

## **Diffuse Groundwater Pollution – current and potential future management in England & Wales**

Tony Marsland, Policy Manager, Groundwater Quality & Protection, Environment Agency

A brief review of the sources and mechanisms of diffuse pollution, monitoring systems and current regulatory controls indicates significant weaknesses in our ability to manage this problem in the UK. As point sources of pollution are dealt with the effects of diffuse pollution have become more apparent. Some pollutants show continued rising trends and for both surface waters and groundwater diffuse pollution has become one of the top priorities for action.

Despite a substantial research effort in individual disciplines there are substantial gaps in understanding of the impact of groundwater diffuse pollution on surface water systems. The Water Framework Directive is now the main driver for both research and a new approach to tackling this issue. However, providing the evidence to clearly demonstrate that there are causal links between sources and impacts that can be effectively tackled by specific controls is much more difficult than for point source pollution. Government, operators (potential polluters) and other regulators will demand such evidence if some of the more radical changes that are likely to be needed to bring diffuse pollution under control are to be introduced.

The presentation will illustrate some of the above problems and describe the requirements of, and controls that may be envisaged under, the Water Framework Directive and the proposed new Groundwater Directive.

## **Diffuse Pollution Threats to Groundwaters – A Water Company Perspective**

Meryl Knapp, Water Quality Regulation, Yorkshire Water

Yorkshire Water Services supplies water to more than 4.7 million customers and 142,000 businesses throughout Yorkshire. Groundwater provides about 22% of the average daily demand of 1275 Megalitres from more than 100 sources. Groundwater has traditionally been considered to be of high quality, generally requiring a minimum of treatment, but data will be presented on pollution threats to groundwaters from nitrate, pesticide and microbiological diffuse sources, to demonstrate some of the consequences of such pollution for a public water supply utility:

- the long time scale between cause and consequence
- the difficulty of defining groundwater catchments
- the influence of abstraction patterns on catchment area and abstracted water quality
- vulnerability of upland spring sources to pesticide and microbiological contamination
- the difficulty of defining the catchments of upland spring sources
- the steady rise in nitrate levels in borehole abstractions and evidence of a band of nitrate moving through the unsaturated zone
- effects of Nitrate Sensitive Areas on leaching of nitrate
- evidence of pesticide contamination of a major public supply aquifer
- value of pro-active, co-operative management of pesticide use in upland gaming estates

- shortcomings of legal framework to facilitate such management (and consequent opportunities)
- security of supply vulnerability from pollution of major aquifers used in public supplies
- the disproportionate cost of the loss of small sources in remote areas
- costs to a water company of contamination of groundwaters

One consequence of pollution of groundwaters is the displacement of groundwater for surface (mainly river) water for public water supplies. This may result in a water company becoming too dependent on a small number of large surface water abstractions and vulnerable to a major pollution incident in a river.

The presentation will reflect on the problems for a water company in the management of its supplies, arising in part from the conflict between policies based on the 5-year time bites of Asset Management Plans (AMPs) and Parliamentary Election timetables rather than the need for a long term vision. Europe may well be doing us a good turn in providing the long-term drivers for this longer vision, through the Water Framework Directive and other policies.

### **Pesticides in groundwater: what we know and what we still need to know**

John Chilton, Marianne Stuart and Daren Goody, British Geological Survey

Richard Williams and Andrew Johnson, Centre for Ecology and Hydrology

Nitrate has been recognised as an important diffuse pollutant of groundwater for the past 25-30 years, and this led naturally to a consideration of the pollution hazard posed by agricultural pesticides. While this potential has been recognised for some time, research was initially hampered by the technical sophistication and high cost of analyses at the required detection limits, and the wide range of compounds in common usage. However, as monitoring programmes have been developed, an increasing number of pesticides were detected. The paper discusses the possible pathways by which pesticides might move from soils to groundwater, and the factors such as adsorption and degradation that determine the behaviour of pesticides in the subsurface. These discussions are illustrated by the results of recent field and laboratory studies on pesticides jointly undertaken by BGS and CEH, which have shown that, from normal agricultural applications, pesticide residues are likely to reach the water table only at low concentrations, in the same range as drinking water standards. These results are briefly compared the contrasting picture of the potential impact from improper disposal of agricultural pesticides and or amenity use. Some remaining gaps and uncertainties in our knowledge of the fate and behaviour of pesticides are highlighted.

