Nitrate transport in Chalk catchments-monitoring, modelling and policy implications

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Abstract

Rising nitrate levels have been observed in UK Chalk catchments in recent decades, with concentrations now approaching or exceeding legislated maximum values in many areas. In response, strategies seeking to contain concentrations through appropriate land management are now in place. However, there is an increasing consensus that Chalk systems, a predominant landscape type over England and indeed northwest Europe, can retard decades of prior nitrate loading within their deep unsaturated zones. Current levels may not fully reflect the long-term impact of present-day practices, and stringent land management controls may not be enough to avert further medium-term rises. This paper discusses these issues in the context of the EU Water Framework Directive, drawing on data from recent experimental work and a new model (INCA-Chalk) that allows the impacts of different land use management practices to be explored. Results strongly imply that timelines for water quality improvement demanded by the Water Framework directive are not realistic for the Chalk, and give an indication of timescales over which improvements might be achieved. However, important unresolved scientific issues remain, and further monitoring and targeted data collection is recommended to reduce prediction uncertainties and allow cost effective strategies for mitigation to be designed and implemented.

Introduction

Nitrate is one of the most problematic and widespread of potential groundwater contaminants. It is (indirectly) toxic to humans, as post-ingestion reduction to nitrite causes a form of oxygen starvation that in extreme cases leads to death (Canter, 1997). There is also evidence linking nitrate ingestion with increased risk of gastric cancer (Sandor *et al.*, 2001). Livestock, crops and industrial processes can be seriously affected by excessive levels of nitrate in groundwater (Canter, 1997), while elevated nitrate levels in surface water systems have a detrimental impact on river ecology (Hayes and Greene, 1984). Due to these hazards, conservative legislation exists regarding allowable nitrate levels in groundwater and water supplies. Satisfying this legislation is becoming increasingly difficult due to the rising upward trend in nitrate concentrations observed in both surface waters and groundwater over the last decades. Nitrate levels in Cretaceous Chalk aquifers within southern and eastern England are of particular concern, as these aquifers provide 20% of all national water supplies, and up to 60% of the groundwater supply (Downing, 1998). In some systems, concentrations are now hugely above inferred values in pristine conditions; typical baseline nitrate concentrations in UK Chalk groundwaters are thought to be between 2 and 4 mg l^{-1}, with an absolute maximum of 5 mg l^{-1} (Buss et al, 2005) but concentrations in excess of 50 mg l^{-1} (the maximum legal limit) have been recorded in Chalk groundwaters since the early 1970's (Foster & Crease, 1974).

It is generally accepted that these increases are in main due to intensification of agricultural practices (Foster & Crease, 1974, Limbrick, 2003, Wade *et al.*, 2004). While such a link implies that, with appropriate farm management, a reversal of this trend is possible, there have been increasing concerns regarding the short-to-medium term prognosis of such a reversal in the Chalk. Growing consensus that the Chalk unsaturated zone highly retards a variety of chemicals (Foster, 1993; Mathias *et al.*, 2006, Gooddy *et al.*, 2006, Jackson *et al*., 2007) suggests that much of the historical agricultural loading is still en route to the groundwater within this unsaturated zone. It is likely that this retardation is currently masking the extent of the water quality problem, with negative impacts of present-day practices partially buffered by the less intensive land management earlier within the 20th century.

This paper discusses the above issues, and explains why conventional water quality models fail to represent adequately the important unsaturated zone processes and the complexity of the groundwater response. Recent work has extended an established catchment-scale nitrogen model (INCA-N, Wade *et al.*, 2002) to provide an appropriate representation of these processes for the Chalk to evaluate nutrient management options (INCA-Chalk, Jackson *et al.*, 2007). Land use management scenario predictions from this model suggest that the timescales demanded by the incoming EU Water Framework Directive are not achievable for many Chalk systems, and provide information on what deadlines and management strategies may be appropriate. However, considerable prediction uncertainties remain due to sparse data, spatial heterogeneity observed in subsurface profiles, and unresolved hypotheses of process response. An evaluation of available data in two Chalk catchments (the Pang and Lambourn, UK) is used to interrogate performance of individual components of the INCA-Chalk model, and suggest where further effort might best be directed to improve understanding and better inform policy.

Nitrate legislation in the United Kingdom

The main directives controlling nitrogen levels in water bodies and drinking supplies in the United Kingdom are the European Union Drinking Water Directive (98/83/EEC), Groundwater Directive (80/68/EEC), and the Nitrates Directive. In the UK, the first two apply nationwide, while the Nitrates directive applies only to designated Nitrate Vulnerable Zones (NVZs). These are integrated through the EU Water Framework Directive (WFD) which came into force in December 2000 to expand the scope of water protection to all water bodies: surface water and groundwater; and to achieve 'good' status in all by 2015.

The Drinking Water Directive sets guide and maximum admissible concentrations of 25 and 50 mg NO_3 l^{-1} respectively for public supply water; these correspond with the 1993 WHO guidelines (DEFRA, 2000). There is already a degree of non-compliance:

in 1989, about 1% of the UK population was receiving water with nitrate levels above the maximum legal limit of 50 mg l^{-1} and over 200 public supply sources exceeded the limit at some time (UK Groundwater Forum, 2004). In other cases, treatment and dilution have been used in order to reduce the concentration in abstracted groundwater before distribution. The economic cost of this is significant (Buss et al, 2005); Dalton and Brand-Hardy (2003) estimated an annual cost to the UK water industry of £16.4 million for the period 1992-1997 incurred through treatment alone. Additional expenses are incurred as boreholes with excessive nitrate concentrations are abandoned (Knapp, 2005).

The current Groundwater Directive was conceived in a context of point source control of a limited range of substances only (Skinner, 1999), however the WFD provides for the production of a new directive which will go far beyond this. One major advance will be the introduction of regulatory control on diffuse pollution. More generally 'good' groundwater status will require that a balance is maintained between abstraction and recharge, the groundwater body does not exhibit effects of saline or other intrusions, does not exceed the Community quality standards and would not result in failure to achieve environmental objectives of associated surface water or terrestrial ecosystems (UK Groundwater Forum, 2004).

The Nitrates Directive (91/676/EC) deals explicitly and exclusively with pollution resulting from agricultural activities (direct or indirect). It has a dual objective – the reduction of water 'pollution caused or induced by nitrates from agricultural sources', and 'preventing further such pollution' (Environmental Resources Management, 1999). Nitrate polluted waters are identified under the Nitrates Directive as:

- Surface freshwaters or groundwaters which contain or could contain, if preventative action is not taken, nitrate concentrations greater than 50 mg l^{-1} (11.3 NO_3-N mg l^{-1}).

- Natural freshwater lakes, or other freshwater bodies, estuaries, coastal waters and marine waters which are eutrophic or may become so in the near future if protective action is not taken.

