8 Nitrate in Groundwater

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8.1 NITRATE AS A GROUNDWATER CONTAMINANT

8.1.1 INTRODUCTION

Nitrate is the pollutant most commonly identified in groundwater (Freeze and Cherry, 1979). Nitrate contamination of aquifers is becoming widespread for a whole variety of reasons, notably because of increasing use of inorganic fertilisers, ploughing of old grassland and disposal of organic material (farmyard manure, slurry, sewage sludge) on or beneath the land surface. Though nitrate (NO_3^-) is the main form in which nitrogen occurs in groundwater, dissolved nitrogen may also be present as ammonium (NH_4^+), nitrite (NO_2^-), nitrogen (N_2), nitrous oxide (N_2O) and as organic nitrogen.

Figure 8.1 shows the sources and pathways of nitrate in groundwater. Nitrate in groundwater may originate from organic matter or ammonium. These are converted into nitrate by the processes of mineralisation (decomposition of organic matter into inorganic ammonium) and nitrification (oxidation of ammonium to form nitrate). These are aerobic processes which commonly take place above the water table. Nitrate may be lost from groundwater by denitrification which, because it takes place in an anaerobic environment, is most likely under saturated conditions (i.e. below the water table). Denitrification is principally a biologically mediated process, though it may occur chemically or biologically. NO_3 is first reduced to NO_2 and then to N_2O. Complete reduction results in N_2, though often a trace of N_2O is left; these remain in solution until degassing can take place. Chemodenitrification can occur if the redox potential of the groundwater is low enough (Freeze and Cherry, 1979, p. 414). Biological denitrification may be limited in groundwater because of the lack of a carbon substrate. Its operation in groundwater systems is little known though much debated since it is potentially an important nitrate loss mechanism (see Section 8.2.3 below). Sprent (1987, p. 25) notes that some bacteria can reduce nitrate to ammonium. Being a cation, this ammonium may then be adsorbed by clay minerals present in the rock.

The division between 'soil water' and 'groundwater' is necessarily somewhat arbitrary. Nitrogen cycling in soils is described in Chapters 3 and 4 in some detail. In Chapter 9, the drainage of nitrate through soil to streams is considered; this is essentially an aspect of hillslope hydrology, the dominant flow direction being horizontal (downslope) rather than vertical. Here, we must necessarily concentrate both on vertical percolation through the unsaturated zone (initiated by vertical drainage through the soil profile) and on lateral flow within the saturated zone. However, the distinction between subsurface flow in deep soils and in shallow

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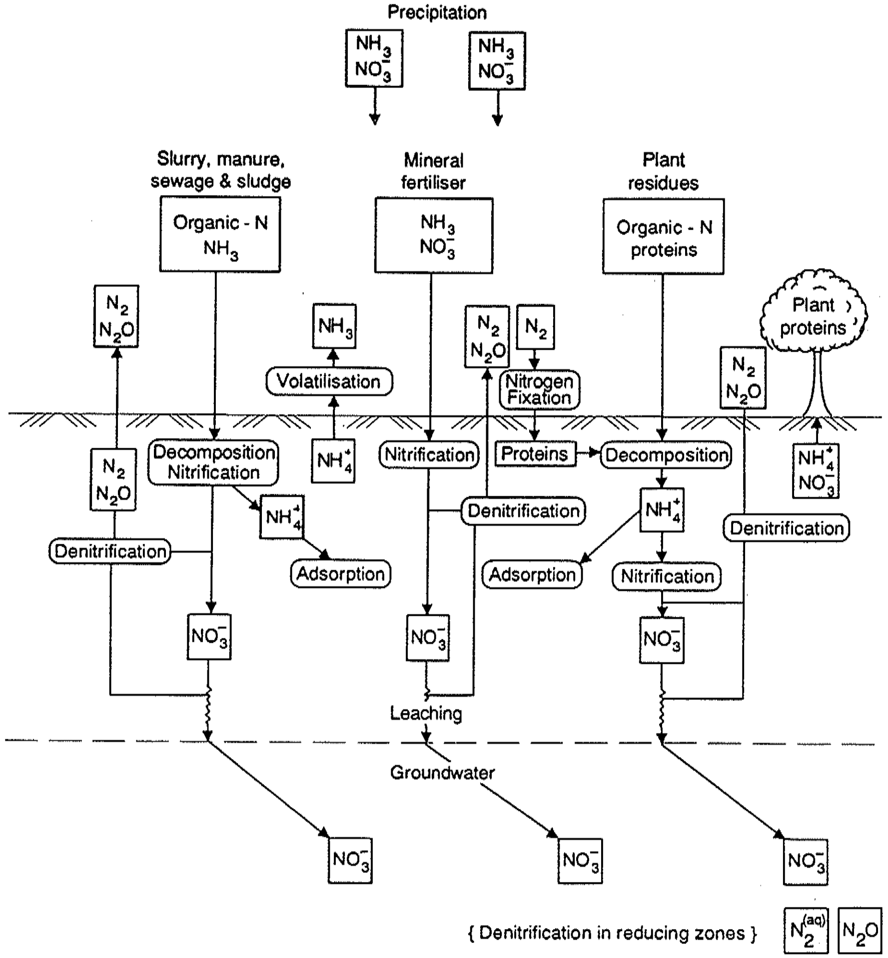

Figure 8.1 Sources and pathways of nitrate in groundwater (adapted from Freeze and Cherry, 1979)

aquifers can sometimes be hard to make, so that there is inevitably some overlap between this and the next chapter. Finally, it should be pointed out that soil scientists have, naturally enough, concentrated their efforts on vertical drainage in soils, especially within the root zone. In both Chapter 9 and here we refer to soil water flow where it is relevant to do so.

8.1.2 AQUIFER PROPERTIES

Two types of flow occur through rock: laminar flow through the rock matrix and turbulent flow through large fractures. Because flow through a porous medium is complex, attempts to estimate flow using simple measures of pore geometry have met with little success. Darcy's Law (1856) shows that the flow of water through a porous medium is proportional to the driving force acting on the liquid (i.e. the hydraulic gradient) and to the ability of the medium to transmit the liquid (i.e. the hydraulic conductivity). Darcy was not concerned with flow through individual pores, referred to as the microscopic level, but rather with flow at the

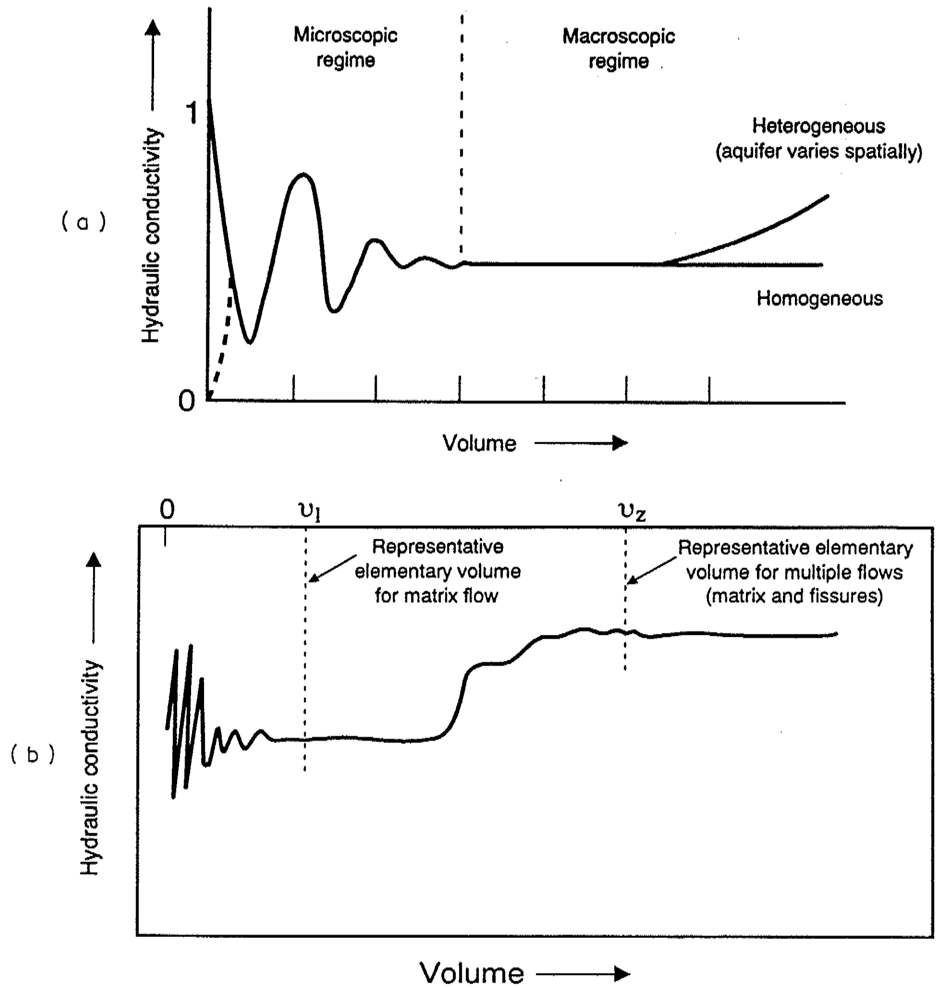

Figure 8.2 Diagrams illustrating representative elementary volumes for (a) homogenous, porous rock and (b) porous rock with fractures (adapted from Domenico and Schwartz, 1990)

macroscopic scale. Darcy experimented with a volume of sand that was large with respect to a single pore but small with respect to the space within which significant variations of macroscopic properties may be anticipated (Domenico and Schwartz, 1990). At the microscopic level, the size and tortuousity of pores varies widely; as volume increases, variability decreases markedly until the point where there are no longer any variations with the size of sample. Hence Darcy sought the smallest possible sample that exhibited an acceptable level of homogeneity, as shown in Figure 8.2(a). At larger scales, some measure of heterogeneity is reintroduced since bedrock properties vary spatially. Though variance will increase with scale, it may still be possible to define a mean value of hydraulic conductivity with acceptable accuracy.

