The Vulnerability of British Groundwater Resources to Pollution by Agricultural Leachates

S.S.D.Foster
Institute of Geological Sciences,
Hydrogeological Department,
London.

Summary

The outcrops of the major British aquifers, the Chalk and the Permo-Triassic Sandstones, form extensive tracts of valuable agricultural land in central, southern and eastern England. Their groundwater resources in the main originate as rainfall which infiltrates farming land in these areas. As such they are, and always have been, directly vulnerable to diffuse pollution by agricultural practices.

Evidence of widespread pollution at significant or serious levels is mainly limited to nitrate, but the monitoring of many sources is rather scanty. Rapid rises of NO_3-N in groundwater supplies from various parts of eastern England since 1968–70 are the greatest cause of current concern; for the most part these rises are in regions of intensive cereal growing.

The interpretation of the chemistry of water supplies pumped from an aquifer requires considerable caution, since their origin is liable to be complex. Many misconceptions result from a lack of understanding of the groundwater flow regime both above and below the water-table. A major part of the paper is thus devoted to a review of the physical properties, chemical characters and hydrological regimes of the two major aquifers. The effect of stratification of recharge below the water-table in the deep Permo-Triassic basins and of slow intergranular seepage in the thick unsaturated zone of many Chalk aquifers *could mean* that only a small proportion of water supplies at present abstracted will be recent (post-1970) infiltration. Both effects require further study; the Chalk unsaturated zone, in particular, being a highly controversial topic. *But,* if small components of recent infiltration do prove responsible for the recent increases, then these rises might be only 'the tip of the iceberg' as far as NO_3-N levels in groundwater supplies are concerned.

The nature of groundwater systems, and the British aquifers in particular, is such that monitoring of the chemistry of water supplies alone is an inadequate basis, albeit the only one currently employed, for the management of groundwater quality.

Significance of groundwater in British water supply

Some 25–30 per cent of all authorized water supply development in England and Wales is from groundwater resources. Coal mine drainage and cooling water for electricity generation are excluded from this estimate. If potable supplies only are considered then the proportion approaches 40 per cent.

Total groundwater development is in the order of 7,000 Ml/d; of this more than 50 per cent is derived from the Chalk and about 30 per cent from the Permo-Triassic Sandstones.

Although direct groundwater abstraction has in many places reached, and in some places surpassed, reliable yield calculated from the replenishment (Ineson, 1970), it is thought that by more effective deployment groundwater can satisfy about 25 per cent of the demand for new supplies anticipated to the end of this century (Water Resources Board, 1974). Fuller exploitation of the vast volumes of subsurface storage is the objective, in conjunctive use with surface water supplies, for river regulation by groundwater abstraction and by artificial groundwater recharge with surplus surface run-off.

The increasingly complex effluent load in many lowland rivers may threaten the potability of water supplies obtained from them, particularly through a wide variety of trace pollutants. It further strengthens the case for protection of the high quality of most groundwater supplies and the prevention of levels of pollution incompatible with potability.

In view of the importance of the Chalk and Permo-Triassic Sandstone formations in water supply at the national level, it is the intention to concentrate exclusively upon them in this paper. It should be noted in passing, however, that groundwater from other formations (Jurassic and Carboniferous Limestones, Cretaceous Greensands and Alluvial/Glacial Gravels) is significant in the local water supply of some areas.

The distribution of the Chalk Aquifer is shown in Fig. 1; in considering the risk of agricultural pollution the primary concern is with the groundwater intake areas, which are also volumetrically more important in water supply. They are essentially contiguous with the outcrop and comprise extensive wolds and downs in the counties of East Yorkshire, Lincolnshire, Norfolk, Cambridgeshire, Kent, Buckinghamshire, Berkshire, Wiltshire, Hampshire and Dorset. The Permo-Triassic Sandstones generally occupy lower-lying land, often have a thick cover of drift or superficial deposits (Fig. 1) and a more complex recharge regime.

Physical and chemical characteristics of the major aquifers

CHALK

The Chalk is a uniform, highly-pure and exceedingly fine-grained sequence of white limestones. The bulk of the rock is normally composed of fragments of calcareous microfossils (known as coccoliths) of 0·5–5·0 μm diameter (Plate I) together with scattered larger particles (mainly broken mollusc shells and foraminifera) of 20–100 μm diameter (Black, 1953). The overall lithology of the rock depends on the relative proportions of the above constituents and on diagenetic factors (Bathurst, 1971). Soft porous white chalks are composed principally of coccoliths and have fairly scant cementation (Hancock and Kennedy, 1967); they dominate the sequence in the 'southern depositional province' (as far north as Norfolk). Allowing for intragranular in addition to intergranular pore space, the total porosity on deposition probably exceeded 0·50 and in the case of the Upper Chalk of Berkshire for example, 0·45 is still preserved at some points in the sequence (Edmunds *et al.,* 1973). At occasional horizons (e.g., the Chalk Rock), hardgrounds formed with a porosity reduction to less than 0·15 by calcite

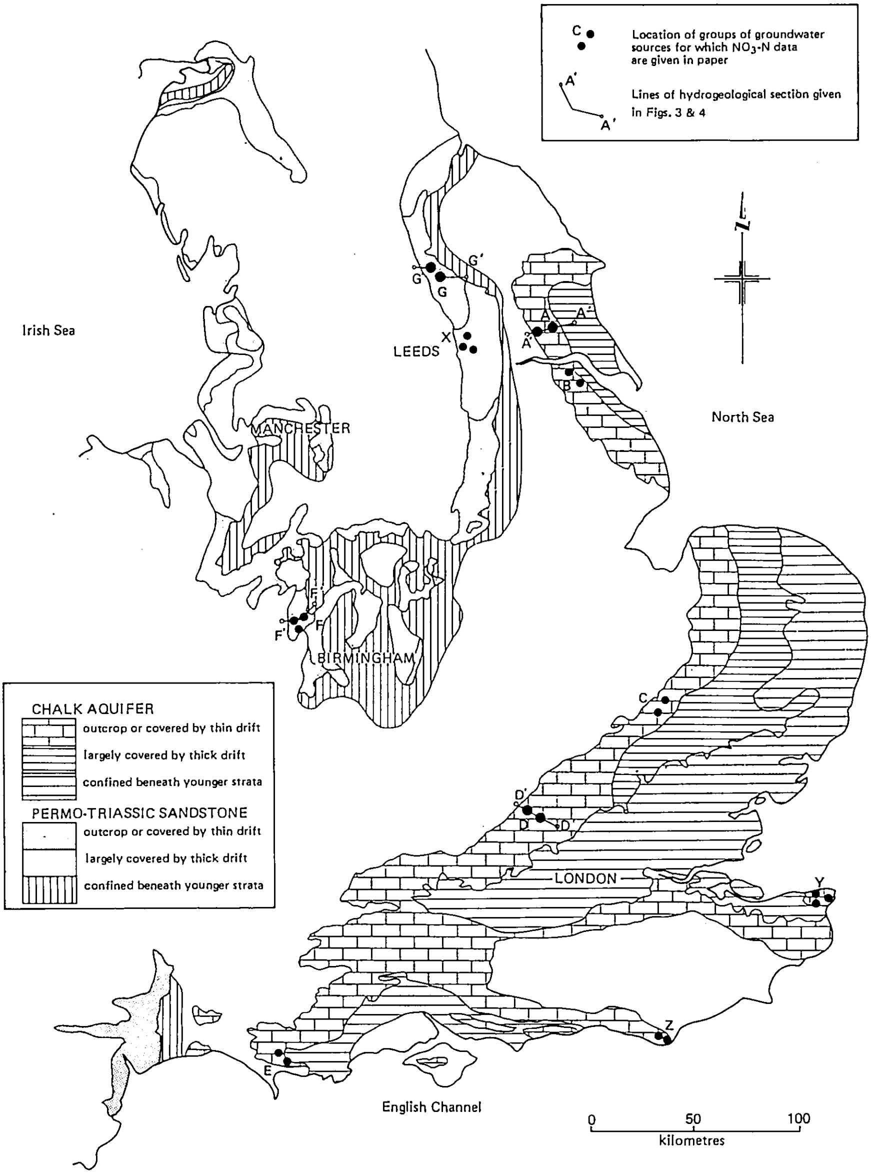


Fig. 1. Location map showing distribution of Chalk and Permo-Triassic Sandstone Aquifers.

