

# **A historical perspective on groundwater nitrate research in the UK**

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Research on the origin, transport, fate and behaviour of nitrate in groundwater has been undertaken by the UK groundwater community for more than 30 years. The paper reviews the work over this period, from the time in the early 1970s when rising trends in groundwater nitrate concentrations were beginning to be widely noticed. Early work was largely field-based, comprising unsaturated zone coring to obtain profiles of nitrate leaching beneath cereal cultivation on the Chalk aquifer. This was extended through the late 1970s and 1980s to the Sherwood Sandstone aquifer, and to the saturated zone.

Having broadly demonstrated the scale and scope of the groundwater nitrate problem associated with intensive farming, research attention began to embrace possible mitigation measures. This meant extending the profiling to other land use types such as grassland and woodland, which might be adopted to help control nitrate pollution. Early approaches to controlling nitrate concentrations in abstracted water included “engineering” solutions, in which sources were modified by casing out shallow, high-nitrate water or drilling deeper to draw lower-nitrate water for blending from an underlying aquifer. These required detailed, site-specific hydrogeological investigations. If there were widespread and significant denitrification in groundwater systems this would also help to reduce eventual concentrations, and a range of techniques have been used to assess denitrification potential.

By the 1980s, the interest of hydrogeologists had also turned to predictive modelling of future groundwater nitrate concentrations. This historical perspective allows us to look back at some of the early modelling and compare the results against subsequent nitrate observations. Modelling of nitrate concentrations at site and catchment scale has continued to be a main thrust of diffuse pollution research.

## Screening for long-term trends in groundwater nitrate monitoring data

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A large dataset of groundwater nitrate data has been analysed using a semi-automated linear regression methodology to define past trends and to make estimates of future concentrations. Tests were included for lack of linearity, outliers, seasonality and breaks in the trend. 21% of the series analysed showed a significant improvement in the overall fit when such a break was included and half of these indicated an increase in trend with time. An assessment of seasonality in nitrate concentrations was also made by including a term for the month of sampling in the regression model. Significant seasonality was found in about one third of the series. In 2000, 34% of sites analysed exceeded the 50 mg/L standard. If present trends continue, 41% of groundwater sources could exceed the standard by 2015.

The WFD concept of calculating trends for groundwater bodies rather than for individual monitoring sites has required new approaches to aggregating groundwater quality data. An alternative to the recommended approach, the 'median trend' approach, was tested. This determines the trend at individual sites within a groundwater body and then finds the median of these trends to give the trend for the groundwater body as a whole. This approach allows an informed analysis of systematic variations within the body, and it is less sensitive to missing data.

# **Identifying the significant factors influencing chronological and spatial trends in nitrate concentrations in the Dorset and Hampshire Basin Chalk Aquifer of Southern England**

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Groundwater in the major aquifer of the Dorset and Hampshire Basin Chalk makes up over 70% of water abstracted from the environment for public water supply in Southern England. Rising nitrate levels in the chalk aquifer are of concern to water suppliers who must provide safe drinking water in compliance with drinking water standards (DWI, 2001). Land use over the aquifer is mainly agricultural. The presence of the thin soils usually associated with Chalk bedrock, makes the aquifer highly vulnerable to contamination from surface activities.

As part of its statutory duties the Environment Agency (UK) collects groundwater quality data throughout England and Wales in order to comply with European and UK legislation. Here nitrate data collected over a 30 year period from 172 sites is used to describe the chronological evolution of the spatial distribution of nitrate concentrations in the Dorset and Hampshire Basin Chalk aquifer. Contours of equal nitrate (as mg N/l) concentration are plotted over the study area using average values for each decade between 1976 and 2006 at 172 points. Concentrations of nitrate have increased by around 90% at some sites over the study period, although most appear to have increased by 40-60%. A comparison of the spatial distribution of nitrate concentration with land-use confirms that areas of semi-natural vegetation coincide with low nitrate concentrations in groundwater. Groundwater flow direction may also control the spatial distribution of elevated nitrate concentration. Time series analysis was performed on the data to identify long term trends and any seasonality in the data set. Seasonal variability in nitrate concentrations is more pronounced in the east of the aquifer with winter peaks taking the nitrate concentration over the DWI standard. Multivariate analysis of geochemical data was also carried out in an effort to identify the significance of factors controlling nitrate concentrations within the aquifer.