Hydraulic conductivity is maximal when all pores are filled with water; this is referred to as the saturated hydraulic conductivity. For a given porosity, pore size is the principal factor controlling hydraulic conductivity. Thus a massive rock containing only a few large fractures may have a much higher hydraulic conductivity than a porous but fine-grained rock whose pores are all of very small radius. For fractured rocks, it is likely that as the volume increases beyond that which is representative of the macroscopic properties of the rock matrix, the flow parameters will start to vary again before becoming constant once more for large volumes of rock (Domenico and Schwartz, 1990). Thus the representative volume may exist on more than one scale, this being shown schematically in Figure 8.2(b). Not surprisingly, the saturated hydraulic conductivity of many rocks is determined by its secondary (or bulk) porosity rather than by the primary porosity of the matrix. This is illustrated in Figure 8.3. Each rock type is represented by two fields, of which the one to the left of the diagram shows the primary porosity and pore size. The second field shows the total rock porosity and the range of size of the secondary voids. There is very little change in porosity between primary and secondary fields, but the secondary pore size is two to three orders of magnitude larger; it is this latter variable that mainly determines the saturated hydraulic conductivity of a rock (Smith, Atkinson and Drew, 1976). In the zone of saturation, flow is likely to remain Darcian, even in a well-fissured rock, since the hydraulic gradient is usually low, though clearly the highest *individual* pore velocities are associated with the largest fractures (see Section 8.1.3).

As a rock becomes progressively unsaturated, so its hydraulic conductivity is reduced, often by several orders of magnitude. As the degree of saturation is reduced, flow is confined to

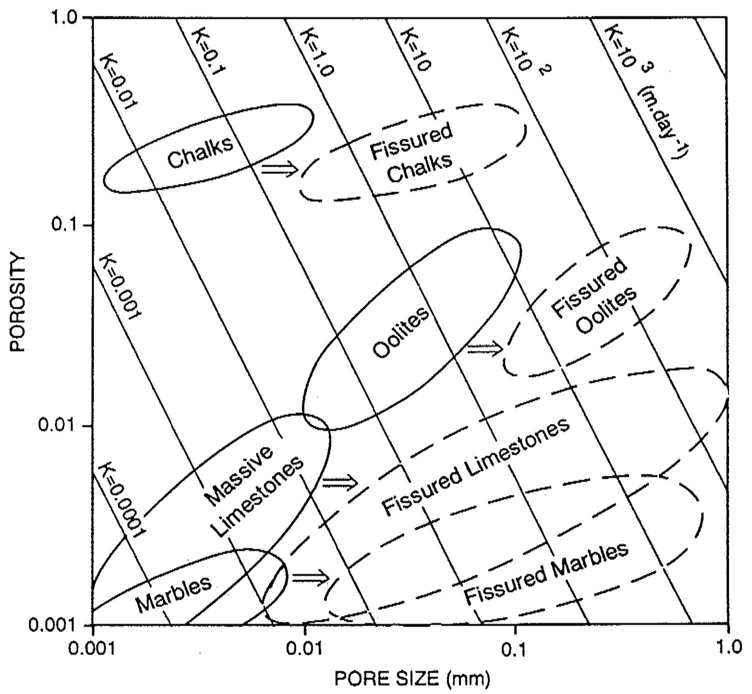

Figure 8.3 Primary and secondary porosity, pore size and hydraulic conductivity (K) of carbonate rocks (adapted from Smith, Atkinson and Drew, 1976). Contour values of K are based on the assumption that the rock behaves as a bundle of straight, parallel capillary tubes. Solid lines indicate primary conductivities of the rock matrix; dashed lines are secondary or total conductivity

smaller pores and to less of the pore space, and conductivity decreases. The largest pores drain first. This may leave the smaller pores which remain full of water poorly interconnected. Thus, drainage of large fractures is very likely to cause a severe reduction in flow and the hydraulic conductivity can fall by several orders of magnitude (Figure 8.3). If the vertical flux in an unsaturated fractured rock is less than the saturated hydraulic conductivity of the matrix, the flow will tend to remain in the smaller sized pores within the matrix and flow will be slow. As the flux increases, the water content of the rock matrix will become higher and some flow will then take place within larger pores. In other words, though the rock as a whole remains unsaturated, the capillary suction in the rock matrix has fallen sufficiently that larger pores (but only those which are of capillary size) can now hold water; these provide pathways for more rapid flow. If the flux is greater than the saturated hydraulic conductivity of the matrix, the matrix will saturate. Some water must then enter the fractures (those cavities too large to function as capillaries) where flow is likely to be much more rapid than through the small pores.

Recent research on cracked clay soils has shown that this is not the only mechanism whereby large fractures can conduct flow rapidly down through the unsaturated zone (Beven and Germann, 1982). In soils where the rainfall rate exceeds the infiltration rate of the soil matrix, excess water will enter the structural voids (or 'macropores') and water may move quickly down through the soil profile, even though the matrix remains unsaturated. The depth of movement is determined by the rate of input and by losses of water absorbed into the soil matrix through the walls of the macropore. The magnitude of absorption losses into the soil depends on the matric suction of the soil water, which itself is a function of soil moisture content. Where soil macropores connect with fractures in the rock or where drainage from the soil exceeds the infiltration rate of the rock matrix, percolating water may enter large rock fissures and may therefore by-pass the rock matrix.

The important point is that, depending on rock type, the downward movement of water through the unsaturated zone may or may not be uniform. This has particular implications for the speed with which nitrate is carried down to the zone of saturation.

8.1.3 SOLUTE TRANSPORT PROCESSES

Considerations of solute movement in porous media often begin with Fick's first law which refers to solute flux in relation to solute gradient (Nye and Tinker, 1977). Even in static water, solutes diffuse along the concentration gradient from high to low concentration. If the water itself is moving, convection also occurs: that is, the mass transport of water and any solute dissolved in it from one location to another. However, the solute will move down any concentration gradient simultaneously with the convection process, so the two components of solute movement (diffusion and convection) must be combined. A further complication in a porous medium is that some portions of water (and its solutes) travel faster than others, in large pores and/or by more direct routes (Burt and Trudgill, 1985). The combined movement of convection and diffusion is referred to as dispersion (or, more formally, hydrodynamic dispersion). Dispersion causes a zone of mixing to develop between a fluid of one composition that is adjacent to or being displaced by a fluid of another composition (Domenico and Schwartz, 1990).

Dispersion can be demonstrated by the displacement of water by solute in a simple column apparatus (Figure 8.4(a)). For a saturated rock with initially no solute present, simple convection (or 'piston flow') for a solute pulse would yield a breakthrough curve as shown

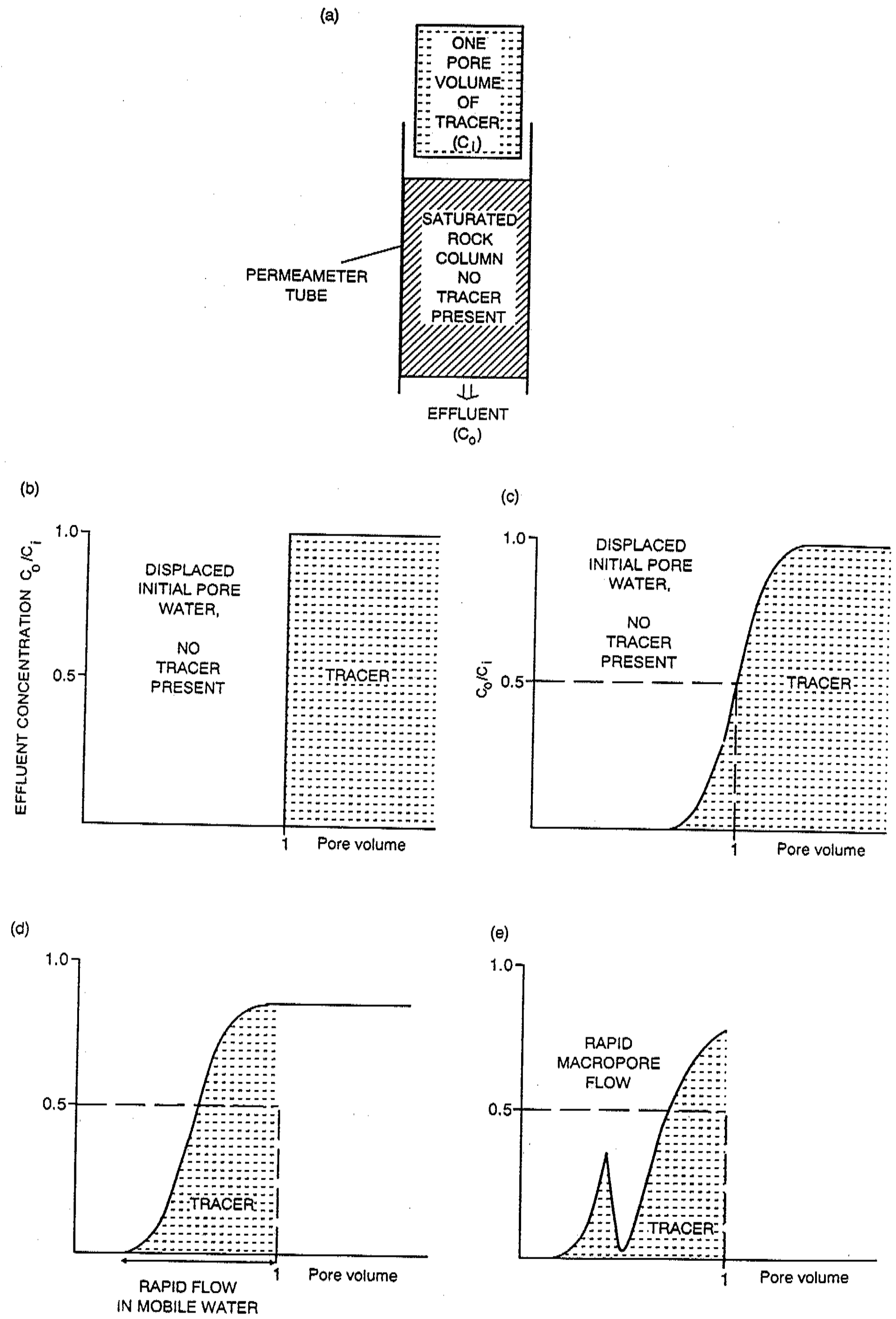

Figure 8.4 Movement of solute through a saturated rock sample (adapted from Burt and Trudgill, 1985)

in Figure 8.4(b) when one pore volume has been displaced. The effect of dispersion is to spread the solute mass beyond the region it would normally occupy due to convection alone, with more rapid faster appearance in the faster flow paths and some tailing in the slower, more tortuous paths (Figure 8.4(c)). This pattern can be greatly exaggerated by the presence of large fractures which cause the solute to arrive in the outflow considerably in advance of one pore volume or even giving initial peaks of solute (Figures 8.4(d) and (e)).