### **Characterisation & Field Evaluation of Sheep Dip Chemical Disposal**

D J Arnold, T Pepper, S Rose, Cambridge Environmental Assessments

R J Williams, A Johnson, N Parekh, Centre for Ecology and Hydrology

An investigation into the potential for sheep dip chemicals, diazinon and cis-cypermethrin, applied to land, to leach through the soil profile to groundwater or to enter nearby surface waters from surface run-off or drainage is in progress. The project is funded by the Environment Agency: National R&D Project P2-250: Ref 12116. The first Phase of a two Phase project comprised an investigation into the way sheep dipping is carried out on farm accompanied by chemical analysis of dip from selected "spent" dipping solutions. Soil degradation studies were carried out on samples of spent dip which, together with soil sorption studies data, will provide inputs to a conceptual model being developed for three field

study sites. A broad hydrogeological characterisation of three field sites has been done and risk characterisation using the conceptual model is underway. It is intended that leaching and overland/drainage losses of sheep dip chemicals will be monitored in future field studies, accompanied by concurrent small scale lysimeter experiments to investigate the effect of variables, such as application frequency, use of slurries, microbial adaptation and influence on degradation, etc. Preliminary results of the Phase 1 study will be presented.

### **Mapping the risk to groundwater resources from farm waste stores in England and Wales**

Helen Rutter (BGS), Adrian Armstrong (ADAS), Hester Lyons (ADAS) and Daren Goody (BGS)

Unlined farm waste stores present a potential, but unquantified, risk to groundwater. Field studies of porewater retrieved from beneath active slurry stores indicate there is a potential for pollutants to be transported down through the unsaturated zone of the aquifer. The highest risk to groundwater is where the water table is shallow and/or where there is no protection offered to the aquifer by low permeability soil or drift layers. A preliminary screening tool is presented which highlights vulnerable areas of aquifer, based on the protection offered by superficial layers. Two different approaches were applied, one utilising soils data and the other making use of superficial geology data. Some of the differences between the approaches are considered, and their influence on the resulting risk assessment is discussed.

### **Have Nitrate Sensitive Areas been effective in reducing groundwater nitrate concentrations?**

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Concerns over the impact of nitrate leaching from agricultural land on groundwater quality led to the establishment of the Nitrate Sensitive Areas (NSAs) Scheme. NSAs overlie vulnerable aquifers where nitrate concentrations exceed, or are at risk of exceeding, the 50 mg NO<sub>3</sub>/l limit in the Drinking Water Directive (80/778/EEC) and Nitrates Directive (91/676/EEC). In total 32 NSAs were established (10 in 1990/1 and 22 in 1994/5) where voluntary, compensated agricultural management measures were introduced to reduce the levels of nitrate reaching boreholes. The Scheme ends in summer 2003. This study assessed the potential effectiveness of the NSA Scheme in reducing nitrate concentrations in groundwater by analysing existing monitoring data and application of appropriate modelling techniques.

The project had four phases. Phase 1 included the collation of data, including porous pot nitrate leaching data, borehole water level and chemistry timeseries, into a unified project database. Phase 2 included a review and analysis of datasets and the selection of NSAs for modelling. Phase 3 involved modelling nitrate leaching from the soil root zone, while Phase 4 used these results as inputs to groundwater models to predict the impact of the Scheme on groundwater concentrations.

In Phase 2, monitoring results revealed that mean leaching losses were 42 kg N/ha/a following fertilised winter wheat *managed under NSA Scheme rules* compared to 16 kg N/ha/a under long-term woodland receiving only atmospheric deposition. Results suggest that the NSA Scheme reduced mean root zone nitrate concentrations by around 50% in the Pilot Scheme and 34% in the Main Scheme, compared to measurements under comparable non-Scheme land uses and depending on variations in soils, land use and drainage volume. The NSA with the most significant change in nitrate concentrations was Old Chalford, where an

increasing annual trend of 0.2 mg NO<sub>3</sub>/l pre-NSA changed to a decreasing annual trend of 2.6 mg NO<sub>3</sub>/l.

