESS AIR” AS TRACERS OF GROUNDWATER RECHARGE PROCESSES IN THE CRETACEOUS AQUIFERS OF WEST NORFOLK**

Richard G.S. Ingram, Kevin M. Hiscock, Paul F. Dennis  
School of Environmental Sciences, University of East Anglia, Norwich

The Sandringham Sands aquifer system in west Norfolk is confined to the east of outcrop by two impersistent clay formations, separating the Sands from the overlying Chalk. The manner in which the confined aquifer is recharged is unclear from groundwater head observations due to a sparse monitoring network but three possible mechanisms are suggested: 1) recharge from outcrop areas; 2) recharge by leakage from the Chalk around the confining clay formations or 3) recharge from the Chalk near the confined/unconfined transition zone where the clays have been partially eroded. Measurements of strontium (Sr) isotope ratios and noble gas concentrations in groundwater samples from the Sandringham Sands provide evidence that the confined aquifer is recharged from the Chalk by a combination of mechanisms 2 and 3. Enriched  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios (0.7087 – 0.7115) observed over the Sands outcrop imply that silicate dissolution dominates groundwater chemistry in the Sands. Depleted  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios ( $\leq 0.7084$ ) found in the confined groundwater show that carbonate dissolution is more important in the chemical evolution of this groundwater, which is incompatible with the outcrop recharge scenario. Groundwater recharged by leakage from the Chalk (mechanism 2) is differentiated from marginal recharge (mechanism 3) using noble gas “excess air” concentrations. Excess air concentrations in groundwater recharged by leakage are very high (~ 100% Neon excess relative to saturation,  $\Delta\text{Ne}$ ). This results from the large annual fluctuations of the Chalk water table over the recharge area that trap air bubbles during wetting periods. Marginal recharge has lower  $\Delta\text{Ne}$  values of  $40 \pm 10\%$  due to re-equilibration between groundwater and the atmosphere where Chalk water tables are shallow over the transition zone. Higher Cl concentrations and Ca:Mg ratios indicate a shorter residence time for this groundwater than that recharged by leakage.

### **DATING GROUNDWATERS IN THE UK USING CFCs AND $\text{SF}_6$**

George Darling<sup>1</sup>, Daren Gooddy<sup>1</sup>, Alan MacDonald<sup>2</sup>, Brian Morris<sup>1</sup>

<sup>1</sup>British Geological Survey, Wallingford

<sup>2</sup>British Geological Survey, Edinburgh

The British Geological Survey has been using the chlorofluorocarbons (CFCs) and sulphur hexafluoride ( $\text{SF}_6$ ) as environmental tracers in its hydrogeological investigations over the past eight years. During this time a wide range of aquifer types has been investigated, from Dalradian metasediments in the Highlands of Scotland to Chalk in the south of England. Under ideal circumstances, the CFCs can be used to date groundwaters less than fifty years old with considerable precision. Cross-plotting of CFC against  $\text{SF}_6$  concentration can then be used to resolve mixing from piston flow processes. However, contamination of groundwater by excess CFCs from industrial or landfill sources is by no means unknown. In such cases, the CFCs can be used as tracers of water origin and movement while  $\text{SF}_6$ , which is largely immune to contamination, can still provide a bulk age. Examples of both types of usage will be presented, and the future of the techniques briefly discussed.

**DARCY LECTURE: "INERT GAS TRACERS IN GROUND WATER"**

D Kip Solomon

Department of Geology and Geophysics, University of Utah, USA

The presentation will illustrate the basic concepts of using inert gas tracers along with case studies that describe their applications to real ground water flow problems. The case studies will focus on ground water dating, noble gas thermometry or inject gas tracers.