

EFFECTS OF AGRICULTURAL LAND-USE ON GROUNDWATER QUALITY WITH SPECIAL REFERENCE TO NITRATE

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ABSTRACT

Groundwater provides over 30% of potable water supplies in Britain. It is mainly derived from the Chalk and Triassic Sandstone formations, which occur widely as unconfined and semi-confined fissured aquifers (with significant primary porosity), the recharge areas of which form extensive tracts of valuable agricultural land. Nitrate (NO_3-N) levels in many sources, particularly in eastern England, are now considerably above 10 mg/l though, in many cases, there is no obvious point source of pollution. In consequence, two national research programmes are in progress and their interim results are summarized. Very high NO_3-N concentrations (over 20 mg/l) have been widely observed in the interstitial water of the unsaturated zone beneath arable farmland. Their implication for future groundwater quality is discussed in the light of probable rates of pollutant transport and of possible attenuating processes.

INTRODUCTION

Background to British research

Although instances of individual wells and boreholes producing nitrate-rich groundwater (with more than the current lower WHO limit for NO_3-N of 11.3 mg/l) have been recorded at least since the end of the 19th century (Whitaker 1908), the contamination could be confidently assigned in the majority of cases to nearby discrete or point sources, such as cess pits, leaking sewage mains or farmyard drainage. In recent years, however, an increasing number of examples of high and/or rising nitrate levels have been reported from Chalk, Triassic Sandstone and other aquifers, especially in eastern England (Davey 1970, Greene & Walker 1970, Satchell & Edworthy 1972, Foster & Crease 1974, Severn-Trent Water Authority 1976, Foster 1976, and Greene 1977). Their widespread distribution in outcrop or recharge areas suggested that the major component of nitrate input to groundwater systems was derived from diffuse, as distinct from point, sources.

Foster and Crease (1974) postulated a relationship between rising nitrate concentrations and changes in agricultural practice, particularly the increasingly regular cropping of cereals sustained by greatly increased use of inorganic nitrogenous fertilizers. They also expressed serious apprehension over long-term trends found in groundwater sources, because the possibility of very slow movement of pollutants down through the unsaturated zone to the water table of certain aquifers (especially the Chalk) implied that the full effect of the major changes in arable agriculture during the period 1950-65 might not be perceived for many years thereafter. Young, Oakes and Wilkinson (1976) confirmed the presence of major accumulations of nitrate in the Chalk unsaturated zone and suggested that the major increases in arable acreage, associated with the ploughing of long-standing grassland during the 1939-1945 war, was another significant factor in the increased leaching of nitrate from agricultural land in certain parts of the Chalk outcrop area.

The increasing nitrate concentrations in groundwater are of concern to public water-supply authorities because of an established risk to the health of infants (Comley 1945) and older children (Petakhov & Ivanov 1970) and of its possible role in the etiology of gastric cancer (Tannebaum *et al.* 1977). Over 30% of public water-supplies in Britain are derived from groundwater, the proportion being in excess of 80% in parts of south-eastern England. In 1973, the Anglian Water Authority, for example, inherited a situation in which 50 groundwater sources, representing a total supply of about 160 Ml/d, already had recorded NO_3-N concentrations in excess of 11.3 mg/l (Greene 1977).

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Scope and status of British research

Growing awareness of the groundwater nitrate problem in the 1970s led to the commissioning of two major national programmes of hydrogeological research — one at the Water Research Centre (WRC) and the other at the Institute of Geological Sciences (IGS) — to establish in detail the effects of agricultural land-use on groundwater quality; the Central Water Planning Unit of the Department of the Environment co-ordinated the work.

The objectives of the programmes are:

- (a) To determine the extent of nitrate pollution in the principal aquifers, primarily in their unsaturated zones;
- (b) To evaluate the mechanisms and rates of movement of potential groundwater pollutants, derived from the land surface, through the unsaturated zone;
- (c) To estimate future trends in nitrate concentrations.

Dedication of a substantial proportion of the total research effort on the unsaturated zone was justified because of its critical importance (as a consequence of the relatively high porosity and specific retention of the principal British aquifers) in the estimation of future trends and the almost complete lack of published work on unsaturated zone groundwater chemistry.

The WRC and IGS research, beginning late in 1974 and 1975 respectively, involves extensive borehole drilling programmes. The former primarily comprises drilling and sampling, on a nationwide basis (figure 1), at selected sites (such as experimental farms) with detailed historical landuse and fertilizer application records. The latter involves detailed drilling, sampling and monitoring of small groundwater catchments to public water-supply sources already displaying a substantial nitrate problem; two such catchments have been investigated to date (figure 1).

As both programmes are still in progress, the interpretation of results presented here is, to some degree, interim. An essential part of the research programmes was redrilling of the unsaturated zone at selected sites after a hydrologically significant period, say four or five water years. To date, investigation has also been limited almost entirely to the outcrop or recharge areas, that is the unconfined aquifers; no systematic study has yet been made of the fate of nitrate migrating down-dip into confined aquifers.

