NITRATE POLLUTION OF CHALK GROUNDWATER IN EAST YORKSHIRE—A HYDROGEOLOGICAL APPRAISAL*

By S. S. D. FOSTER, BSC, CENG, MICE (*Member*)**
R. I. CREASE, BSC (*Tech*), CENG, MICE, AMBIM (*Fellow*)***

SYNOPSIS

During 1970–72 there have been marked increases of nitrate level in Chalk groundwaters from widely-distributed locations in East Yorkshire. The most likely cause appears to be some change in agricultural practice; indicating an urgent need for collaborative studies by water-supply and farming interests.

Hydrogeological investigations show the situation to be complex. Tritium determinations suggest that, even below intake or recharge areas, the polluted groundwater could be more than 10 years old. The hydraulics of the implied slow-transit system above the water-table, in what had always assumed to be predominantly a fissure-flow formation, are not readily understood. The dilemma is defined in detail.

If such a system is controlling subsurface flow, the steady increase in applications of nitrogenous fertiliser since 1959 gives rise to a most pressing question. How much nitrate is contained in the groundwater of the unsaturated zone, already in transit to the water-table? Preliminary investigations have revealed levels of 10–35 mgl NO_3-N in Chalk pore-water from shallow depths below fertilised arable land.

BACKGROUND TO NITRATE POLLUTION PROBLEM

Introduction

Prior to 1970, routine monitoring had shown Chalk groundwaters from East Yorkshire (Wolds Area) Water Board (EYWB) sources to contain 2·5–4·5 mgl NO_3-N. Since 1970 levels ranging up to 7·5–11·5 mgl NO_3-N have been recorded for these widely-distributed supplies. Somewhat similar rises have been reported from comparable areas in Sussex and Lincolnshire by Green & Walker[9] and Davey[6], who attempted to correlate the pollution with coincident changes in local agricultural practice or regional land-use.

In East Yorkshire the apparently sharp rises in nitrate level are alarming but the maximum concentrations experienced are not yet critical. This paper, based on the synthesis of largely pre-existing data amplified by limited field investigation, defines and discusses the state of knowledge of the problem, especially its hydrogeological aspects.

Limitation on Nitrate in Water Supplies

The effect of increasing nitrate on the potability of water continues to be a subject of debate among medical research workers. A health hazard results from nitrate reduction on ingestion; the build-up of stable nitrate compounds in the bloodstream reducing its

---

* The authors presented this topic in outline at the WRA Conference on "Groundwater Pollution" at the University of Reading on 25–27th September 1972.

** Senior Scientific Officer, Institute of Geological Sciences (Hydrogeological Department).

*** Formerly Deputy Engineer, East Yorkshire (Wolds Area) Water Board; now Distribution Engineer, Yorkshire Water Authority (Eastern Division).

Note. Details of numerical references are given on p. 194.

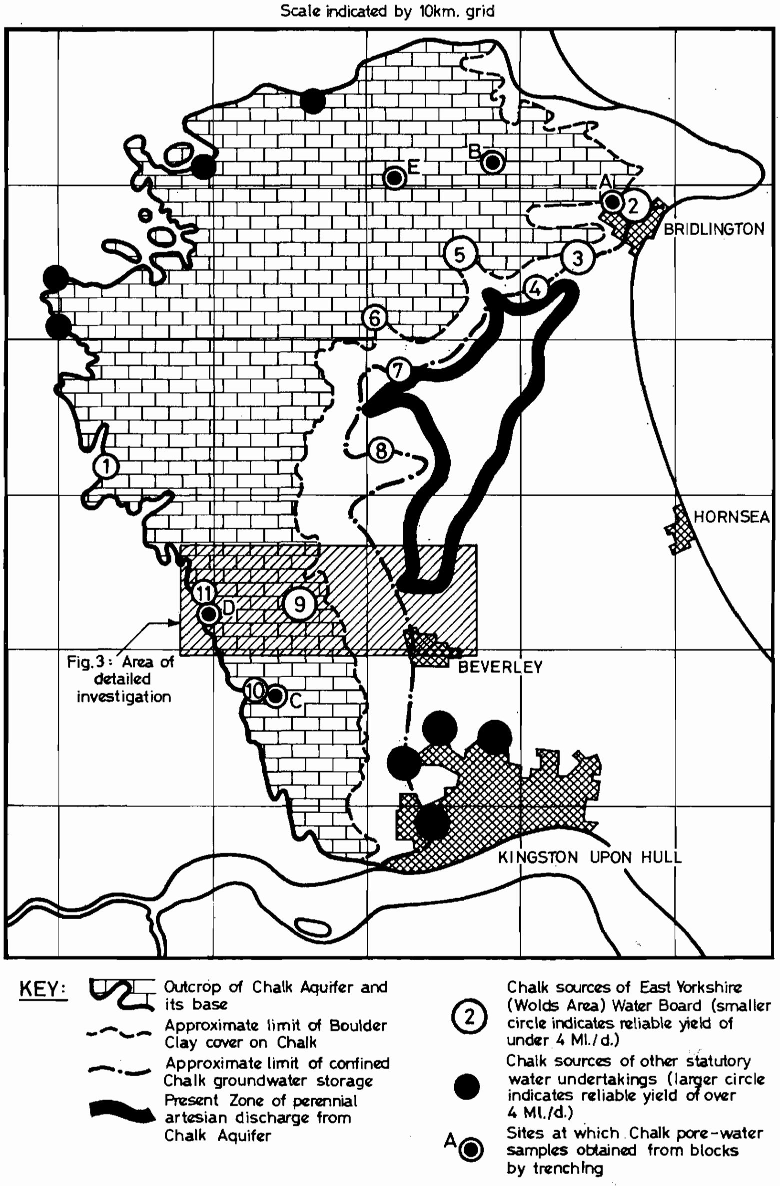


Fig. 1. Distribution of public water supply sources in East Yorkshire Chalk

oxygen-carrying capacity. Infants under 1 year old are most vulnerable but there remains significant variation of medical opinion on hazard levels and secondary factors and thus standards are liable to periodic revision. Those at present adopted for European drinking waters[22] suggest that concentrations should not exceed 11·3 mgl NO_3-N (50 mgl NO_3), but occasional levels of up to 22·6 mgl NO_3-N (100 mgl NO_3) might be acceptable*. In the latter case closer observation by the medical authorities or special arrangements for the supply of drinking water for infants would be required.[15]

The total relaxation of the lower recommended limit has been called for but a recent study in North America[21] concludes that there is insufficient medical evidence to safely justify such action and recent work[14] points to other reasons for minimising the total volumes of ingested nitrate. Nitrate poisoning can also occur in livestock, and high nitrate levels in process waters can be troublesome in certain industries.