Phase 3 model results suggest the NSA Scheme reduced mean root zone nitrate concentrations from 98 mg/l in 1994 to 69 mg/l in 1998 at Pollington NSA, and from 43 mg/l in 1990 to 37 mg/l in 1998 at Old Chalford NSA. These results are broadly comparable with the monitoring data reported under Phase 2. For near-future (2017) scenarios, a return to pre-NSA conditions resulted in a consistent increase in modelled nitrate losses at both NSAs. Scenarios involving increased grass areas at the expense of arable land (assuming similar stocking densities) and/or a reduction in livestock numbers proved effective in reducing modelled nitrate leaching losses in both NSAs. Reductions in stocking density relate to Nitrate Vulnerable Zone (NVZ) regulations which impose a limit on total N inputs to agricultural land, and thereby implicitly lead either to a limit on stock density or a requirement to export surplus manures off-farm.

Groundwater flow modelling and particle tracking was used during Phase 4 of the project to quantify the effect of the measured changes in the soil zone on groundwater concentrations. At Old Chalford there was a very short lag (about two years) between changes in the soil zone and a measurable effect at the abstraction points. This was expected from statistical analysis of measured data. In contrast, Pollington NSA showed little effect of the NSA Scheme on abstracted groundwater concentrations, with geology and geometry of the source catchment zones leading to a noticeable impact only after 30 years or more. For example at Pollington, decreasing soil zone nitrate leaching from 80 mg/l in 2002 to 30 mg/l in 2012 has the effect of reducing modelled nitrate concentrations in abstracted water in 2025 from 44 mg/l to 39 mg/l.

A combination of factors including fertiliser and manure N loadings and timings, soil leaching risk (soil type, drainage volume), and nitrate being a highly soluble anion (e.g. compared to phosphate) all contribute to the "leachability" of nitrate from soils to groundwaters. Results show the NSA Scheme has had a measurable beneficial impact on reducing root zone nitrate leaching, and that this will *eventually* lead to a reduction in nitrate concentrations in groundwaters. However, the typically long timescales involved in groundwater responses mean that, in many areas, the impact of short-term (i.e. 8-13 year duration) agricultural control schemes such as NSAs will not be realised for several decades.

### **Previous experience and some recent developments in oil degrading porous pavement systems**

Alan Newman, Head of Environmental Biosciences, School of Science and the Environment, Coventry University

Porous pavements constitute one part of the approach to sustainable drainage which involves infiltration or temporary storage to reduce localised flooding. However, with the infiltration of contaminated stormwater, there is a potential pollution problem. Hydrocarbon contamination has been addressed by the Coventry group for several years. It has been shown that oil can be effectively trapped on porous pavements and it has also been established that oil retention in a porous pavement is closely related to the nature of the geotextile used in the system to separate the subbase from the upper bedding layer. It is the belief of our group that the formation of a temporary pool of water on the geotextile during rain, leading to effective separation of oil and water, is the first step in the retention process. This initial interception is followed by the sorption of oil into the structure of the geotextile until it is eventually scavenged out again by microorganisms seeking to use it as an energy source. Previous work has also highlighted the role of the geotextile in maintaining the biofilm necessary for the biodegradation of hydrocarbons. Because of the mechanism of entrapment, the amount of oil which a typical granite based porous pavement system will retain is limited.

Extensive work has been carried out looking at a range of car parking surfaces, and at porous pavement models. Experience shows that single applications of as little as 30 ml, applied directly to a single position on a porous pavement model can sometimes cause significant

free oil to be observed in the effluent in subsequent simulated rain events. Even when making long-term, drop wise, applications over the model surface, applications exceeding about 0.5 l/m<sup>2</sup> have been shown to result in significant levels of oil being measured in the effluent.

An overview of previous work will be used to set the scene and then an initial report will be made on a large scale outdoor experiment involving the addition of very large quantities (150 ml/m<sup>2</sup>) of used motor oil to the surface of block paved car parking surfaces based on both granite and recycled plastic box subbases. These outdoor models consisting of at least four car parking bays per model have provision for both effluent collection and gas monitoring below the bedding layer. This presentation will also introduce a new design of porous pavement which can significantly improve upon current performance.