INVESTIGATIONS OF CHALK AQUIFER AND THEIR RESULTS

Chalk aquifer

The Chalk is the most important British aquifer. Geologically, it comprises a uniform sequence of very fine-grained, pure white limestones composed predominantly of the remains of planktonic organisms with variable, often scant, calcite cementation (Hancock 1975). Hydrogeologically, the formation has very low interstitial permeability (generally less than 10^{-3} m/d), despite moderate-to-high porosity (mainly in the range 0.20–0.40, according to region and horizon), because of its exceedingly small pore diameters (Price, Bird & Foster 1976). Borehole water supplies thus depend upon joints and fissures; these are generally well-developed beneath the outcrop area (Foster & Milton 1974, Owen & Robinson 1978), where individual borehole yields of more than 20 l/s for 5 m drawdown are commonplace. The outcrop area represents the principal recharge zone for groundwater resources and also forms extensive tracts of rich agricultural land.

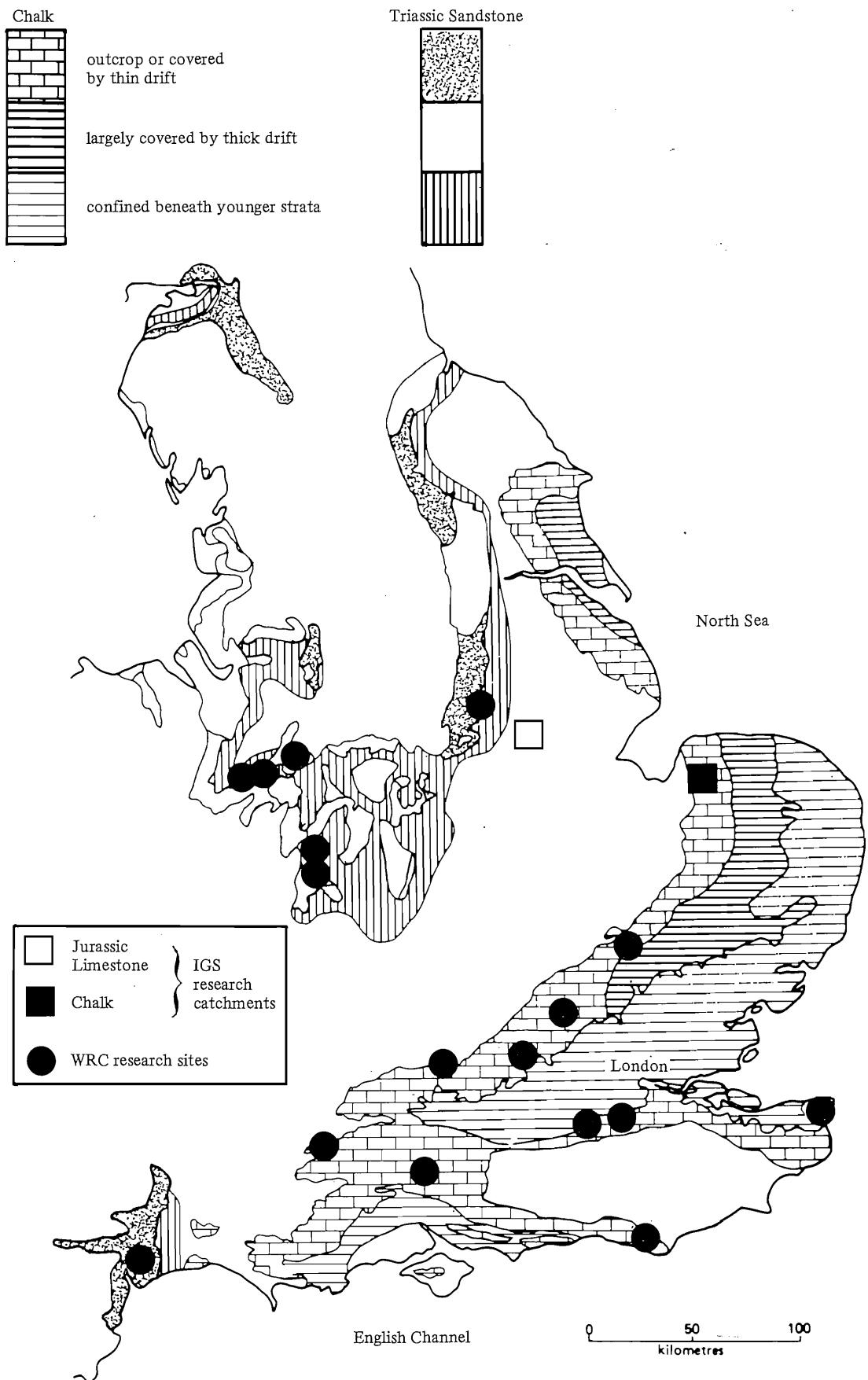


Figure 1. Location map showing distribution of Chalk and Triassic Sandstone aquifers and sites of research work.