Nitrate Vulnerable Zones (NVZs) are identified as all known areas of land draining into nitrate polluted waters (Osborn & Cook, 1997), which are identified through monitoring data. The Nitrate Directive currently states these designations and associated action programmes should be reviewed on a 4 year cycle. Farmers within these zones are required to adhere to an action programme of measures in order to reduce the amount of nitrate lost from their land to polluted waters. These action programmes are mandatory and uncompensated; DEFRA estimates a net cost to the agricultural industry of £20 million per year and admits that intensive dairy and livestock farmers in NVZs can be particularly economically disadvantaged. The original NVZ designations in 1996 covered 8% of England. Since October 2002 55% of England is categorised as lying within a NVZ and a review of these designations is expected imminently (mid-2007). In April 2006, the Catchment Sensitive Farming Initiative began in forty priority catchments in England. Advisers in these catchments provide dedicated support to farmers, assisting mitigation of diffuse water pollution through promotion of best practice in the use of fertilisers, manures and pesticides, reduced stocking density, maintained or improved soil structure and reduced soil erosion.

Nitrate level predictions in Chalk catchments

Catchment-scale nitrogen models can be broadly classified into metric, conceptual and physics-based models (Wheater *et al.*, 1993). Models in all categories have utility for aspects of nitrogen management (Quinn, 2004; Lacriox *et al.*, 2006); however discussion here is restricted to consideration of their predictive capacity. Metric models are essentially statistical relationships between existing input and output data-sets with rudimentary, if any, physical basis; extrapolation of predictions to conditions for which data has not been collected is generally meaningless and they are not considered further here. Conceptual models involve specifying a model structure *a priori*, normally on the basis of a system of conceptual stores (which may be spatially lumped or semi-distributed); where these are derived through simplification of physical processes they are often referred to as “physically-based”. Physics-based fully distributed models seek to capture a system's response by incorporating significant processes through fundamental physical equations. The distinction between physically based semi-distributed conceptual models and fully distributed physics-based models can become blurred depending on the level of simplification and abstraction from reality, spatial resolution, and number of non-measurable or empirical parameters. Strong trade offs also exist between the level of complexity represented and the cost and technical expertise needed for implementation.

Physics-based distributed nitrogen models at the catchment scale include adaptions of MikeShe (Refsgaard *et al.*, 1999), NPSM (Carruba, 2000) and SHETRAN (Birkinshaw and Ewen, 2000). Particularly complex site specific models also exist (e.g. Wriedt and Rode, 2006). Nitrogen implementations of the well-established SWAT model (e.g. Santhi *et al.*, 2001 and Chu *et al.*, 2004) lie somewhat at the interface between physics-based and conceptual. Fully dynamic conceptual models include SWIM (Krysanova and Becker, 2000), INCA-N (Wade *et al.*, 2002) and HBV-N (Andersson and Arheimer, 2003); other established distributed or conceptual models such as PolFlow (de Wit, 2001), MONERIS (Behrendt *et al.*, 2000), TOPCAT-N (Quinn, 2004), and RIVERSTRAHLER (Billen and Garnier, 2000) include static (time-invariant) and/or metric based representations of important processes and have limited applicability for scenario impact assessments (Andersson *et al*., 2005). Although it has been contested that the fully distributed physics-based models are most suitable for predictions of the effects of land use changes (Abbot *et al*., 1986), appropriate measurable parameters are rarely obtainable, and extensive calibration is generally required (Beven, 2001). Such calibration can lead to a similar problem to that seen with the metric models: extrapolation to situations not covered by the calibration period is misleading. Although they have great potential for scientific exploration and understanding, the calibration issue and the costs of implementation limit their potential as management tools. As a result, the computationally and parametrically cheaper dynamic conceptual models are increasingly used for predictive modelling (Wade *et al.*, 2004, Andersson *et al.*, 2005, Lacroix *et al.* (2006). These retain the flexibility to represent process response explicitly and to deal with sub-annual time scales (Jackson *et al.*, 2007). Implementation is also less resource-intensive. SWAT, SWIM, INCA-N and HBV-N have been noted specifically as having the level of process description considered most appropriate for general management scenarios (Andersson *et al.*, 2005).

Although the appropriateness of using such a level of process description for predictive modelling of nitrate levels at catchment scales seems apparent, problems arise when attempting to use current conceptual models to predict the impact of changes in systems such as the Chalk. This is a particularly complex medium, characterised by a fine-pored matrix and the presence of (spatially heterogeneous) fracture networks. Although fractures are the dominant transport pathway within Chalk groundwaters, they are only activated within the unsaturated zone under intense infiltration conditions; indeed flux calculations from experimental data suggest most rainfall events are almost completely accommodated by the Chalk matrix rather than causing fracture flow due to attenuation of infiltrating water within the topsoil (Cooper *et al.*, 1990; Ireson *et al.*, 2006). Water table response is strongly correlated to major infiltration episodes, with a lag time of the order of days to weeks over tens of metres (Headworth, 1972; Ireson *et al.*, 2006). Conversely, contaminants including tritium, nitrate and chlorine migrate slowly downward at rates below 1m per year (Smith *et al.*, 1970; Wellings & Bell, 1980; Oakes *et al.*, 1981; Barraclough *et al.*, 1994). Profiles also generally show strong peak preservation consistent with the assumption that matrix flow dominates and dispersion is low (Foster and Smith-Carington, 1980; Geake and Foster, 1989; Mathias *et al.*, 2005), although there are exceptions to this which appear to be correlated to particularly small pore sizes (Geake and Foster, 1989). It is generally assumed that in the deep unsaturated zone and unconfined groundwater, nitrate is effectively conservative (Brouyere *et al.*, 2004; Price *et al*., 1993), although there is some evidence that this is not true under some geochemical conditions (Buss *et al.*, 2005) and further research on this is required. It has historically been difficult to reconcile the rapid response of the water table with the absence of fracture flow and slow contaminant migration rates due to the limitations in hydraulic conductivity and storage within the Chalk under specific pressure conditions. Headworth (1972) interpreted the recharge mechanism as a system of displacement, with “new water” entering the top of the partially saturated Chalk displacing a similar quantity of “old water” at the bottom. This explanation is now well-supported by both experimental and modelling studies (Brouyere *et al.*, 2004, Mathias *et al.*, 2006, Brouyere, 2006, Ireson *et al.*, 2006).

The depths within the Chalk unsaturated zone vary significantly over both space and time, dependant on distance from rivers and streams and on season; but are typically of the order of tens of metres. Interfluvial values approaching one hundred metres are not uncommon, see for example the depth distribution of the Lambourn catchment (Figure 1). As a result of the slow travel times and the spatial variation in vertical distance of the unsaturated zones, water exiting from the unsaturated zone is of varying age, with a corresponding mixed history of nutrient loading. Adequate representation in models of both this distribution of travel times and the contrasting slow nutrient/ fast water table response is necessary for meaningful consideration of the implications of previous loadings on future concentrations, and to allow estimates of the time-scales over which future changes in land use change might impact (Jackson et al., 2006). Representing such effects in fully distributed physics-based models, where pressure and gravity drive water transport, is possible (although difficult to calibrate appropriately). However, conceptual models, typically consisting of a limited number of linear stores which act as “buckets” releasing water, are unable to represent both the fast water response and the slow chemical transport in an integrated manner. Accordingly, Jackson et al. (2006) draw on insights from data and the physically based modelling described in Mathias *et al*. (2006) to present a simple methodology for representing the unsaturated zone, appropriate for large scale models. To account for the different periods over which responses occur, transport of solute and water is treated separately within the unsaturated zone and combined at the water table. The history of application is accounted for through routing solutes through a distribution of travel times, obtained through combining digital elevation and groundwater maps and scaling the resultant distribution of unsaturated zone depths by the rate of average vertical nitrate movement. The approach is both consistent with current understanding of the dominant processes, and simple to implement within most catchment scale hydrological models. The only significant modifications required are the addition of a single difference equation and storage of the history of soil concentrations accumulated as a simulation progresses (see Jackson *et al*., 2006 for a full description of the algorithm). It is also parsimonious; assuming digital elevation data and sufficient information on groundwater levels is available, only one additional parameter (travel time within the unsaturated zone) is required. Although it might initially seem reasonable to relate this rate of movement to hydrologically effective rainfall and rock porosity rather than defining it directly, such an approach is not appropriate in the Chalk, due to its fine-pored matrix which drains negligibly under typical field pressure conditions. It is better characterised through data from the isotope and other tracer studies described previously.