# **Catchment-scale modelling of flow and nitrate transport in the Chalk unsaturated zone**

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The LOCAR research programme has provided a unique set of comprehensively instrumented groundwater-dominated catchments, with the Pang and Lambourn, tributaries of the Thames near Reading, a particular focus for research into subsurface processes and surface water-groundwater interactions. The Chalk unsaturated zone is crucial in controlling the delivery of nitrate to Chalk streams, yet flow and transport processes in this complex, dual-porosity medium have remained controversial. We present results from a new dual permeability numerical model of the Chalk unsaturated zone to explore the relative roles of matrix and fracture flow, and use these to interpret detailed unsaturated zone monitoring data from the LOCAR programme in the Pang and Lambourn. A major challenge arises in representing the deep unsaturated zone within catchment-scale models for nutrient management. These have generally been based on simple conceptual stores to represent soils and groundwater. A new conceptualisation is presented and applied to the Lambourn within a catchment-scale nutrient model. Preliminary results are encouraging, but clearly illustrate the decadal time-scales that need to be considered in the context of nutrient management and the Water Framework Directive.

# **Evaluation of the behaviour of wastewater discharges of nitrate within the unsaturated zone - mechanisms of storage and attenuation within Chalk downlands, Southern England.**

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This paper presents the findings of a programme of investigations characterizing wastewater discharges onto Chalk. Five separate treatment plants were evaluated by installing a groundwater monitoring network, including geological and geophysical core logging, pore water extraction and chemical analysis, hydraulic conductivity testing, water level measurement and groundwater sampling.

The results have been assessed with respect to nitrate and ammonia discharge and transport through the unsaturated zone. The assessment initially evaluated the physical layout of the discharges which exert a control over groundwater mounding and the loading of organic nitrogen. A detailed view of the hydrogeology and groundwater chemistry is given in profile through the unsaturated zone by reference to geophysical and pore water sample results. Concentrations of nitrate in excess of  $150\text{mg.L}^{-1}$  were recorded in the unsaturated zone at discrete intervals. The concentration profiles have been assessed to indicate the mode of nitrate transport and storage within the unsaturated zone. Pore water concentrations are noted in some instances to be significantly higher than recorded in the underlying groundwater. The processes that control the formation of nitrate within the subsurface, in particular the effect of redox during varying conditions of saturation are examined and an approximate chemical mass balance presented. The rate of nitrate transport and attenuation as it migrates through the unsaturated zone and flows with groundwater is estimated.

The results suggest that at some sites, the amount of organic nitrogen stored in the unsaturated zone is greater than can be predicted from a leaching model. Where the physical layout of the disposal system encourages wide dispersal there tends to be less nitrate stored in the unsaturated zone. Coupling physical and chemical data, a conceptual model of the sites suggests that where there are high driving heads either at surface or in groundwater mounds, organic nitrogen-rich sediments can be driven into the subsurface and be emplaced in deep Chalk fractures. This material continues to generate nitrate in the unsaturated zone at high concentrations leading to increased leaching and impact to groundwater.

# **Quantification of the attenuation of nitrate within riparian floodplains and the role of hyporheic zone processes**

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Hydrological processes in riparian floodplains are often controlled by exchange fluxes across the groundwater - surface water interface. The intensity and directions of these fluxes can be subjected to a high spatial and temporal variability. However, groundwater – surface water exchange fluxes strongly determine the advective transport of nutrients as nitrate or pollutants between the riparian floodplain and the river.

Due to denitrification processes in anoxic groundwater riparian floodplains can act as nitrate sinks. On the other hand riparian floodplains can also represent nitrate sources when nitrate rich groundwater is exfiltrating into the river. These processes strongly depend on hydraulic gradients and connectivity, in situ concentrations, geological background and sources of pollution.

This study presents approaches to analyse the nitrate transport and metabolism between river and groundwater in order to quantify the importance of natural attenuation in the groundwater of riparian floodplains.

The analyses of groundwater – surface water interactions in riparian floodplains of North-German catchments detected temporal dynamics of the floodplain being a sink for nitrate during surface water infiltration periods in winter and acting as a nitrate source during base flow periods in summer. Although within the research area the contribution of groundwater born nitrate to the total loads within the river is less significant for the annual loads the delivery of nitrate from groundwater can be seasonally very important and represent up to 28 % of the total nitrate delivery of the catchment.