Role of Chalk Aquifer in Regional Water Supply

The East Yorkshire Chalk provides the bulk of all water-supplies in a region with a population of over 500 000; the licensed abstraction of all Chalk sources totalling in excess of 200 Ml/d. In particular the EYWB have 11 Chalk sources (Fig. 1), mainly large-diameter boreholes, with a combined drought yield of some 53 Ml/d. The protection of the Chalk Aquifer from a level of pollution incompatible with its water-supply function is thus of regional significance. Moreover its large unexploited storage capacity in the northern part of East Yorkshire would appear to have a role in meeting the future demands of the North Humberside conurbation.[8]

Some 80–90 per cent of the flow of the River Hull is derived from Chalk springs. Nitrate enrichment could lead to fertilization of weeds in the river itself and to algal problems in the water-supply reservoirs at the intake works.

INTERPRETATION OF HYDROCHEMICAL DATA

Trends of NO_3-N in Chalk Water Supplies

The long-term trends in NO_3-N concentration for selected sources are shown in Fig. 2. During 1962–69 all had relatively constant nitrate levels of around 3·0 to 4·0 mgl NO_3-N. In 1970 more variable results with some increases were recorded. An apparently sharp rise followed in 1971 and 1972; the worst-affected source reaching a peak of 11·5 mgl NO_3-N in May 1972. Other sources had comparable, though less steeply rising trends (Fig. 2 and Table 1). There are seasonal variations with late spring/early summer maxima and autumn minima but daily and weekly samples have not revealed any flashy fluctuation. Elsewhere in the Chalk, a change from 7·2 to 16·0 mgl NO_3-N over only 10 days in a borehole water supply has been reported.[9]

TABLE I. SUMMARY OF INCREASES IN NITRATE LEVELS IN EYWB SOURCES (*not presented in Fig. 2*)

Source No. (Fig. 1.)		1	2	3	4	6	7	8	10
pre-1970 background	NO_3-N mgl	2·9	3·2	3·4	2·9	3·2	3·4	3·4	3·4
1972 peak		6·8	9·3	6·1	7·2	7·9	7·0	6·3	9·5

---

* Throughout the remainder of this paper nitrate concentrations are expressed in mgl NO_3-N units only (multiply NO_3-N by 4·4 for NO_3 units).

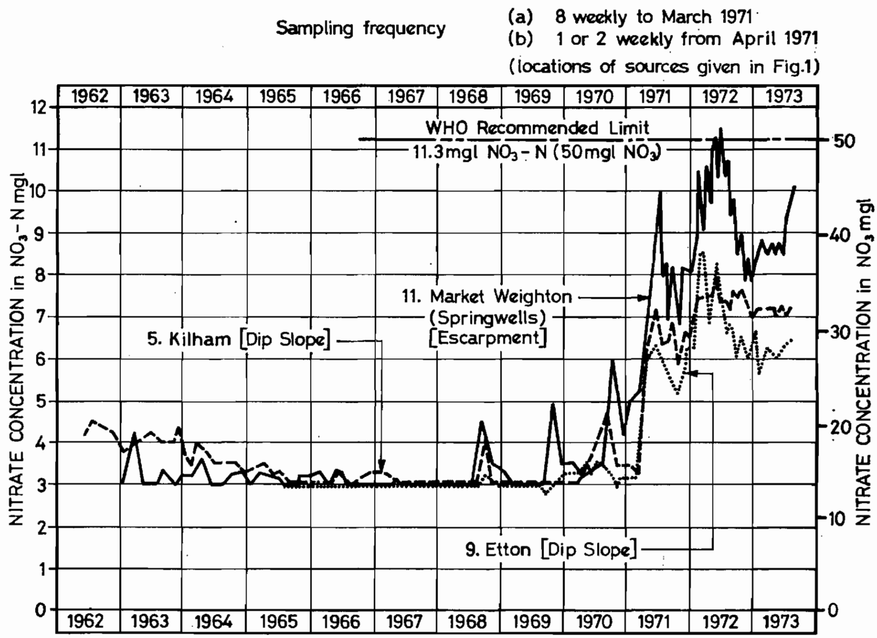


Fig. 2. Trends of nitrate concentration in selected sources

The sources have always had low levels of nitrite and organically-bound nitrogen (ammoniacal and albuminoid N not exceeding 0·04 and 0·05 mgl respectively) and no increases have accompanied the rises in NO_3-N. Neither have there been clear simultaneous changes in other inorganic ions such as chloride, sulphate or potassium, although there are only restricted data in respect of the latter. Chloride levels in Chalk groundwaters of the Yorkshire Wolds are typically close to 20 mgl; the Market Weighton (Springwells) source however records somewhat higher values, which have increased since 1967 from 23–26 mgl to 24–34 mgl. The bacteriological standard of the raw waters from all sources is consistently high, with only very occasional low coliform counts.

Reliability of Analytical Techniques

The interpretation of long-term trend data as evidence for pollution depends to a considerable extent on the accuracy and reliability of nitrate analyses. Numerous analytical techniques are available for the determination of nitrate in waters. Waters[20] reviewed those methods involving colorimetric measurement, both directly and indirectly after reduction. Significant problems arise because of changes in concentration during transport and storage, varying effects of interfering ions and natural colours of water and incomplete conversion of the nitrate ion to the distinct molecular species to be colorimetrically determined. Moreover since the percentage conversion depends considerably on experimental conditions, failure to adhere to standardized procedures leads to irreproducibility of results by the same method.

A study of differences between 10 different laboratories employing various methods, gave a mean result of 4·43 mgl NO_3-N for a standard solution of 4·60 mgl NO_3-N, with a lowest value 0·89 mgl NO_3-N below standard.[3] Interlaboratory work was introduced in the present investigation mainly to aid the interpretation of past data, though rapid analytical methods involving direct observation of the ultra-violet absorption and a specific ion electrode were also included. The results for some split samples (Table II) revealed an absolute variation of more than ±1·0 mgl NO_3-N, both between methods and in repeated determinations with the specific ion electrode. It is thus clear that the analytical problem will, in many cases, restrict the interpretation of historical or sequential nitrate data. A similar problem may also be posed when attempting to implement any recommended limit for water-supply.

