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THE INTERPRETATION OF TRITIUM IN THE CHALK UNSATURATED ZONE

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ABSTRACT

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Pore-water tritium profiles from the Chalk unsaturated zone are presented and the problems and limitations in their interpretation are evaluated in detail. A new model of the physicochemical behaviour of tritium in the soil zone is proposed, which can account for the quantity and distribution of thermonuclear tritium observed at shallow depths in the unconfined Chalk aquifer. The mechanisms of solute movement through the Chalk unsaturated zone are also discussed.

INTRODUCTION

Background to paper

The relevance of thermonuclear tritium (^3H) to groundwater studies on the *unsaturated zone* of the British Chalk was first demonstrated by the far-sighted work of Smith et al. (1970), and Smith and Richards (1972). They recovered uncontaminated cores and determined the tritium distribution in pore water beneath sites in Berkshire (October 1968) and Dorset (September 1970). The tritium profiles at both sites had very clearly defined peaks of over 500 TU*[1] at depths of 4 and 7 m, respectively (Fig.1). After allowing for radioactive decay*[2], these peaks could only have originated from fallout in the spring rainfall*[3] of 1963 and 1964, following a period of frequent thermonuclear weapon testing. Only 15% and 5% of the total thermonuclear tritium present at the respective sites had reached depths of more than 12 m. The profiles were inter-

*[1] The unit of tritium concentration used in this paper, which is defined as one ^3H atom per 10^{18} atoms of all hydrogen species and represents a radioactivity of $3.2 \cdot 10^{-3}$ pCi/ml.
*[2] The half-life of tritium is approximately 12.3 yr.
*[3] The term rainfall is used in this paper for all forms of precipitation; snowfall not being a significant process in the hydrology of lowland Britain.

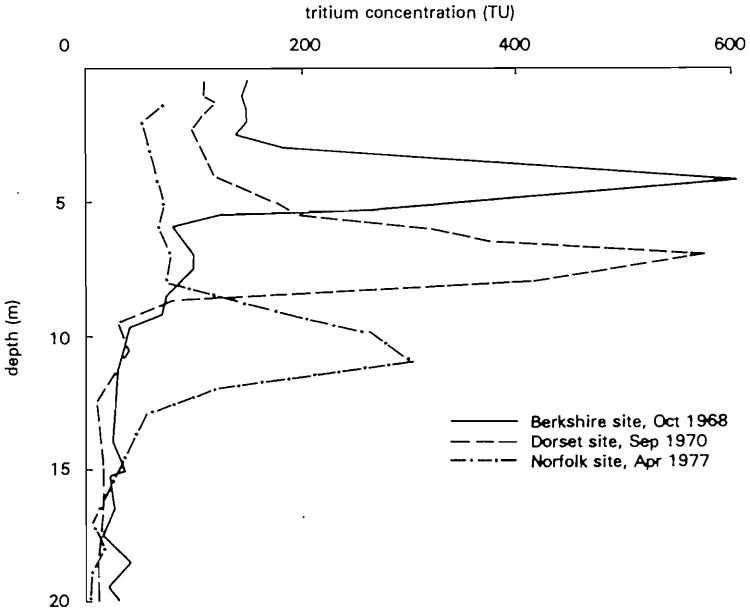


Fig.1. Selected tritium profiles for Chalk unsaturated zone.

preted as indicating that most of the infiltration was moving downwards by *interstitial piston flow* at average rates of about 1 m/yr. It was also noted that the tritium input from infiltration (using excess rainfall calculated from meteorological data and correlated/observed values for tritium concentration in British rainfall) was not sufficient to account for the tritium recovered in the cores, and it was postulated that the classical method of computing infiltration might be over-estimating evaporation rates and/or that significant infiltration of summer rainfall was occurring.

These results had important implications for the estimation of groundwater resources, for water-quality management and for pollution protection in the important Chalk aquifer, from which 15—20% of national water supplies are abstracted.