It was shown that the intensity of interactions between groundwater and surface water, the exchange fluxes and subsequently the attenuation rates in groundwater are controlled by the riverbed connectivity. Experimental investigations at the UK rivers Leith (Cumbria) and Tern (Shropshire) highlight the importance of the passage through the hyporheic zone for the attenuation of the transported nitrate. The physical riverbed conditions (e.g. pressure head gradients, porosity and permeability) strongly control the intensity of exchange fluxes and the composition of interstitial water as well as the residence times within reactive areas. The residence times and the stream bed redox-conditions subsequently control the intensity of nitrate attenuation processes.

It was furthermore tested how far characteristic attenuation pattern as found for pool – riffle sequences can be incorporated into existing model approaches in order to upscale the local results from stream reach to catchment scale.

# Combining $^{18}\text{O}/^{16}\text{O}$ with $^{15}\text{N}/^{14}\text{N}$ data in isotope studies of UK nitrate

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Natural abundance  $^{15}\text{N}/^{14}\text{N}$  ratio analyses have been contributing to studies of the sources and reaction pathways of nitrate for more than 30 years. Here I outline the development of  $^{18}\text{O}/^{16}\text{O}$  ratio analyses in the past 10 years, and show how the combination of  $^{18}\text{O}/^{16}\text{O}$  +  $^{15}\text{N}/^{14}\text{N}$  analysis of nitrate has proved particularly useful in identifying atmospheric nitrate, and distinguishing  $^{15}\text{N}/^{14}\text{N}$  effects due to denitrification. Examples are given of recent studies of catchment systems in the UK – i.e. relating to nitrate movement through the unsaturated zone – and studies of UK groundwaters.

The nitrate status of groundwaters is to a large extent dependent on the ability of the overlying soils to either assimilate and immobilise nitrogen, or to produce and release it in the form of nitrate.

$^{18}\text{O}/^{16}\text{O}$  +  $^{15}\text{N}/^{14}\text{N}$  data are presented from studies of upland catchment areas, and an experimental lowland grassland plot, to examine conclusions based on earlier modelling studies. Contrary to expectations of significant hydrologic, rain-fed contributions of nitrate, the data indicate a dominant soil microbial source.

Whilst increases in the  $^{15}\text{N}/^{14}\text{N}$  ratios of nitrate are known to be associated with denitrification, they can also result from contamination by human/animal sewage waste.  $^{18}\text{O}/^{16}\text{O}$  analysis provides an important second indicator for positively identifying denitrification in different groundwater environments.

## **Nitrate in groundwater – A Water Company Perspective**

*(Wessex Water and Entec)*

### **Rising nitrate - so what?**

*Luke de Vial*

Nitrates are rising at many of Wessex Water 80 groundwater sources. If unchecked this rise will require one new treatment plant to be built each year for the foreseeable future. Treatment for nitrate is expensive, both in capital and operating costs, the treatment plants have short asset lives and the waste water stream can be difficult to dispose of. The treatment requires a lot of power and chemicals and is therefore not sustainable. And remember it is the peak level of nitrate that governs whether or not we have to install treatment.

### **In search of low nitrate water**

*Victoria Ashton*

To overcome high nitrate in the groundwater at one site near Dorchester we are trying to find a source of low nitrate water nearby in the confined Chalk. Drilling and test pumping in the 1990s demonstrated that there was water present in this aquifer and it did have low nitrate. Wessex are currently drilling further boreholes in the confined Chalk a bit closer to where it is needed. Yield, quality and environmental impact are all being examined.

### **Catchment management - what are we doing?**

*Paul Stanfield*

Wessex Water is working with farmers and other organisations in 10 source protection zones. 8 of these sites are to deal with nitrates and 2 to deal with pesticides. Before talking about nitrates the two pesticides sites will be reviewed as they indicated that radical changes in land management can lead to radical changes in water quality. On all of these sites Wessex's two catchment advisers are concentrating on data collection, groundwater levels, nitrate concentrations in boreholes, rivers, springs, land drains, soils and leaves - and then using this information to give advice to farmers to help them reduce their applications of nitrate and therefore, hopefully, to reduce the amount of leaching out of the soil.

### **Catchment management - who are they kidding?**

*Nick Rukin – Entec*

Well that is all very noble, but it won't work of course, and if it does work it will take too long. We all know that water in the Chalk, and the pollution that travels with, moves through the unsaturated zone at 1metre a year. Entec has been working with Wessex Water and the Environment Agency to try and understand why we see the nitrate concentrations that we do, and how those concentrations will change in response to changes in land management. The data collected as part of Wessex's catchment management study has been used to test conceptual models of how nitrate may move through the soil, unsaturated zone and saturated zone to the abstraction wells. Very provisional conclusion - This indicates that whilst reversing the long term trend in nitrate will take a long time, radical land management changes may control the peak level of nitrate observed very quickly - and therefore delay or avoid altogether the need for treatment.