TABLE II. INTER-LABORATORY COMPARISON OF NITRATE ANALYSES ON CHALK GROUNDWATERS FROM EAST YORKSHIRE
Split samples taken on 15 February 1972. All results in mgl NO_3-N

Source No. (Fig. 1)	Lab A		Lab B	Lab C		Lab D		Lab E*	Mean	Absolute Variation from Mean	
	Method		Method	Method		Method		Method			
	DCpda	DCxyl	DCpda	SIonEl	DCbr	UVSp	DCpda	SIonEl		+	−
9	8·4	8·5	8·5	9·0M	7·8	7·8	8·0	7·7m	8·2	0·8	0·5
8	6·3	7·0M	5·9	6·7	5·7	5·4	5·2m	5·5	6·0	1·0	0·8
5	7·1	7·5	7·4	8·2M	7·0	7·0	7·2	6·9m	7·3	0·9	0·4
11	10·5	10·0	9·1	10·9M	8·6	8·3m	8·8	8·4	9·3	1·6	1·0
10	11·0M	10·5	8·7	9·0	8·9	8·2	8·6	8·1m	9·2	1·8	1·1
3	6·7	7·0M	5·5	6·5	4·9	5·0	4·8m	4·9	5·7	1·3	0·9
	+0·7	+0·8	−0·1	+0·6	−0·5	−0·7	−0·5	−0·7	Average Variation from Mean		

M: maxima. m: minima

KEY TO METHODS:

DC: Direct Colorimetric Methods with phenol —2·4 disulphonic acid (pda) or brucine reagent (br) or 2·4 xylenol (xyl)[20]

SIonEl: Specific Ion Electrode[4]

UVSp: Ultra-violet Spectroscopy[12]

* Mean of five determinations in 5 days with variation of about ±1·0 mgl.

This applies in some degree to, but does not invalidate, the trend data for the Chalk groundwaters of East Yorkshire (Fig. 2). All analyses were carried out by the same technique, the direct colorimetric method with phenol-disulphonic acid, although there have been changes of analyst and analytical laboratory including a change (from Lab. A to Lab. B of Table II) in 1971. There must therefore be some doubt as to the absolute magnitude of pre-1971 levels, but the sharp rise in recent years has been confirmed through the detailed and careful work of Lab. B alone. Earlier background values are, to an extent, substantiated by the relationship between the results of Lab. B and Lab. A in the inter-laboratory determinations (Table II).

Distribution of NO_3-N in Chalk Groundwater

The network of sources with long-term trend data (Table I) are scattered throughout the rural parts of the region (Fig. 1). The detailed spatial distribution of nitrate in groundwater of the saturated zone has been investigated within a cross-section 6 km wide

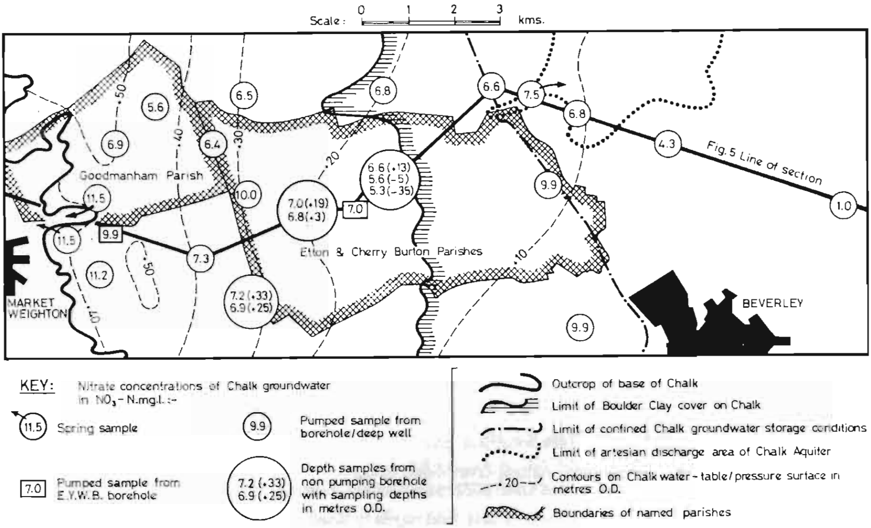


Fig. 3. Nitrate concentrations of Chalk groundwater in the Market Weighton-Beverley area in August 1972

and 16 km long. A sampling programme was carried out during August 1972 and 16 pumped-samples, 3 spring-samples and 7 depth-samples were collected for analyses. The results (Fig. 3) show nearly all groundwaters below the outcrop or intake area to have NO_3-N concentrations in excess of 6·0 mgl, with values exceeding 10·0 mgl NO_3-N near the escarpment. These values are probably some 20–25 per cent below the all-time maxima reached a few months earlier.

An electro-magnetically operated depth-sampler was used to skim the water-table and for sampling at greater depths in three observation boreholes. Little nitrate stratification or submerged zone of nitrate reduction was revealed (Fig. 3). Natural Eh changes, causing reduction of nitrate, appear to occur in the confined zone however, since levels fall to 1·0 mgl NO_3-N some 6 km down-dip (Fig. 3). Conditions down-dip are of somewhat academic interest however, since they cannot be used to significant advantage in water-supply because of the coincident fall-off in permeability and well yields in this direction.[8]

The distribution of NO_3-N in Chalk groundwater above the water-table was also of considerable interest. A few results in respect of pore-water have been produced for 5 sites (Fig. 1) at which Chalk blocks were carefully removed from trenches dug rapidly by mechanical-excavator to depths of 4 metres. Pore-water samples were extracted from the blocks after crushing to a paste; this method may not be ideal and might lead to underestimates if nitrate is not fully-recovered from the smallest pores. The results (Fig. 4) are nevertheless of interest and show Chalk pore-water frequently to contain more than 15 mgl NO_3-N (and sometimes in excess of 30 mgl NO_3-N) at shallow depths beneath fertilized arable land. The corresponding values for unfertilized grasslands were mostly below 2·0 mgl NO_3-N. Differences between the exterior and centre of blocks were observed and it is possible that accumulation of soluble salts might be occurring after evaporation without any net groundwater movement, or through other processes.

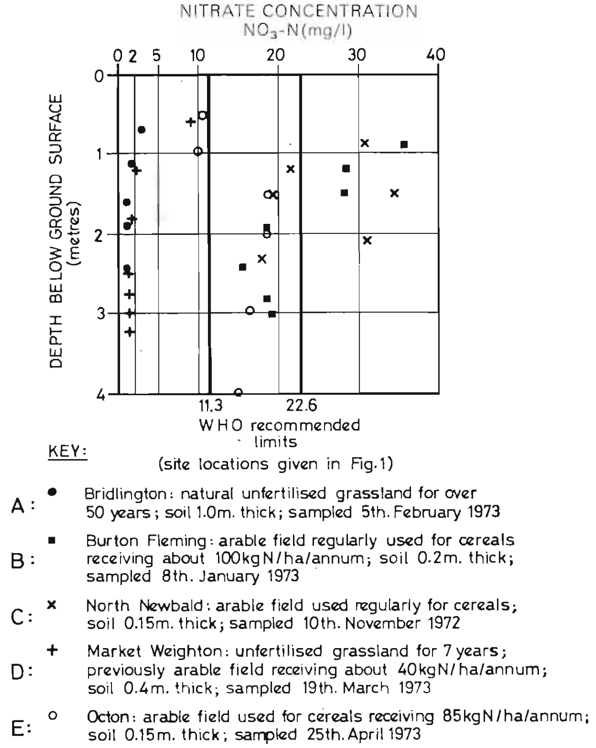


Fig. 4. Nitrate concentrations of Chalk porewater in unsaturated zone

GROUNDWATER FLOW REGIME IN CHALK AQUIFER

Overall Pattern of Recharge, Storage and Throughflow

In the Market Weighton-Beverley area of the Yorkshire Wolds the hydraulic behaviour of the Chalk in its saturated zone has been studied in detail, using hydrological pumping tests, geophysical borehole flow investigations and other methods. The Chalk is a fissure-flow and largely fissure-storage formation with horizontal permeability (k_h) in the range 20–200 metres/day in the active flow zones. Corresponding velocities of throughflow to the discharge areas under natural hydraulic gradients must be in the range 10–50 metres/day (Fig. 5).