Continuous sampling of the Chalk with minimal chemical contamination has been achieved to depths of about 70 m. Samples from mechanically-excavated trenches and from continuous flight augers (100 mm diameter) were cut during preliminary investigation at some sites, but the majority of samples were obtained by dry percussive drilling with a drive core barrel (0.45 m long, 101 mm diameter). In order to obtain satisfactory samples from the harder, more cemented chalks of north-eastern England, air-flush rotary drilling with a lined (triple) core barrel is required at depths greater than 15–25 m. All samples were carefully handled and stored to eliminate or minimize pore water contamination or evaporation (Gray *et al.* 1977, Foster *et al.* 1977) prior to centrifuge extraction of their interstitial water (Edmunds & Bath 1976).

The pore water samples (generally of 10–30 ml) thus extracted were analysed for nitrate and other nitrogen species by standard methods adapted for small volumes on the autoanalyser. In some cases, other anions together with the suite of major cations were determined, the latter on a spectrophotometer. Determination of the tritium content of the interstitial water involved its extraction from cores by distillation to complete dryness, electrolytic enrichment, conversion to ethane and measurement in a scintillation counter (Allen *et al.* 1966). Measurements of some physical properties and limited biochemical studies on core material were undertaken. For the research catchments, various devices for monitoring and sampling soil drainage and mobile groundwater have been installed.

Unsaturated zone

In more than 60 boreholes, the vertical profiles of nitrate concentration in the interstitial water from the Chalk unsaturated zone have been shown to be closely related to the history of agricultural practice on the overlying land. Lateral variation in the overall shape of nitrate profiles, that is between boreholes drilled in the same year within the same field, is considered to be relatively slight, although in detail there is likely to be substantial variability (figure 2).

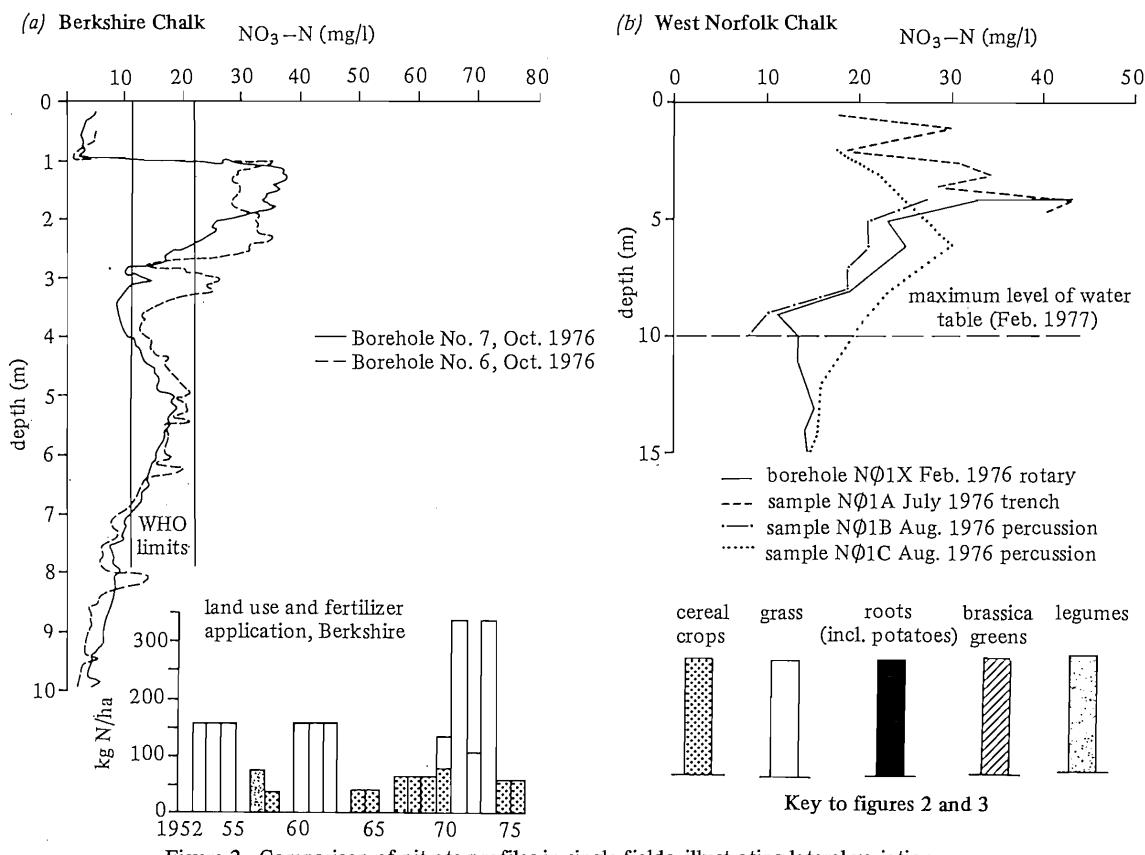


Figure 2. Comparison of nitrate profiles in single fields, illustrating lateral variation.