Burt and Trudgill (1985) have identified three flow domains in soils. These are equally applicable to flow in rock and provide a basis for understanding the movement of nitrate:

(1) Immobile water which is tightly held in the smallest pores; these pores remain saturated at all times. This water does not appear in drainage water, but it is important because nitrate may diffuse into and out of the domain from or to the more mobile water.
(2) Mobile or displaced water, equivalent to capillary or matric water, and is held at intermediate tensions (which vary with rock type). Nitrate concentrations may build up in this domain depending on the pattern of displacement from above and on the exchange of nitrate with immobile water via diffusion.
(3) Transient flow transmitted rapidly through large fissures. This flow will be maintained provided that the supply rate exceeds infiltration losses into the rock matrix.

8.2 NITRATE MOVEMENT IN THE UNSATURATED ZONE

8.2.1 EXTRACTION AND ANALYSIS OF BOREHOLE WATER

A substantial proportion of the total research effort on nitrate in UK groundwater continues to be dedicated to the unsaturated zone (Parker, Young and Chilton, 1991). The research has been based primarily on the extraction of interstitial pore water from rock cores by centrifugal techniques or pressure extraction. A full description of the extraction and analysis of pore water is given, *inter alia*, in Young, Hall and Oakes (1976). Typically, extracted pore water may be analysed for nitrate, nitrite, ammonium, chloride, calcium and tritium. In addition, rock samples may be tested for evolved carbon dioxide, carbohydrate content and bacterial contamination.

Chloride is widely regarded as a stable, conservative, non-reactive ion, not subject to biological transformation. Chloride proiles can therefore represent a useful tool in the interpretation of solute transport in the unsaturated zone. The transport of nitrate is likely to be similar to that of chloride except that denitrification or nitrification within an aquifer cannot be discounted (Whitelaw and Rees, 1980). The determination of tritium (^3H) profiles aids the evaluation of solute transport mechanisms in the unsaturated zone because of its unique temporal distribution in rainfall and infiltration. It can thus be used as an analogue for non-reactive solutes of similar physico-chemical behaviour to nitrate whose temporal patterns of input are less easy to estimate. Many tritium profiles show a distinct peak originating from fallout in rainfall in 1963–5 following atmospheric testing of thermonuclear weapons (Geake and Foster, 1989). Despite attenuation because of radioactive decay and the effects of hydrodynamic dispersion, this peak is still evident in water moving downwards in the unsaturated zone (see next section and Figure 8.3). However, given the assumptions and possible sources of error involved in evaluating the tritium mass balance (particularly uncertainties over the tritium content of rainfall), profiles must be interpreted with some caution (Foster and Smith-Carington, 1980).

8.2.2 RATES OF DOWNWARD MOVEMENT OF NITRATE

Interpretation of pore water profiles requires a detailed understanding of flow mechanisms and dispersion effects in the unsaturated zone. In the UK, three main aquifers have been studied: Cretaceous Chalk, the Jurassic limestones, and the Triassic Sherwood (or Bunter) sandstone (Rodda, Downing and Law, 1976).

8.2.2.1 Cretaceous Chalk

The Chalk of south-east England is the major aquifer in the UK, providing over 40% of the total groundwater abstracted. In recent years, there has been mounting concern about the increasing concentrations of nitrate in water suplied from boreholes and spring in the Chalk; hence the Chalk is the most studied UK aquifer in this respect. The Chalk is a fine-grained limestone frequently traversed by joints and fissures. The matrix (intergranular) porosity is high (0.25–0.5) but the pores are so small (mostly 0.25–0.5 μ– radius) that the hydraulic conductivity is very low (below 10^{-2} d^{-1}; Foster and Smith-Carington, 1980 — see also Figure 8.3). These pores remain full of water almost all the time but the average annual rate of downward movement of the water is very low, approximately 0.9 m a^{-1} (Wellings and Bell, 1980). In addition to these micropores, the Chalk contains a large number of fissures of varying sizes (Reeves, 1979). These can contain water either only when the matric tension is low or, more rarely, if the percolation rate from the soil above exceeds the hydraulic conductivity of the rock matrix. Except in valleys, depth to the water table is often in the range 20–50 m. Given very high nitrate concentrations in the upper part of the unsaturated zone and the slow rate of downward percolation, it is expected that nitrate concentrations in chalk groundwater supplies will increase steadily over the next few decades (see below).

There is no simple universal model for solute transport through the unsaturated zone of the Chalk (Parker, Young and Chilton, 1991). Two mechanisms have been put forward to explain observed nitrate and tritium profiles. Marked tritium peaks have been taken to indicate that most of the infiltration is moving slowly downwards by intergranular flow with very little dispersion. Microfissures and the largest pores of the chalk (0.01–0.2 mm diameter) account for the slow mode of downward tritium movement. Such pores are unlikely to represent more than 1% of the Chalk by volume and probably produce a hydraulic conductivity of less than 0.01 m per day (Foster and Smith-Carington, 1980). Foster (1975) suggested that the main mechanism of recharge was flow through fissures. After intense rainfall, the infiltration capacity of the rock matrix is likely to be exceeded, suctions fall concomitantly and positive potentials develop locally, allowing horizontal groundwater flow to the macrofissures (larger than 0.2 mm in aperture). Diffusion between the moving water in the fissures and the relatively static pore water retards the downward movement of isotopes and solutes so that a virtually non-dispersive solute movement can still occur. This would, however, only hold for low-velocity flow through a dense network of microfissures and for solutes with a high diffusion coefficient. When flow takes place in larger fissures, rates may be too rapid to allow significant difussion exchange with the pore water and solutes may by-pass the normal slow mode of solute transport.

Geake and Foster (1989) conclude that the relative importance of each flow mechanism may vary spatially and with depth; moreover, at any one site, the mode of water flow can vary temporally with excess rainfall intensity and antecedent moisture conditions. Where the matrix hydraulic conductivity is relatively high, intergranular flow will predominate. There is straightforward 'piston flow' displacement of water and least dispersion of the tritium peak, implying that nitrate will itself move downwards without significant dispersion. With much lower matrix hydraulic conductivity, more flow must move through fissures and solutes become more dispersed down the profile. Dispersion is implied where there has been more downward movement of solute than would be expected if piston flow was occurring and where there has been an apparent flattening and broadening of the original solute peak. As a result, there are higher concentrations than expected in the deeper part of the profile (Foster and Smith-Carington, 1980; Parker, Young and Chilton, 1991).

Isotope and solute profiling in the Chalk has been reviewed recently by Geake and Foster (1989) and by Parker, Young and Chilton (1991). Figure 8.5(a) shows a tritium profile from the unsaturated zone of the Chalk at a site in Hampshire where the tritium peak, moving slowly downwards with time, has been preserved despite attenuation because of radioactive decay and the effects of hydrodynamic dispersion. Figures 8.5(b) and (c) show the nitrate profile from an adjacent borehole and the land use since 1949 for the field in which both the tritium and nitrate boreholes were drilled. Young, Hall and Oakes (1976) postulate that the large releases of nitrate accompanying the ploughing of ley (temporary) grassland should be recognisable as major peaks in nitrate concentration in interstitial water. A comparison of the land-use record with the vertical nitrate profile suggests that the peaks at 30–32 m, 20 m, 14 m, 9 m and 2 m may correspond to periods of ploughing after leys in 1948/9, 1955/6, 1960/1, 1965/6 and 1972/3, respectively. This chronology would seem to correspond well with the 1963/4 tritium peak at 8–9 m, which represents a mean downward movement of about 0.8 m a^{-1}.

The preservation of tritium peaks at many sites demonstrates that the bulk of the nitrate transport through the unsaturated zone of the Chalk, by whatever means, is slow. Evidence shows that downward flow takes place with varying degrees of dispersion. At those sites where solutes and isotopes are moving downwards without significant dispersion, all the pore water to the base of the tritium peak can be assumed to be post-1963 in age. Given this assumption, nitrate leaching losses from Chalk soils can be seen to have increased steadily since the mid-1960s. The very high nitrate concentrations in the upper part of the unsaturated zone imply that nitrate concentrations in Chalk groundwater supplies will continue to rise slowly for many years (Geake and Foster, 1989).

8.2.2.2 Jurassic (Cotswold or Lincolnshire) limestones

These are found to the west of the Chalk and form an important aquifer in south-central and eastern England. They are thin formations (20–35 m) with moderate intergranular porosity (0.1–0.25) but with very small pores, giving very low values for matric hydraulic conductivity (0.5–5 $\times$ 10^{-4} m d^{-1}). The limestone, however, is cut by a large number of bedding plane fractures and joints along which the bulk of the groundwater flow occurs. Groundwater levels increase rapidly following the first effective infiltration in late autumn and early winter. This immediate respose to recharge suggests a low storage aquifer with rapid groundwater flow (Smith-Carington *et al.*, 1983). It suggests too that slow percolation through the rock matrix, a feature of the Chalk aquifer, is not very important in this limestone. Since the movement of nitrate down to the water table is so rapid, the history of leaching losses from the soil is not preserved in unsaturated zone profiles. Despite the low rate of recharge (100–250 mm annually), it is likely that the effects of any change in land use, and in the amount of nitrate leached, will be rapidly transmitted to the saturated zone.

8.2.2.3 Triassic (Sherwood) sandstone

This aquifer is located in the Midlands of England and comprises a series of medium- to fine-grained red sandstones underlain by the so-called Pebble Beds, a coarse pebbly sandstone and conglomerate which forms the main part of the aquifer. The unsaturated zone varies from more than 60 m deep beneath higher ground to less than 10 m deep in valleys. Groundwater levels show no substantial seasonal variation. Measurement of the moisture content and physical properties of sandstone cores from investigation boreholes suggests that the rate of downward percolation of water through the unsaturated zone is about 2 m per year (the mean annual rate of recharge is 360 mm a^{-1}). Hence there is a time lag of some 5–30 years before infiltration reaches the water table (STW, 1988). Investigations in the Hatton catchment showed that nitrate concentrations in the unsaturated pore waters vary from 0.5 to 50 mg NO_3-N l^{-1}, reflecting the different land uses (Figure 8.6). Very high leaching losses occur from arable land (60 kg N ha^{-1}) and from grazed grassland which is heavily fertilised (up to 150 kg N ha^{-1}), losses being equivalent to 40% of inputs in both cases.