A well-established semi-distributed catchment-scale model of nitrogen (INCA-N, described in Wade *et al.*, 2002) was extended to include this representation. The revised model (INCA-Chalk) takes account of the retardation caused by the unsaturated zone in addition to the biogeochemical transformations and spatially distributed hydrological routing included within the original INCA model. Jackson *et al.* (2007) used this model to examine historical and predict future nitrate concentrations under different land management scenarios using existing and projected data within a predominantly agricultural Chalk catchment in Southern England (the Lambourn). This and an adjacent catchment (the Pang) have been a focus for extensive multi-disciplinary research within the UK (Neal *et al.*, 2004b; Wheater and Neal, 2006). Sixteen subcatchments, with six land use types, were considered. A travel time of 1m year^{-1} was assumed, and fifty pathways used to represent the unsaturated zone depth distribution (corresponding exactly to that presented in Figure 1); note this implies that, given constant agricultural inputs, over 80 years are needed to reach anything close to an equilibrium level within groundwater and rivers.

Despite the relative wealth of available data due to the research focus on this catchment, obtaining reliable historical land use and fertiliser application data was problematic. National land use records and livestock numbers are based on infrequently collected census data; only six sets of data are available over the last 100 years and periods where rapid land use changes occurred are often not covered (e.g. around the 1939-1945 war). Spatial resolution is also poor, with public domain data averaged over large areas (2km or more) due to privacy laws. Information on fertiliser application rates does not even extend to this level of resolution. In the absence of catchment-specific information, fertiliser application rates for each period and for each of the six land uses for all sixteen subcatchments were taken from Johnes *et al.*

(1998), where application rates are differentiated by geo-climatic region. The timing of the fertiliser applications was assumed to be the same as those observed in a survey of fertiliser practice from the River Ant (Johnes *et al*., 2003). Under these assumptions, the derived current-day annual nitrogen inputs from fertiliser for both cereal and other arable land uses were approximately constant for each sub-catchment at 175 kg N ha^{-1} year^{-1}, while subcatchment input rates to ‘grassland’ varied between 90 and 170 kg N ha^{-1} year^{-1} depending on the ratio of permanent and temporary grassland, and rough grazing (Wade *et al.*, 2006). Inputs from livestock were highly variable between subcatchments, between 60 and 350 kg N ha^{-1} year^{-1}. Table 1 presents available census dates, along with associated proportions of the two dominant land use classes within the Lambourn (arable and grassland), and catchment-averaged agricultural inputs shown as a proportion of current-day application rates. The majority of the census data is applied from the beginning of the year it is collected until the end of the year previous to the next collection. To account for post-war increase in fertiliser use, the census data from 1931 is used from the start of the period of interest, 1920, until the end of 1944. The 1969 census data is then applied to 1945-1975, the post-war period. The model was calibrated over the entire period of available data (1920 to 2003) using the Monte Carlo procedures presented in Mcintyre *et al.* (2005) and least squares measures of fit; the resultant parameterisation provides a visually excellent fit to available flow and nitrate concentration data (see Jackson *et al.*, 2007). To examine the time-scales over which effects from land management changes might take place, two fertiliser application scenarios were considered, the first with current-day practices continuing until 2100, and the second with all agricultural nitrate loading cut from 2003. Further details of the model setup and data used are in Jackson *et al.* (2007); note that projected data utilises B2HADCM3; a relatively conservative climate change scenario assuming slow population growth and technological advances moderating human emissions.

Figure 2 shows groundwater and in-river nitrate concentrations in the Lambourn under the two nutrient loading scenarios; note that the simulation with future loading cut to zero, which can be considered a “better than best case” scenario, has serious implications for the timescale over which improvements in groundwater quality can reasonably be expected, and hence for compliance with the EU Water Framework Directive. Reversal in the in-river nitrate concentration trend is not appreciable until around 2040, while the groundwater problem is even more severe, with significant decreases not occuring until past 2060. This suggests that historical loading of catchments such as the Lambourn will dominate groundwater quality decades into the future, and its impacts must be considered in any predictions and corresponding policy decisions. The implications of doing nothing are much worse; if current nitrogen loading levels continue a steady increase in both mean in-river and groundwater concentrations can be expected for most of the remainder of the century.

The implications of the above results for policy are of great concern, as they suggest that increasing trends in nitrate concentrations in groundwater sources may be impossible to reverse through land management alone in the next few years, and that achievement of ‘good’ chemical status by 2015, as required by the Water Framework Directive, may not be feasible. There is minimal flexibility in nitrate legislation where drinking water is concerned; it is probable that reduction of nitrate levels via groundwater treatment will be increasingly necessary. This may require considerable investment in technology, as current methods for reducing nitrate concentrations are expensive and difficult to implement on large scales (Canter, 1997). In-situ biological denitrification, induced either through the injection of a carbon source (Tomkins *et al.*, 2001) or through constructed wetlands to remove nitrate (Prior and Johnes, 2002), is particularly desirable as infrastructure costs are likely to be reduced and the potential exists to satisfy ecological as well as drinking supply purposes. For either of these to be effective, some knowledge on appropriate placement within a catchment is required; implementation of any in-situ system in a position by-passed by the great majority of water would have negligible effect regardless of its efficiency at the site itself.

Where water is not taken directly for human consumption, more flexibility exists: there is provision for setting less stringent objectives for specific water bodies where it would be unfeasibly or disproportionately expensive to achieve ‘good’ status (due to human activity or otherwise), and the 2015 target date can be extended where there are reasonable grounds (UK Groundwater Forum, 2004). To establish what targets might be reasonable will however require considerable further work. Although INCA-Chalk has been shown to be capable of good reproduction of observed in-river nitrate concentrations, and some confidence in the overall system analysis appears reasonable, considerable prediction uncertainties remain due to sparse data, spatial heterogeneity, and unresolved hypotheses of process response. It is possible that components of the model where limited or no data have been available for calibration possess compensatory errors; indeed Wade *et al.* (2006) note an equifinality problem in the Lambourn catchment, with data insufficient to determine the relative contribution of subsurface or in-river nitrate losses or transformations. It is therefore strongly recommended that further work to discriminate between differing process hypotheses is carried out to improve the predictive capabilities of models such as INCA-Chalk. To provide preliminary guidance on this, we now use an evaluation of subsurface data in two Chalk catchments within the United Kingdom (the Pang and Lambourn) to interrogate individual components of the Chalk system response, and suggest where further effort might best be directed to improve understanding and better inform policy.