Throughout the Chalk outcrop the recharge regime was believed to be relatively simple, with infiltrating precipitation and corresponding recharge at the water-table, at times of zero soil moisture deficit. The unsaturated zone is typically in the range 20–100 metres thick and rapid fissure-flow was thought to dominate downward groundwater movement through this zone to the water-table. However, as will be discussed below, the results of isotope work suggest that a totally different unsaturated flow regime may in fact prevail.

The long term average infiltration in the Yorkshire Wolds is estimated to be about 300 mm/annum. Foster & Milton[8] have computed the maximum monthly infiltration for the northern part of the region during 1962–70 to be in excess of 130 mm with a total of 480 mm during the period September 1965–February 1966. Infiltration is usually concentrated in the months October-March, but there is frequently some post-March and in certain years this can be a significant proportion of the total (e.g. April 1966, May 1967).

The response of the water-table to infiltration as recorded in observation boreholes, appears reasonably predictable, both in magnitude and time-lag. There is generally a small very rapid response (probably in fact partly barometric) with the main recharge to the water-table commencing a few days after the corresponding rainfall and spread over a number of days. The response times in respect of the latter are normally of the order of 0·1–0·3 days/metre of unsaturated zone. On the evidence of groundwater levels in observation boreholes, minor "flash" infiltration during periods of large soil moisutre deficit also appears to occur occasionally after short heavy rainfall.

Determinations of Environmental Tritium

Tritium is a radioactive isotope of hydrogen with a half-life of 12·3 years. Tritiated water occurs both naturally and artifically in the atmosphere from where it enters the groundwater cycle as infiltrating precipitation. The tritium level in precipitation increased from below 10 TU (tritium units or tritium atoms per 10^{18} protium atoms) to a peak in excess of 2000 TU in summer 1963, as a result of thermo-nuclear testing in the preceding 10 years. Observed or correlated tritium levels in British rainfall have been given by Smith *et al*[18] and it is important to note that they did not fall below 50 TU during 1962–70; the annual means, adjusted for decay, have exceeded 100 TU in every year since 1958.

Some 30 tritium determinations were carried out during 1970–72 on Chalk groundwaters from East Yorkshire, by the method of Allen[2]. Most of the samples were pumped from water-supply boreholes but some depth samples and spring samples were also included. The groundwater conditions on the sampling dates were those of moderate drought in October 1970, high water-table in March 1971 and fairly low water-table in August 1972. All of the tritium counts are low (less than 50 TU) and no less than 21 of the samples had counts below 10 TU with a further 5 below 20 TU.

Ten of the sampling stations were located in the area of detailed investigation (Figs. 1 and 3) and the results for this area are illustrated in Fig. 5. It is of note that:

(*a*) Despite major recharge of the Chalk water-table between October 1970 and April 1971, no significant increase in tritium levels was observed at the 3 stations sampled on both dates.

(*b*) Depth samples skimmed from the surface of the water-table in August 1972 had low tritium levels and it appears that tritium layering cannot explain the low values obtained for the pumped samples.

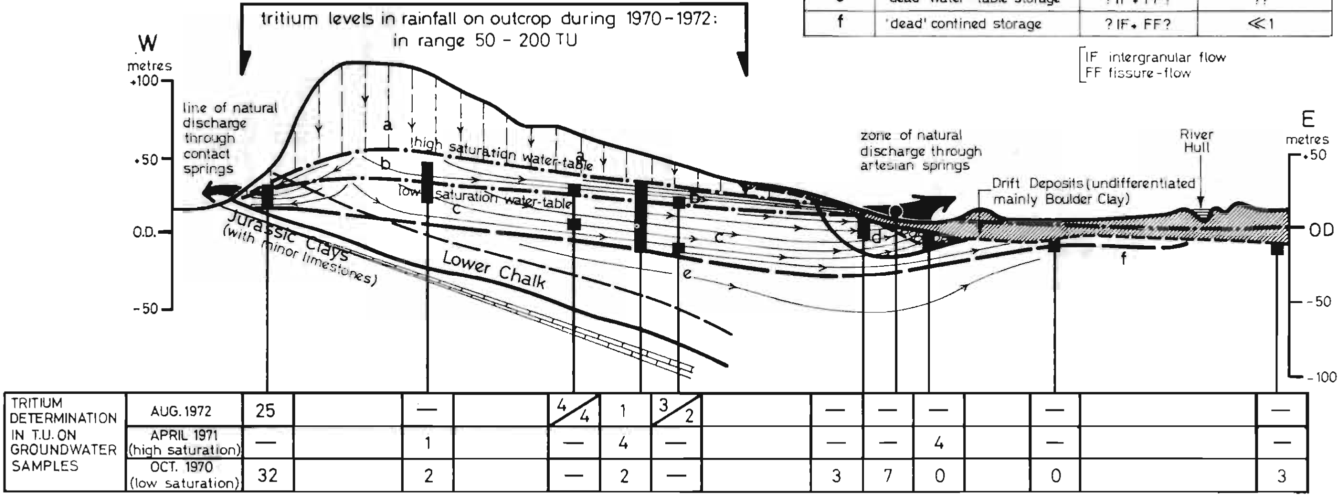
Environmental tritium is considered a particularly suitable tracer for water since it is part of the water molecule. Sample contamination would in most circumstances lead only to increased counts. While limited isotopic concentration in the liquid phase during evaporation has been recorded and in low velocity groundwater flow systems isotopic diffusion may produce significant dispersion, the possibility of any selective delay or retention of tritium by soil or chalk is believed to be remote.