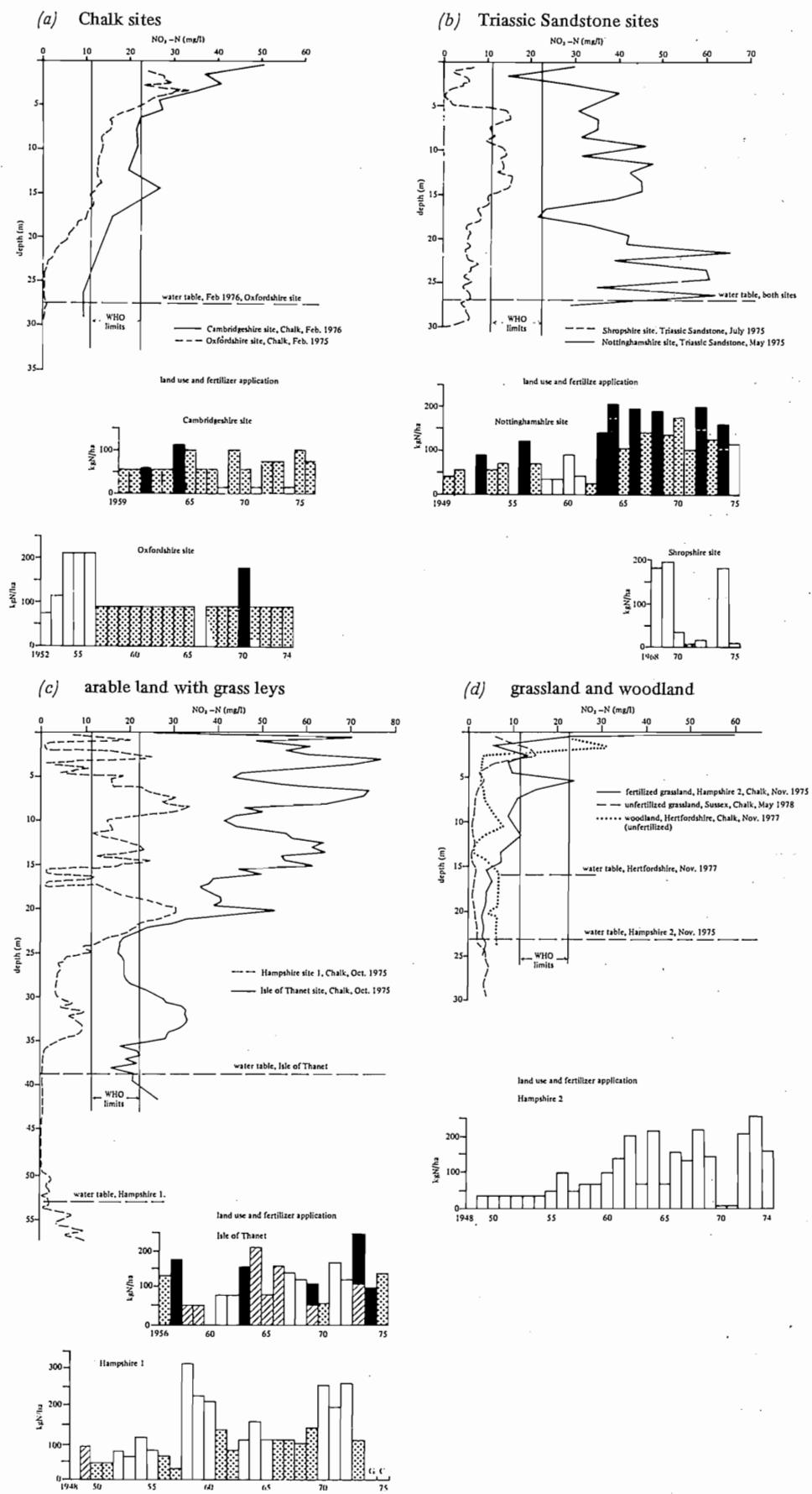


Figure 3. Nitrate profiles beneath sites with different land uses.

Concentrations of NO_3^- -N in excess of 11.3 mg/l, either continuously or intermittently, have been measured in the pore water profiles from beneath *all* the arable and arable/grass-ley sites that have been investigated. At many sites, the NO_3^- -N concentrations have exceeded 22.6 mg/l at numerous depths and individual values well in excess of 50 mg/l have been frequently encountered. The profiles beneath sites, subject to long-term, essentially-continuous arable farming, normally appear to be relatively smooth with nitrate concentrations decreasing with depth (figures 2(b), 3(a)), but those at which arable husbandry has been frequently interrupted by grass-leys are more sinuous (figure 3(c)); in some cases, low concentrations may be reached at depth within the unsaturated zone though, in others, relatively high concentrations continue to the water-table. Carbohydrates have been detected at depths of up to 55 m at concentrations of about 0.1 mg/kg dry chalk (Young & Hall 1977) and this may imply a potential for microbial reduction of nitrate. However, bacteriological studies on the West Norfolk Chalk could not detect the presence of any denitrifying genera at depths below 2 m (Foster *et al.* 1977); until more positive evidence has been gathered, the conservative assumption must be made in profile interpretation that no reduction of nitrate is occurring, or will occur, at depth in the unsaturated zone.