Subsurface data on nitrates in the Chalk

Data from the Pang and Lambourn catchments were obtained and an analysis of solute profile data, land use data, fertiliser application data, groundwater level data and climate data performed. Correlations between features in solute profiles and other data sets were investigated with a view to establishing the source of solute peaks and other characteristics. Recent porewater chemistry profiles collected as part of the LOCAR research initiative described in Wheater and Peach (2004) and Wheater *et al.* (2007) were available from a number of boreholes at five sites located within the Pang and Lambourn catchments (Adams *et al.*, 2003). In addition, a selection of profiles from British Geological Survey (BGS) borehole monitoring during the late 1980s at an additional seven sites within the Pang/Lambourn area was acquired. TON (Total Oxidisable Nitrogen) and NO_3-N data were considered in the context of the hydrology and geology of the area. Difficulties in obtaining agricultural loading data at the catchment scale have already been noted. Attempts to obtain detailed records from specific sites were only partially successful, although some application records and land use information were kindly provided by managers of the land containing the LOCAR boreholes, allowing associated solute profiles to be analysed in the context of localised land use and N applications. Farms within NVZs are now required to hold fertiliser application data for 5 years, however more generally few farmers have kept written records of land use or fertiliser applications and tacit knowledge disappears with time and when changes in land ownership occur. Without such data, it is difficult to define trends in application inputs, and extremes or localised effects cannot be identified. These effects can be significant: although data from Geake and Foster (1989) and predictions from the leaching model SUNDIAL (Goulding *et al*., 1998), suggest that *average* annual leaching losses below Chalk are close to half the rate of nitrogen fertiliser application, differences in soil management methods (e.g. drainage, cultivation systems, rotations, type of fertilizer/sludge applied) cause significant deviations from this at any specific location (Dowdell and Mian, 1982). Andrews et al. (1997) demonstrate a significant link between application methodology and rate of nitrate leaching from topsoil to Chalk; data also shows the most substantial peaks being associated with large sludge applications and ploughing of grass crops. Addiscott (1996) also notes the potential contribution of ploughing to large nitrate peaks within the Chalk based on cores taken twenty years after the ploughing of old permanent grassland.

The porewater TON profiles from each of the five LOCAR sites (presented in Figure 3) indicate that significant variation can exist in TON concentration with depth, with the largest variations occurring within the unsaturated zone. Large peaks in TON concentration were present at three sites; PL10A, PL13A and PL26 at around 17 m, 25 m and 10 m respectively. These peaks were all within the unsaturated zone, according to water table locations taken at the time of drilling. Borehole PL11 was located near the river and hence the profile was, in the main, located within the saturated zone. Low TON concentrations exist throughout this profile, with only relatively small variations. Borehole PL14 is located near the interfluve, and the entire core was within the unsaturated zone at the time of drilling. All profiles exhibited lower TON concentrations in the saturated zone. This is in agreement with current understanding and is presumed to be, in general, due to groundwater mixing, dilution and dispersion. If oxygen is limited in this saturated region (this is currently unknown), the reduction of NO_3-N to N_2 via denitrification may also contribute. At present, TON concentrations within the saturated zone in all boreholes are within the nitrate level limit set by the Water Framework Directive (11.3 mg l^{-1} N, which corresponds to 50 mg l^{-1} of nitrate).

The origin of the LOCAR data peaks within the unsaturated zone are unknown, however examination of soil moisture deficit time series led to speculation that the peaks could be related to high recharge events coinciding with nitrate applications. Lithological information provided an explanation for the low concentrations observed within PL14. Unlike the other sites, where chalk was predominately present within the entire profile, the chalk in PL14 was overlain by 33 metres of Palaeogene deposits. The low concentrations observed in this profile are almost certainly due to a significant reduction in nitrate leaching into the subsurface due to these relatively impermeable deposits. Considering peaks, the lithological borehole logs for PL26 showed ‘putty’ chalk near the zone of increased concentration, with a band between 4.5m and 5.5m, and some localised ‘putty’ chalk around 9.5 m -10.1 m (more generally Seaford Chalk was present from the surface to a depth of around 67m). It may be possible that the ‘putty’ chalk retards flow and thus solute accumulates locally. However, no previous association between putty chalk and high concentrations is known, and it seems unlikely that this would cause such a significant increase as that evident from the TON profile. Unfortunately lithological information was not available for sites PL10A and PL13A and thus a comparison between geological features and TON concentration could not be carried out for these sites.

Data from non-LOCAR sites is also illuminating; showing large spatial variability within profiles within a few hundred metres of each other and with similar histories of fertiliser applications. Figure 4 shows NO_3-N profiles obtained from four boreholes to 21m depth at one site within the Lambourn during the winter of 1988/1999. The water table depth at this site is between 30 m and 40 m below ground level; hence all profiles are fully within the unsaturated zone. Boreholes BE01A and BE02A are located in land with a history of permanent pasture for more than 25 years previous to sampling, while boreholes BE03A and BE04A are located in land that has been under permanent pasture since 1981 and possessed a kale crop during 1979 and 1980. The land use prior to this is unknown. At all four sites, the history of nitrogen fertiliser applications is 166 kg ha^{-1} yr^{-1} (nitrogen) from 1979-1989. All profiles show extremely high NO_3-N concentrations at some point, but peak depths between the profiles do not correspond, either with ordnance datum elevation or depth below ground level. Given the close proximity of the boreholes and their similar land use histories, these differences do not appear to be due to changes in meteorological or cropping conditions. The differences may be caused by a variation in soil types or very local scale agricultural effects (e.g. stock preferences for particular locations, impacts of drainage or farm machinery); it is also possible that there is a geological explanation. Variation in peak depths has important implications for predictive scenarios.

A pressing question given the ambiguities present in the above data is to what degree models like INCA-Chalk can represent nitrate leaching to the unsaturated zone at any particular point in the catchment. Direct comparisons were difficult, due to the very sparse fertiliser input data available. Nitrate profiles from INCA-Chalk (derived through taking the nitrate mass entering the unsaturated zone from the soil and assuming a travel time of 1m per year), for both grassland and cereal, are shown in Figure 5. However model outputs and experimental data were not comparable, perhaps in average magnitude but certainly not in form; the INCA-Chalk profiles had clearly defined annual peaks present in most years along with substantial intra-annual variability, although the magnitude of these peaks vary according to atmospheric conditions around the time of fertiliser applications. The discrepancy may be in main due to poor nutrient loading data quality but also raises questions as to the adequacy of current soil representations for systems such as the Chalk. INCA-Chalk follows the hydrological representation of INCA-N (Wade *et al.*, 2002), a classic hydrological conceptualisation in which contributions from the soil component are partitioned between the deeper subsurface (percolation) and the river (through-flow) using a baseflow index. Hence concentrations entering the deeper subsurface and exiting to the river are equal at any one time. Data does not necessarily support this assumption. Soil concentrations near the surface are very variable due to biogeochemical influences and temporal variation in surface applications (e.g. fertilisers and atmospheric deposition), and the effect of this is seen in in-river concentration data. However most of the variation observed in deeper subsurface data appears to be a consequence of changes over longer time periods; there is little obvious seasonal variation. This may partially be an artefact of the sampling process, which necessarily integrates water taken over tens of centimetres within each discrete measurement;

however a smoothing effect on concentrations in the deeper part of the soil would be consistent with the advection dispersion processes governing the transport of nitrate in soils. Some form of differentiation between the two output concentrations may be required to improve subsurface representation. However, experimental data examining variations in nitrogen transport and speciation with depth in Chalk soils and associated physically based modelling studies would be required to achieve this satisfactorily.