Despite moderate-to-high porosity (mainly in the range 0.15—0.45, according to region and horizon), the Chalk matrix has very low permeability (rarely exceeding $5 \cdot 10^{-3}$ m/day). Thus it was widely believed that downward groundwater movement through the unsaturated zone (like the horizontal flow in the saturated zone below) occurred mainly or exclusively in the frequent fissures, joints and other discontinuities of the rock mass (Foster and Crease, 1974). The tritium profiles appeared to contradict this concept. However, the exceedingly small pores (mainly less than 1 μm diameter) mean that gravity drainage of the Chalk matrix is almost entirely inhibited (Price et al., 1976), and within most of the *unsaturated zone* it must remain very close to full saturation. Foster (1975) thus postulated that relatively rapid unsaturated

groundwater flow could occur in fissures, but with the downward movement of tritium (and other solutes) being largely retarded as a result of exchange by molecular diffusion between the mobile fissure water and the static pore water. It has been shown mathematically that such a mechanism can produce similar vertical distributions of tritium to those resulting from interstitial piston flow (Oakes, 1977), and this has gained acceptance by British hydrogeologists (Young et al., 1976; Downing et al., 1978, 1979). Nevertheless it must be noted that this only applies for certain combinations of matrix porosity, molecular diffusion coefficient, fissure aperture and spacing; quite different distributions being produced with other combinations of these parameters (J.A. Barker, pers. commun., 1979).

In recent years it has become steadily more apparent (Foster and Crease, 1974; Young et al., 1976; Foster and Young, 1980) that at shallow depths below arable fields the pore waters of the Chalk unsaturated zone contain very high concentrations of nitrate and other ions, notably sulphate. This has given rise to serious apprehension about the long-term future of groundwater quality. The interpretation of thermonuclear tritium in the Chalk unsaturated zone is thus a topic of immediate practical relevance to the British water industry, because of the insight that it can provide on the movement of troublesome water-soluble pollutants (Foster, 1976).

Scope of paper

The importance of the topic has necessitated a *thorough* reassessment of all the factors that enter, or might enter, into the evaluation of the mass balance for thermonuclear tritium. Of particular interest is the interpretation of the proportion of the total tritium input involved in the slow mode of movement down to the water table, and the nature and degree of any "bypass" of this route.

In addition to a reconsideration of the original data from the Berkshire and Dorset sites (Fig.2), *new* data are presented and analysed from the following investigations:

(a) Multiple profiling of adjacent sites, mainly in arable land use, on the West Norfolk Chalk during 1976—1977.

(b) Re-drilling of the original Dorset site on permanent rough grassland in 1977.

All the profiles from Norfolk (Fig.3A), which are 0.1—10 km apart, show remarkable lateral uniformity. Tritium profiles with single pronounced peaks have also been found at numerous other sites on the Middle/Upper Chalk of southeastern England* with sufficiently thick unsaturated zones (Foster and Young, 1980). The relative magnitude and depth of the TU peaks are broadly

*The relevance and interpretation of tritium profiles in the hydrogeological study of Chalk areas with a known capping of *low-permeability* residual soils, glacial drift, or Tertiary deposits, from which localised surface runoff often occurs, are *outside* the scope of this paper.

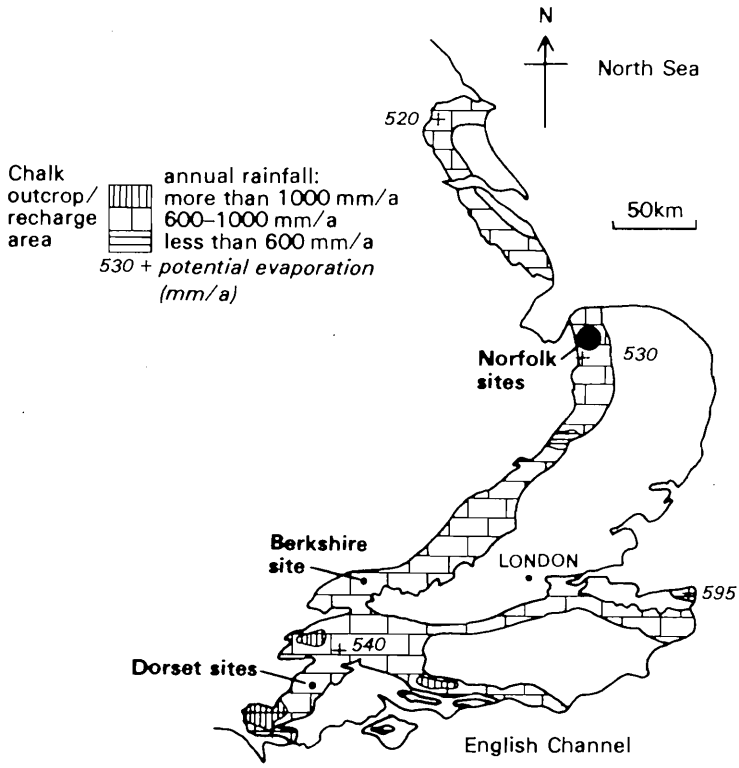


Fig. 2. Location and climate of investigation sites.