In sharp contrast to arable sites, pore water profiles from beneath areas of permanent unfertilized vegetation, such as rough grassland, downland and woodland, have been found to be characterized by NO_3^- -N concentrations mainly below 5 mg/l, and frequently below 1 mg/l (figure 3(d)). Long-term fertilized grassland has been found to be underlain by pore waters with 5–10 mg/l of NO_3^- nitrogen (figure 3(d)), except where abnormal amounts of inorganic nitrogen fertilizer (over 500 kg nitrogen per hectare each year) have been applied or where fields have been used temporarily for the storage of manures or as intensive stock-pens.

In West Norfolk, high sulphate and moderate chloride concentrations (over 100 and 50 mg/l, respectively) have been widely encountered in the interstitial water of the Chalk unsaturated zone beneath long-standing arable fields (figure 4), and this is believed to be the norm. It is interesting to note that SO_4^{2-} or NO_3^- (rather than HCO_3^-) was found to be the *major* anion at depths from 1 to 10 m, calcium being overwhelmingly the dominant cation. In contrast, SO_4^{2-} and Cl concentrations beneath unfertilized grassland at inland sites were typically in the range of 20–50 and 15–40 mg/l, respectively, and compatible with the known input from rainfall. Sulphate and chloride are not nutrients, but, to a degree, may be taken-up by plants. However, they are normally added in substantial quantities to agricultural soils in combination with the principal nutrient elements (N, P and K). The amounts of sulphate have decreased significantly during the present decade as a result of changes in fertilizer chemistry and is probably the cause of the peak SO_4^{2-} concentrations in West Norfolk Chalk pore water profiles almost always occurring about 3–7 m below those for nitrate.

The practical relevance of tritium (${}^3\text{H}$) as a natural tracer in groundwater studies in the Chalk unsaturated zone was first demonstrated by Smith *et al.* (1970) who determined its distribution at a site in Berkshire in 1969 (figure 5). The existence of a clearly-defined peak at a depth of around 4 m was interpreted as indicating that about 85% of the infiltration was moving downwards by interstitial piston flow at the surprisingly slow rate of about 0.8 m/a since, after allowing for radioactive decay, the ${}^3\text{H}$ values observed in the peak (about 600 TU) could only have originated from rainfall during the springs of 1963 and 1964. Similar ${}^3\text{H}$ profiles, with a single pronounced peak (always of more than 200 TU) at depths between 5 and 14 m, have been found at *all* sites on the Middle/Upper Chalk (with sufficiently thick unsaturated zones) so investigated during 1975–77 in the course of the current research programmes. The peak concentrations and the depths to the peaks (see figure 5 and table 1) are broadly consistent with expectation, after allowing for radioactive decay and considering the average local infiltration rate. However, instances of significant differences in ${}^3\text{H}$ profiles from adjacent sites at comparable times are also known.

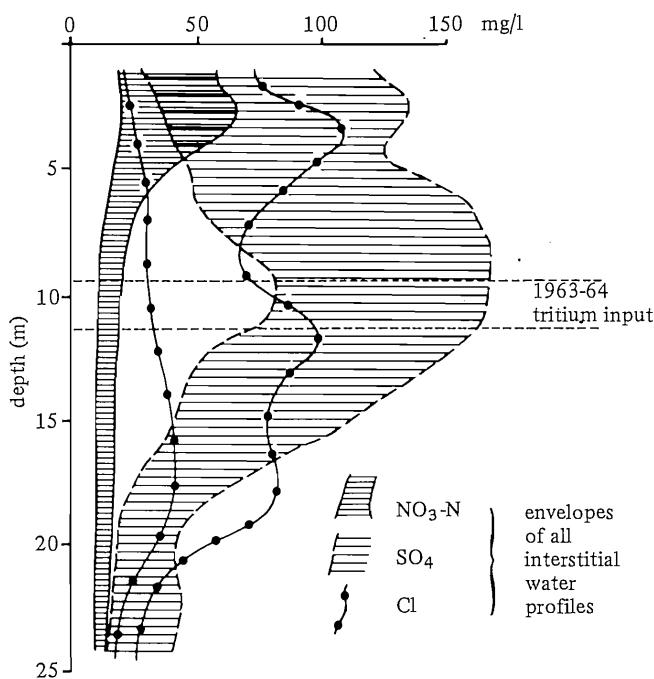


Figure 4. Partial summary of chemical profiles of interstitial water for Chalk unsaturated zone beneath arable sites in West Norfolk.

Moreover, careful study of individual profiles reveals that a confident evaluation of the mass ^3H balance is not always possible for a variety of reasons, and suggests that reliable interpretation will have to await the collection of a number of time sequences of ^3H profiles for selected sites (Foster & Smith-Carington 1980). Available data, for sites on the Hampshire and Dorset Chalk, confirm that the tritium peak is moving slowly downwards though, at the Dorset site, there is some doubt as to the proportion of the total tritium input involved in the slow component of movement. *This is a critical question.*