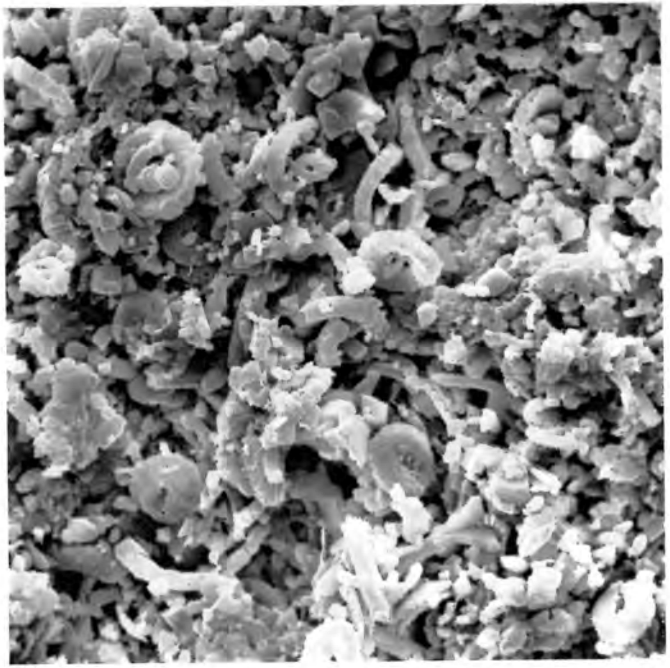


PLATE I

Electronmicrograph of a sample of Middle Chalk from a Berkshire borehole (overall width of field of view about 30μm)

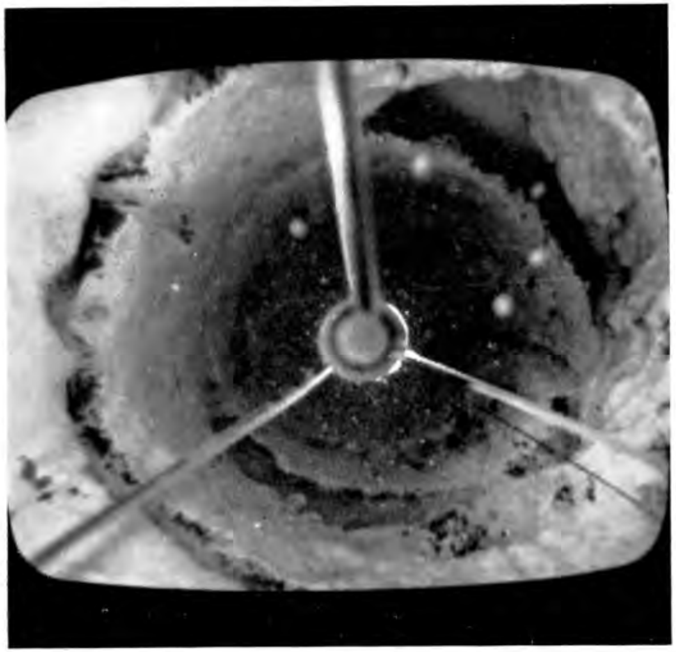


PLATE II

Axial cc tv view down a 900 mm diameter borehole in the Upper Chalk of Norfolk, showing fissure development on horizontal discontinuities

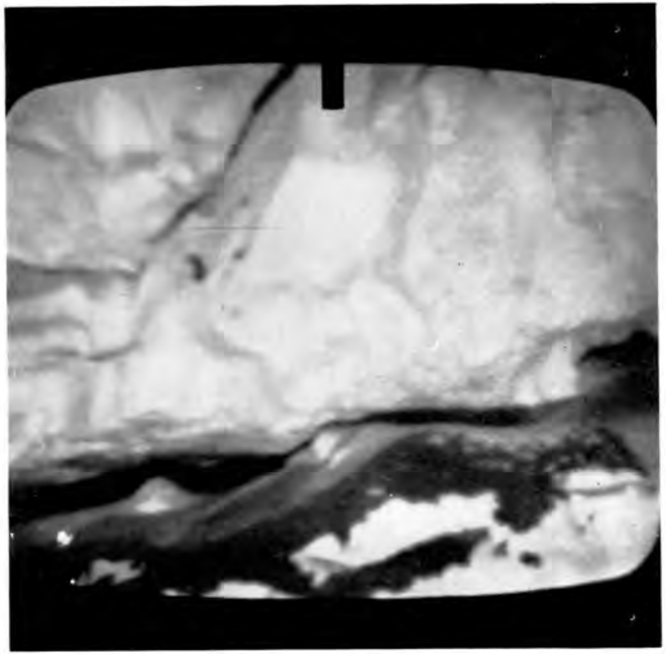


PLATE III

Radial cc tv view of part of a single fissure from Plate II with marl seam below (overall width of field of view about 150 mm)

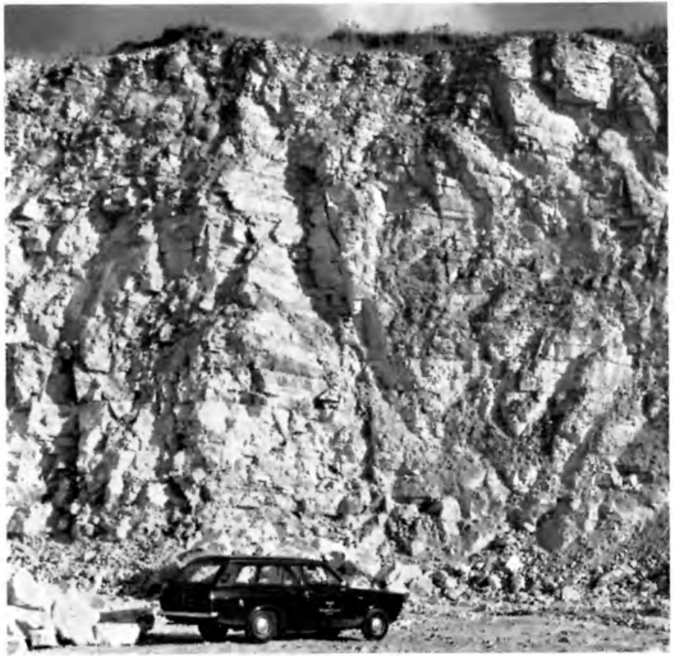


PLATE IV

Typical quarry exposure showing jointing and horizontal discontinuities in the Upper Chalk of East Yorkshire cementation, with the development of glauconite and apatite and other distinctive features.

In the Chalk of the 'northern depositional province', including Lincolnshire and East Yorkshire, cementation and hardening are more common features and dominate the sequence. Porosities are typically in the range 0·13–0·21 (Foster and Crease, 1974).

The Upper and Middle Chalk sequence is broken only occasionally by primary marl bands (0·01–0·20 m thick) and more often by secondary flints and stylolites with their associated marl seams.

The chalk of this sequence is itself an exceptionally pure limestone, the acid insoluble fraction being only 0–5 per cent, with montmorillonite and clay mica as the most frequent clay minerals (Weir and Catt, 1965; Young in Gray, 1965; Jeans, 1968). The Lower Chalk is distinctive by its more marly character, by the presence of other impurities imparting colour to certain horizons and by the general absence of flints. Acid insoluble residues of 5–30 per cent are common and kaolinite is often present as an additional clay mineral. Other frequent trace impurities in the Chalk are quartz, apatite and disseminated pyrite, the latter being commonly oxidized to calcium sulphate.

Despite high porosity, laboratory samples of Chalk exhibit very low permeability, rarely exceeding 10^{-3} m/d (Table 1). This combination of physical properties is a reflection of the exceedingly small particle sizes and pore diameters (Plate I). PSD determinations by the mercury-injection method (Fig. 2) show the bulk of the pores to have equivalent capillary diameters of 0·3–1·5 μm. Drainage will occur only under tensions of the order of 2–5 atmospheres, explaining the very low specific yields and very high specific retentions obtained in centrifuge tests on core samples (Table 1). The values of less than 0·01 and frequently less than 0·005 for the former, probably represent drainage from an occasional pore of larger diameter.

In its saturated zone the Chalk Aquifer is thus an entirely fissure-flow and largely fissure-storage aquifer, the pore-water being for the most part physically immobile. The flow of groundwater through the rock mass is controlled by the geometry of discontinuities (inclined joints, bedding planes, less regular fissures and cavities and solution openings) with respect to natural or applied heads. Very high transmissivities (more than 100,000 times the intergranular component) are frequently reported from the outcrop area (Table 1). It is thought that high permeability has developed due to limited calcite solution mainly on horizontal discontinuities (Plates II and III) during long-term circulation of fresh groundwater to existing and pre-existing base levels (Foster and Milton, 1974). Such horizontal discontinuities are particularly well developed in the Chalk of the 'northern depositional province' but occur fairly frequently in the south also. Permeability is not evenly developed throughout the entire thickness of the formation and is frequently concentrated at shallow depths below the water-table and in the zone of seasonal water-table fluctuation. At depth there is often little groundwater flow.

The significance of inclined jointing in the development of secondary permeability is not well understood; it is believed that the *in situ* horizontal permeability normally exceeds that in the vertical direction by more than one order of magnitude. In quarry exposures the rock mass is normally traversed by relatively large numbers of inclined joints (Plate IV). These may appear

Table 1

Comparison between laboratory and field values for hydraulic properties of Chalk and Permo-Triassic Sandstones at selected sites

Formation	Location	Laboratory samples							Field tests		Type of flow regime	Reference
		Mean k_H (m/d)	k_H range (m/d)	Mean k_V (m/d)	Mean Ø	Ø Range	T_i (m²/d)	Mean cSy	T_t (m²/d)	S_t		
Upper and Middle Chalk	Berkshire Downs	10^{-3}	$3 \cdot 10^{-4}$ to $5 \cdot 10^{-3}$	10^{-3}	0·35	0·25–0·45	10^{-2}	0·01	2,800	?0·02	F	Edmunds *et al.* (1973)
Upper/Middle Chalk	Yorkshire Wolds	$2 \cdot 10^{-4}$	$5 \cdot 10^{-5}$ to $6 \cdot 10^{-4}$	10^{-4}	0·17	0·13–0·21	10^{-2}	0·005	1,000	0·005	F	Foster and Milton (1974)
Bunter Sandstone	Sherwood Forest, Notts.	4	$2 \cdot 10^{-2}$ to 10	3	0·29	0·14–0·34	300	0·22	1,500	—	F + I	Williams *et al.* (1972)
Penrith Sandstone	Eden Valley, Cumbria	3	10^{-1} to 20	1	0·26	0·20–0·32	155	0·14	2,500	0·001	F	Price (personal communication)
Bunter Pebble Beds	Cannock Chase, Staffs.	9	—	—	—	0·26–0·33	270	—	2,800	0·0005	F + i	Lovelock (1972)
Bunter Sandstone	Fylde, Lancs.	0·5	10^{-1} to 10	0·2	—	—	65	—	1,100	0·002	F	Brereton and Skinner (1974)

k_H	horizontal intergranular permeability	cSy	centrifuge specific yield	F	fissure component dominant
k_V	vertical intergranular permeability	T_t	total *in situ* transmissivity	I	major intergranular component
T_i	computed intergranular transmissivity	S_t	*in situ* storage coefficient	i	minor intergranular component.
Ø	porosity				