Although it is evident that the soil exerts a strong control on nitrate levels in the Chalk, there are also questions regarding a "deeper" subsurface effect; i.e. that caused by variations in water table level within the Chalk aquifer. Analysis of groundwater level data in the Pang and Lambourn over a thirty year period showed groundwater heads to vary significantly within the catchment, with strong seasonal fluctuations but also substantial intra-annual variability. Figure 6 presents three example timeseries. Groundwater heads generally increase with distance from the river, as well as distance upstream within the catchment. Fluctuations tend to be small close to the river, and large close to the interfluve, although small fluctuation magnitudes also exist close to dry valleys and tributaries, perhaps due to increased permeability, or in some cases, impeding layers. In locations towards the interfluve, fluctuations of over 35m were observed; this is consistent with data from other Chalk catchments where fluctuations as great as 40m have been noted (Price *et al.*, 1993). As the effective aquifer is generally only the upper 50-60 m of saturated chalk due to a decrease in permeability with depth (Price et. al, 1993), this "seasonally unsaturated zone" can be a significant component of the total aquifer thickness. It has been shown by examination of the effect of fluctuating water table on solute concentrations in mobile fissures and solute distribution in matrix pore-water that the scale of water table fluctuations can be the dominant control on solute concentration in mobile groundwater (Fretwell *et. al*, 2000). At two of the three cores containing the high peaks, nearby groundwater levels were spatially similar and temporal water table variations (around 8m near PL26 and 13m near PL13) were superimposed. Both showed some indication that a decrease in concentration is occurring with depth over this range of fluctuation. It is important to establish whether the effects of this fluctuating region on solute transfer have significant consequences for future timescales of trend reversal or absolute magnitudes of concentrations reached.

While the causes of the distinct peaks in the obtained profiles could not be satisfactorily resolved given data limitations, it is clear that they will result in an increase of nutrient input to groundwater some time in the future. It is unclear how large an impact this will have on overall groundwater concentration, due to unknown spatial variability as well as the possibility of diffusion in the seasonally unsaturated zone which may attenuate the effects. In order to better explore the causes and long term effects of solute profile peaks and other characteristics, a long record of historic land use and nitrate applications is desired in addition to climatic data such as precipitation and soil moisture deficit and detailed geological data.

Conclusions

More than half of UK groundwater supplies are abstracted from the Chalk aquifers of eastern and southern England, many of which are becoming nitrate polluted as a consequence of UK agricultural practices. While changes in land use management are arguably the most effective long term means of controlling this, there are wellfounded concerns that the unsaturated zone in lowland Chalk will prevent control of nitrogen levels being achieved within the timescales demanded by incoming European and UK legislation. Chalk catchments, in the UK and elsewhere in Europe, will require detailed assessment to confirm whether they will be in breach of the EU Water Framework Directive's target for "good" status by 2015 and well beyond, and assess the timescales in which "good" status may be achievable. Until very recently, no catchment-scale models capable of treating the complexities of the Chalk were available; a suitable management tool has only recently been developed.

Although this represents a significant advance in predictive capabilities of nitrates in Chalk systems, INCA-Chalk or subsequent models require further data support and refinement to better inform strategies to contain nitrate pollution. Key areas for further work include improving the spatio-temporal resolution of nutrient loading input data and information on topsoil nitrogen speciation and leaching, as well as the representation of diffusion in the seasonally unsaturated zone. Collection of spatially representative porewater and groundwater nitrate concentration samples to allow further subsurface calibration would also reduce the equifinality problem outlined in Wade *et al.* (2006). It is clear that although INCA-Chalk provides an effective tool for catchment-scale simulation, an improved understanding of nitrogen movement through the soil-unsaturated chalk-groundwater continuum (through targeted studies examining nitrogen transport and transformations within Chalk topsoils, further subsurface data analysis and process modelling) is required before further notable progress in nitrate modelling of Chalk catchments can be achieved.

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References

Abbot, M.B., Bathurst, J.C., Cunge, J.A., O'Connell, P.E., Rasmussen, J., 1986. An introduction to the European Hydrological System - Systeme Hydrologique Europeen, "SHE", 1: History and philosophy of a physically-based, distributed modelling system. J. Hydrol. 87, 45-59.

Adams, B., Peach, D.W., Bloomfield, J.P., 2003. The LOCAR Hydrogeological Infrastructure for the Pang/Lambourn Catchment. British Geological Survey Internal Report, IR/03/178, available from BGS, Keyworth, Nottingham, UK.

Addiscott, T., 1996. Fertilisers and nitrate leaching. Issues Envir. Sci. 5, 1-26.

Andersson, L., Arheimer, B., 2003. Modelling of human and climatic impact on nitrogen load in a Swedish river 1885-1994. Hydrobiologia 497, 63-77.

Andersson, L., Rosberg, J., Pers, B.C., Olsson, J., Arheimer, B., 2005. Estimating Catchment Nutrient Flow with the HBV-NP Model: Sensitivity To Input Data. Ambio 34(7), 521-532.

Andrews, R. J., Lloyd, J. W., Lerner, D. N., 1997. Modelling of nitrate leaching from arable land into unsaturated soil and chalk 2. Model confirmation and application to agricultural and sewage sludge management,. J. Hydrol. 200, 198-221.

Beven, K., 2001. The Dalton lecture: how far can we go in distributed hydrological modeling? Hydrol. Earth Syst. Sci. 5, 1–12.

Barraclough, D., Gardner, C.M.K., Wellings, S.R., Cooper, J.D., 1994. A tracer investigation into the importance of fissure flow in the unsaturated zone of the British Upper Chalk. J. Hydrol. 156, 459-469.

Behrendt, H., Huber, P., Kornmilch, M., Optiz, D., Schmoll, O., Scholz G., Ueber, G., 2000. Nutrient balances of German river basins. UBA-Texte 23/2000, 261pp.

Billen G., Garnier J., 2000. Nitrogen transfers through the Seine drainage network: a budget based on the application of the Riverstrahler model. Hydrobiologia 410, 139-150.

Birkinshaw, S. J. and Ewen, J., 2000. Nitrogen transformation component for SHETRAN catchment nitrate transport modelling. J. Hydrol 230, 1-17.

Brouyere, S., Dassargues, A., Hallet, V., 2004. Migration of contaminants through the unsaturated zone overlying the Hesbaye chalky aquifer in Belgium: a field investigation. J. Contam. Hydrol. 72, 135-164.

Brouyere, S, 2006. Modelling the migration of contaminants through variably saturated dual porosity, dual permeability chalk. J. Contam. Hydrol. 82(4), 195-219.

Buss, S.R., Rivett, M.O., Morgan., P., Bemment, C.D., 2005. Attenuation of nitrate in the sub-surface environment. Environment Agency of England and Wales Science Report SCO30155/SR2.

Canter, L.W., 1997. Nitrates in Groundwater. CRC Press, USA.

Carrubba, L., 2000. Hydrologic Modeling at the Watershed Scale Using NPSM. J. Amer. Water Resour. Assoc. 36, 1237-1246.