8.2.3 CLIMATIC AND LAND-USE CONTROLS

Parker, Young and Chilton (1991) have reviewed the relationship between land use and nitrate leaching. Where it can be assumed that the nitrate and tritium in pore water profiles is moving down without dispersion, then it is possible to interpret the history of recent nitrate leaching losses in relation to cultivation history (e.g. Figure 8.5) and mass balance calculations may be made to quantify the amount of nitrate leached. In the discussion below, the word 'equivalent' indicates that most of the nitrate leached does not come directly from the nitrogen applied in the previous season. Most of the applied nitrogen which is not taken up by the crop, or that which is returned to the soil in plant residues or as in dung and urine, will become incorporated into the soil organic matter and microbial biomass. It is this nitrogen which is subsequently mineralised to leachable nitrate (STW, 1988; Dowdell and Webster, 1980).

Many investigations under arable land have revealed marked peaks in nitrate concentration in the upper part of the unsaturated zone; Figures 8.5 and 8.6 show typical results. Maximum concentrations range from 20 to 70 mg NO_3-N l^{-1} in the upper 10 m (well in excess of EC limits) compared with typical values of the order of 5–20 mg NO_3-N l^{-1} at depth. Foster, Cripps and Smith-Carington (1982, table 1) estimated annual leaching losses since 1963 in the range 40–70 kg N ha^{-1}, equivalent to between 26% and 78% (mean 49%) of the N fertiliser applied. Note that one site listed by Foster, Cripps and Smith-Carington (1982) is excluded here because of the complication that grassland was ploughed during the study period. The ploughing out of ley grassland is a particularly important source of nitrate, resulting in an estimated leaching loss of 280 kg ha^{-1} over the three years following ploughing and 150 kg ha^{-1} in the first year alone. Parker, Young and Chilton (1991) note that current estimates of the average leaching of nitrate under arable land are equivalent to about 25% of applied nitrogen. This lower figure may relate in part to the indirect benefits of the recent moves to autumn-sown cereals and to the use of minimal cultivation techniques, both of which might reasonably be hoped to reduce leaching losses in winter.

Apart from the ploughing up of grassland, many studies in the 1970s concluded that nitrate leaching losses were low under grassland. However, in many cases such studies were confined to unimproved or unfertilised grassland, and recent studies have shown that nitrate concentrations found under grazed grassland are often greater than those found under

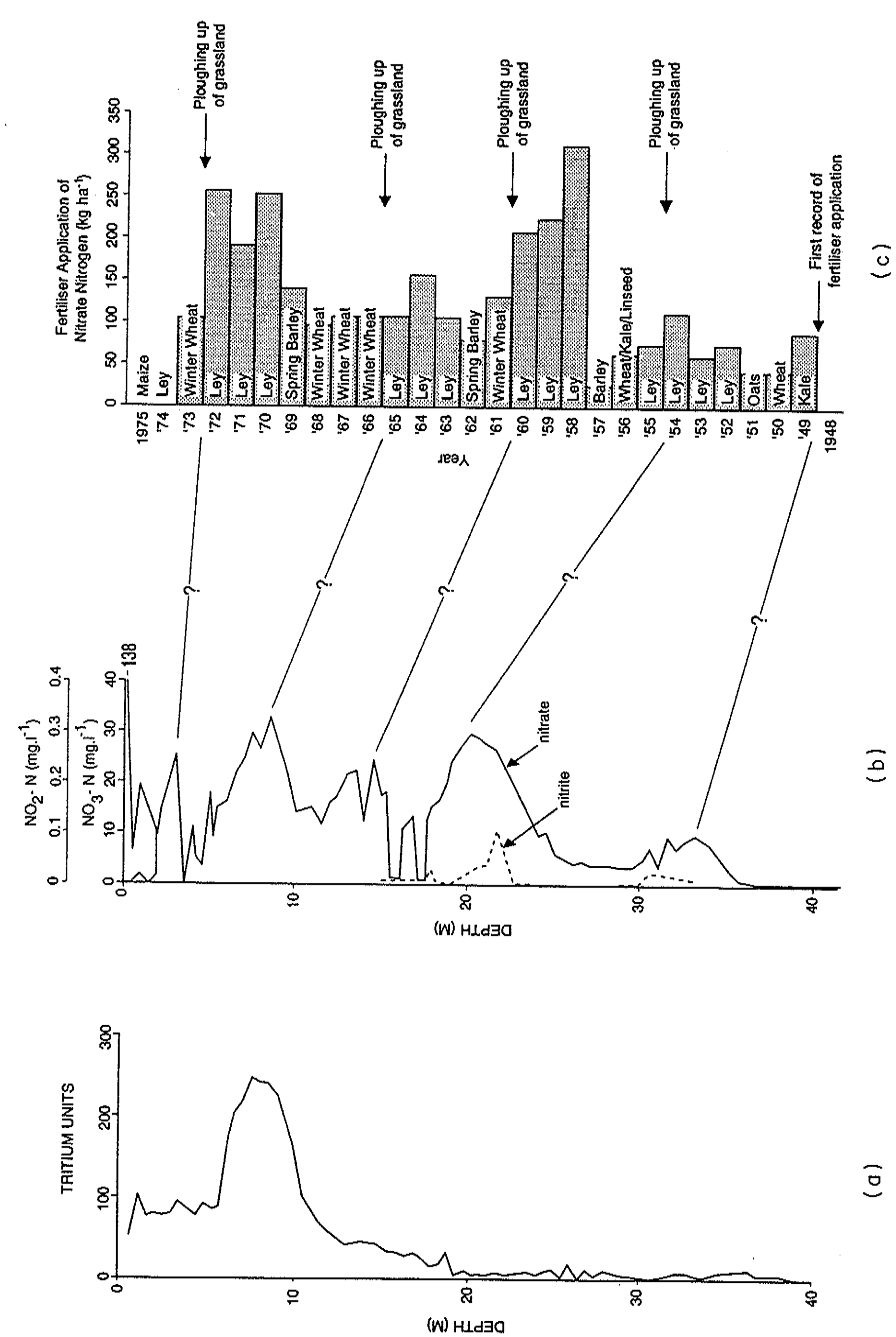

Figure 8.5 Tritium (a) and nitrate (b) profiles, together with land use since 1949 for land in the vicinity of the boreholes (c) for a site on the Chalk near Winchester (based on Young, Hall and Oakes, 1976, by permission of WRc)

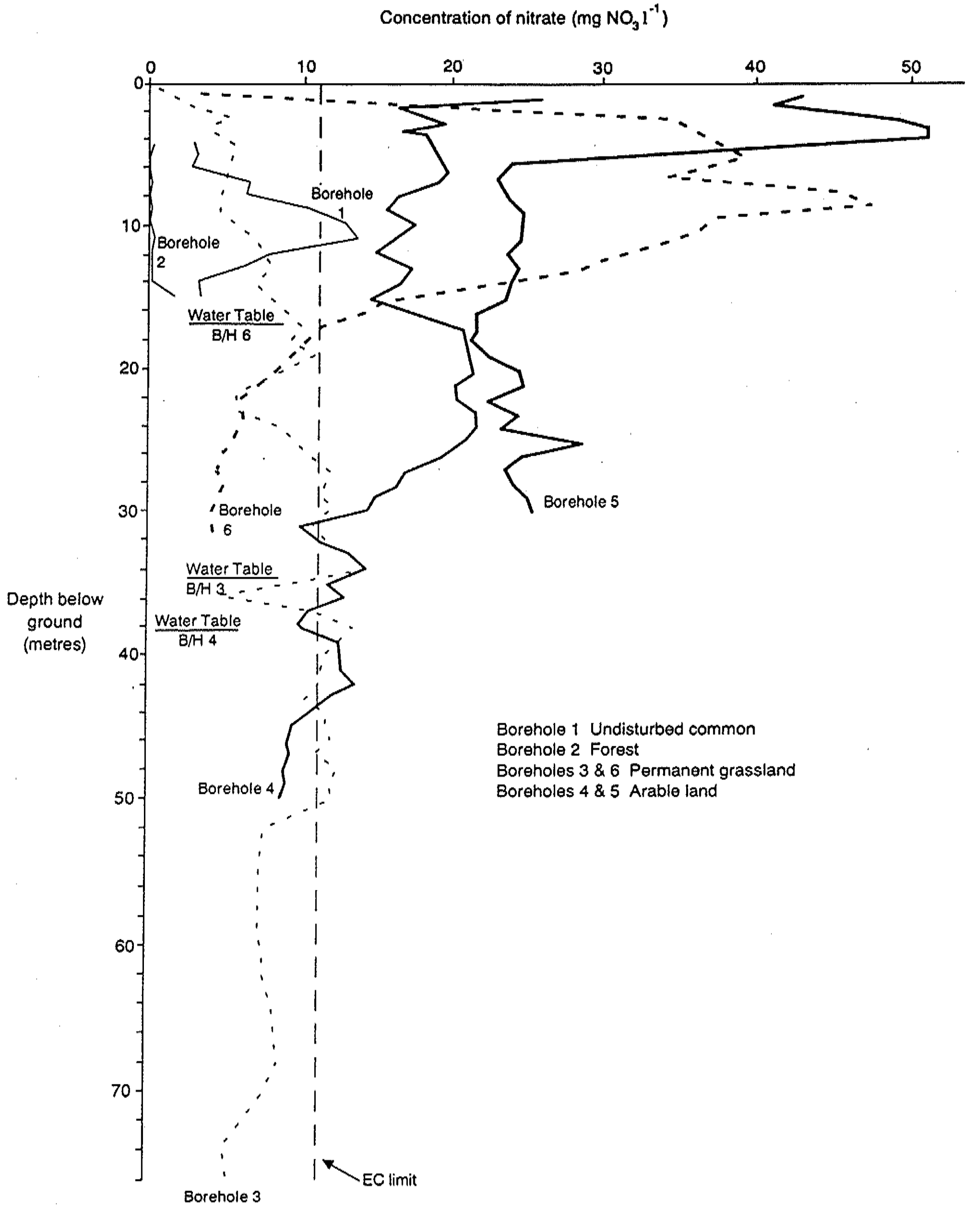

Figure 8.6 Nitrate profiles of cored boreholes in the Hatton catchment study area (reproduced by kind permission of the National Rivers Authority, Severn-Trent Region)