The most satisfactory explanation of the low tritium levels in the Chalk groundwater of East Yorkshire, when compared to recent rainfall, is that the bulk of the recharge to the water-table must reside more than 10 years, and probably more than 18 years, in the unsaturated zone during downward percolation. Low tritium levels are being recorded from the saturated zone of the Chalk over much of the country, including North Lincolnshire where nitrate pollution is also reported. Direct investigation of the unsaturated

KEY TO GROUNDWATER FLOW REGIME

SYMBOL	ZONE OF	TYPE OF GROUNDWATER FLOW REGIME	ACTUAL NATURAL GROUNDWATER FLOW RATES metres/day
a	unsaturation	? IF + FF ?	??
b	water-table fluctuation	FF	25 - 50
c	'active' water - table storage	FF	10 - 30
d	natural discharge	FF	
e	'dead' water - table storage	? IF + FF?	??
f	'dead' confined storage	? IF + FF?	≪1

IF intergranular flow
FF fissure-flow



TRITIUM DETERMINATION IN T.U. ON GROUNDWATER SAMPLES																
	AUG. 1972	25		—		4/4	1	3/2		—	—	—		—		—
	APRIL 1971 (high saturation)	—		1		—	4	—		—	—	4		—		—
	OCT. 1970 (low saturation)	32		2		—	2	—		3	7	0		0		3

Fig. 5. Hydrogeological cross-section of the Yorkshire Wolds in the Market Weighton-Beverley area to show groundwater flow regime and tritium age determination

zone however has been relatively limited. Smith *et al*[18] determined the total tritium of unsaturated zone pore-water from a cored Chalk borehole on the Berkshire Downs in 1968 It was concluded that 85 per cent of the total downward movement was intergranular seepage at a net flow rate of only 0·88 metres/annum; the 1963 tritium peak being clearly in evidence at just below 4 metres depth.

In East Yorkshire, only at sampling sites on the escarpment and near some dip-slope springheads, were somewhat higher tritium levels recorded and components of more recent water implied. These included the source at Market Weighton (Fig. 5) the worst affected by nitrate pollution. On the available evidence, it is not possible to say whether such levels result from the limited thickness of the unsaturated zone in parts of these areas, from the existence here of a significant rapid-transit fissure-flow component or from other factors.

Dilemma of the Unsaturated Zone

The existence of a dominantly slow-transit intergranular flow regime in the unsaturated zone is not easy to reconcile with the known hydraulic properties of the Chalk.

The physical and hydraulic properties of 28 selected samples of East Yorkshire Chalk have been determined[8] and more comprehensive laboratory core analysis of an individual Chalk borehole in Berkshire has been reported.[7] It should be noted however that cementation is more extensive in the East Yorkshire Chalk and that there are significant differences between its properties and those of the southern Chalk. Although weathering, the presence of stylolites and minor changes in lithology have a measurable effect on physical properties at the intergranular level, and there may be a tendency for porosity to reduce with depth, it is possible to quote order-of-magnitude values for the purpose of the present discussion. In the Yorkshire Wolds, inter-connected porosity (ϕ) is only moderately high and unlikely on average to exceed 0·20 in the unweathered state; in strong contrast the inter-granular permeability is extraordinarily low, with k_V (saturated vertical permeability) in the order of 10^{-4} metres/day. This combination clearly implies exceedingly small particle sizes and pore-channel diameters and such have been demonstrated by scanning electron microscopy.[11] The bulk of the particles in the fabric are coccolith plates, believed to be in the order of 1 μm diameter, with even smaller pore-sizes. The Chalk must be amongst the finest of naturally-occurring granular materials and if an unbroken intergranular column existed, it could be expected to support a capillary fringe of unusual height. Pores of such diameter would drain only under suctions in the order of 3 atmospheres and explain the very high specific retentions. Centrifuge specific yield tests on core samples from East Yorkshire gave values up to 0·009 with an average of about 0·003 and the drainage probably derives entirely from occasional pores of larger diameter.[8]

In quarry exposures the rock mass is traversed by frequent major joints of multi-directional steeply-inclined aspect and even larger numbers of minor joints; the typical density of the major inclined jointing is reported to be 0·7–1·3 per metre.[8] There is evidence from the Chalk of Norfolk that many of these inclined joints may be closed 'tight' at relatively shallow depths of burial, but it should be borne in mind that very small openings can impart high permeability to a rock mass. If, for example, each joint of a set of 1 metre spacing had an effective opening of 0·1 mm, they would develop a permeability of 0·05 metres/day (about 500 times the intergranular k_v). Horizontal discontinuities must also be present in the unsaturated zone. In the East Yorkshire quarries their density of occurrence ranges from 0·6–3·6 per metre and solution on them is believed to be responsible for the very high permeability (about 120 metres/day) of the zone of water-table fluctuation at Etton.

Given this framework of hydraulic properties, specific questions concerning the dilemma of unsaturated groundwater flow in the Chalk originating in the tritium results should be discussed.

(A) Does the unsaturated zone have sufficient storage capacity, in absolute terms, to hold 10 or 20 years infiltration?

Taking $\phi = 0{\cdot}20$ and an average annual infiltration of 300 mm, 10 and 20 years recharge could be stored in thicknesses of 15 and 30 metres, which are present over most of the intake area except in escarpment dry valleys and near some dip-slope springheads. The potential fissure-storage of the unsaturated zone is almost certainly an order-of-magnitude smaller.

(B) What order of vertical intergranular flow rates are physically possible?

Any downward movement at the intergranular level for partial saturation will be under the complex interaction of capillarity and gravity; both the unsaturated k_v and the suction head being a function of moisture content and pore diameter. Saturated downward movement under unity gradient is the limiting case and, taking $k_v = 10^{-4}$ m/day and $\phi = 0{\cdot}20$, actual flow rates would not exceed 0·2 m/annum. Higher k_v and ϕ (5×10^{-4} m/day and 0·25), due to weathering could increase the upper limiting flow rate to about 0·7 m/annum at shallow depths.

(C) Do mechanisms exist for the pore-space to accept an annual infiltration of up to 480 mm in 6 months at maximum rates probably exceeding 130 mm/month and 30 mm/day?

In view of the Chalk's extremely high specific retention it is assumed that high saturations, probably in excess of 98 per cent, must exist throughout most of the unsaturated profile; though this has not been confirmed. Evapotranspiration and possibly direct evaporation from the walls of fissures seem the only possible processes available to further reduce saturation. Such processes would be significant probably only to limited depth below the thin soil zone and their existence could imply significant departures from the classical evaporation model or would require re-appraisal of the root constant. Assuming an average $\phi = 0{\cdot}25$ at shallow depths, the mean saturation down to 3 m would have to be reduced to about 36 per cent (i.e. a water content (θ) of 0·09) to accommodate the above annual infiltration in that depth range. The corresponding saturation for a 300 mm infiltration would be 60 per cent ($\theta = 0{\cdot}15$). Comprehensive field saturation profiles are not available but in the limited investigations to date such low water contents have not been encountered; the saturation of the blocks obtained for pore-water sampling (including pit C (Fig. 1) excavated during moderate drought) being consistently in the range 80–90 per cent. At these saturations the top 3 m of Chalk could not accommodate much more than the first 150 mm of infiltration. Further infiltration could only be accepted into the pore-space through downward displacement, that is by some mode of piston-flow. At full saturation any excess external head at the top of the intergranular column would generate a downward-moving pressure front with rapid displacement of water at the base.