Chu, T.W., Shirmohammadi, A., Montas, H., Sadeghi, A., 2004. Evaluation of the SWAT model's sediment and nutrient components in the Piedmont Physiographic Region of Maryland. Trans. ASAE 47(5), 1523-1538.

Cooper, J.D., Gardner, C.M.K., MacKensie, N., 1990. Soil water controls on recharge to aquifers. J. Soil Sci. 41, 613-630.

Dalton, H, Brand-Hardy, R., 2003. Nitrogen- the essential public enemy. J. App. Ecol. 40, 771-781.

de Wit, M., 2001. Nutrients fluxes at the river basin scale. I: the PolFlow model. Hydrological Processes 15, 743-759.

Department of the Environment, Food & Rural Affairs (DEFRA), 2000. The Water Supply (Water Quality) Regulations 2000. S.I. 2000 No. 3184.

Dowdell, R. J., Mian, M. H., 1982. Fate of nitrogen applied to agricultural crops with particular reference to denitrification. Phil. Trans. Roy. Soc. Lon. B., 363-373.

Downing R. A., 1998. Groundwater: our Hidden Asset. British Geological Survey, available from BGS, Keyworth, Nottingham, UK.

Environmental Resources Management, 1999. Verification of Vulnerable Zones Identified Under the Nitrate Directive and Sensitive Areas Identified Under the Urban Waste Water Treatment Directive. UK. European Commission Directorate General.

Foster, S. S. D., 1993. The Chalk aquifer- its vulnerability to pollution, in The Hydrogeology of the Chalk of North-West Europe. In R. A. Downing, M. Price, G. P. Jones (ed). Clarendon Press, Oxford, pp1-13.

Foster, S.S.D, Crease, R.I., 1974. Nitrate pollution of Chalk groundwater in East Yorkshire – a hydrogeological appraisal. J. Instit. Wat. Eng. 28, 178-194.

Foster, S. S. D, Smith-Carington, A. 1980. The interpretation of tritium in the Chalk unsaturated zone. J. Hydrol. 46, 343-364.

Fretwell, B.A., Burgess, W., Barker, J.A., 2000. Contaminant retardation within the seasonally unsaturated zone of the Chalk aquifer: the SUZ process. In: Dassargues, A. (ed). Tracers and modelling in Hydrogeology. IAHS Press, Wallingford, pp. 385-390.

Geake, A.K., Foster, S.D., 1989. Sequential isotope and solute profiling in the unsaturated zone of British Chalk. Hyd. Sci. J. 34, 79-95.

Gooddy, D. C. W, Darling, G., Shand, P., Abesser, C., 2006. Using Chlorofluorocarbons (CFCs) & Sulphur Hexafluoride (SF6) to characterise groundwater movement and residence time in a lowland Chalk catchment. J. Hydrol. 330(1-2), 44-52.

Goulding, K.W.T., Bailey, N. J., Bradbury, N. J., 1998. A modelling study of nitrogen deposited to arable land from the atmosphere and its contribution to nitrate leaching, Soil Use Manag. 14, 70-77.

Hayes, C.R., Greene, L. A., 1984. The evaluation of eutrophication impact in public water supply reservoirs in East Anglia. Wat. Poll. Contr. 83, 45-51.

Headworth, H.G.,1972. The analysis of natural groundwater level fluctuations in the Chalk of Hampshire. J. Instit. of Wat. Eng. 26, 107-124.

Ireson, A., Wheater, H.S., Butler, A.P., Mathias, S.A., Finch, J., Cooper, J.D., 2006. Hydrological processes in the Chalk unsaturated zone- insights from an intensive field monitoring programme. J. Hydrol. 330, 29-43.

Jackson, B.M., Wheater, H.S., Mathias, S.A., McIntyre, N., Butler, A.P., 2006. A simple model of variable residence time flow and nutrient transport in the Chalk, J. Hydrol. 330, 221-234.

Jackson, B.M., Wheater, H.S., Wade, A.J., Butterfield, D., Mathias, S.A., Ireson, A.M., Butler, A.P., McIntyre, N.R., Whitehead, P.G., 2007. Catchment-scale modelling of flow and nutrient transport in the Chalk unsaturated zone. Ecol.Model. (2007), doi:10.1016/j.ecolmodel.2007.07.005.

Johnes, P.J., Bennion, H., Curtis, C., Moss, B., Whitehead, P., Patrick, S., 1998. Trial Classification of Lake Water Quality in England and Wales. Report from Environment Agency Project E2-i721, Environment Agency, Bristol, p. 264.

Johnes, P.J., Whitehead, P.G, Davies, S., Wade, A.J., Butterfield, D., 2003. Effectiveness of Eutrophication Control by Phosphorus Reduction. Environment Agency R&D Technical Report, Bristol, 149pp

Knapp, M. F., 2005. Diffuse pollution threats to groundwater: a UK water company perspective. Quat. J. Eng. Geol. Hydr. 38, 39-51.

Krysanova, V. and Becker, A., 2000. Integrated modeling of hydrological processes and nutrient dynamics at the river basin scale. Hydrobiologia 410, 131–138.

Lacroix, A., Laurent, F., Ruelland, D., Sauboua, E., 2006. Nitrate pollution risk assessment: from the model to the indicator, Intern. J. Agric. Resour.Gov. Ecol. 5, 206–223.

Limbrick, K.J., 2003. Baseline nitrate concentration in groundwater of the Chalk in south Dorset, UK. Sci. Tot. Envir. 314-316, 89-98.

Mathias, S.A., Butler, A.P., McIntyre, N., Wheater, H.S., 2005. The significance of flow in the matrix of the Chalk unsaturated zone, Journal of Hydrology, 310, 62 - 77.

Mathias, S.A., Butler, A.P., Jackson, B.M., Wheater, H.S., 2006. Transient simulations of flow and transport in the Chalk unsaturated zone. J. Hydrol. 330, 10-28.

McIntyre, N., Jackson, B.M., Wade, A.J., Butterfield, D., Wheater, H.S., 2005. Sensitivity analysis of a catchment-scale nitrogen model. J Hydrol. 315, 71 – 92.

Neal, C., Jarvie, H. P., Wade, A. J., Neal, M., Wyatt, R., Turner, H., Hill, L., Hewitt, N., 2004. The water quality of the LOCAR Pang and Lambourn catchments. Hydrol. Earth Sys. Sciences 8, 614–635.

Oakes, D.B., Young, C.P., Foster, S.S.D, 1981. The effects of farming practices on groundwater quality in the United Kingdom. Sci. Tot. Env. 21, 17-30.

Osborn, S., Cook, H.F., 1997. Nitrate Vulnerable Zones and Nitrate Sensitive Areas: A policy and technical analysis of groundwater source protection in England and Wales. J. Envir. Plan. Manag. 40(2), 217-233.

Price, M., Downing, R. A., W. M. Edmunds, 1993. The Chalk as an aquifer. In: The Hydrogeology of the Chalk of north-west Europe, Downing R.A., Price M. and G.P. Jones (eds.), Clarendon Press, Oxford, pp. 35-58.

Prior, H., Johnes, P. J., 2002. Regulation of surface water quality in a Chalk catchment, UK: an assessment of the relative importance of instream and wetland processes. Sci. Tot. Env. 282/283, 159-174.

Quinn, P. 2004. Scale appropriate modeling: representing cause-and-effect relationships in nitrate pollution at the catchment scale for the purpose of catchments scale planning. J. Hydrol. 291, 197–217.