intensively managed arable land (Parker, Young and Chilton, 1991). Grassland production responds more to higher rates of fertiliser application than do most other crops. Optimum rates of application are in the range 350–450 kg N ha^{-1} a^{-1} and have increased considerably over the last 30 years. Ryden, Ball and Garwood (1984) emphasised the possibility of significant leaching from intensively managed, grazed grassland; they estimated an equivalent leaching loss of 160 kg N ha^{-1} a^{-1} from an application of 420 kg N ha^{-1} a^{-1}, significantly

greater than that beneath a comparable cut grass sward from which most of the nitrogen is removed in hay or silage. Parker, Young and Chilton (1991) conclude that mean leaching losses are between 75 and 150 kg N ha^{-1} a^{-1} from intensively managed grazed grassland, equivalent to at least 20% of the applied nitrogen. Such losses are likely to give rise to nitrate concentrations above the EC maximum. As noted above, leaching losses from cut grass systems are low, typically around 10 kg N ha^{-1} a^{-1}, except where large amounts of fertiliser are added (applications over 250 kg N ha^{-1} a^{-1}), because most of the nitrogen is removed when the grass is cut.

8.2.4 EVIDENCE FOR N-CYCLING AND NITRATE LOSS

The transport of nitrate downwards through the unsaturated zone is likely to be similar to that of chloride and tritium, unless the processes of nitrification or denitrification take place, in which case the concentration of nitrate will change independently of any dispersive effects. Such processes cannot be discounted since the presence of both the required bacteria and suitable carbon substrates has been shown. Whitelaw and Rees (1980) found significant bacterial populations throughout the whole of the unsaturated zone of the Chalk. Nitrate-reducing and ammonium-oxidising bacteria were detected in substantial numbers at various horizons. Denitrification was identified beneath permanent grassland whereas the unsaturated zone beneath fertiliser arable land was essentially aerobic and little (if any) attentuation of nitrate by denitrification was occurring. They concluded that nitrate seems certain to be involved in biological reactions in the unsaturated zone of the Chalk, although quantification of the rate and extent of such reactions was not possible. Young, Hall and Oakes, (1976) took the occurrence of small concentrations of nitrite at various points within the Chalk to be an indication of biological activity at depth (Figure 8.5(b)). Moreover, the content of organic carbon in the form of carbohydrate was more than sufficient to support biological activity within the aquifer. Once again, however, they were unable to establish the extent to which denitrification has occurred or could take place. The general implications of such studies are that denitrification rates are low, since the unsaturated zone is predominantly aerobic, so that biological reduction of nitrate concentrations is likely to be minimal. However, in aquifers like the Chalk, with slow percolation rates through the unsaturated zone, significant rates of denitrification could influence the pattern of decreasing nitrate concentration with depth.

8.3 NITRATE MOVEMENT IN THE SATURATED ZONE

The distinction is often made between unconfined and confined groundwater because of hydraulic differences between the flow of water under pressure in a confined aquifer and the flow of free, unconfined groundwater. In the case of unconfined groundwater, the upper boundary of the zone of saturation is the water table; its shape tends to follow that of the overlying topography, albeit in more subdued form. Recharge to an unconfined aquifer takes place directly by percolation from the land surface above. In the case of a confined aquifer, the upper boundary of the water body is formed by an overlying, less permeable bed which prevents direct recharge from above. Recharge to a confined aquifer can only take place at those locations where the aquifer is unconfined; hence the distinction drawn above is, to some extent, an arbitrary one (Ward and Robinson, 1990).

In order to forecast nitrate concentrations from groundwater sources, research has been carried out to determine the input, migration and attentuation of nitrate within the saturated zone. The input of nitrate to the saturated zone via percolation was considered in the previous section. Research on the saturated zone has included detailed catchment investigations in unconfined aquifers to establish the origin and distribution of nitrate within the saturated zone and to understand the factors controlling the concentration of nitrate in groundwater supplies (whether pumped supplies or spring-fed). Investigations in confined aquifers have sought to understand the origin and security of low-nitrate groundwater; these studies have necessarily included consideration of the transition zone between the unconfined and truly confined parts of the aquifer (Parker, Young and Chilton, 1991).

8.3.1 UNCONFINED AQUIFERS

The precise pattern of nitrate leached from soils into the aquifer below is rarely known, but lysimeter studies suggest that the highest nitrate concentrations occur in autumn and early winter, this nitrate being derived from mineralisation of the soil biomass. Later in the winter, concentations tend to fall as the nitrate available for leaching becomes less (see Chapters 3 and 9). Nitrate concentrations in groundwater increase immediately and rapidly with the first infiltration of soil drainage water into the aquifer in autumn. Both groundwater levels and nitrate concentration rise to a peak in late winter; thereafter both decline through the spring and summer until further recharge takes place. Such marked seasonal fluctuations tend to happen even in aquifers with a generally deep unsaturated zone, indicating that rapid recharge to the saturated zone must take place locally, most usually in valleys where depth to the water table is least. The dispersion of nitrate from the autumn peak in infiltration to the winter peak in the saturated zone may happen for several reasons (Smith-Carington *et al.*, 1983): dilution by pre-existing groundwater, diffusion exchange with immobile pore water and slow movement of a component of the infiltrating water through the upper part of the permanently saturated zone.

The distribution of nitrate within the saturated zone depends on several factors: the depth of the unsaturated zone, the saturated hydraulic conductivity of the aquifer, the degree to which any pumping induces vertical groundwater flow, and lithological variations within the aquifer. Parker, Young and Chilton (1991) report the case of the Sherwood Sandstone in Yorkshire (England): the unsaturated zone is thin (about 10 m), encouraging rapid recharge, and deep penetration of nitrate into the sandstone is thought to occur as a result of groundwater abstraction from boreholes drilled down to the bottom of the aquifer. The occurrence of major fissuring in a rock and the presence of less permeable beds may block or attentuate the downward movement of polluted water. The Chalk limestone is generally more fissured in its upper levels, so that significantly higher nitrate concentrations occur than in the less-fissured rock below. In the Lincolnshire Limestone, the Kirton Cementstones appear to act as an important aquiclude between the upper and lower limestone beds, creating chemical stratification between the two aquifers. Where they occur, faults allow transfer of groundwater between the two limestone aquifers, and the boreholes themselves may act in a similar way (Smith-Carington *et al.*, 1983).

The occurrence of stratified groundwater can cause uncertainty in terms of the effectiveness of water sampling from boreholes. The nitrate content of pumped samples can vary according to borehole depth, length of solid casing, intersection of fissure flow, the proportion of inflow from various depths in the aquifer and the degree to which changes in the pumping regime

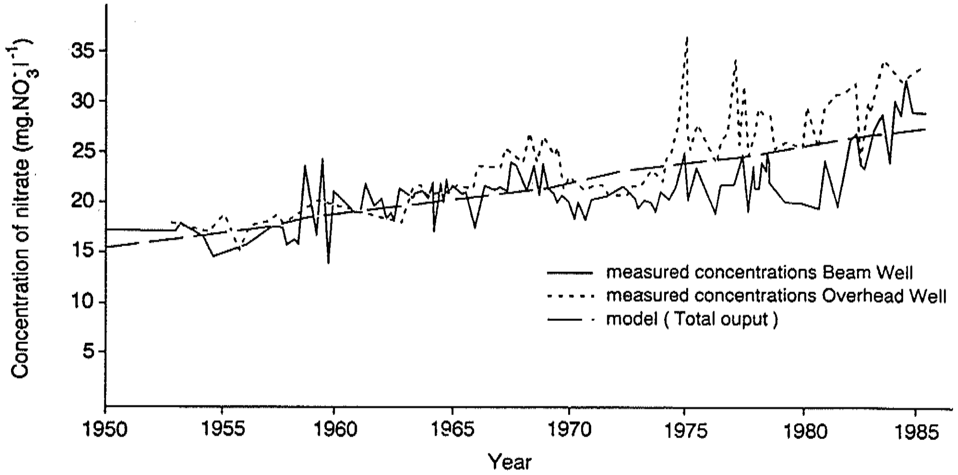

Figure 8.7 Nitrate concentrations for two wells in the Hatton catchment, 1950–1986 (reproduced by kind permission of the National Rivers Authority, Severn-Trent Region)

cause water to be withdrawn from different levels in the aquifer. For the early detection of diffuse pollution from agricultural sources, sampling from shallow depths in the aquifer will be most effective (Parker, Young and Chilton, 1991). Sampling from boreholes which fully penetrate an aquifer is suspect since samples are likely to represent an integrated value of concentrations of contaminants for the thickness of saturated aquifer that has been penetrated. By contrast, interstitial water extracted from cores recovered from beneath the water table may reflect more accurately the composition of water at various levels (Young, Hall and Oakes, 1976). Water taken from neighbouring boreholes may well yield different nitrate concentrations, although exhibiting similar trends, if the water is drawn from different depths in the aquifer. An example of this is given in Figure 8.7.