consistent with what might be expected, after allowing for radioactive decay and considering both the mean infiltration rate and the Chalk porosity in the areas concerned. However, it should also be noted that substantial differences between tritium profiles from closely adjacent sites drilled at comparable times are known from two areas, and various other minor anomalies have been observed in certain profiles.

Investigation methods

The majority of samples were obtained by dry, percussion drilling with a 0.45 m long, 100-mm diameter, drive core barrel. In order to obtain satisfactory samples from the somewhat harder and more cemented Chalk in Norfolk, air-flush rotary drilling with a lined double core barrel was required at depths greater than 15—20 m. Mechanically-excavated trenches were also used for obtaining samples at shallow depths and studying the weathering profiles of the Chalk rock mass. A comparison of laboratory results between the three sampling methods showed good agreement.

All samples were carefully handled and stored to eliminate, or to minimise,

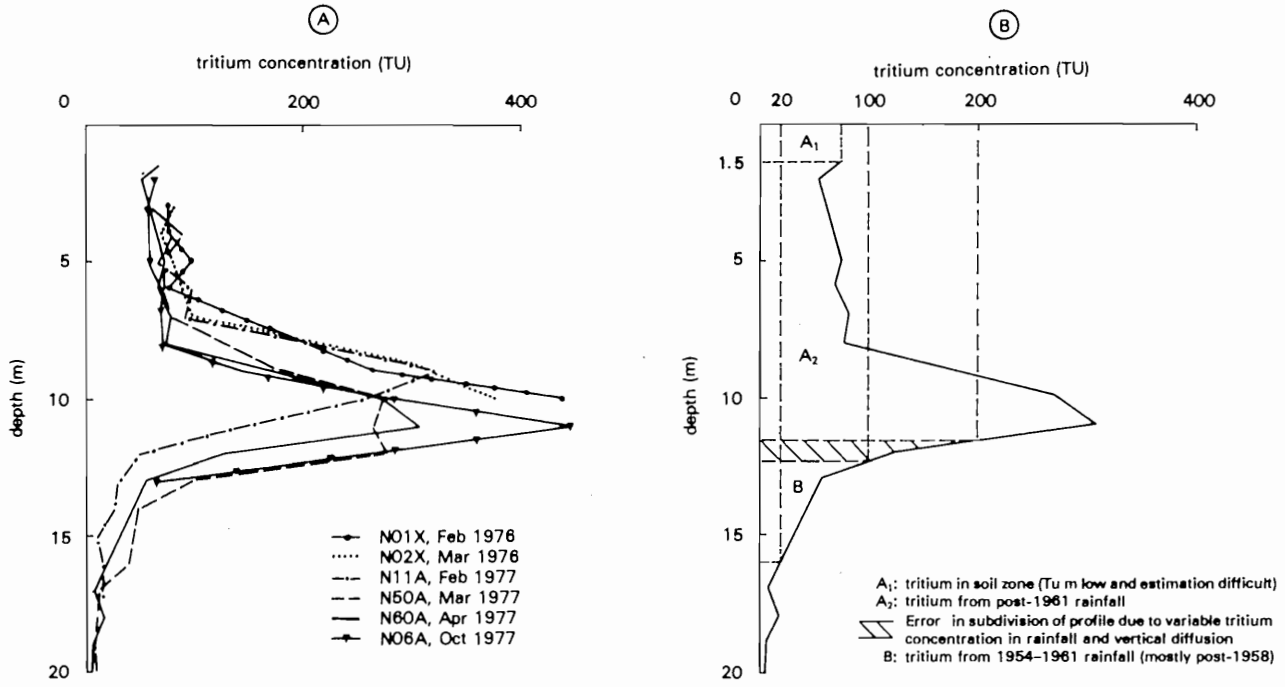


Fig. 3. Tritium profiles for Norfolk sites and their analyses.

pore-water contamination or evaporation prior to analysis. The determination of the tritium content involved its extraction from cores by distillation to complete dryness, electrolytic enrichment, conversion to ethane and measurement in a proportional counter (Allen et al., 1966). The overall sampling and analytical costs for a 20-m tritium profile totalled £ 2,000—2,500 at 1977 U.K. prices.