# **An Integrated Approach for Groundwater Nitrate Risk Assessment from Agricultural Diffuse Sources at Catchment Scale**

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Groundwater pollution prevention at catchment scale is more important and more feasible than remediation of polluted groundwater during the implementation of the EU WFD by year 2015. Quantification of the impact of nitrate in surface water and overland flow on groundwater quality can reduce the uncertainty in groundwater risk assessment.

We have developed an integrated GIS D-DRASTIC modelling approach for a better groundwater risk assessment from nitrate pollution at catchment scale, taking the Upper Bann Catchment (NI) as an example, which will support decision makers to efficiently and effectively carry out groundwater diffuse pollution prevention. This method considers not only the hydrogeologic factors controlling water pollution pathway, but also the nitrate quantitative dynamics along the pathway to groundwater. The pollutant inputs from different land uses, surface water movement, the dynamic nature of nitrate and their potential impacts on groundwater were combined to reduce uncertainty of the modelling results. This method is more accurate and reliable by adopting risk concept for nitrate estimation with surface and ground water interaction at catchment scale. This approach may provide a good starting point for tackling diffuse pollution problems at catchment scale in the WFD participatory process.

# **Integrated assessment of nitrate for the designation of groundwater NVZs in England and Wales.**

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The project had two main aims. Firstly to identify surface and groundwater that is exceeding, or likely to exceed, 50 mg/l nitrate with agricultural input as a significant source. Secondly to identify the parcels of land that drain to these waters. The work brings together and develops the 2000 nitrates review methodologies for surface and groundwater and is focused on providing the underpinning evidence for both the Nitrates Directive 2006 review and the WFD.

The work has been carried out in three phases; National scale risk assessment and source attribution; local expert elicitation, source attribution and delineation of NVZ boundaries and finally national QA of the outputs.

This paper will give an overview of all three phases of the project but will focus on the second phase of the groundwater section of the work. This has been one of the most rewarding parts of the project. It is the phase that brings a national scale risk assessment down to a local scale and transfers ownership of risk assessment to the local experts. It is also a critical phase in helping to ensure that the measures are targeted as accurately as possible.

## **A spatial planning approach to reduce the impact of nitrate on groundwater quality – the *Water4All* experience**

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The *Water4All* project aimed to demonstrate groundwater protection in the context of spatial planning and the implementation of the EU Water Framework Directive. Through a series of workshops, the four partner countries (Denmark, Germany, The Netherlands and UK) developed a handbook containing a methodology for risk-based land and water management to reduce diffuse pollution of groundwater from agricultural sources. Best practice guidelines were catalogued as a matrix of compensated and non-compensated ‘soft’ to ‘hard’ measures and were supported by illustrative case studies. The *Water4All* project also showed that spatially targeted measures can have wider benefits as part of a ‘whole landscape’ approach to planning and management. The sharing of expertise between the partner countries enabled the UK partner to explore a set of theoretical land use scenarios, developed in consultation with stakeholders, for reducing nitrate concentrations in the regionally important Lincolnshire Limestone aquifer in the Slea catchment in eastern England. The results of a combined export coefficient and numerical groundwater modelling approach showed that a reduction in groundwater nitrate concentrations can be achieved over several decades with the implementation of groundwater protection zones in which there is a significant element of land conversion from arable to woodland and grass. Hence, a long-term commitment to land management is required if alternative, end-of-pipe water treatment is to be avoided.

# Monitoring nitrate in groundwater: what do the data really tell us?

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Effectively monitoring nitrate concentrations in groundwater is fundamental to both the European Nitrate Directive (91/676/EEC) and Water Framework Directive (2000/60/EC). Although most countries expend considerable resources collecting and reporting nitrate data from national groundwater quality monitoring networks, less consideration is given to evaluating how effective the network and individual monitoring points are, and what the data actually tell us about nitrate in the groundwater environment. In this paper we discuss the results of a project to evaluate nitrate data from the Scottish groundwater monitoring network.

For all 219 monitoring sites on the network, a zone of influence was estimated using a semi-quantitative method. These zones were used to focus field surveys and also to characterise each site using national datasets. These data were then used to conduct an analysis of the factors controlling nitrate concentrations across the network.