The mechanism by which water and solutes move downward through the Chalk unsaturated zone also remains a subject of uncertainty and controversy. The exceedingly small pore diameters (mainly less than 1 μm) mean that gravity drainage is almost entirely inhibited and that, *even within the unsaturated zone*, most of the Chalk matrix remains very close to saturation (Price, Bird & Foster 1976). In view of the observed frequent vertical jointing, Foster (1975) postulated that relatively rapid infiltration and groundwater flow in unsaturated zones may occur with ^3H (and other solutes) diffusing between the mobile 'fissure' water and the almost-static pore water. This general concept has been extended by Young, Oakes & Wilkinson (1976) and Oakes (1977) who demonstrated that such a mechanism could, under certain conditions, produce a similar vertical distribution of solutes to interstitial piston flow. The detailed picture is likely to be complex and to involve combinations of mechanisms. Obviously the ultimate aim must be to produce a satisfactory mathematical model of unsaturated zone solute transport, starting with tritium and extending to include nitrate and other constituents of interest. If this were possible, it would generate, by way of calibration, an evaluation of the rates of leaching of nitrate from permeable agricultural land with various husbandries and, given assumptions as to future climate and cropping practice, a prediction of future nitrate concentrations reaching the water-table. Modelling of the sites on the Hampshire Chalk (Young, Oakes & Wilkinson (1976)) has provided satisfactory simulation of unsaturated zone profiles of nitrate, chloride and tritium. Simulations have been achieved of some other Chalk sites but these require modifications to the model. The model assumes that a high proportion of the solutes are transported via the slow component of flow and that no nitrate reduction occurs. Preliminary investigation of the presence of nitrogen-transforming bacteria in Chalk indicates that denitrification is slight and restricted to the upper few metres of rock.

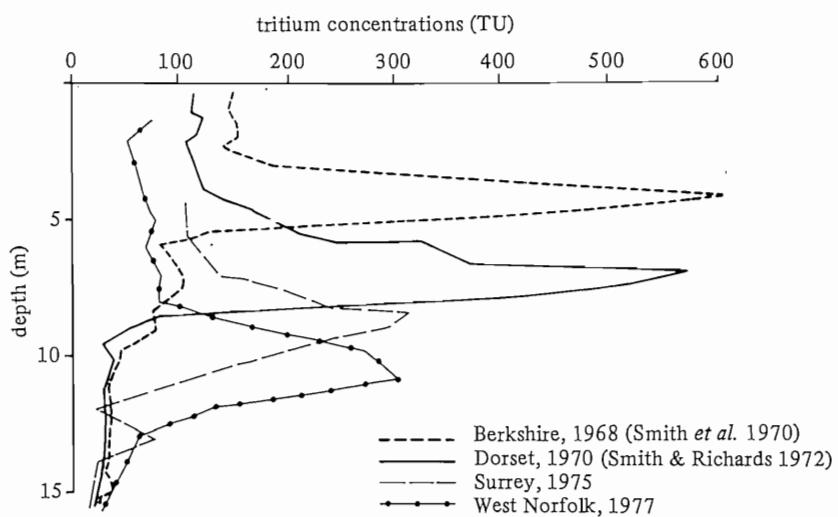


Figure 5. Selected tritium profiles for Chalk unsaturated zone pore-water samples.

Table 1. Depths below ground level to peak tritium concentrations in the Chalk

location	no. of boreholes	sampling date	depth to peak (m)	long-term average effective rainfall (mm) assuming 75 mm root constant
Cambridgeshire	1	1976	5	130
West Norfolk	5	1976/77	9 – 12	160
Isle of Thanet	1	1975	7.5	200
Oxfordshire	1	1975	7.5	210
Surrey	2	1975/77	8 – 11	240
Hampshire	1	1975	8 – 11	315
Sussex	1	1977	12.5	330

Saturated zone

In the research catchment on the West Norfolk Chalk, three cored boreholes were drilled to about 50 m below the water-table to facilitate chemical and isotopic analyses of interstitial water and thus establish the extent to which storage and/or reduction of nitrate might delay or attenuate the migration of high concentrations reaching the saturated zone. Some risk of contamination of pore water samples from depth with mobile groundwater in overlying major flow zone existed, but it is believed that the effect was minimized by the core drilling and handling procedures employed.

The distinctive features of the profiles obtained (figure 6) are:

- (a) Variable and often high concentrations of all constituents in the upper part of the zone of seasonal water-table fluctuation, where downward moving solutes must come into intermittent contact with horizontal groundwater flows;
- (b) Relatively high NO_3-N concentrations (8–15 mg/l) through a considerable thickness of the permanently saturated zone, suggesting that inputs from the land surface in

long-standing entirely arable areas must have contained similar mean concentrations over fairly long periods;

(c) Decrease of the $\text{NO}_3\text{-N}$ concentrations to low or very low levels below the Plenus Marl, because of the absence of significant groundwater circulation at this depth and/or of denitrification.

(Similar distributions of nitrate in the saturated zone have been measured in the Chalk in Sussex and on the Isle of Thanet, but at one site in Surrey nitrate concentrations were reduced to low levels at about 20 m below the water table).