### **Impact of urban land use on groundwater quality in relation to groundwater quality in agriculture and natural areas. Example from the Netherlands**

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Urban pollution of groundwater is often considered to be diffuse pollution. Scattered point sources such as ordinary city waste, oil and fuels, PAH/gas factories, leaking sewage systems, herbicide and pesticide use in parks etc affect the urban groundwater quality. In densely populated regions such as the Netherlands impact of urban areas may result in a distinctive urban groundwater quality, when compared to other land uses, such as nature or agricultural land use. Knowledge on the groundwater quality development in urban areas is important for the potential use of urban groundwater, and should also be considered in land use planning. However, studying urban groundwater quality in relation to other land uses is complicated because in general groundwater quality shows high natural variation, while aquifer sediment reactivity may attenuate the groundwater quality during transport. This attenuation masks the impact of diffuse urban pollution, especially for naturally occurring compounds such as macro ions and trace metals.

For agricultural and natural land use functions, deterministic and/or empirical relations are used to quantify the interrelationship between the diffuse source and the groundwater system. An example is the impact of manure application on nitrate concentration. In the case of urban activities this impact is less known due to the highly heterogeneous activities and actors in the urban areas. We applied an inverse approach using existing ground water quality monitoring network data to: 1) portray differences between urban, rural and natural groundwater composition, and 2) determine specific water quality parameters that do change the groundwater quality due to urban land use.

For this inverse approach we used the ground water composition (macro chemistry, trace metals) and water temperature from 615 well screens of the Dutch groundwater quality monitoring networks, that monitors groundwater in rural, natural and urban areas. The shallowest well screens between 5 to 10 mbs (meter below surface) of the network were used to minimize effects of (natural) attenuation. The data were from the 1997 sampling round. A set of micro-pollutants was measured in 1987 in a selection of the well screens of the national network and added to assess impact of non natural compounds.

To deal with natural variations of groundwater quality, the well screen water compositions were grouped into four water types by (fuzzy c-means) cluster analysis. In the Netherlands natural variation ranges from very fresh to saline, oxic to methanogenic and acid to slightly alkaline. Four water types reflect the major natural groundwater features: redox state (oxic and anoxic), carbonate mineral dissolution and salinity. Subsequently within these water types different water qualities related to the functions 'rural' (agricultural polluted), 'nature' (no pollution) and 'urban' (urban pollution) are assessed.

Many major ions and trace metals did not show statistically significant differences of concentrations between rural and urban functions, and even between urban and nature functions. Their variations seem to be mainly related to hydrogeological processes (infiltration or exfiltration), and natural hydrogeochemical composition of the sediment. However, despite the high natural variation in groundwater composition, statistically significant differences of water compositions as a result of land use were detected for bicarbonate, boron, chloride, nitrate, potassium, sodium, and temperature and conductivity. If we compare 'urban' groundwater composition to 'nature', generally 3 to 4 times more boron (although natural variation is very high due to high boron concentrations in brackish water) and 2 to 4 times more sodium is measured, while temperature is 1-2 degrees C higher in 'urban' groundwater. This is illustrated by box- and whisker plots per water type with a subdivision for land use/diffuse pollution source. In addition, most of the 26 organic micro pollutants that were studied did not show significant differences, because they are predominantly not detected in groundwater at all. However, 1,2 DCE and 6 Borneff PAH have higher probability of detection in 'urban' groundwater. 'Rural' groundwater contains significantly higher concentrations of nitrate, potassium and shows higher conductivity than 'urban' and 'nature' water.

### **Diffuse Pollution of Groundwater by Pesticides in the Triassic Sandstone Aquifer of South Yorkshire**

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Following the wet autumn and winter of 2000-2001 water levels in many aquifers rose to exceptionally high levels and remained high for extended periods of time. Associated with this rise, concentrations of nitrate in abstracted groundwater have increased considerably. Against this background a possible upturn in trace pesticide concentrations in blended water from the Triassic Sandstone aquifer for supply in the Doncaster area has also been detected. A programme of analysis of groundwater from individual supply boreholes has shown that a number have been affected by pesticides, possibly from both agricultural and amenity use.

To assess the temporal and spatial variations in pesticide concentrations across the study area groundwater samples were collected over a period of more than 12 months from representative observation wells and extraction points. These were analysed for a complete spectrum of commonly detected pesticides as well as chloride and nitrate with the ultimate goal of forecasting likely future groundwater concentrations. The study found 19 different pesticides present within the sampling area. Pesticide concentrations were commonly in excess of the EU MAC for individual pesticides of 0.1 µg/L. Very high concentrations of mecoprop (7 µg/L) were consistently found at two of the sampling sites. High concentrations of atrazine (1 µg/L) were also found at three sites and high concentrations of isoproturon (0.98 µg/L) were also found at one of the sites that has very high mecoprop concentrations. The distribution of analytes throughout the study area is extremely heterogeneous stressing the importance of understanding the varying land use, drift cover and geology. Different pesticides detected at the same site often showed no correlation. No relation was observed between pesticide concentration and chloride or nitrate.