The velocity of the downward-moving pressure front will clearly vary considerably, for a given porous medium, with such factors as saturation and the distribution and state of confinement of the air phase. In the laboratory response rates in excess of 1 m/day have been demonstrated for small increases in external head at nearly full saturation and could explain in part the observed recharge response of the water-table to infiltration. However, without substantial prolonged ponding in the thin soil zone and superficial fissures, whose available storage above field capacity is in any case quite limited, the actual rate of acceptance of infiltrating rainfall by this mechanism would be more-or-less limited to that Darcy flow rate corresponding to the saturated k_v and a hydraulic gradient only marginally above unity, that is about 0·5 mm/day. This does not approach the higher infiltration rates or rainfall intensities.

(D) Why are the inclined discontinuities not more significant in the unsaturated groundwater flow regime?

It is perhaps possible that individual inclined joints are not continuous in depth and the overall flow process might be controlled by intergranular seepage between discontinuities at various levels. High suctions will certainly prevail at shallow depths if saturations are significantly reduced and the initial part of the annual infiltration would be drawn into the pores. However, if continuous joints, even of microscopic aperture, are present in depth and any near surface pore-water deficiencies have been satisfied, it remains difficult to understand why preferred-route (fissure) flow would not become rapidly established, particularly when rainfall intensities and infiltration rates are high. Overland flow or shallow lateral groundwater movement (interflow) might also be expected to develop locally over short distances in any non-fissured locations.

To summarize, no adequate explanation of the inferred slow-transit system is available and the overall regime of infiltration, evaporation and unsaturated flow in the Chalk must remain uncertain. Flow rates could be more than 5 m/hour through some fissures, less than 1 m/year through the pores or variable components of both systems.

TABLE III. OUTLINE OF CURRENT FERTILISER PRACTICE IN THE YORKSHIRE WOLDS

Month Crop-Type	J	F	M	A	M	J	J	A	S	O	N	D
Winter Cereals				top dressing 50–100 kgN/ha (S)						seed bed approx. 20 kgN/ha (C)		
Spring Cereals			seed bed 75–100 kgN/ha (C)									
Grassland				intermittent dressings of up to 90 kgN/ha total 0–375 kgN/ha (S or C) mean 150 kgN/ha								
Potatoes				seed bed 125–190 kgN/ha(C)								
Root Crops					seed bed 75–125 kgN/ha (C)							
Peas			seed bed up to 20 kgN/ha (C)				after harvest 'haulms' are ploughed-in					

125 kgN/ha = 100 N units/acre = 1 cwtN/acre

(S) straight nitrogenous fertiliser

(C) combined N/P/K fertiliser

AGRICULTURAL PRACTICE IN THE YORKSHIRE WOLDS

Present Land-Use and Cropping Pattern

The widespread and relatively even distribution of the rising nitrate levels, together with the high organic and bacteriological quality of the affected groundwaters, appear to eliminate many possible sources of pollution and it is concluded that it must be due to some change in the land and the way that it is farmed. The uncertainty about the age of the polluted waters questions the relevance of discussion on the present land-use and cropping pattern. Nevertheless, this is a convenient starting point for looking at the overall changes in agricultural practice which have occurred over the last 30 years.

The Yorkshire Wolds are a rich agricultural region with light-textured freely-drained soils resting directly on shattered Chalk. Over wide areas the soil zone is less than 0·2 m in thickness and only in the bottom of the dry valleys does it reach 1 m and have a more clayey character.

Arable farming dominates the region and as much as 60 per cent of the land area is dedicated to cereal growing. There is very little woodland or rough pasture; only locally does such land-use exceed 10 per cent of the total and overall it may less than 5 per cent.

Barley is by far the most important crop. It is sown in March and April, with a fertiliser application of 75–100 kgN/ha as shown in Table III. This is by no means a high application rate. Many unfertilised agricultural soils contain in excess of 1000 kgN/ha in the top 0·15 m, the bulk of which is organically-combined and derives from the decay of plant residues and direct fixation from the atmosphere. In Britain mineralization of these soil reserves typically generates some 50 kgN/ha/annum and is largely associated with intense microbial activity in late spring and to a lesser extent in autumn.[5] In excess of 150 kgN/ha/annum is required for high yields of most non-leguminous crops, the greatest deficiency occurring in the lighter soils farmed with continuous or frequent cereals.

Typical fertiliser practices for other crops are also illustrated in Table III; that for grassland varies widely, even within restricted areas.

Long-term Changes in Land-Use and Fertiliser Application

A detailed consideration of three typical parishes, in the area of detailed investigation marked in Fig. 3, has been undertaken. The greatest change is the doubling of the area devoted to barley between 1955 and 1966. This increase has been achieved more by the gradual replacement of traditional crop rotations with repeated cereal growing, than by expansion of the arable acreage. Grassland has remained stable at 25–35% of the total land use. The increased barley production has been possible only through the use of fertilisers and is reflected by the increase in the application rate from 20 kgN/ha/annum in 1957 to 93 kgN/ha/annum in 1971 (Fig. 6). Unfortunately data on fertiliser application cannot readily be related to parish or crop type and application rates may vary widely. Local investigations suggest that, in the three selected parishes, the county picture is probably representative. In recent years $(NH_4)_2SO_4$-based fertilisers have been progressively replaced by NH_4NO_3-types.

The cultivation of peas and beans for processing has increased in certain areas recently, though only locally to exceed 5 per cent of the total land-use. Peas are leguminous and the crop residues (haulms) are rich in nitrogen. They are ploughed in after harvest (Table III) and have been suggested as a possible source of nitrate pollution in other areas.[6] The cultivation of the processing pea is however fairly localised in East Yorkshire and it appears unlikely to be a significant regional factor.

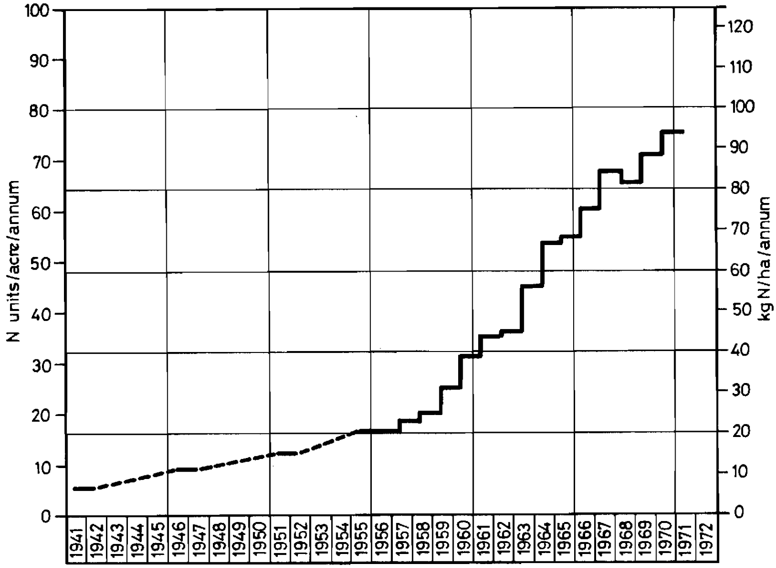

n.b. Based on data supplied by
M.A.F.F. & I.C.I.