The data from the network indicate that land use has a large influence on the nitrate concentrations measured in the monitoring network: arable areas, mixed cultivation of both arable & grassland, and where dairy, pigs and poultry are reared contribute to the highest nitrate concentrations, with 18% of sites in these areas exceeding 50 mg NO<sub>3</sub> l<sup>-1</sup>. The most significant control on nitrate concentrations in the monitoring network is the presence of dairy, pigs or poultry within the zone of influence of the monitoring point.

Further analysis of the variance in nitrate concentrations from the monitoring network was undertaken by comparing measured concentrations with modelled predictions of based on the nitrogen available for leaching at the end of the growing season and the dilution effect of rainfall. This indicated that a considerable number of monitoring sites have lower nitrate concentrations than would be expected. The data indicated that there were several reasons for the discrepancy: mixing with older waters (identified from CFC and SF<sub>6</sub>); denitrification (identified from chemistry data); and the nature of the soil cover and superficial deposits (identified by statistical analysis of collected data).

In summary, additional information on groundwater monitoring sites is fundamental to understanding variations in nitrate concentrations in our aquifers. Information on land use, geology, soil type and recharge can be combined with groundwater chemistry and residence time data to give a much clearer picture of nitrate concentrations in groundwater.

# **Determining nitrate distribution and groundwater flow in the Permo-Triassic Sandstones of the Eden Valley, Cumbria.**

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The Eden Valley in west Cumbria is underlain by Permo-Triassic sandstone, the major aquifer in Northwest England. Whilst groundwater quality is generally good, rising nitrate trends in some boreholes where concentrations exceed  $30 \text{ mg l}^{-1}$  (as  $\text{NO}_3$ ) has prompted collaborative research into flow systems and timescales in the area.

The use of slurry and artificial fertilisers following agricultural intensification during the 1980s is believed to be responsible for the rise in nitrate concentrations. The broad aim of this research is to enable prediction of future nitrate concentrations at abstraction boreholes and in groundwater discharge to surface water.

Previous research during the same project focused on determining the lag time between leaching from the soil and arrival at the water table using a combination of historic chemical tracers and modelling. This investigation focuses on processes at and below the water table at a research borehole.

A combination of porewater sampling during coring, discrete interval sampling using a packer system (for matrix and fissure flow), geophysical logging and imaging were employed in conjunction with modern dating techniques (CFC and SF6) and hydrochemical analysis. Physical and hydrochemical profiles were developed and key fractures or fracture zones were identified and sampled.

The hydrochemistry (particularly nitrate) of samples from discrete intervals in the profile exhibited a remarkably good relationship with the proportion of modern water (and year of recharge) with the age of groundwater increasing to c. 1950 towards the bottom of the 90m borehole.

This work demonstrates that the combination of discrete sampling and dating of groundwater is a powerful tool in characterising groundwater movement and timescales in boreholes and hence in parts of aquifers where pollution is most significant. With timescales and processes better constrained, a more reliable prediction of nitrate (and other) trends can be made.

Further work applying the same approach along a groundwater flowline is underway.

## **RESERVE TALK**

### **Assessment of natural attenuation as a viable management strategy for former sewage disposal site, Coventry. UK**

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*Wardell Armstrong LLP*

Owned and operated by Severn Trent Water Ltd (STWL), the Rock Farm site was a disposal site for wastes generated from different sewage works in Midlands. Situated immediately to the south of Coventry Airport and Middlemarch Business Park. The site is located adjacently and hydraulically connected with the River Avon. In January 2002 STWL appointed Wardell Armstrong to carry out quarterly groundwater quality monitoring, undertake annual review of monitoring results to assess groundwater conditions beneath the site and help inform STWL for the most appropriate management strategy for the site. Evolution of monitored parameters under investigation during the 2002-2006 period and across the site was examined. Unlike the other monitored determinands, high concentrations of nitrate have been observed mainly in the outer parts of the site and are relatively low in the central part where the other determinands are often found in higher concentrations. The spatial variation of ammoniacal nitrogen shows a strong inverse correlation with nitrate and demonstrates that oxidation of ammonia by micro-organisms is taking place, which is clearly confirmed by the spatial variation of oxygen across the site. Once in a nitrate form, a partial denitrification of this is observed downgradient due to the presence of organic carbon in groundwater and prevailing anaerobic groundwater conditions after decrease of oxygen concentration. Nitrification/denitrification processes explain to a large extent the loss in nitrogen mass during the transport, and the increase of nitrate down-gradient. It is concluded that natural attenuation is taking place and represents a viable management strategy for this site, though, its efficiency and capacity will depend on factors such as the amount and rate of discharge to the lagoons.