The concentration of nitrate in a groundwater sample from beneath a particular investigation site is a function not only of the concentrations entering the saturated zone by vertical drainage but also of the additions to the groundwater in an up-gradient direction. This laterally flowing water may be of higher or lower nitrate content so that at a given site the infiltrating groundwater may become more concentrated or more dilute. If vertical mixing within the saturated zone is minimal, inputs of differing concentrations to the water table along a flow path may remain distinct for some distance, leading to vertical variations in concentration below the water table (Young, Hall and Oakes, 1976). Figure 8.8 shows a section through the Chalk parallel to the groundwater flow lines; a single borehole has been drilled into the saturated zone. The section shows that the unsaturated zone is of variable thickness. Young, Hall and Oakes (1976) postulate that the higher concentrations of nitrate at 3 m depth below the water table demonstrates the earlier arrival of higher concentrations of nitrate in interstitial water from an area of reduced unsaturated zone thickness upgradient of the borehole. Young, Hall and Oakes (1976) used their model to predict the rate at which nitrate already in the unsaturated zone and future surface inputs would move down to the water table in response to infiltration. Estimates of the expected nitrate concentrations in groundwater were obtained from a catchment model in which infiltrating water and nitrate were routed through the

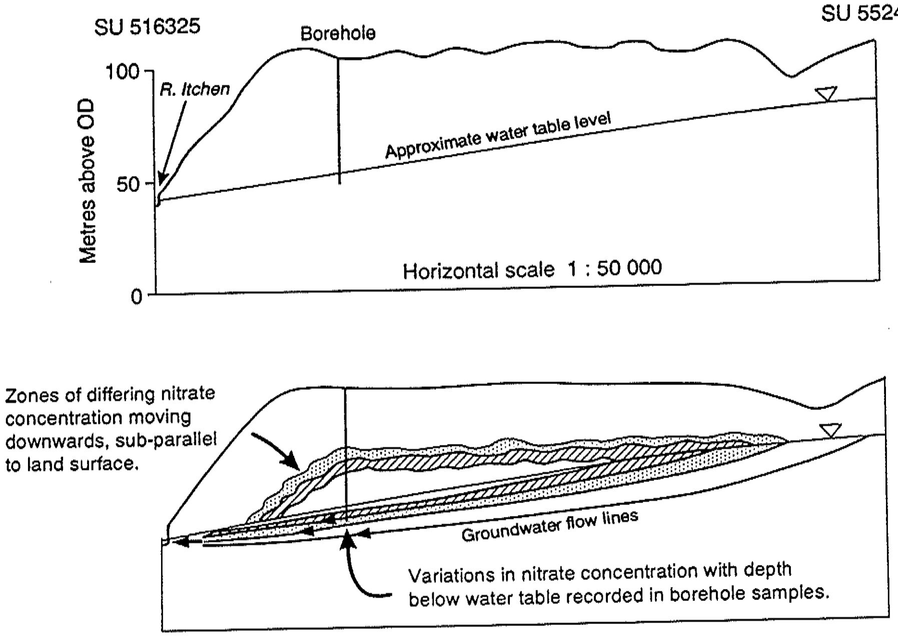

Figure 8.8 Section parallel to groundwater flow through the Chalk near the Itchen valley, Hampshire, England (above) and sketch showing postulated mechanism responsible for variation in nitrate concentration with depth below water table at the borehole (from Young, Hall and Oakes, 1976, reproduced by permission of WRc)

saturated zone of the aquifer. A vertical flow model was used to estimate the nitrate flux across the water table from 1950 to 2030 with the assumption that past agricultural practice and infiltration rates would be repeated cyclically in the future. A downward migration rate through the unsaturated zone of 1 m per annum was assumed. Because of the large difference in the hydraulic conductivities between the saturated and unsaturated zones, times of transit through the saturated aquifer were estimated to be small in comparison, having a maximum of about 5 years. Model predictions of the nitrate concentration of water reaching the water table in the vicinity of the borehole and for the mean nitrate concentration in groundwater beneath the borehole are shown in Figure 8.9. The steady rise in groundwater concentration from 1970 onwards is the result of contributions from up-gradient zones where the unsaturated thickness is less than at the borehole. The large depth of the unsaturated zone at the borehole site means that the increase in nitrate concentration of water entering the saturated zone at that point lags considerably behind the overall response of the groundwater.

8.3.2 CONFINED AQUIFERS

To date, the impact of agricultural pollution on confined aquifers in the UK has been small and groundwater in these aquifers is generally characterised by low or zero nitrate concentrations (Parker, Young and Chilton, 1991). The importance of such aquifers is not the volume of water which such sources provide but the fact that they are an important source of low-nitrate water which can be used to blend with polluted supplies from unconfined aquifers. This is especially important in the east of England where supplies of low-nitrate

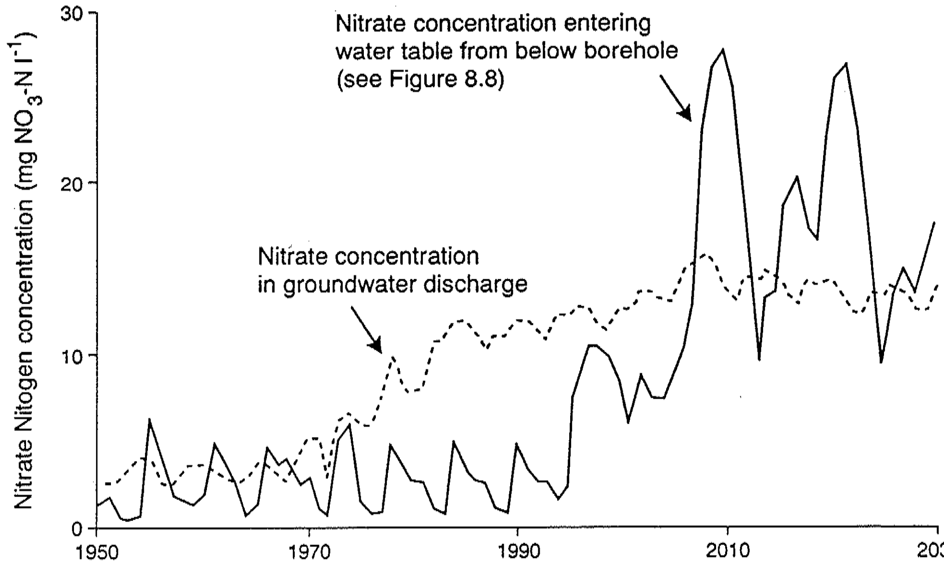

Figure 8.9 Model predictions of nitrate concentration in water reaching the water table for the borehole site shown in Figure 8.8 (from Young, Hall and Oakes, 1976, reproduced by permission of WRc)

water for blending are increasingly rare. Not surprisingly, the principal focus for research has been the security of such supplies. A major concern is that the significant pollution noted in recent years in the unconfined sections of certain aquifers will migrate into the confined strata. In some cases, the flow direction is naturally down-dip from the unconfined outcrop at higher elevation to the confined strata at lower elevation. In other cases, pumping may establish a hydraulic gradient towards the confined layer.

A front of groundwater contaminated by agrochemicals has migrated into the confined section of the Lincolnshire Limestone (Figure 8.10); tritium in the pore water proves this water to be recent in origin. Nitrate and dissolved oxygen diminish to negligible concentrations some 10 km from the edge of the aquifer outcrop. Dissolved oxygen concentrations gradually fall due to bacterial demand and also as a result of oxidation of finely disseminated pyrite and other ferrous minerals (Edmunds and Walton, 1983). This reduction in dissolved oxygen apparently provides a stimulus for the process of denitrification. Pore water samples from a borehole some 4 km from the outcrop contain significant nitrate which demonstrates that diffusion from the fissure water to the limestone matrix occurs (Parker, Young and Chilton, 1991). Much lower nitrate concentrations were found in pore water at greater distances into the confined aquifer. However, significant tritium concentrations were found in this water, which indicates that the water is of modern (post-1963) origin and should theoretically have contained nitrate also. The absence of this associated nitrate implies that denitrification is occurring. Smith-Carington *et al.* (1983) argue that the decreasing nitrate concentrations across this zone could not be the result of bacterial denitrification, since the relevant bacteria, even if present in sufficient numbers, would be unlikely to denitrify in the presence of dissolved oxygen. They argue that the major attenuation of nitrate in the marginally aerobic zone, and the relatively small increases in the decade 1969–79 (Edmunds and Walton, 1983), may be due primarily to transient dilution resulting from the diffusion of nitrate into the rock matrix. Bacterial denitrification would be more likely further down-gradient, beyond the point where

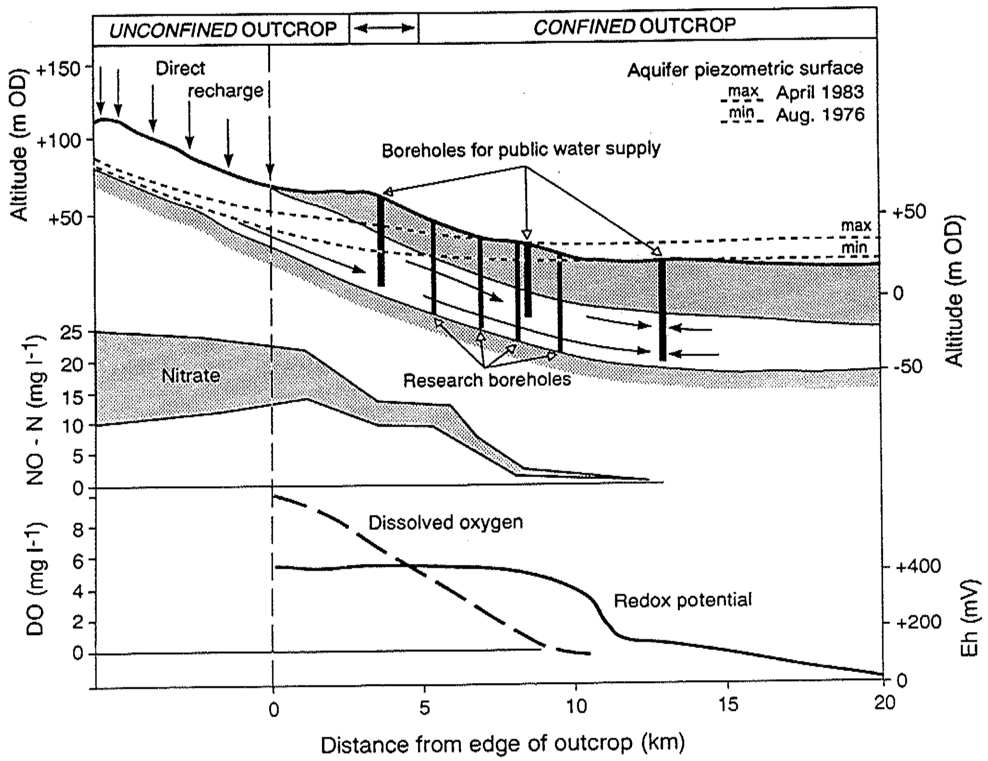

Figure 8.10 Down-dip hydrogeological and hydrochemical section through the Lincolnshire Limestone of south Lincolnshire (after Smith-Carington *et al.*, 1983; Parker, Young and Chilton, 1991)

there is a sharp reduction in Eh below 400 mV (Sprent, 1987, p. 61); the decrease in sulphate concentrations beyond 18 km suggests reduction via anaerobic microbial respiration. However, the parallel decrease of dissolved osygen and nitrate concentrations does imply that denitrification processes are also active in the marginally aerobic zone upstream of the Eh boundary. This might occur because of deoxygenation of micropore water, despite the availability of oxygen close by in the larger fissures; this situation is also thought to occur in soils (Umarov, 1990). A similar pattern to that shown in Figure 8.10 is reported by Parker, Young and Chilton (1991) for the Sherwood Sandstone aquifer. Despite 10 years of abstraction, there has been virtually no movement of nitrate polluted water from the recharge area of the outcrop into the confined aquifer.