Measurements of the physical properties (moisture content by weight, bulk density at field saturation, interconnected porosity, intergranular permeability, pore-size distribution) were also made on selected Chalk samples.

TRITIUM CONTENT OF PORE-WATER PROFILES

The evaluation of the tritium mass balance requires a detailed, critical comparison of the tritium content of pore-water profiles with the tritium input from infiltration. Both can be expressed in TU metres (TU m); this unit being the product of tritium concentration (TU) and the respective volume per unit area of pore water or infiltration.

The tritium contents of selected Chalk pore-water profiles (Fig.1) are given in Table I, but it must be recognised that these figures are subject to several assumptions and possible sources of error, whose significance must be analysed in some detail.

TABLE I

Tritium content of pore-water profiles

Location	Berkshire	Dorset	Norfolk (N60A)
Sampling date	Oct. 1968	Sep. 1970	Apr. 1977
Mean chalk porosity (%)	38*	43	36
A_2—B boundary (Fig.3B) (adjusted for radioactive decay; in TU)	250	200	150
Tritium content (TU m)			
A_2	510	760	460
A_1 (estimated)	15	10	20
$A_1 + A_2$	520	770	480
$A_1 + A_2 + B$	730*	810*	560

*After Smith et al. (1970), and Smith and Richards (1972).

The accuracy of TU determinations themselves is quoted at ± 10% (Allen et al., 1966), which becomes significant when estimating the TUm associated with the principal peak in the profiles. The determinations were performed on lithologically-representative core samples of 0.3 m length for every 0.5 m, 1.0 m, or, occasionally, 2.0 m of borehole depth. Any variation in pore-water concentration in the rock mass, for example that with distance from joints or other discontinuities, would thus be averaged. The concentrations in the un-