In addition to the groundwater sampling a series of cored boreholes were constructed between a mixed arable farm and an adjacent pumping station in an attempt to demonstrate the origin of herbicide contamination in the supply wells. Analysis of extracted porewaters for four diagnostic herbicides (atrazine, bentazone, isoproturon and mecoprop) indicated that although the farm pesticide disposal practise may account for elevated concentrations of

isoproturon in the supply well, it could not explain the presence of the other three compounds which must originate from elsewhere.

### **Can variations in groundwater pesticide degradation be attributed to special bugs, or special groundwater chemistry?**

Andrew Johnson, CEH Wallingford

The important water bearing aquifers in the UK are chalk, limestone and sandstone. Cereal crop production on outcrops of these aquifers leads to detectable, but low levels of pesticide contamination. Microcosm studies over a number of years have revealed consistently fast isoproturon degradation in groundwater collected from sandstone sites, but generally slower from the chalk and Limestone. Similarly, groundwater from the sandstone sites degraded mecoprop and atrazine quicker than at the other sites. No relationship could be seen with DOC, number of viable heterotrophic bacteria or pH. We have two competing hypotheses:

- Fast degradation is dependent on the presence of specialist degrading bacteria
- The degrading bacteria are everywhere but fast degradation is dependent on the groundwater chemistry stimulating pesticide degradation.

It might be predicted that constant sub-culturing into sterile groundwater containing isoproturon would stimulate the formation of a fast degrading microbial population. Following 3 sub-culturing runs, the results indicated that in many cases the degradation rate remained the same or slowed down. However, in one replicate from a chalk site, a very rapid degrading population developed.

To assess the importance of the groundwater chemistry, bacteria from existing microcosms were filtered onto 0.2 mm HDPE filter discs. The discs were then placed in filter-sterilized groundwater from a different rock aquifer type. Incubating bacteria normally resident in chalk groundwater with sterile sandstone groundwater caused their isoproturon degradation rate to increase! The degradation rate of the sandstone bacteria was reduced when incubated in the chalk groundwater. These results unequivocally indicate that components of the groundwater chemistry influence pesticide degradation rate.

### **Can bioremediation reduce nitrate levels?**

Luke de Vial, Head of Water Resources, Wessex Water

Bioremediation has rarely been applied to groundwater contaminated with nitrate. This is despite nitrate reduction occurring naturally in confined aquifers and bioremediation being an established technology for dealing with land contaminated with petrochemicals.

Wessex Water and WRc conducted a small scale trial at a lower Chalk public water supply source near Devizes, Wiltshire. A glucose solution was injected into small diameter boreholes approximately 50 metres from the abstraction point. Nitrate, nitrite and dissolved oxygen levels were monitored in the injection, abstraction and intermediate observation boreholes.

Nitrate levels were significantly reduced towards the end of the three month test period. No harmful bi-products were generated and the chlorination system was able to deal with the bacteria produced. Following discussions with the DWI the water was used for public water supply towards the end of the trial.

### **Nitrate in Groundwater: A Water Company Perspective**

Sarah Beeson (Mott MacDonald, seconded to Anglian Water Services)

Mike C Cook (Groundwater and Surface Water Manager, Anglian Water Services)

Anglian Water Services (AWS) abstracts approximately 600 MI/d of groundwater for public water supply from 195 sources located in a variety of aquifers. Many of the sources are vulnerable to both diffuse and point pollution and about 45 sources have nitrate concentrations in excess of 50 mg/l. AWS has used various analytical approaches to define trends and variations in nitrate concentrations and has established a reliable and robust method for predicting future concentrations. Fieldwork has been carried out to define how nitrate concentrations vary with depth in a borehole, with the duration of pumping, and with the pumping rate. Time series graphs show that nitrate concentrations 'recess' to a long term baseline trend, and that seasonal variations and/or data scatter are superimposed upon this trend. Depth profiling indicates that low nitrate groundwater is present at depth in some aquifers. The methods used by AWS have allowed a rigorous definition of capital investment requirements to maintain compliance with drinking water standards under the AMP4 process.