There is obviously still much uncertainty about the potential role of denitrification in confined aquifers. Nevertheless, a continued supply of low-nitrate water from these aquifers depends on the effectiveness of the processes of oxygen removal and nitrate reduction.

8.3.3 MODELLING STUDIES

In the UK, the mathematical model developed by the Water Research Centre has been extensively used to model nitrate movement in groundwater (Oakes, 1982, 1987). The groundwater catchment is divided by a grid into square cells, with an edge length of 0.25 km. The simulation involves in three stages with the calculation of:

(1) Nitrate leaching losses from the soil zone to the underlying aquifer;
(2) Transport of water and nitrate through the unsaturated zone to the water table; and
(3) Transport of water and nitrate through the saturated zone to pumping wells or springs (DOE, 1986).

The model is run in two parts: in the first, the movement of water through the aquifer is calculated; in the second part, the quantity of nitrate carried by the water is estimated. Leaching losses of nitrate are calculated from a simple set of rules which identify different types of crops with the average annual loss expressed as a percentage equivalent of the nitrate applied (see Table 12.2). These rules, derived from evidence such as that presented in Section 8.2, have been the subject of some criticism (Addiscott and Powlson, 1989) and it is likely that future versions of the model will incorporate physically based leaching models such as that of Addiscott and Whitmore (1991) and Whelan (1992). The fissure flow and molecular diffusion processes described in Section 8.2 are incorporated into the unsaturated zone component of the model. Nitrate which has reached the water table is assumed to move horizontally towards springs and pumping wells at velocities and in directions determined by groundwater gradients. A necessary prerequisite to running the nitrate model is to run the corresponding groundwater flow model to provide the groundwater gradients (Oakes and Pontin, 1976). To calculate the diluting effect of recharge water mixing with water from the saturated zone it is necessary to assume an effective depth of flow in the aquifer over which this mixing occurs (DOE, 1986). The model has been used extensively to predict future nitrate trends in groundwater and to assess the impact of land-use changes on those trends (DOE, 1986; STW, 1988). In the case of the Hatton catchment study (STW, 1988), the model results have been combined with a financial analysis to indicate the benefits and costs of particular solutions (see also Chapter 12).

8.4 PATTERNS OF NITRATE DISCHARGE FROM AQUIFERS

8.4.1 ANNUAL REGIME

Discharge from aquifers may be via springs, diffuse seepage into streams and lakes, or from pumped wells. Depending on the nature of the aquifer, peak groundwater discharge may lag significantly behind precipitation inputs. There is a continuum of rainfall–runoff responses: cavernous (karst) limestones and thin aquifers provide the most rapid, peaked groundwater hydrographs while deep aquifers like the Chalk yield the most subdued and lagged hydrographs. Deep aquifers such as the Chalk have low flows only slightly below the mean flow because the response time for discharging water in storage is comparable to the time between wet and dry seasons. In such aquifers, there will be a long lag before a discharge increase occurs in response to the reasonal recharge, with a slow rise to the peak groundwater discharge and a low rate of recession (Burt, 1992). However, even in a deep aquifer like the Chalk, groundwater discharge is noticeably seasonal. One result of this is that many headwater streams are seasonally ephemeral. Prolonged summer discharge lowers the water table to such an extent that the source of the river migrates several kilometres downstream. Autumn recharge eventually raises the water table and the intermittent ('bourne') stream reappears, though perhaps not until several months after the main period of rainfall.

The seasonal variation in groundwater discharge is in many cases paralleled by a similar fluctuation in nitrate concentration; usually the two are positively correlated (see also Sections

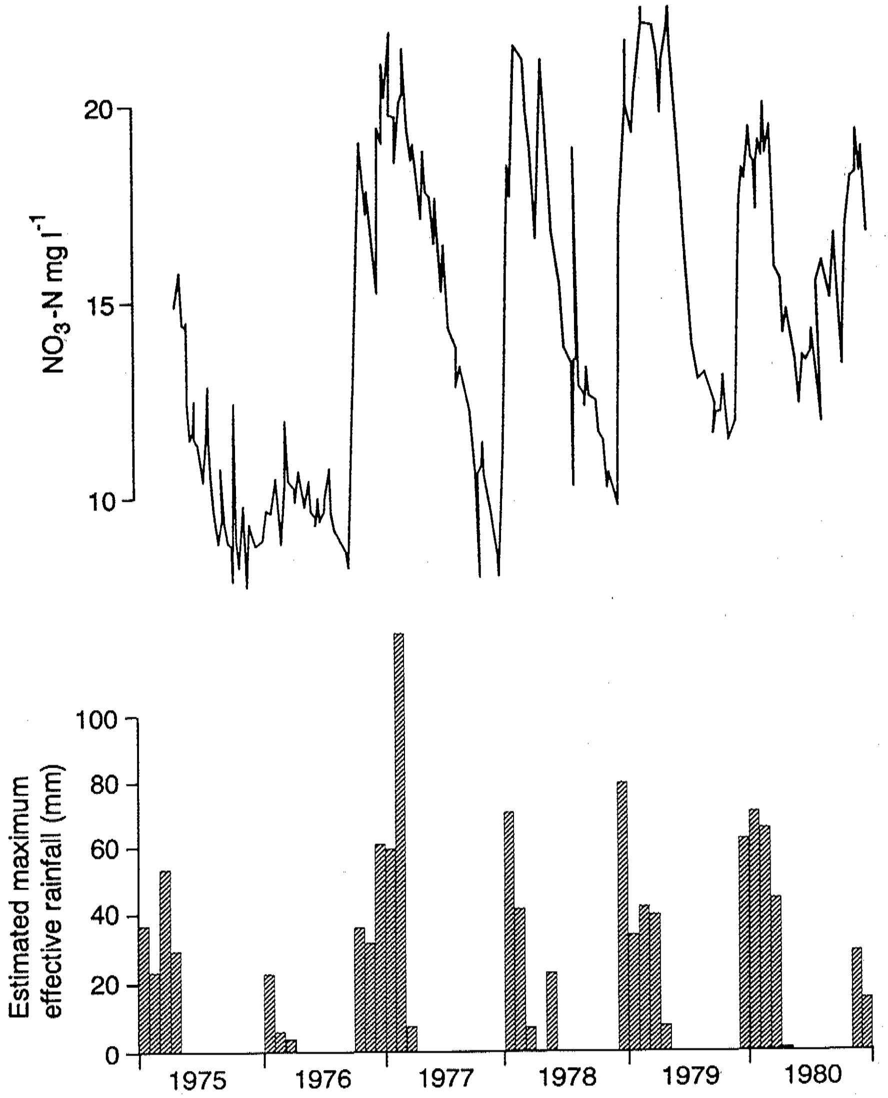

Figure 8.11 Nitrate concentrations from a public supply well in the Lincolnshire Limestone (after Smith-Carington *et al.*, 1983)

10.3 and 12.4). Groundwater discharge and nitrate concentration often increase sharply with the first recharge to the water table in late autumn or early winter; both then rise to peak in middle to late winter and thereafter both decline through the spring and summer until further recharge takes place. Figure 8.11 provides an example of marked seasonal fluctuations in the nitrate concentration of borehole water in the Lincolnshire Limestone. The sharp increases in nitrate concentration in the autumn, particularly after the drought of 1976, are especially notable. By contrast, in the previous winter, which was remarkably dry, minimal leaching of soils took place and there was little increase in the nitrate concentration of groundwater during that winter as a result.

As noted above (Section 8.3.1), the attenuation of nitrate from a sharp autumn peak in infiltration to a winter peak in discharge may happen for several reasons, notably because of dilution by pre-existing groundwater and dispersion as the infiltrating water percolates through the rock. Peak discharge often precedes peak nitrate concentration because the flood peak propagates more rapidly through the aquifer than the movement of the water itself and its solute load; dispersion may further delay the nitrate peak. The relationship between percolation and groundwater discharge is shown schematically in Figure 8.12 (which is based in part on Figure 12.6).

Results from Haigh and White (1986) and from Roberts (1987) show a decrease in the nitrate concentration of soil drainage water through the winter. The seasonal pattern of groundwater discharge is based on results from Burt *et al.* (1983), Burt and Arkell (1987) and Haycock (1991). A strongly seasonal response is seen even for a deep aquifer like the Chalk: over most of the aquifer, recharge is considerably delayed by the great depth of the unsaturated zone, but in the valleys, where depth to the water table is much less, recharge to the water table is rapid and the linkage between infiltration and discharge is clear.

Many examples exist in the published literature which show the annual nitrate regime for groundwater-fed rivers. For example, Casey and Clarke (1979) examined weekly nitrate samples for the river Frome which drains a Chalk catchment in southern England. Using multiple regression analysis they found that weekly nitrate concentrations over an 11-year period could be explained most successfully using a linear trend to describe the long-term increase and a cosine function to describe the seasonal variation. Discharge was a less useful independent variable. Although discharge was closely related to the seasonal variation in nitrate concentration when both were based on weekly data averaged over several years ($r = 0.858$), the individual discharges and nitrate concentrations were much less closely related, because both can vary considerably and independently from week to week. There is further discussion of the annual nitrate regime in rivers in Sections 10.3.1 and 12.4.

8.4.2 STORM HYDROGRAPHS

Except for cavernous limestones, it is unusual for aquifers to provide flood hydrographs. If there are no significant sources of overland flow, floods may be generated by groundwater. Otherwise high discharges are generated by surface and near-surface runoff processes and groundwater provides the prolonged recession flow associated with the falling limb of the hydrograph.