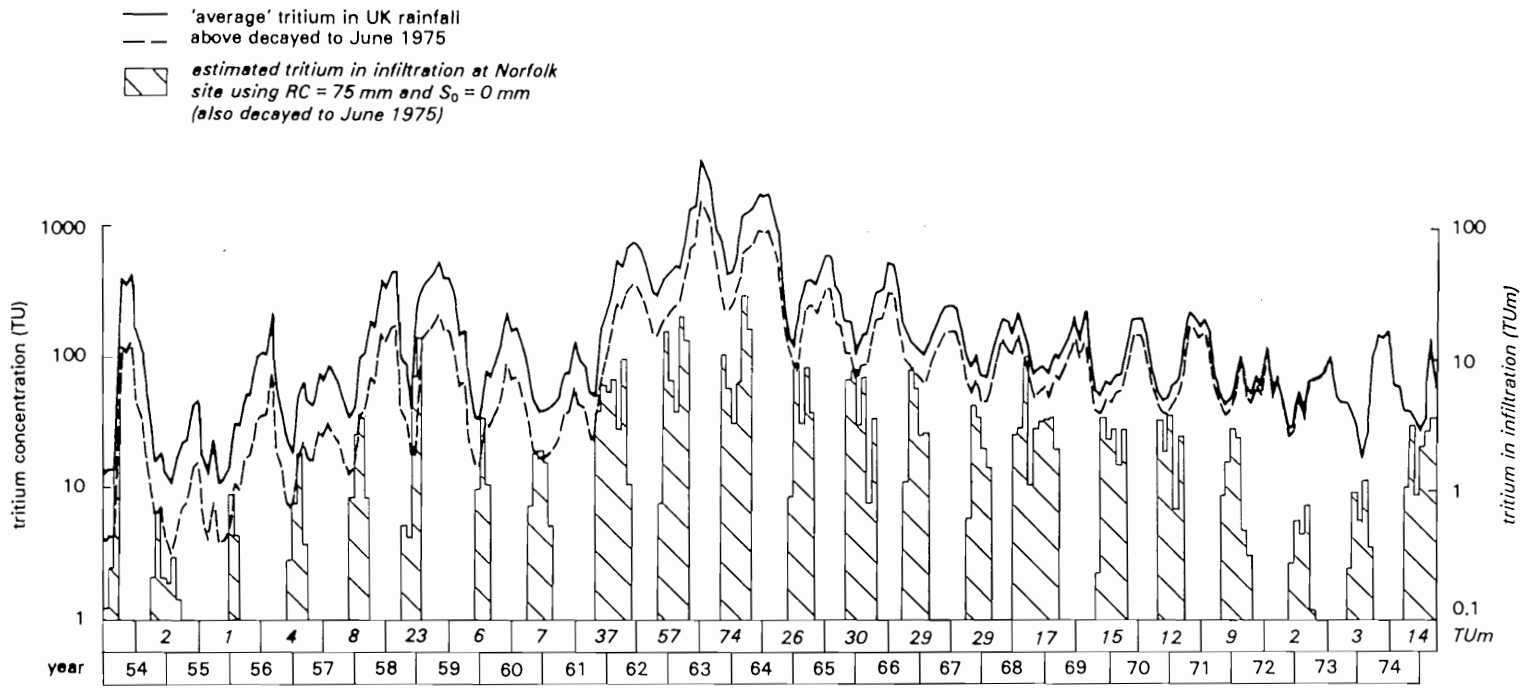


Fig.4. Long-term variation of tritium in rainfall and infiltration.

TABLE II

Tritium input from infiltration

Location	Berkshire	Dorset	Norfolk
(A) Summary of basic meteorological and tritium data:			
Period of analysis	Sep. 1961—Oct. 1968	Sep. 1961—Sep. 1970	Sep. 1961—Apr. 1977
Mean annual rainfall (mm)	740	880	700
Mean annual infiltration (mm):			
RC = 75 mm	240	410	230
RC = 25 mm	280	450	280
Total rainfall (mm)	5,360	8,040	10,920
Total infiltration (mm):			
RC = 75 mm	1,700	3,680	3,650
RC = 25 mm	1,980	4,060	4,420
Total TUm in rainfall*	2,140	2,230	1,700
Peak TU in rainfall*	2,470	2,220	1,540
(B) Estimation by method of Smith et al. (1970):			
Total TUm in infiltration*:	Sep. 1961—Oct. 1968	Sep. 1961—Sep. 1970	Sep. 1961—Apr. 1977
RC = 75 mm (S_0 = 0)	450	700	330
RC = 25 mm (S_0 = 0)	490	760	430
Peak TU in infiltration*:			
RC = 75 mm (S_0 = 0)	1,050	880	610
RC = 25 mm (S_0 = 0)	1,050	880	1,250
(C) Estimation using revised soil-moisture model:			
Total TUm in infiltration*:	Sep. 1961—Oct. 1968	Sep. 1961—Sep. 1970	Sep. 1961—Apr. 1977
RC = 25 mm, S_0 = 500 mm	690	1,040	610
RC = 25 mm, S_0 = 300 mm	650	990	580
RC = 75 mm, S_0 = 300 mm	540	840	430
RC = 25 mm, S_0 = 100 mm	500	790	460
Peak TU in infiltration*:			
RC = 25 mm, S_0 = 500 mm	790	870	650
RC = 25 mm, S_0 = 300 mm	840	1,070	830
RC = 75 mm, S_0 = 300 mm	820	990	620
RC = 25 mm, S_0 = 100 mm	780	1,170	1,150

*Corrected for radioactive decay to appropriate sampling date.

sampled core were assumed to vary linearly between the sampled lengths. It should also be noted that the date quoted for any given profile is that of sampling, but in certain cases there may have been a delay of some months before laboratory analysis, during which time additional radioactive decay would have occurred. This, however, is not considered significant in relation to other sources of error.

Estimates of volumetric moisture content are required to convert the TU measurements to TUm. Moisture content by weight was measured in the field laboratory, but possible loss of moisture during sampling/handling together with difficulty in obtaining accurate measurements of bulk density at field saturation for use in the conversion to volumetric content lead to the pos-

sibility of a ± 15% error. However, the physical properties of the Chalk are such that, in situ, the pores will everywhere remain close to full saturation, except in the uppermost metre or so of the profile. Thus porosity measurements can also serve for volumetric moisture content; these were made by the water resaturation method, with an estimated accuracy of ± 10%.