Fig. 6. Regional trend in application rates of fertiliser nitrogen to all cropped land

Overall the numbers of livestock in the Yorkshire Wolds have not shown marked consistent increases during the period 1941–72, but the character of some livestock feeding operations has changed radically. There are uncertainties about estimating the nitrogen content of animal excreta but it appears that in many parishes at least 50 kgN/ha/annum are being generated. This traditionally was returned to the land; although evaporative losses must have been high, the manure being heaped in mounds on fields to dry before autumn and then ploughed-in. The recent concentration of the animal population, particularly pigs, as a result of the development of intensive rearing units, presents a waste disposal problem especially where little land is available.

Vulnerability of Nitrogenous Fertilisers to Leaching

Among all elements nitrogen is the most commonly deficient in agricultural soils. Whatever the form in which fertiliser nitrogen is applied, in aerobic soils it is fairly rapidly transformed to the nitrate ion by biological activity.[13] The process is normally complete within a few weeks and $(NO_3)^-$ (unlike $(NH_4)^+$) is neither absorbed or precipitated in soil and thus highly mobile and readily leached. Shaw showed that 200 mm of infiltrating rainfall completely removed a fertiliser application of 134 kgN/ha from the top 0·15 m of a sandy soil; the leachate must have contained 67 mgl NO_3-N.[17]

The nitrogen cycle in fertilised soils has been a research subject in agricultural chemistry for many years. Leaching, together with other mechanisms of loss of fertiliser nitrogen have received less attention than utilisation by crops and immobilization or fixation in the soil. It is difficult to relate much of the published work on leaching losses to actual agricultural practices in given field conditions of other areas, due principally to differences in soil properties, variation and variability of weather conditions and diversity of soil management and cropping procedures. Nevertheless many important results are presented in some of the works.

Cooke & Williams[5] have summarized the many decades of lysimeter and field drainage experiments on the Chalk at Rothampsted, Herts. Significant nitrate leaching has been observed from unfertilized fallowed soils particularly when rainfall intensity exceeded 20 mm/day in the spring. Peak nitrate levels in the drainage water from plots of fertilised or manured winter-wheat (receiving 95 kgN/ha) approached 30 mgl NO_3-N, but the long-term average was 7·2 mgl NO_3-N; for 250 mm of drainage the latter would represent a loss of 18 kgN/ha. Unfertilized plots had drainage waters with an average of about 4·0 mgl NO_3-N and a three-fold reduction in crop yields. They point out that losses of nitrate from spring-sown cereals could be expected to be greater than for winter-wheat, which both reduces drainage due to spring transpiration and takes-up nitrate significantly earlier, in March or April. In contrast to arable land, drainage from Rothampsted grassland contains very little $(NO_3)^-$, even when fertilised or manured at typical rates.

Stewart *et al*[19] and Olsen *et al*[16] have used destructive core-sampling methods to study losses of nitrate from agricultural land in Colorado and Wisconsin, U.S.A. respectively. Both works illustrate the pollution potential of arable farming using fertiliser applications of 150–170 kgN/ha/annum and the latter suggests that, as a result of the slow average rate of downward movement of NO_3-N through the soil profile (0·4 m/annum), this might not be apparent in groundwater supplies for some years. A comprehensive survey of a shallow unconsolidated aquifer in the North German lowlands has shown nitrate levels consistently in excess of 20 mgl NO_3-N in the groundwater below extensive intensively-cropped tracts of arable land, contrasting to 1·0 mgl NO_3-N below areas of forest and meadow with intermediate values in areas of mixed land-use.[1]

In the Yorkshire Wolds the 75–100 kgN/ha applied on sowing spring cereals will be particularly vulnerable to leaching for perhaps 6–8 weeks until it begins to be taken-up by the growing crop in May. The long-term average infiltration is around 300 mm/annum and about 60 per cent of the total land area is now devoted to cereals; overall rates of leaching of 46 and 102 kgN/ha/annum would thus be required to raise the mean nitrate levels in groundwater to 10 and 20 mgl NO_3-N respectively. This assumes the drainage from the remaining 40 per cent of the land area, not utilized for cereal farming, to contain only 2·0 mgl NO_3-N. Any tendency for this value to be exceeded, as a result of uncontrolled slurrying on grassland for example, would further aggravate this situation.

SUMMATION AND APPRAISAL

Current Situation in East Yorkshire

It is now well-established that the Chalk groundwaters of the saturated zone in the aquifer's intake area currently have nitrate levels approaching the lower recommended WHO limit for potable supplies. At the same time most of these groundwaters appear to contain very little, if any, thermonuclear tritium and would appear by implication to be 10 years or perhaps even 20 years old; though significant hydraulic objections to this interpretation can be raised.

The Yorkshire Wolds have become an area of increasingly intensive cereal growing, with barley as the dominant crop, and it appears likely that changes in agricultural practice, in particular the increased use of nitrogenous fertiliser, are either directly or indirectly the cause of the rising nitrate levels in groundwater. It is tempting to link the steady rise in fertiliser application rates, which commenced in about 1959, with the rise in NO_3-N of the groundwater supplies in 1971. If the available evidence is interpreted to imply that the bulk of the nitrate pollution currently being experienced is of such age, it could be inferred that further increases will occur because the rate of application of nitrogenous fertilizers has more than quadrupled. Thus a most pressing question is "How much nitrate is in the water of the unsaturated zone already in passage to the water-table?" This could be answered by direct investigation, though the work may be expensive, time-consuming and be confronted with practical difficulties.

Examination of Chalk pore-water at shallow depths below fertilized arable land has already revealed nitrate concentrations in excess of 15 mgl NO_3-N and locally in excess of 30 mgl NO_3-N; in strong contrast to those below unfertilized grassland. While it has not been demonstrated that such pore-water is in motion downwards towards the water-table, the concentrations show the pollution potential of nitrogenous fertilizers as currently used in cereal growing in East Yorkshire. It arises because of the rapid conversion of fertilizer nitrogen to nitrate in the soil, the time which elapses between application and uptake by the growing crop and the fairly high probability of infiltration during this period. Other sources of pollution also could be present locally.

Implications for Water-Supply Engineering and Agriculture

While the maximum nitrate concentrations experienced to date are not critical, they give grounds for concern inasmuch as the increase might be sustained. Since most of the Chalk groundwater sources of the region could be affected, the scope for alleviating the impact of pollution by mixing is currently limited.