A number of studies of hillslope hydrology have identified the occurrence of double-peaked storm hydrographs (Dunne, 1978). In addition to an immediate runoff response at the time of the rainfall, a second hydrograph peaking several days after the rainfall input can occur in some basins, especially in the winter when soil moisture deficits are minimal. The second peak is entirely subsurface flow. Such hydrographs are usually the major volumatric response and may also provide the peak discharge. Burt and Butcher (1985) have analysed the occurrence of such hydrographs in catchments where permeable soils overlie impermeable bedrock. The delayed hydorgraph has also been identified as a time of maximum nitrate concentration (Burt *et al.*, 1983; Burt and Arkell, 1987). Given the coincidence of high discharge and high nitrate concentration, this means that such hydrographs can represent the major period of nitrate loss from a catchment (see also Section 9.4). Haycock (1991) has identified a similar runoff response for a small basin draining the Cotswold Limestone (a southern version of the Lincolnshire Limestone discussed above). The results in Figure 12.6 (p. 360 below) show

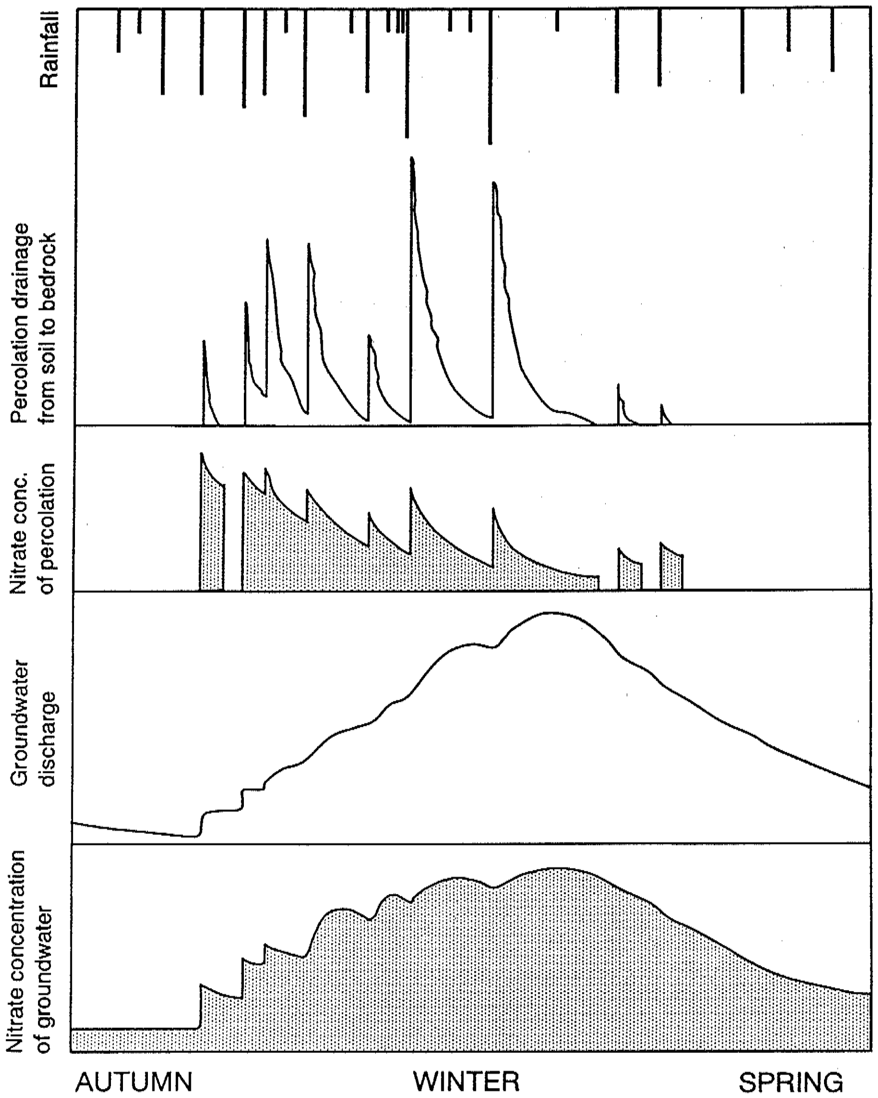

Figure 8.12 Schematic diagram showing percolation drainage into and discharge out of an aquifer. Also shown are the nitrate concentrations of percolation and discharge waters

that a thin aquifer can produce individually recognisable storm hydrographs and that each delayed hydrograph is associated with enhanced nitrate leaching. It is clear that deep throughflow in permeable soil and shallow groundwater flow may produce identical hydrological responses, and the distinction between the two is therefore necessarily an arbitrary one.

8.4.3 LONG-TERM TRENDS

Many groundwater sources in the UK have shown a steady rise in nitrate concentration since the 1960s, which must reflect post-war changes in farming practice. Smith-Carington *et al.*

(1983) note that there are several possible causes of a rising trend but that their relative importance is difficult to assess. If agricultural changes are slow, it is to be expected that nitrate concentrations will also respond slowly. However, in aquifers with a deep unsaturated zone, the effects of even relatively sharp increases in nitrate leaching associated with modern farming methods may be greatly attenuated by slow percolation through the unsaturated zone. Even where nitrate reaches the saturated zone quickly, diffusion of nitrate into the immobile storage could lead to an attenuation of surface-derived nitrate in the mobile fissure water.

In many cases, detailed sampling of groundwater and rivers in the UK began in 1975; the limited amount of data and the unusual meteorological sequence at the beginning of the period make trend analysis difficult. Johnes (1990) examined the nitrate concentrations for the river Windrush which drains an area of Cotswold Limestone in the upper Thames basin. For thin aquifers, where there is intimate linkage between recharge and discharge, it is possible to distinguish between the effects of climate and land-use change in relation to the changing nitrate concentration of groundwater. Using partial correlation analysis, Johnes (1990) showed that the annual mean nitrate concentration of the Windrush was most successfully explained by a long-term trend. The year number (*Anno Domini*) was used in the regression to denote the time trend; this variable alone accounted for 73% of the explained variance in nitrate concentration. Discharge, though significantly correlated with nitrate concentration, alone accounted for only 20% of the explained variance in annual mean nitrate concentration. A small joint effect (7%) indicated that higher nitrate concentrations had occurred in later, wetter years. These results mirror those found by Burt *et al.* (1988) for the Slapton Wood catchment and suggest that changes in land use provide a more significant explanation of changing nitrate concentrations over recent times than do climatic conditions. Further discussion of long-term trends is to be found in Section 10.3.3.

8.5 CONCLUSIONS: PREVENTION OR CURE?

Considerable quantities of freshwater are stored naturally in permeable strata. In England and Wales, the most important aquifers are the Chalk and the Sherwood (Triassic) sandstone which together yield about 60% of the groundwater abstracted; groundwater supplies 35% of the water used for public supply. Where groundwater is available in sufficient quantities, it is generally preferred as a source of water because of its low cost, good quality, relatively constant temperature and the fact that it is not so susceptible to pollution as surface storage (Rodda, Downing and Law, 1976). However, as the evidence reviewed above demonstrates, the security of groundwater is now under threat. Over the last two decades, nitrate concentrations in some groundwater sources have risen to levels which may intermittently or continuously exceed the EC limit of 11.3 mg NO_3-N l^{-1} (e.g. Figure 8.5). It is such nitrate concentrations, and the upward trend, which are of concern to the UK water industry, which has initiated a programme of field and laboratory investigations designed to determine the extent of nitrate contamination in the unsaturated and saturated zones of the principal aquifers; to evaluate the mechanisms and rates of movement of nitrate derived from the land surface; and to estimate future trends in groundwater nitrate concentrations (Royal Society, 1983). Investigations have revealed large concentrations of nitrate in the unsaturated zones of the principal aquifers. The evidence indicates that this nitrate is moving slowly downwards towards the main groundwater body. The slow rate of percolation and the great depth of the unsaturated zone mean that maximum nitrate concentrations in many supplies may not occur until well the twenty-first century (Figure 8.7). By then, the nitrate concentration of groundwater will be well above the current EC maximum acceptable concentration in some cases.

Two possible strategies are available to control nitrate concentrations in potable waters obtained from aquifers. Curative engineering solutions include blending of waters from different sources, installation of treatment processes for nitrate removal from water supplies (Chapter 13) and the relocation of wells within the confined sections of an aquifer. Recently much more attention has been given to preventative measures which tackle the problem at source (Chapter 12). In the Hatton Catchment Study (STW, 1988) a computer simulation model (Oakes, 1987) was used to assess options for the control of nitrate in water supply. The simulations showed that, unless there is a change in land-use practice, groundwater in the Hatton area will exceed the EC nitrate limit early next century. Blending supplies could defer the impact, but it will eventually be necessary to install a treatment plant to remove nitrate. Chemical treatment could be avoided if land use in the catchment is modified to reduce the amount of nitrate being leached. In the Hatton area it would be relatively cheap to provide blending and treatment; even so, the costs are not significantly less than solutions involving land-use controls. In other areas where favourable engineering solutions are not available, options involving a modification of land use might well offer clear financial advantages. In the Hatton catchment, a small 'local protection zone' was favoured, largely on practical grounds, as the means to control land use. This would impose stringent land-use controls on a small area in the vicinity of the borehole. Catchment-wide restrictions would be more expensive to implement and police; though they have a lower financial impact on individual farmers, the total cost can be greater.

The Hatton Catchment Study did not consider the social implications of the possible land-use changes, though these could be significant. Nor did it take account of wider issues of agricultural and environmental policy, the costs and benefits which may be associated with these or the question of who should pay compensation to farmers for loss of income. DOE (1988) also favoured a local protection zone policy and concluded that it would be in the national interest to compensate farmers for income lost in complying with the restrictions imposed in a local protection zone. Though water treatment may be the marginally cheaper option, other considerations, such as more strategic use of funds already being used to take farmland out of production, may favour the land-use change option. On this basis, the UK has introduced a pilot Nitrate Sensitive Area scheme (Section 12.3.3) aimed at controlling land use around selected boreholes. This scheme marks the first concerted attempt by government to use agricultural restrictions to prevent the pollution of groundwater supplies. This theme is explored in greater detail in Chapter 12.

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