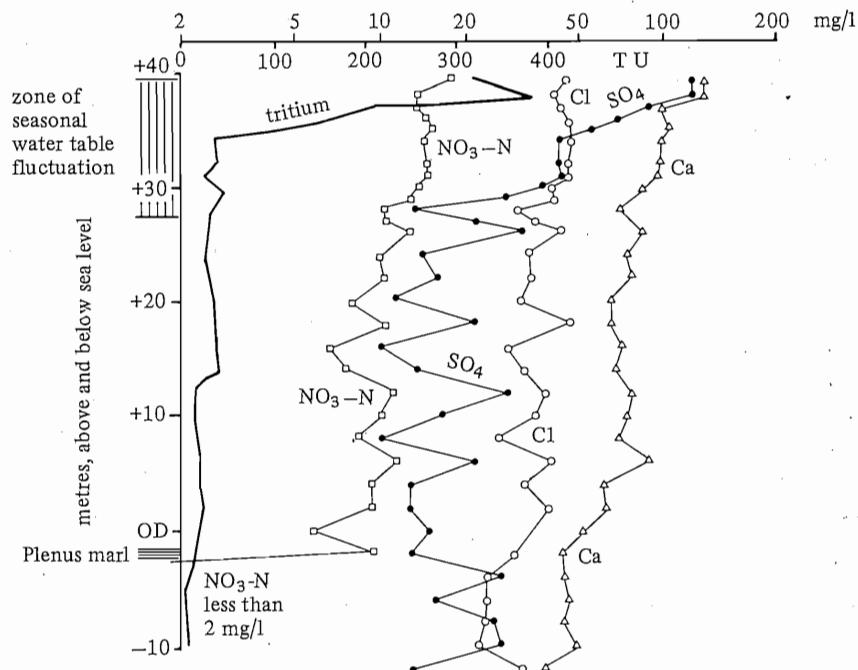


Figure 6. Chemical and isotopic profiles of saturated zone interstitial waters from individual boreholes in West Norfolk Chalk.

By way of comparison, careful and regular sampling from observation boreholes of different depths in the West Norfolk catchment have shown the deeper of the major groundwater flows to contain 11–13 mg/l of $\text{NO}_3\text{-N}$. Following heavy infiltration in February 1977, the zone of water table fluctuation filled with groundwater containing 17–21 mg/l of $\text{NO}_3\text{-N}$, although it is extremely unlikely that the actual infiltration from the soil had anything like this level of nitrate. An adjacent water-supply borehole, normally producing groundwater with 12–15 mg/l of $\text{NO}_3\text{-N}$, peaked to 17 mg/l in February 1977. The levels of other chemical constituents in this borehole are: SO_4 , 35–50 mg/l; Cl , 30–40 mg/l; Ca , 105–135 mg/l.

Other aquifers

Triassic Sandstone

The Triassic Sandstone, which outcrops mainly in central and northern England (figure 1), is composed of consolidated, red, in part pebbly, sandstones of continental deposition. Extensive areas of the outcrop are mantled by glacial deposits; where this cover is absent, weathering to depths of 10 m or more is common. As dry percussive coring was generally impractical because of the formation lithologies, continuous flight augering was employed for shallow exploratory boreholes, and air-flush rotary core drilling for deeper boreholes. The handling, storage and pore water extraction techniques

were similar to those used with Chalk cores, but the majority of samples were deep-frozen to prevent drainage.

The general relationship between land use and pore water nitrate profiles observed at Chalk sites is repeated in the Triassic Sandstone: $\text{NO}_3\text{-N}$ concentrations in the range 10–50 mg/l are characteristic of arable land (figure 3(b)), while levels of 10–20 mg/l and less than 5 mg/l have been measured beneath fertilized and unfertilized grassland, respectively. The high degree of vertical anisotropy, resulting from the sedimentary character of the sandstones, was found to be reflected in the form of the interstitial water profiles. Lateral variability in the Sandstones, when compared to the Chalk, was responsible for the lack of close correspondence in shape of adjacent profiles from individual arable sites. Determination of reliable ^3H pore water profiles in the unsaturated zone has been restricted by the low moisture content of the rock and the difficulty of obtaining satisfactory cores without the use of a drilling fluid; those that have been determined (Brereton & Wilkinson 1977) have shown irregular forms, with maxima in the range 200–300 TU at depths of around 20 m. This suggests a more rapid (and possibly less uniform) rate of downward movement than in the Chalk.

Cored boreholes to depths of 150 and 200 m were drilled in a Staffordshire valley, close to boreholes producing groundwater having $\text{NO}_3\text{-N}$ levels of 7–8 and 3–4 mg/l. The saturated zone profile from the former site (figure 7(a)) showed high $\text{NO}_3\text{-N}$ concentrations between 40–90 m depth, while concentrations of 6–10 mg/l were measured at the latter site (figure 7(b)) to a depth of about 60 m. Lithological examination of the cores from both sites showed that the higher concentrations were confined to the Bunter Pebble Beds and geophysical borehole logging revealed that the main groundwater flows occur within this part of the Triassic sequence. Tritium determinations showed the groundwater moving through the Bunter Pebble Beds, at both sites, to be significantly younger than that in the underlying Lower Mottled Sandstone, suggesting the nitrate to be of relatively recent origin. A survey of land use in the groundwater catchments contributing to each pumped borehole showed a greater proportion of arable cropping in the catchment of the source producing the higher nitrate concentration groundwater.