Rising NO_3-N levels in groundwater supplies may well prove to be a national problem; though in all cases regional trends throughout an extensive aquifer must be distinguished from local ones, which may be related to totally different origins. The mechanism of pollution will generally be difficult to determine but a fuller understanding than at present is essential if a realistic policy for future water-supply and land-use is to be formulated. Knowledge of the process of leaching of the nitrogenous fertilizer is required to suggest optimum application rates and times for the local conditions. Control over leaching might be exercised by limiting and splitting applications or by introduction of new fertilizer types, though climatic variation and unpredictability would always constitute a problem.[1]

It might be argued that nitrate pollution of groundwater is an inevitable by-product of efficient high-yield arable farming, the problem not being how to eliminate nitrates but how to live with them; eventually weighing the cost of water treatment against the value of the increased crop yield. However, there is no well proven economical method of removing nitrate from drinking water.[21] The present distribution of nitrate in the unsaturated zone and its rate of movement to the water-table could be critical in putting a time-scale on the urgency for development of techniques.

Groundwater pollution frequently can be insidious, not being recognized until aquifers are irrevocably affected; quality monitoring alone, without sound understanding of the groundwater flow regime, is often ineffective as a safeguard to water-supplies. There is also danger in linking deteriorations in water-quality somewhat casually with likely-looking sources of pollution without consideration of the hydrogeological processes operating in the vast volumes of intervening rock.

ACKNOWLEDGEMENTS

The paper is published by permission of the Director of the Institute of Geological Sciences and of the East Yorkshire (Wolds Area) Water Board. The authors were encouraged by the active interest of Mr. D. A. Gray and Mr. Harold Ackroyd, the Chief Hydrogeologist and the Engineer of the respective organizations.

People from various organisations provided important data, performed essential work or contributed valuable discussion and the following especially are acknowledged; P. W. Izzard (Chemist, Kingston-upon-Hull CBC); D. B. Smith (UKAEA, Harwell Laboratories); J. Webber (MAFF, Leeds); S. C. Wyatt (MAFF, Beverley); P. E. R. Lovelock (Institute of Geological Sciences); N. G. Bunton (DTI Laboratory of the Government Chemist); A. E. M. Hood (ICI, Jearott Hill Research Station); M. J. R. Holmes (Fisons, Levington Research Station); C. Renn (University of Hull); R. Williamson (East Yorkshire (Wolds Area) Water Board).

Local well owners/operators and farmers are thanked for their interest and co-operation.

REFERENCES

1. Aldrich, S. R. 1970 Proc. 12th Sanit. Eng. Conf. (University of Illinois, College of Engineering) pp. 153–176, "The influence of cropping patterns, soil management and fertilizer on nitrates".
2. Allen, R. A., Smith, D. B., Otlet, R. L., and Rawson, D. S. 1966 *Nuclear Inst.& Methods*, vol. 45, pp. 61–71, "Low-level tritium measurements in water".
3. Anon. 1971 *Water Treat. & Exam.*, vol. 20, pp. 70–73, "Determination of total hardness and nitrate in water: an experimental study of interlaboratory errors".
4. Bunton, N. G., and Crosby, N. T. 1969 *Water Treat. & Exam.*, vol. 18, pp. 338–342, "The determination of nitrate in water and effluents using a specific ion electrode".
5. Cooke, G. W., and Williams, R. J. B. 1970 *Water Treat. & Exam.*, vol. 19, pp. 253–276, "Losses of nitrogen and phosphorus from agricultural land".
6. Davey, K. W. 1970 North Lindsey Water Board, Scunthorpe, "An investigation into the nitrate pollution of Chalk borehole water-supplies".
7. Edmunds, W. M., Lovelock, P. E. R., and Gray, D. A. 1973 *Jour. Hydrol.*, vol. 19, pp. 21–31, "Interstitial water chemistry and aquifer properties in the Upper and Middle Chalk of Berkshire England".
8. Foster, S. S. D., and Milton, V. A. (in press). IGS Report Series, "Hydrological basis for large scale development of groundwater storage capacity in the East Yorkshire Chalk".
9. Greene, L. A., and Walker, P. 1970 *Water Treat. & Exam.*, vol. 19, pp. 169–182, "Nitrate pollution of Chalk waters".
10. Groba, E. and Hahn, J. 1972 Proc. 24th Int. Geol. Cong. (Montreal), section 11, pp. 270–281 "Variations of groundwater chemistry by anthropogenic factors in northwest Germany".
11. Hancock, J. M., and Kennedy, W. J. 1967 *Proc. Geol. Soc. London*, no. 1643, pp. 249–252, "Photographs of hard and soft chalks taken with a scanning electron microscope".
12. Hoather, R. C., and Rackham, P. F. 1959 *The Analyst*, vol. 84, pp. 548–551, "Oxidised nitrogen in water and sewage effluents observed by ultraviolet spectrophotometry".
13. Kurtz, L. T. 1970 *Jour. Agr. Food Chem.*, vol. 18, pp. 773–780, "The fate of applied nutrients in soils".
14. Lijinsky, W., and Epstein, S. S. 1970 *Nature*, vol. 225, pp. 21–23, "Nitrosamines as environmental carcinogens".
15. Martin, A. E. 1972 *Water Treat. & Exam.*, vol. 21, pp. 202–212, "Medical considerations in the abstraction of potable waters from polluted sources".
16. Olsen, R. J., Hensler, R. F., Attoe, O. J., Witzel, S. A., and Peterson, L. A. 1970 *Soil Sci. Soc. Amer. Proc.*, vol. 34, pp. 448–452, "Fertilizer nitrogen and crop rotation in relation to movement of nitrate nitrogen through soil profiles".
17. Shaw, K. 1962 *Jour. Agr. Sci.*, vol. 58, pp. 145–152, "Loss of mineral nitrogen from soil".
18. Smith, D. B., Wearn, P. L., Richards, H. J., and Rowe, P. C. 1970 Proc. Symp., "Isotope Hydrology", I.A.E.A. Vienna, pp. 73–87, "Water movement in the unsaturated zone of high and low permeability strata by measuring natural tritium".
19. Stewart, B. A., Viets, F. G. Jr., Huchinson, G. L., and Kemper, W. D. 1967 *Environ. Sci. Tech.* vol. 1, pp. 736–739, "Nitrate and other water pollutants under fields and feedlots".
20. Waters, W. F. 1964 *Water Treat. & Exam.*, vol. 13, pp. 298–315, "The determination of nitrate in water".
21. Winton, E. F., Tardiff, R. G., and McCabe, L. J. 1971 *Jour. Amer. Waterwks. Assoc.*, vol. 129, pp. 112–116, "Cyanosis in infants caused by nitrates in well water".
22. World Health Organisation. 1970 W.H.O. Geneva, 2nd edition, "European standards for drinking water".