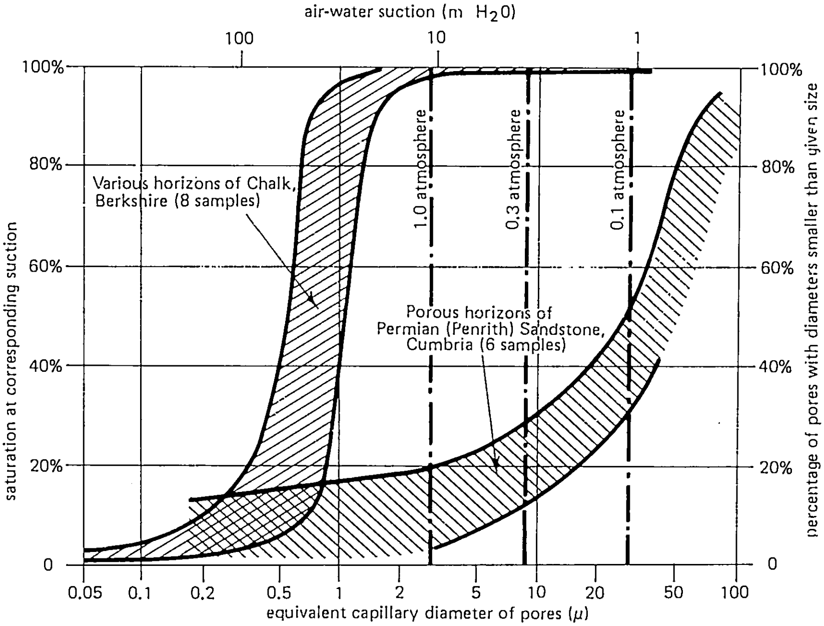


Fig. 2. Pore size distribution (PSD) envelopes.

closed 'tight' at relatively shallow depths of burial but it should be borne in mind that small openings can impart high permeability to a rock mass (Foster and Milton, 1974). For example, if each joint of a parallel set with 1 metre spacing had an effective opening of only 0·2 mm, a permeability of 400-4,000 times the vertical intergranular value would be developed.

In summary the Chalk is a most unusual aquifer containing two contrasting physical components – a small volume /high permeability fissure porosity and a large volume/very low permeability intergranular porosity. By virtue of the minute pore diameters, the latter will be almost always fully saturated, even in the unsaturated zone. In addition to the small volume of minerals of high cation exchange capacity, there thus must be a large capacity for straightforward dilution of new constituents in the fissure-water by aqueous diffusion with the pore-water system (Foster, 1975). Major pollution of the aquifer will probably have occurred before it is recognized by the associated pollution of groundwater supplies and will remain long after the source of pollution has been eradicated.

PERMO-TRIASSIC SANDSTONES

In contrast to the Chalk, the Permo-Triassic Sandstones are more normal aquifers, with significant intergranular permeability accompanying moderate porosity at most horizons.

They are, however, also essentially consolidated formations and in recent years (Lovelock, 1972; Williams *et al.*, 1972; Brereton and Skinner, 1974) it has become increasingly apparent that fissure-flow normally plays a significant or dominant role in their hydraulics (Table 1).

The Permo-Triassic Sandstones show wide vertical and lateral lithological variation on all scales. In each area where they are present a number of lithological sub-divisions are usually recognized. A comprehensive work on the lithological and hydraulic characteristics of the sub-divisions in the various regions is available (Lovelock, 1972) and indicates that the physical parameters also vary widely within a given sub-division in any given area. This is a reflection of their largely fluvial environment of deposition. A typical sedimentary feature is the fining-upward cycle from basal pebbly sandstones through laminated fine-to-medium grain sandstones and siltstones, the topmost member of the cycle being a thin impersistent mudstone or marl. The thickness of individual cycles and the relative thickness of each part of the cycle varies widely from formation to formation. Aeolian sandstones are also well developed at some horizons in certain areas.

For the present purpose it is practical to give only a general idea of the range of physical properties likely to be encountered, by reference to specific examples. At a site in Nottinghamshire, Williams *et al.* (1972) recognized four distinct lithologies within the Lower Mottled Sandstone and the Bunter Pebble Beds (known collectively as the Bunter Sandstone). The commonest rock type was a fine-to-medium grained sandstone characterized by a permeability of 4–6 m/d but exceptionally reaching 16 m/d, a high porosity (0·30) and a centrifuge specific yield of over 0·20. Other rock types present included highly-laminated sandstones with permeability ranging from less than 1 m/d to 8 m/d with lower porosity and centrifuge specific yield, well-cemented sandstones with a porosity of about 0·20 and permeabilities of only about 0·3 m/d and mudstones with permeabilities of less than 10^{-2} m/d. Average overall horizontal permeability determined from field pumping tests proved to be about 5 times the value calculated for intergranular permeability from tests on laboratory samples and the lithological log. The range of physical properties of the Bunter Sandstone in Nottinghamshire is fairly representative of the characteristics of the Permo-Triassic Sandstones in other areas (Table 1) although fine-grained, well-cemented sandstones of less than 1 m/d permeability dominate in some areas, notably North Yorkshire and the Cumbrian coast (Lovelock, 1972).

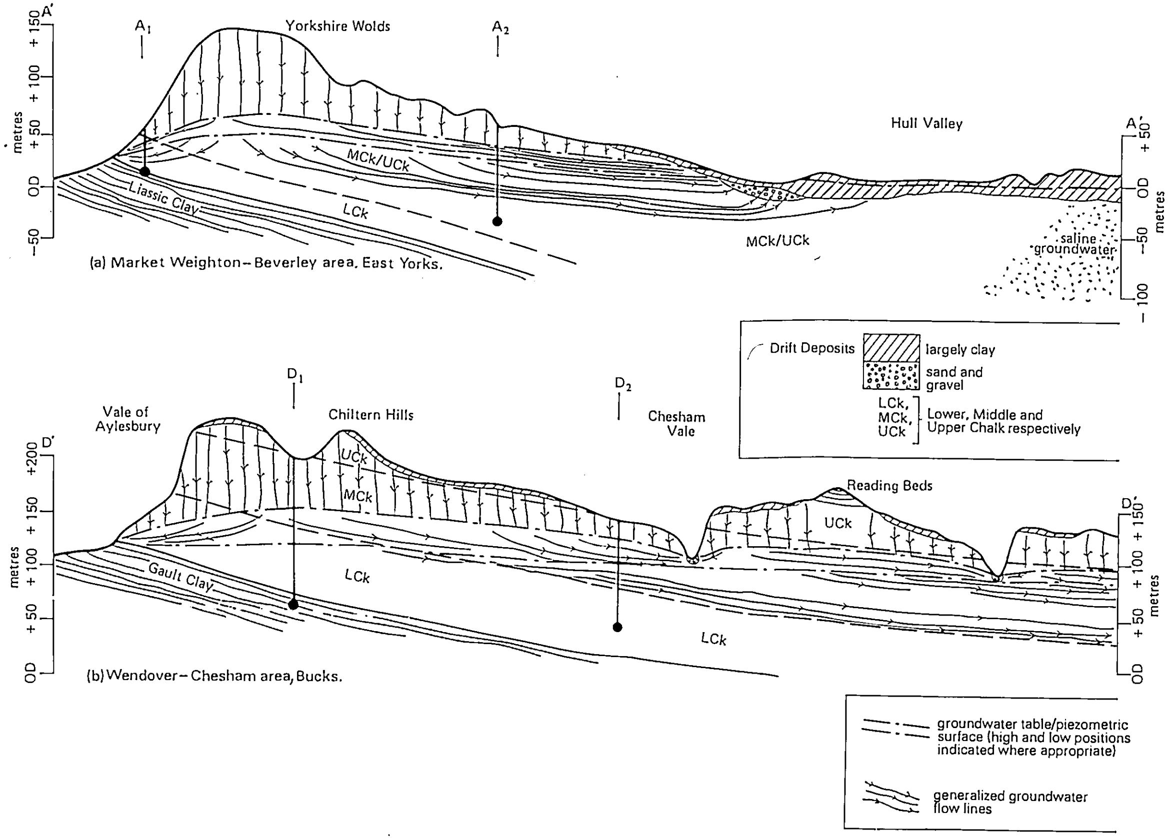
The bulk of the sandstones are formed of quartz and feldspar, which are relatively unreactive. Clay minerals (kaolinite, montmorillonite and clay mica) and various species of hydrated ferric oxides are normally abundant in the matrix (Taylor in Sylvester-Bradley and Ford, 1968; Morgan-Jones, personal communication). The sandstones are predominantly red, the abundance of haematite being directly related to the colour; green or white mottling is fairly common and resulted from syndepositional or diagenetic reduction of the primary red iron oxides.