Refsgaard, J.C., Thorsen, M., Jensen, J.B., Kleeschulte, S., Hansen, S., 1999. Large scale modeling of groundwater contamination from nitrate leaching. J. Hydrol. 221, 117-140.

Santhi, C., Arnold, J.G., Williams, J.R., Dugas,W.A., Hauck, L., 2001. Validation of the SWAT model on a large river basin with point and nonpoint sources. Tech Publ. Ser. Am. Water Resour. Assoc. 37, 1169–1188.

Sandor, J., Kiss, I., Farkas, O., Ember, I., 2001. Association between gastric cancer mortality and nitrate content of drinking water: Ecological study on small area inequalities. Eur. J. Epidem. 17, 443-447.

Skinner, A., 1999. Groundwater Protection – an Overview of Current Issues, Proceedings of the Seminar "Groundwater Protection in Ireland", Enniskillen, 8 October 1999.

Smith, D.B., Wearn, P.L., Richards, H.J., Rowe, P.C., 1970. Water movement in the unsaturated zone of high and low permeability strata using natural tritium. In: Isotope Hydrology, pp.73-87. Atomic Energy Agency, Vienna.

Tompkins, J. A., Smith, S. R., Cartmell, E., Wheater, H. S., 2001. In-situ bioremediation is a viable option for denitrification of Chalk groundwaters. Quat. J. of Eng. Geol. Hydr. 34, 111-125.

UK Groundwater Forum, 2004. Nitrate and pesticide pollution, British Geological Survey publication IPR/47-4, available from BGS, Keyworth, Nottingham, UK.

Wade, A. J., Butterfield, D., Whitehead, P. G., 2006. Towards an improved understanding of the nitrate dynamics in lowland, permeable river-systems: Applications of INCA-N. J. Hydrol. 330, 185-203.

Wade, A.J., Durand, P., Beaujouan, V., Wessel, W.W., Raat, K.J., Whitehead, P.G., Butterfield, D., Rankinen, K., Lepisto, A., 2002. A nitrogen model for European catchments: INCA, new model structure and equations. Hydrol. Earth Syst. Sci. 6(3), 559-582.

Wade, A. J., Whitehead, P.G., Jarvie, H. P., Neal, C., Prior, H., Johnes, P. J., 2004. Nutrient monitoring, simulation and management within a major lowland UK river system: the Kennet. Math. Comp. Sim. 64, 307-317.

Wellings, S.R., Bell , J.P., 1980. Movement of water and nitrate in the unsaturated zone of the upper Chalk near Winchester, Hants, England. J.Hydrol. 48, 119-136.

Wheater, H. S., Neal, C. (eds), 2006. Hydro-ecological functioning of the Pang and Lambourn catchments, UK: Results from the LOwland CAtchment Research (LOCAR) initiative, special issue of J. Hydrol, 330(1-2).

Wheater, H.S., Peach, D, 2004. Developing interdisciplinary science for integrated catchment management: the UK LOwland CAtchment Research (LOCAR) programme. Intern. J. Water Resour. Devel. 20, 369-385.

Wheater, H.S., Jakeman, A.J., Beven, K.J., 1993. Progress and Directions in Rainfall-runoff Modelling, in Modelling Change in Environmental Systems, edited by Jakeman, A.J., Beck, M.B, McAleer, M.J., John Wiley And Sons, Chichester.

Wheater, H. S., Peach, D and Binley, A., 2007. Characterising groundwater-dominated lowland catchments: the UK Lowland Catchment Research Programme (LOCAR), Hydrol. Earth Syst. Sci. 11(1), 108-124.

Wriedt, G. and Rode, M., 2006. Modelling nitrate transport and turnover in a lowland catchment system, J. Hydrol. 328, pp157-176.

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List of tables and figures

Table 1: Census dates with associated relative proportions of dominant land uses and historical agricultural loadings as a proportion of current-day agricultural loadings

Agricultural census year	Grassland Area (%)	Cereal area (%)	Grassland agricultural input as proportion of current day loading	Cereal agricultural input as proportion of current day loading
1931	60	25	0.71	0.03
1969	32	60	1.27	0.51
1976	34	55	1.38	0.46
1981	30	62	1.30	0.72
1988	25	67	1.03	1.05
2000	31	64	1.00	1.00

Figure 1: The unsaturated zone depth distribution (derived from interpolated elevation and water table level data) over the 236 km^2 Lambourn catchment, UK (modified from Jackson *et al.*, 2006).

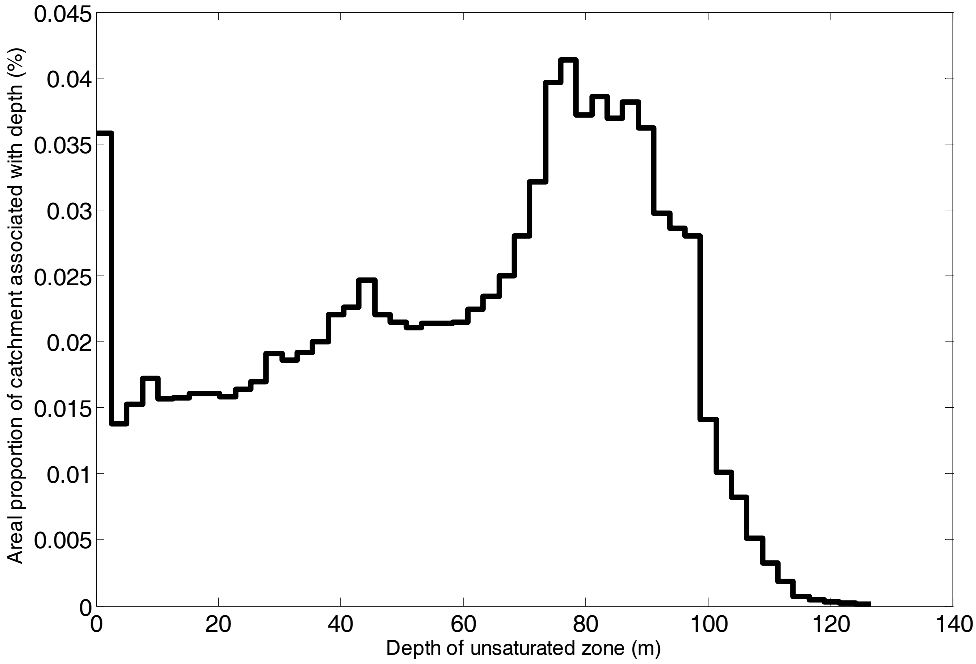

Figure 2: Projected end of century groundwater and in-river nitrate levels under present-day and no agricultural loading scenarios for the Lambourn catchment, UK