Jurassic Limestone

Research is being undertaken on a groundwater catchment in the Lincolnshire Limestone, the land use of which has been about 90% arable since the 1930s or even earlier. The presence of some massive cementstones and numerous marl bands within the Limestone

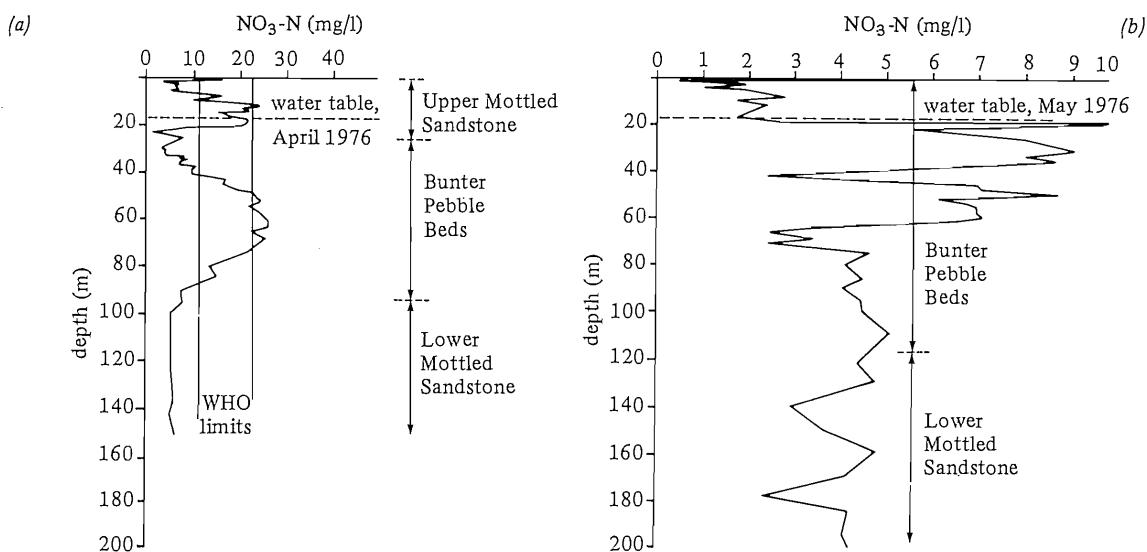


Figure 7. Nitrate profiles of saturated zone interstitial waters from boreholes in the Triassic Sandstone, Staffordshire.

sequence causes many perched water-tables and significant lateral groundwater movement, above the regional water-table, following major infiltration. This invalidates an analytical approach to the vertical profiles of interstitial water chemistry, though most of the more porous lithologies throughout the formation were found to have high or very high pore water nitrate concentrations.

The formation and its permanently saturated zone rarely exceed 30 m and 10 m thickness, respectively; in consequence, the aquifer has very low storage, both in respect of total and mobile water content. It is thus probable that the overall groundwater system more nearly approaches equilibrium with current arable farming practice than do other groundwater systems. It is therefore of considerable interest that the groundwater produced by the water-supply borehole tapping the catchment exhibits marked seasonal fluctuation in the concentration of nitrate and other constituents; NO_3-N and SO_4 , peaking at about 22 mg/l and 150 mg/l and falling during the groundwater recession to 12–16 mg/l and 110–130 mg/l, respectively.

CONCLUDING REMARKS

Prior to the 1970s, hydrogeological factors were often ignored in groundwater quality investigations, especially when such investigations were limited to pumped sampling. In particular, no study of physical and chemical processes in the unsaturated zones of aquifers had been attempted.

The current British research programmes have produced a substantial and possibly unique body of data on the unsaturated zone, especially of the Chalk. They are bringing about a realization of the great influence of agricultural practice on groundwater chemistry and of the extent of the build-up of nitrate and other solutes beneath arable farmland.

If the physico-chemical behaviour of these solutes is similar to that of tritium, the rates of leaching from arable fields appear to have increased substantially since 1963–64. In West Norfolk, for example, the Chalk pore waters above the ${}^3\text{H}$ peak at 10 m depth are estimated to contain the following concentrations of SO_4 and Cl : 600–1000 kg/ha, 2000–4500 kg per hectare and 1000–2400 kg per hectare corresponding to average losses of at least 40–70 kg (nitrogen) per hectare per year, 150–350 kg (sulphate) per hectare per year and 70–180 kg (chloride) per hectare per year. The sinuous pore water nitrate profiles beneath arable/grass-ley sites suggest that significant quantities of nitrate are released and lost after ploughing-in grass.

The first attempts at using mathematical modelling techniques to simulate the movement of nitrate through the unsaturated zone of the Chalk have been encouraging. While it is recognized that confident prediction of movement of solute under all conditions is dependent on a more detailed knowledge of the mechanism of unsaturated flow solute transport, it is hoped that the current research programmes will go a long way to resolving the outstanding problems. Time-dependent changes, however, can only be established by redrilling and resampling at selected sites after elapse of a suitable period.

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