Typical hydrological regimes and hydrochemical environments

CHALK

The Chalk Aquifer tends to develop similar hydrological regimes wherever it occurs; cross-sections of two areas are given (Fig. 3). In the present paper the main concern is with the intake area of the aquifer, since here exists the greatest risk of pollution from the surface. The following discussion is accordingly biased.

Over much of the intake area the Chalk itself is at outcrop with only a thin



(a) Market Weighton–Beverley area, East Yorks.

(b) Wendover–Chesham area, Bucks.

Fig. 3. Hydrogeological sections of the Chalk Aquifer (vertical exaggeration ×20 approx.).

soil cover; elsewhere 0·5–3 m of superficial deposits (upland Boulder Clay, residual clay-with-flints) may also be present. In these areas most, if not all, the excess rainfall infiltrates and aquifer recharge rates in the range 100–500 mm/a result, depending on the meteorological variables. Long-term average annual infiltration is usually 200–300 mm. In contrast recharge through a Boulder Clay cover of 10 m or more thickness, in the sub-artesian confined areas of East Anglia for example, is less than 100 mm/a, and may only be induced by groundwater abstraction. Infiltration in any year is mainly limited to a few weeks during September–March but minor infiltration is sometimes observed following high intensity rainfall outside these months.

The unsaturated zone is normally 10–100 m thick. For many years it was thought that fissure-flow at rapid rates dominated downward groundwater movement through the zone after infiltration, in the same way as horizontal flow in the saturated zone is localized in fissures. However, the low-level of thermonuclear tritium in the saturated zone throughout most of the intake areas and the form of the unsaturated zone tritium profiles at two sites (Smith *et al.*, 1970; Smith, 1973), have been interpreted to indicate a largely intergranular flow regime in the unsaturated zone with average seepage rates of less than 1 m/a. Such a flow regime is not easy to reconcile with the hydraulic properties of the Chalk (Foster and Crease, 1974); it is particularly difficult to explain the higher of the short-term infiltration rates (over, say, 20 mm/d) during periods of zero soil moisture deficit, without evoking a major component of fissure-flow. Surface run-off might be expected from non-jointed Chalk. The case for a dominantly slow regime of downward flow in the unsaturated zone is still far from proven. Resolution of the controversy is of major relevance to the understanding of pollution from the land surface in Chalk outcrop areas (Foster and Crease, 1974). Attention has been drawn to the unusual physical properties of the Chalk; it appears possible that these might lead to a manifold dilution of new constituents in circulation in the fissure-water (such as thermonuclear tritium), by aqueous diffusion into the apparently older and immobile pore-water (Foster, 1975). It is interesting to note that Chalk pore-waters can be more highly mineralized than the present fissure-water at the same horizons (Edmunds, personal communication).

It has been recognized for some years (Buchan, 1958) that many of the chemical characteristics of Chalk groundwaters in the saturated zone are acquired before the recharge has infiltrated more than 1–2 m through the soil and surficial layers. Some further solution of Chalk is indicated by the subsequent increases in alkalinity reported (from 80–170 mg/litre to in excess of 210 mg/litre). Throughout the intake area solution reactions predominate; the rain water taking up carbon dioxide produced by microbiological activity in the soil and dissolving calcite to produce an essentially Ca^{++}, HCO_3^- water with other ions subordinate (Ineson and Downing, 1963). Most groundwaters of carbonate aquifers are saturated with respect to calcite at the given field temperature, pressure and pH (Hem, 1963) and precipitation may occur if conditions change. Na^+, Mg^{++}, SO_4^{--} and Cl^- are commonly higher in Chalk groundwater in those intake areas where a thin clay cover is present.

Not enough is known about the capacity of the Chalk and chalk soils for self-purification of polluted recharge. Any heavy metals may be co-precipitated and ion exchange processes may immobilize the exchangeable cations, though no quantitative data are available. Although the bacteriological quality of Chalk groundwaters is usually high, incidents of contamination are known for most sources sited on the outcrop, even in areas without water-table quarries or other direct pollution threats; natural mechanical filtration is thus not as effective as in unconsolidated formations.

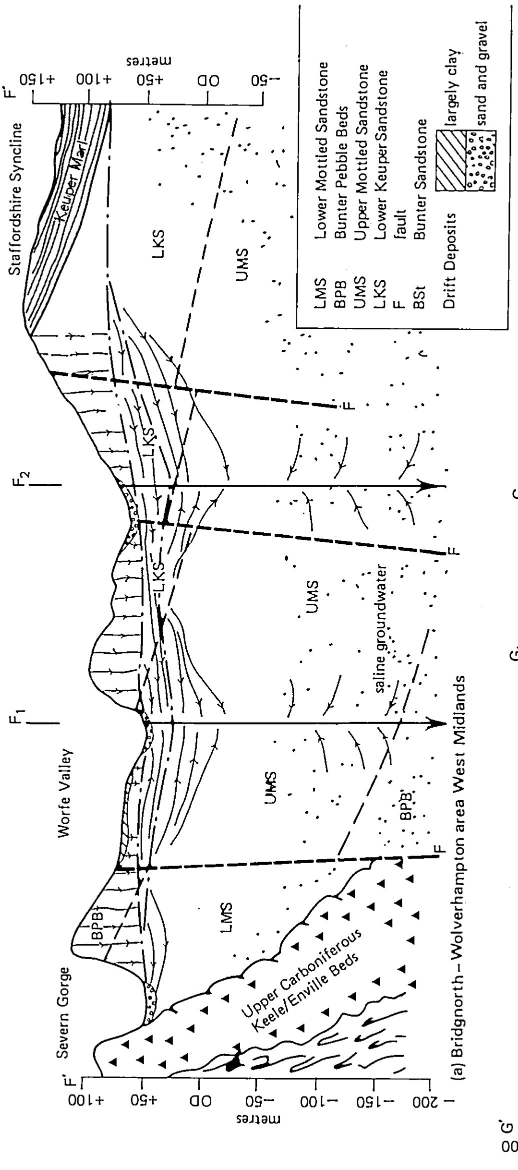
The permeability heterogeneity in the saturated zone has already been described, the major development of fissure permeability frequently being localized at restricted levels. At these levels natural groundwater flowrates will frequently exceed 100 m/d and perhaps reach 500 m/d locally. (Karstic solution features, however, are uncommon even on a small scale, except where rather exceptional local conditions occur.) At depth there is often minor or insignificant development of fissure permeability, and in the absence of a significant intergranular component, water supply boreholes derive no measurable inflows (e.g., Foster and Milton, 1974).

There is little evidence to suggest that even marginally anaerobic conditions are likely to be established anywhere beneath the aquifer intake area, except at times in the soil horizon and possibly also at greater depth beneath some intensive animal feeding areas. A plentiful supply of air is presumably present during the infiltration process and will probably be maintained by diffusion through the unsaturated zone, though *in situ* measurement of Eh in groundwater is subject to difficulties (Hem, 1963). Groundwater chemistry may be affected by slow changes in the input of oxygen to aquifers due to groundwater development or to differing agricultural practices. Down-dip in the confined zones, beyond the areas of major groundwater circulation, flowrates are reduced by more than two orders of magnitude and a complex chain of hydrochemical changes occurs (Ineson and Downing, 1963; Edmunds, 1973), including cation exchange reactions with the clay minerals of the confining bed, development of reducing conditions and mixing with connate water.

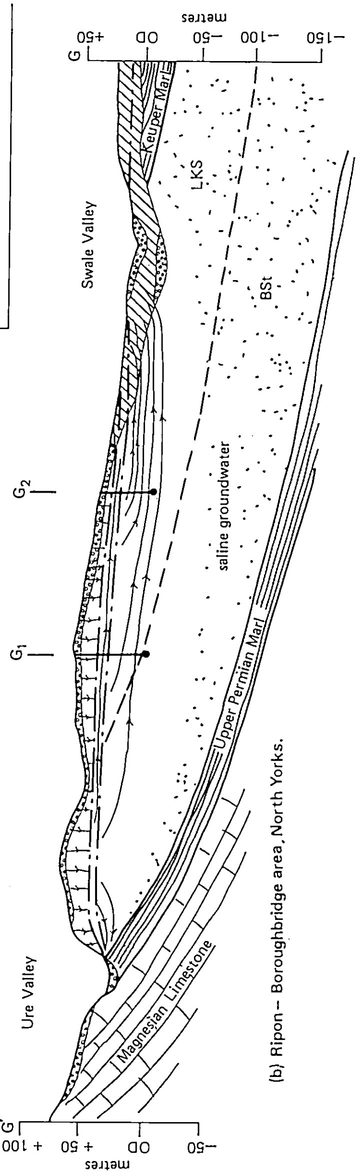
PERMO-TRIASSIC SANDSTONES

The hydrological regimes and hydrochemical environments associated with the intake areas of the Permo-Triassic Sandstones differ in a number of significant ways from those associated with the Chalk.

In general, the formation has a greater thickness than the Chalk, most of this thickness being located below local hydrological base-level (Fig. 4) and possessing moderate intergranular permeability. The ratio of the available aquifer storage in the intake area to average annual throughput is probably more than 50 for many Permo-Triassic Sandstones compared with less than 5 for the Chalk. In the absence of heavy pumping, localized shallow flow regimes tend to develop around the natural discharge areas with stratification of the recharge. The most recent recharge is likely to be found in a thin layer immediately below the water-table with older fresh water below and invariably giving way to connate, increasingly-saline water in depth. Deep pumping boreholes frequently tap a mixture of groundwaters of various origins and recharge histories and the chemistry of their discharge may vary widely depending on the details of production regime and construction (Fig. 5). Supplies from neighbouring boreholes of different depth may have widely different concentrations of any pollutants derived from the surface and present only in recent recharge. Groundwater quality monitoring can



(a) Bridgnorth – Wolverhampton area West Midlands



(b) Ripon – Boroughbridge area, North Yorks.