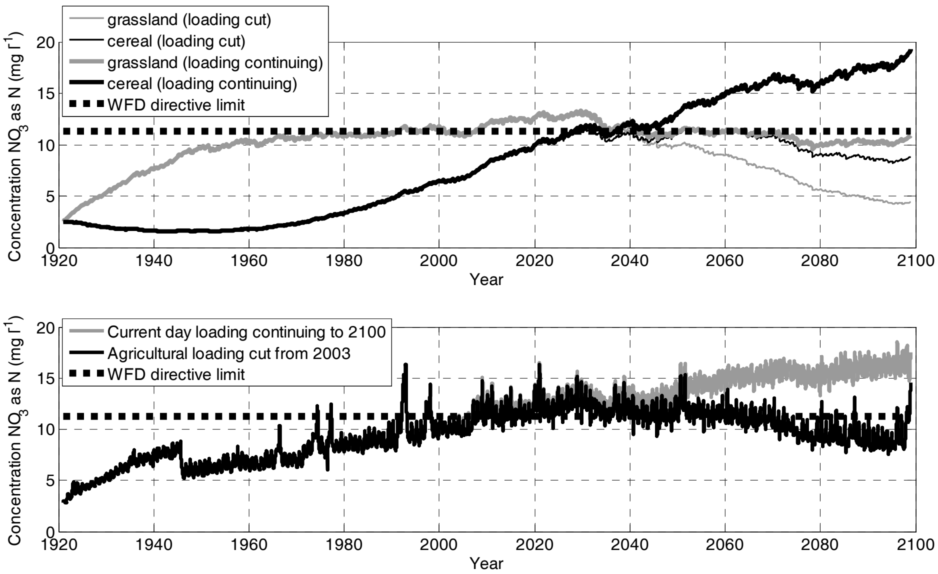

Figure 3: TON profiles from the five LOCAR boreholes, UK; dotted lines indicate position of water table at time of coring (PL14 remained unsaturated through entire depth of core).

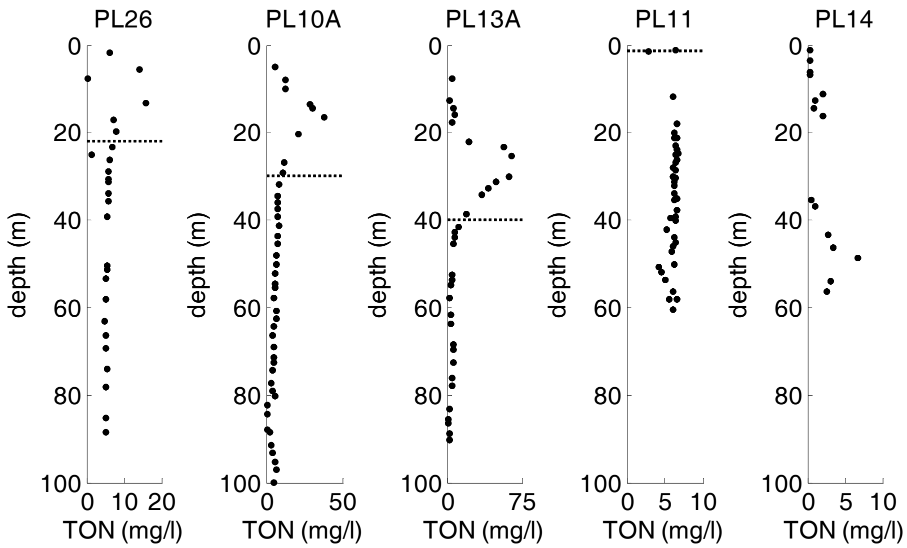

Figure 4: NO_3-N profiles during the 1988/1999 winter from closely located boreholes in the Lambourn catchment, UK

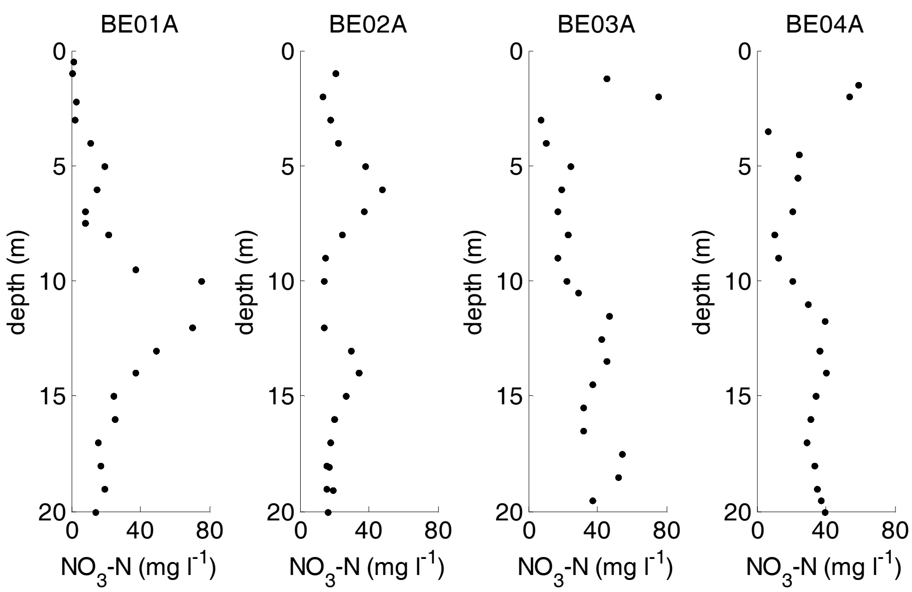

Figure 5: Unsaturated zone profiles derived from INCA-Chalk

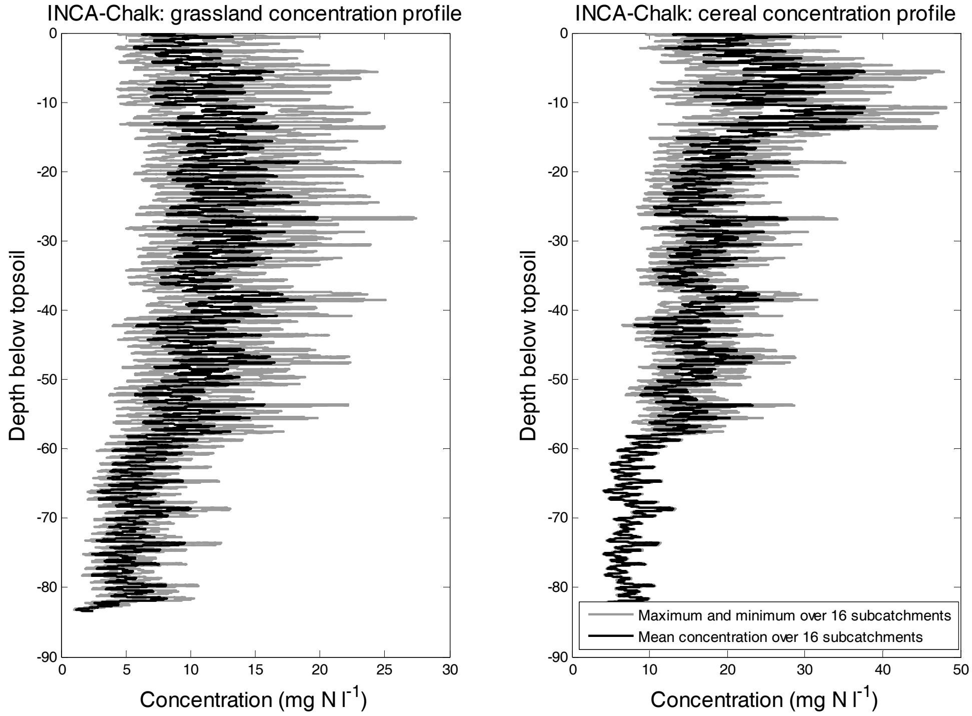

Figure 6: Spatial and temporal variations in water table level within the lower Lambourn