Fig. 4. Hydrogeological sections of Permo-Triassic Sandstone areas (vertical exaggeration ×20 approx.).

only be effectively undertaken at a three-dimensional level with accurately located depth samples being regularly obtained from purpose-drilled boreholes. Such data are rarely available even locally.

The outcrop of the Permo-Triassic Sandstones tends to form lower-lying land than that of the Chalk and is frequently transected by naturally effluent rivers, which may become influent with heavy groundwater development. The outcrop is frequently drift covered and in general develops thicker soils than the Chalk.

Groundwater flowrates will still be relatively high when a fissure-flow component is present but at many horizons where fissure permeability development is minimal natural flowrates are unlikely to exceed 5 m/d.

Precise data on the hydrochemical environments are very limited. In the West Midlands aerobic conditions generally appear to exist to at least 100 m bgl and carbonate saturation is only encountered in the lithological units with calcareous cement (Edmunds, personal communication).

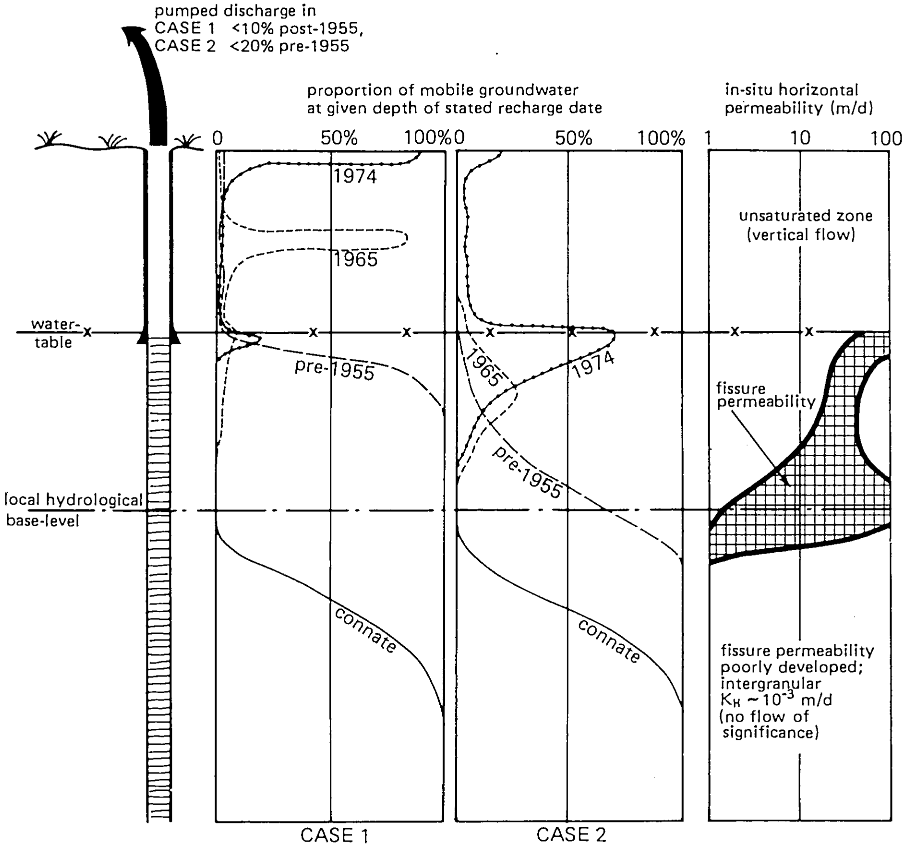
Evidence for regional groundwater pollution by agriculture

It is now of interest to examine any evidence for regional pollution of our major aquifers by agriculture. In this connection it is important to distinguish diffuse pollution at a regional level, resulting from efficient farming practices, from localized incidents originating at point sources.

Many facets of soil and crop management clearly have the potential to cause deterioration in groundwater quality, particularly bearing in mind that the hydrochemical characteristics are largely acquired during initial infiltration through the soil layers (Buchan, 1958). Included are manuring and slurrying, fertilizer application and the use of pesticides and herbicides. Numerous compounds are applied for soil fertilization and management: NH_4OH, NH_4NO_3, $(NH_2)_2CO$, $(NH_4)_2SO_4$, $NH_4H_2PO_4$, $Ca(H_2PO_4)_2$, KCl, $CaSO_4$, $CaCO_3$. Among the fertilizer constituents K, NH_4 and P have strong affinity for soil minerals and do not usually migrate far from the point of application but the anions NO_3, Cl and SO_4 are highly mobile in soil water (Kurtz, 1970). Since nitrate is unique, being the most soluble and being added in the largest amount to soils and representing a health hazard at relatively low concentrations in water supplies (World Health Organization, 1970), it is of primary interest. Leaching by drainage waters, though difficult to quantify, is always potentially a major process in the fate of fertilizer nitrogen. Among other changes in agricultural practice the application of fertilizer nitrogen has increased many fold in Britain during the past decade.

The only data available for the identification of long-term NO_3-N trends in British groundwaters are derived from the routine quality monitoring of raw waters from public supply sources. In many cases even these data are relatively sparse prior to 1965. There are other obstacles to interpretation. The problems of nitrate determination in natural waters are well known (Waters, 1964) and pose questions on the reliability of routine analyses (Foster and Crease, 1974). Pumped groundwater samples are invariably mixtures of different origins (Fig. 5) and long-term trends in the aquifer recharge chemistry may be damped or masked by dilution with older water in storage or by intermittent local pollution. The source of nitrate pollution may be in part other than agricultural (e.g., from an influent polluted river or

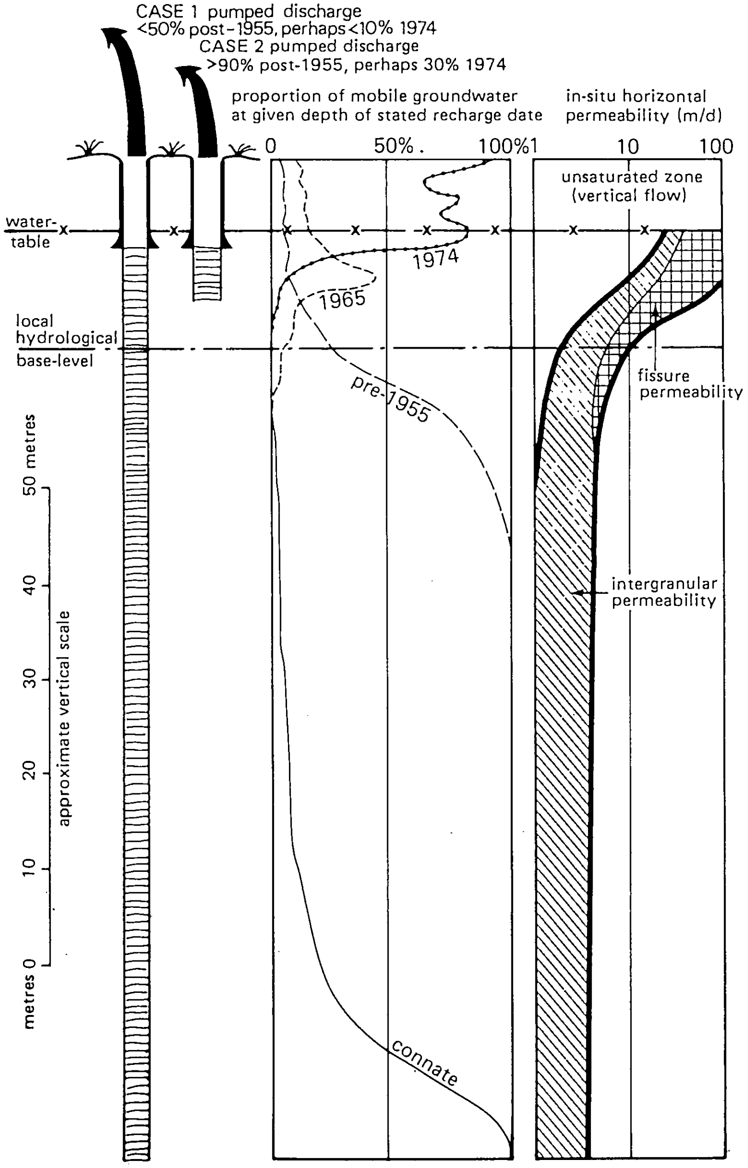
[continued on page 82]



(a) Chalk Aquifer; CASE 1 slow intergranular seepage dominant in unsaturated zone ('tritium profile interpretation'), CASE 2 rapid fissure-flow dominant in unsaturated zone

Fig. 5. Hypothetical aquifer profiles to illustrate potentially complex origin of pumped groundwater supplies/samples.

(b) Triassic Sandstone (thick sequence, in-situ vertical permeability ≪horizontal permeability); CASE 1 deep borehole, CASE 2 shallow borehole



from direct seepage of sewage effluent). Such factors should be remembered when viewing the data presented in Figs. 6 and 7; they have, however, been minimized by considering annual mean NO_3-N levels and by selecting pairs or groups of adjacent sources with comparable trends, which are free from persistent organic or bacteriological pollution and in most respects of high quality. The data from East Yorkshire, North Lincolnshire and the Eastbourne area of Sussex are after the published work of Foster and Crease (1974), Davey (1970) and Sumner (1973), and Greene and Walker (1970) respectively.

In Fig. 6 the NO_3-N trends for five pairs of Chalk groundwater sources in different regions are compared. All the sources concerned have comparable

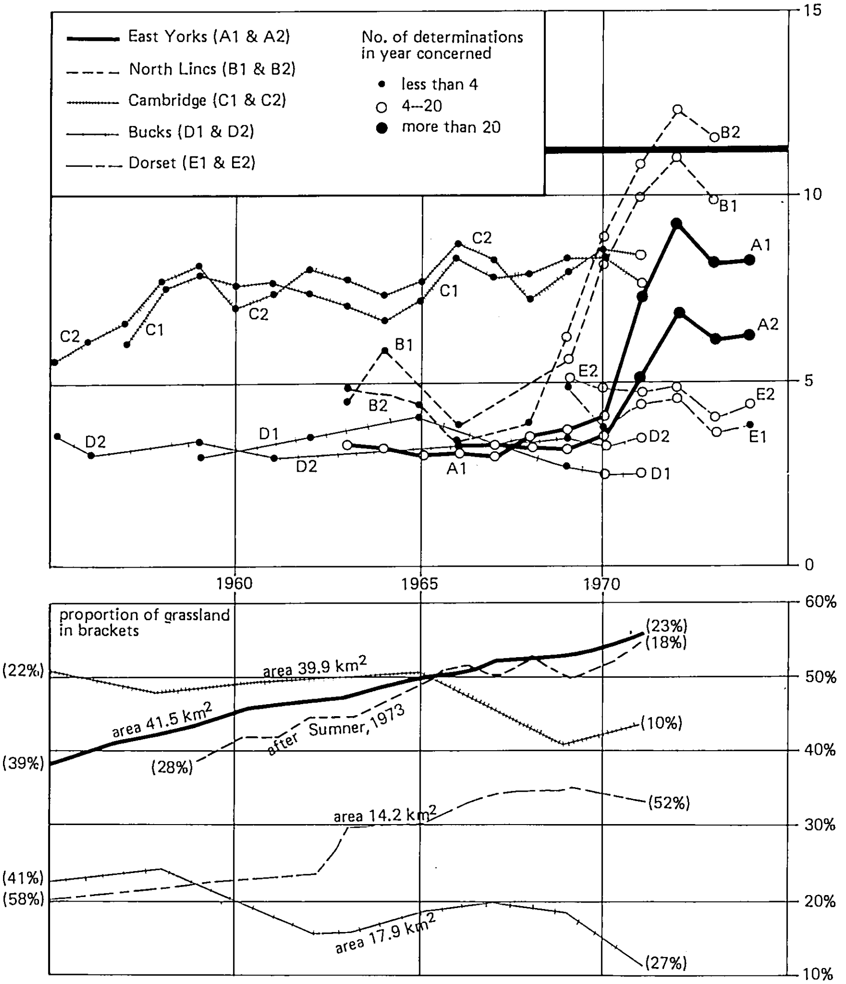


Fig. 6. Trends in NO_3-N levels for selected pairs of Chalk groundwater sources with land use data for corresponding catchments.

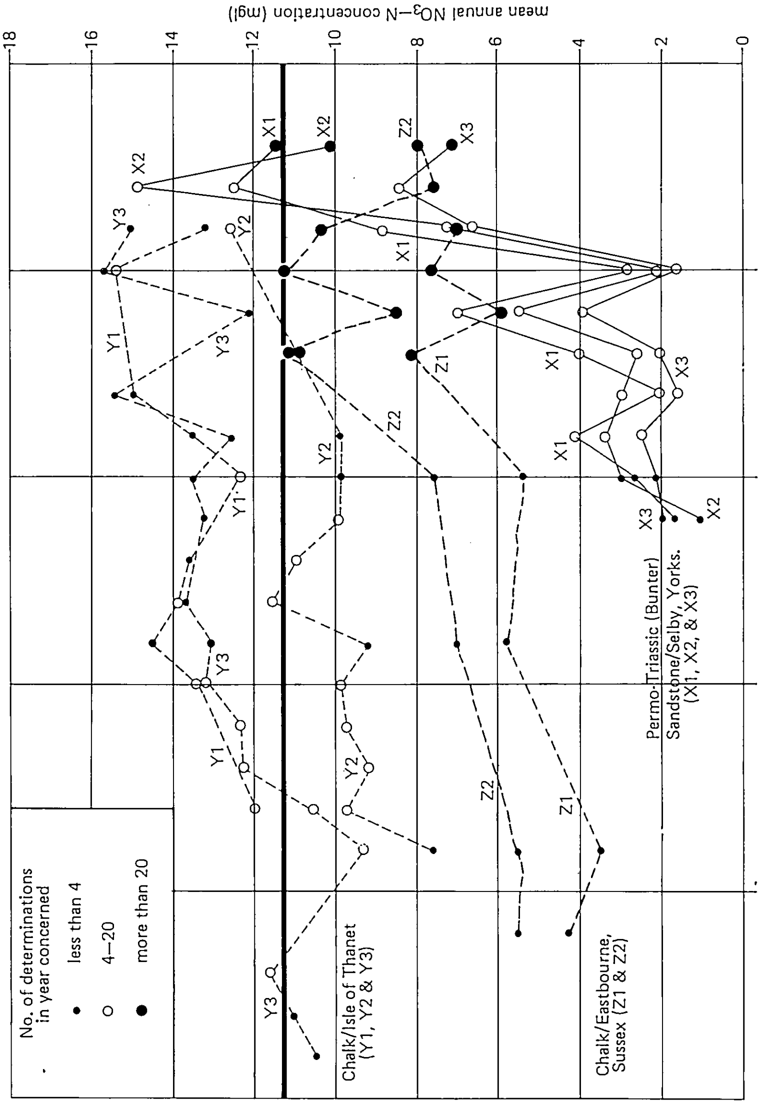


Fig. 7. Trends in NO_3-N levels for groups of groundwater sources with marked nitrate pollution.

hydrogeological environments, though there are differences in Chalk stratigraphy and the character of the Drift cover. The proportion of cereals in the land use of the parishes forming the groundwater catchment of the sources is also given; a broad correlation is apparent and has perhaps been accentuated by the major increase in fertilizer nitrogen application to cereals in the last decade. Some seasonal fluctuation in NO_3-N levels is normally present (Fig. 8) and leads to significantly higher maxima (Table 2) than are apparent in Fig. 6, where annual means only are considered. In North Lincolnshire in particular a substantial increase in mean NO_3-N levels has occurred and the lower W.H.O. limit (11·3 mg NO_3-N/l) is now frequently

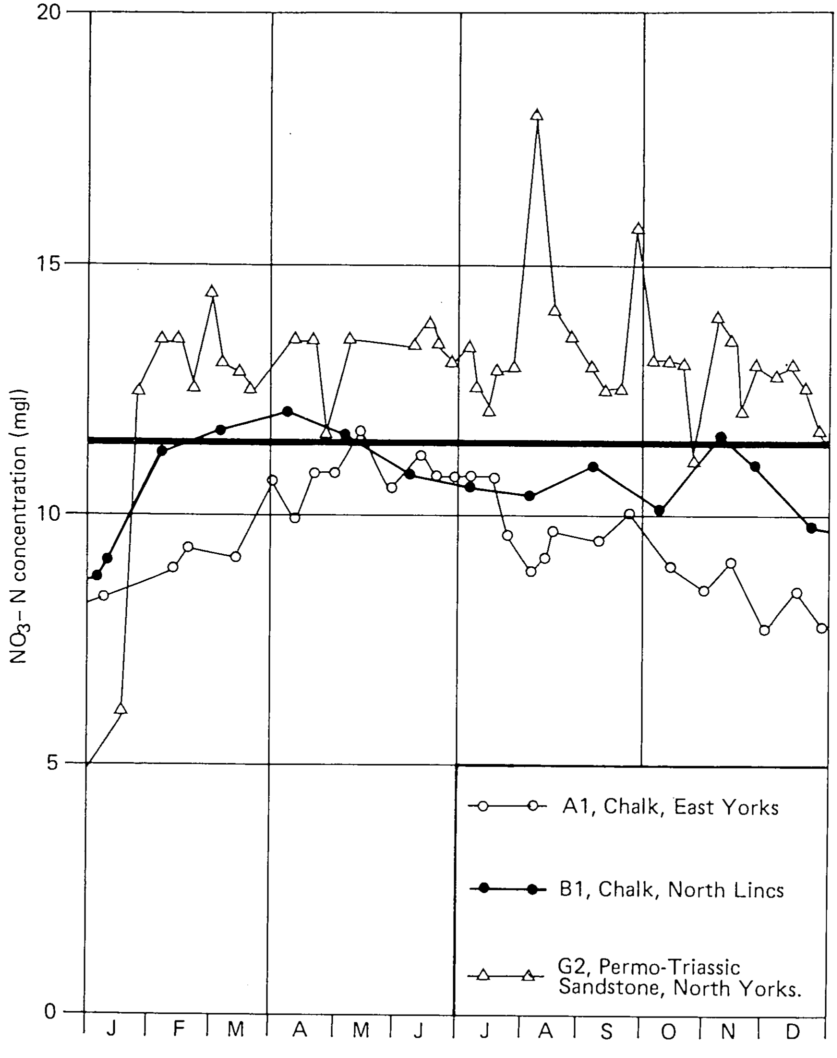


Fig. 8. Fluctuation of NO_3-N levels in selected groundwater sources during 1972.

Table 2

Summary of NO_3-N determinations in selected groundwater sources for 1970, 1971 or 1972

Area	Source no.	Aquifer	Drift cover	Yield Ml/d	Year	No. of analysis	Mean NO_3-N mgl	Peak NO_3-N mgl	Min. NO_3-N mgl	Max. variation of NO_3-N in 10 (mgl)	Percentage of year with NO_3-N	Proportion of cereals in catchment
East Yorks.	A1 A2	LCk MCk/UCk	none	2 14	1972 1972	27 28	9 7	12* 9*	7 6	2 2	< 10 0	56%
North Lincs.	B1 B2	MCk/UCk MCk/UCk	none	15 4	1972 1972	14 12	11 12	12* 14*	8 11	n.d. n.d.	30 90	55%
Cambridge	C1 C2	MCk, LCk MCk, LCk	isolated Boulder Clay and Glacial Gravel	5 12	1971 1971	5 5	8 9	8 10*	7 7	n.d. n.d.	0 ? 0	43%
Bucks.	D1 D2	LCk MCk, LCk	extensive thin clay-with-flints	1 5	1971 1971	6 8	3 4	3 4	2 3	n.d. n.d.	0 0	12%
Dorset	E1 E2	UCk UCk	none	2 3	1972 1972	5 4	4 5	5 5	4 4	n.d. n.d.	0 0	33%
West Midlands	F1 F2 F3	UMS, BPB LKS, UMS UMS, BPB	some Boulder Clay and Glacial Gravel	8 4 14	1972 1972 1970	2 2 2	4 5 7	n.k. n.k. n.k.	n.k. n.k. n.k.	n.d. n.d. n.d.	0 0 ? 0	30%
North Yorks.	G1 G2	LKS LKS	extensive Glacial Gravel some Boulder Clay	< 1 < 1	1972 1972	48 41	17 14	22* 18*	4 6	11† 6†	90 90	59%
Selby, Yorks.	X1 X2 X3	BSt BSt BSt	thick alluvium except on 'bedrock islands'	5 4 5	1972 1972 1972	6 6 6	13 15 9	16 27* 14*	11 10 5	n.d. n.d. n.d.	90 80 10	
Isle of Thanet	Y1 Y2 Y3	UCk, MCk UCk, MCk UCk, MCk	some thin head/ brickearth	3 1 2	1970 1971 1971	5 5 2	15 13 15	17 15 n.k.	13 11 n.k.	n.d. n.d. n.d.	?100 ? 80 ?100	25—35%
Eastbourne, Sussex	Z1 Z2	UCk, MCk UCk, MCk	isolated thin clay-with-flints	3 4	1970 1970	278 143	11 7	23* 14*	5 3	6† 5†	? 50 ? 30	30—40%

Chalk Aquifer

UCk	Upper Chalk
MCk	Middle Chalk
LCk	Lower Chalk

Permo-Triassic Sandstones

LKS	Lower Keuper Sandstone
UMS	Upper Mottled Sandstone
BPB	Bunter Pebble Beds
BSt	Bunter Sandstone

* distinct seasonal fluctuation in NO_3-N levels

†flashy fluctuation in NO_3-N levels also

n.d. – not determined.

n.k. – not known.

exceeded. Concomitant increases in SO_4 from 65 to 90 mg/l and Cl from 30 to 40 mg/l are reported (Sumner, 1973). Significantly lower NO_3-N levels are characteristic of the selected sources in Buckinghamshire and Dorset, where the corresponding land use data indicate less than 35 per cent dedicated to cereal growing.

Few data were available to the author on Permo-Triassic Sandstone groundwater sources (Table 2). Values for the two areas illustrated in Fig. 4, West Midlands and North Yorkshire, are given, the latter having high NO_3-N levels and being an area of intensive cereal growing. It should be noted, however, that fairly wide variations in NO_3-N concentrations have been observed between adjacent boreholes throughout both these regions (Edmunds and Edwards, personal communications) and probably reflect stratification of groundwater recharge and complex origin of pumped samples. Some high NO_3-N levels (above 15 mg/l) are frequently reported from farm boreholes. These may be due to adjacent point sources of pollution or to the shallow depth of the boreholes concerned, or to both.

In Fig. 7 the annual mean NO_3-N trends are presented for three further sets of important groundwater sources, all of which are experiencing very marked nitrate pollution. While the leaching of fertilizers applied to cereals could also be a major factor in these areas, the more restricted acreages suggest that either another source of pollution may be present or that, for some reason, the soils are more vulnerable to leaching. Similar trends to that of source Y2 (Fig. 7) have also been reported for Chalk groundwater supplies in the Sutton area of Surrey (McCanlis in Greene and Walker, 1970).

As statistical study of groundwater chemistry, employing over 400 samples in an area of 1,000 km^2, of an outcrop glacial sand-and-gravel aquifer in the North German Lowlands has been reported by Groba and Hahn (1972). Strong evidence of the influence of land use and of the pollution potential of extensive areas of intensive cereal growing was revealed. In such areas groundwater nitrate levels normally exceeded 10 mg NO_3-N/l and reached 40 mg NO_3-N/l. There was some evidence of an increasing trend. In contrast samples from below extensive tracts of meadow and forest were less than 1 and 4 mg NO_3-N/l respectively. In areas of mixed land use intermediate levels were recorded.

Malpractice in the handling, storage or disposal of agricultural feedstuffs, chemicals and wastes clearly also threatens groundwater quality locally. Normally incidents have to be assessed on an individual basis. In a detailed study, Gilham and Webber (1969) report nitrate levels of 15 mg NO_3-N/l up to 30 m from a manure storage area on a shallow unconsolidated aquifer, whose background levels were about 2 mg NO_3-N/l. The polluted recharge was of very small volume and was rapidly dispersed by dilution. It was estimated that the rate of leaching did not exceed 0·03 kg N/d (and was probably less than 5 kg N/a). By taking core samples Stewart *et al.* (1967) found low Eh values beneath similar sources of pollution and that lack of oxygen was apparently inhibiting NO_3^- formation from the relatively immobile NH_4^+ ions in the leachate. Richards (1972) has discussed the pollution potential of silage clamps sited on the Chalk outcrop, which are likely to generate a small volume (less than 0·1 Ml/a) of liquor with very high NH_4^+, B.O.D. and phenols.

Most pesticides and herbicides are believed to be rapidly immobilized by absorption in soils (Eye, 1968; Scalf *et al.*, 1969) and Croll (1972) was unable to detect any pollution in an area of the Chalk of Kent with shallow water-table and the highest rates of pesticide application in Britain. Comprehensive investigations, however, have not been undertaken.

Discussion of the problem of groundwater quality management

It is now well established that groundwater supplies abstracted from numerous areas of the major British aquifers are significantly polluted by nitrate. The evidence suggests a rising trend in these areas but problems in the routine chemical analysis for nitrate together with the general sparseness of pre-1965 data, make it difficult to establish with certainty the precise rate of rise. It appears likely that changes in land use and agricultural practice, in particular the increased acreages devoted to cereals and the increased use of nitrate fertilizers to sustain them, are either directly or indirectly the cause of the rising levels. In some cases there may also be other sources of pollution present.

The predominance of rapid fissure-flow in the saturated zone of the Chalk and, to a degree, in the Permo-Triassic Sandstones, limits the effectiveness of 'protected areas' around major water supply sources, although such areas do afford a degree of protection against heavy bacteriological pollution. The self-same process of fissure-flow, however, should ensure relatively thorough mixing between groundwater recharge from immediately adjacent areas and down streamlines. This factor probably accounts for the fairly even distribution of nitrate revealed in detailed surveys of Chalk groundwater chemistry in parts of East Yorkshire (Foster and Crease, 1974) and North Lincolnshire (Sumner, 1973). It is suspected that only immediately after groundwater recharge will differences be observed in the groundwater chemistry between directly adjacent areas of differing land use.

Where diffuse groundwater pollution by agriculture is concerned, the management of the pollution at tolerable levels appears on numerous grounds to be a more practical approach than measures for its prevention or elimination, except where trace toxic compounds are concerned. The most important process in groundwater quality management will probably in many instances be dilution.

There is a pressing need to predict the maximum likely NO_3-N levels that may be encountered in the future and it is thus of interest to discuss the sources of dilution in this context. Since there is, as yet, no evidence for the widespread presence of anaerobic conditions beneath the intake areas of the major aquifers, denitrification cannot be assumed to reduce the NO_3-N levels of the groundwater recharge. Now Cooke and Williams (1970) reported that the maximum NO_3-N concentrations in drainage water from plots of winter wheat receiving 95 kg N/ha on the Chalk at Rothamsted did not exceed 30 mg NO_3-N/l. If the drainage waters from adjacent grassland and other fields contained 4 mg NO_3-N/l then the groundwater recharge would rapidly be diluted to 20 mg NO_3-N/l, in an area with 60 per cent of the land employed in cereal growing. Leaching at similar or higher levels would presumably result only for short periods under unfavourable conditions with heavy spring rainfall. Groundwater already in storage and largely originating from winter recharge would be likely to have lower NO_3-N levels and to provide further dilution in the case of supplies pumped from aquifers. Nevertheless such conditions will always be liable to produce troublesome levels intermittently.

Long-term average nitrate levels in the drainage water from the Rothamsted fertilized winter wheat plots were about 7 mg NO_3-N/l (Cooke and Williams, 1970), representing a loss of some 18 kg N/ha for 250 mm of infiltration. It should be noted that larger leaching losses are to be expected from spring sown cereals and from less-controlled fertilizer application, and that the Chalk at Rothamsted has a cover of residual clay-with-flints and may not be typical of the thin light sandy soils associated with most Chalk wold and downland.

A serious situation would develop if losses of, say, 50 kg N/ha were more representative of intensive (60 per cent) cereal growing areas. For 250 mm of infiltration the *average* NO_3-N in the groundwater system would eventually rise to 14 mg/l; for less infiltration (200 mm) the corresponding level would be 17 mg NO_3-N/l. It is of interest to note that the annual average NO_3-N level of the selected sources in North Lincolnshire, the Selby area and the Isle of Thanet are currently in the range 11–15 mg/l (Table 2). Any increase above 4 mg NO_3-N/l in the amount of NO_3-N 'leaking' from grassland would further aggravate the position. Since it is on grassland that the greatest scope for increased fertilization probably exists, this situation requires careful observation.

Moreover it is most important to bear in mind that all the reported cases of rising NO_3-N levels refer to the levels in supplies pumped from an aquifer, the origin of which is liable to be complex (Fig. 5). While the case for a dominantly slow regime of downward flow in the unsaturated zone of the Chalk, for example, is still far from proven, its existence would imply that only a small proportion of present Chalk water supplies will be post-1970 infiltration. A similar effect produced by an entirely different process could occur for some Permo-Triassic Sandstone boreholes (Fig. 5).

Since, in theory at least, these small components of recent infiltration could alone be responsible for the rises in NO_3-N levels, the aquifers concerned could already be more extensively polluted than the current NO_3-N levels in the pumped supplies might suggest. There can be no grounds for complacency until active surveys have been undertaken in various areas to establish the spatial distribution of NO_3-N (and other constituents) throughout the aquifers both above and below the water-table and to determine the rates of physical movement and chemical modification in the component parts of the groundwater system. Monitoring of the chemistry of groundwater supplies alone will not safeguard against the cumulative effects of diffuse pollution and is an inadequate basis for the management of groundwater quality.

Acknowledgments

The paper is published by permission of the Director of the Institute of Geological Sciences. It is essentially a review and the author is indebted to many colleagues for data and discussion, particularly M.J.Bird, Dr.W.M.Edmunds, M.Morgan-Jones, M.Price and T.K.Tate. A.C.Cripps gave energetic and able assistance throughout compilation.

A.H.Goodman (Department of the Environment/Directorate General of Water Engineering) is thanked for drawing the author's attention to sources of additional data. K.Guiver and H.G.Headworth (Southern Water Authority), D.P.Black (Cambridge Water Company), Mrs. Sheila Bloxham (Severn-Trent Water Authority/Wolverhampton Water Supply Division), Dr. A.M.C.Edwards (Yorkshire Water Authority) and J.L.Fisher (Wessex Water Authority/Avon and Dorset Supply Division) are thanked for their generous provision of unpublished data and the corresponding organizations for permission to publish. The land use data quoted were derived from the records of the M.A.F.F. Statistics Branch.

References

BATHURST, R.G.C. (1971). Carbonate sediments and their diagensis. *Developments in Sedimentology,* **12.** Elsevier Publ. Co., Amsterdam.

BLACK, M. (1953). The constitution of the Chalk. *Proceedings of the Geological Society of London,* 1499, 181–6.

BRERETON, N.R. and SKINNER, A.C. (1974). Groundwater flow characteristics in the Triassic sandstones in the Fylde area of Lancashire. *Water Services,* **78,** 275–9.

BUCHAN, S. (1958). Variations in mineral content of some groundwaters. *Proceedings of the Society for Water Treatment and Examination,* **7,** 11–29.

COOKE, G.W. and WILLIAMS, R.J.B. (1970). Losses of nitrogen and phosphorus from agricultural land. *Water Treatment and Examination,* **19,** 253–76.

CROLL, B.T. (1972). The impact of organic pesticides and herbicides upon groundwater pollution. *Proceedings of Conference on Groundwater Pollution,* **1,** 219–32. WRA, Medmenham.

DAVEY, K.W. (1970). An investigation into the nitrate pollution of Chalk borehole water supplies. North Lindsey Water Board, Scunthorpe.

EDMUNDS, W.M. (1973). Trace element variations across an oxidation-reduction barrier in a limestone aquifer. *Proceedings of Symposium on Hydrogeochemistry and Biogeochemistry,* 500–26. Tokyo (1970).

EDMUNDS, W.M., LOVELOCK, P.E.R. and GRAY, D.A. (1973). Interstitial water chemistry and aquifer properties in the Upper and Middle Chalk of Berkshire, England. *Journal of Hydrology,* **19,** 21–31.

EYE, J.P. (1968). Aqueous transport of Dieldrin residues in soil. *Journal of the Water Pollution Control Federation,* **40,** R316–32.

FOSTER, S.S.D. (1975). The Chalk groundwater tritium anomaly – a possible explanation. *Journal of Hydrology,* **25,** 159–65.

FOSTER, S.S.D. and CREASE, R.I. (1974). Nitrate pollution of Chalk groundwater in East Yorkshire – a hydrogeological appraisal. *Journal of the Institution of Water Engineers,* **28,** 178–94.

FOSTER, S.S.D. and MILTON, V.A. (1974). The permeability and storage of an unconfined Chalk aquifer. *Hydrological Sciences Bulletin (IAHS), 19,* 485–500.

GILHAM, R.W. and WEBBER, L.R. (1969). Nitrogen contamination of groundwater by barnyard leachates. *Journal of the Water Pollution Control Federation,* **41,** 1,752–62.

GRAY, D.A. (1965). The stratigraphic significance of electrical resistivity marker bands in the Cretaceous strata of the Leatherhead (Fetcham Mill) borehole, Surrey. *Bulletin of the Geological Survey of Great Britain No. 23,* 65–114.

GREENE, L.A. and WALKER, P. (1970). Nitrate pollution of Chalk waters. *Water Treatment and Examination,* **19**, 169–82.

GROBA, E. and HAHN, J. (1972). Variations of groundwater chemistry by anthropogenic factors in north-west Germany. *Proceedings of 24th International Geological Congress (Montreal)* **11**, 270–81.

HANCOCK, J.M. and KENNEDY, W.J. (1967). Photographs of hard and soft chalks taken with a scanning electron microscope. *Proceedings of the Geological Society of London,* 1643, 249–52.

HEM, J.D. (1963). Some aspects of chemical equilibrium in groundwater. *Ground Water,* **1**, 30–4.

INESON, J. (1970). Development of groundwater resources in England and Wales. *Journal of the Institution of Water Engineers,* **24**, 155–77.

INESON, J. and DOWNING, R.A. (1963). Changes in chemistry of groundwater of the Chalk passing beneath argillaceous strata. *Bulletin of the Geological Survey of Great Britain No. 20,* 176–92.

JEANS, C.V. (1968). The origin of the montmorillonites of the European Chalk with special references to the Lower Chalk of England. *Clay Minerals,* **7**, 311–30.

KURTZ, L.T. (1970). The fate of applied nutrients in soils. *Journal of Agricultural and Food Chemistry,* **18**, 773–80.

LOVELOCK, P.E.R. (1972). Aquifer properties of the Permo-Triassic sandstone of the United Kingdom. Ph.D. thesis, University of London.

RICHARDS, H.J. (1972). Infiltration from farm silage. *Proceedings of Conference on Groundwater Pollution,* **1**, A1-12. WRA, Medmenham.

SCALF, M.R., DUNLAP, W.J., MCMILLION, L.G. and KEELEY, J.W. (1969). Movement of DDT and nitrates during groundwater recharge. *Water Resources Research,* **5**, 1,041–52.

SMITH, D.B. (1973). Tritium water tracing. *Water Treatment and Examination,* **22**, 250–8.

SMITH, D.B., WEARN, P.L., RICHARDS, H.J. and ROWE, P.C. (1970). Water movement in the unsaturated zone of high and low permeability strata by measuring natural tritium. *Proceedings of Symposium on Isotope Hydrology,* 73–87. IAEA, Vienna.

STEWART, B.A., VIETS, F.G.Jr., HUTCHINSON, G.L. and KEMPER, W.D. (1967). Nitrate and other water pollutants under fields and feedlots. *Environmental Science and Technology,* **1**, 736–9.

SUMNER, M.E. (1973). Further investigation into the nitrate pollution of Chalk borehole water supplies. North Lindsey Water Board, Scunthorpe.

SYLVESTER-BRADLEY, P.C. and FORD, T.D. (1968). *The Geology of the East Midlands.* Leicester University Press, Leicester.

WATER RESOURCES BOARD (1974). *Water Resources in England and Wales.* H.M.S.O., London.

WATERS, W.F. (1964). The determination of nitrate in water. *Water Treatment and Examination,* **13**, 298–315.

WEIR, A.H. and CATT, J.A. (1965). The mineralogy of some Upper Chalk samples from the Arundel area, Sussex. *Clay Minerals,* **6**, 97–110.

WILLIAMS, B.P.J., DOWNING, R.A. and LOVELOCK, P.E.R. (1972). Aquifer properties of the Bunter Sandstone in Nottinghamshire, England. *Proceedings of 24th International Geological Congress (Montreal),* **11,** 169–76.

WORLD HEALTH ORGANIZATION (1970). *European Standards for Drinking Water*. W.H.O. Geneva, 2nd edition.