Subdivision of profiles

To attempt an evaluation of the tritium mass balance, it is necessary to attribute the pore-water tritium content down to some depth as being derived from infiltration during a known period. Implicit in this approach is the assumption that the downward movement of tritium in the profiles concerned has conformed to an *apparent* piston flow.

In view of the major rise of TU in rainfall during the spring of 1962 (Fig.4 and Table IIA) it is thought most practical to treat all the tritium above the base of the corresponding peak in the groundwater profiles as post-1961 in origin. However, the selection of this depth boundary is somewhat arbitrary (Fig.3B), and, in the case of the broader peaks of recent profiles, is aggravated by vertical diffusion. This may lead to errors of ± 25 TU m. An alternative approach is to attempt to integrate all of the thermonuclear tritium in the profiles, including the lower levels derived from 1954—1961 rainfall, but this involves a similar element of subjectivity in deciding the position of the lower depth boundary. Additionally, although the tritium content in the soil and Chalk-derived drifts is low, it is difficult to estimate accurately because of highly variable physical properties (Table III).

TABLE III

Summary of physical properties of soil—rock profiles

Location	Dorset	Norfolk
Soil drift cover:		
Lithological description	brown calcareous earths	brown (calcareous) earths over sandy glacial drift
Thickness (m)	0.3—0.5	0.5—2.5
Acid residual (%)	?	2—60 (locally)
Field bulk density (g/cm^3)	?	1.8—2.2
Estimated volume moisture content at field capacity (%)	15—20	15—20
Chalk:		
Depth to base of Chalk zone V* (m)	3	3—5
Acid residual (%)	0.5—2.0	1.0—2.5
Porosity (%)	40—47	30—40
Field bulk density (g/cm^3)	1.9	2.0
Moisture content (% by volume)	? 40—47	30—40

*Deeply weathered "structureless" Chalk, as defined by Ward et al. (1968).

TRITIUM INPUT FROM INFILTRATION

The estimates of the tritium input function used by Smith et al. (1970) were derived by summing the products of monthly excess rainfall, computed by the classical Penman—Grindley method with a RC*[1] of 75 mm, and the "average" correlated/observed tritium concentrations in British rainfall. Similar data extended and decayed to June 1975 are shown in Fig.4. The TUm in post-1961 infiltration estimated in this way, and in each case integrated and decayed to the date of sampling at the corresponding site, are given in Table II, (*B*). In Norfolk, as in Berkshire (Smith et al., 1970), such estimates are not nearly sufficient to account for the corresponding TUm in the pore-water profiles (Table I), despite ample TUm in the rainfall itself [Table II, (*A*)]; nor are the infiltration volumes capable of displacing the main tritium peak to the observed depths. These anomalies led to a more detailed consideration of all the factors affecting the estimation of tritium input from infiltration. In Dorset, however, the deficit of TUm in post-1961 infiltration is only minor [Tables I and II, (*B*)].

Reliability of tritium data for rainfall

The data on TU in British rainfall have been produced from several different sources. For the period 1953—1958 the British values were derived by correlation from measurements for Ottawa (Canada), and for 1956—1964, a particularly critical period, from measurements for Valentia (Ireland). TU determinations on British rainfall began in 1965, and the average British values given (Fig.4) are the arithmetic mean of results from up to five sites, after the elimination of any results suspected of contamination from those sites near to nuclear power stations.

Statistical analyses of the monthly data from two of the longest-standing British monitoring stations (Orfordness and Milford Haven) together with those for Valentia*[2] were carried out to investigate the spatial variation of tritium in rainfall. Student's *t*-tests showed the undecayed TU at all three stations to be significantly different (Table IV); Valentia having the lowest TU and Orfordness the highest. It is suspected that the former is subject to a much higher degree of oceanic dilution than the British stations. Using linear regression analysis only moderate correlation coefficients (r^2) are obtained (Table IV), and because, for the peak 1962—1964 period, considerable extrapolation is required to estimate monthly TU in rainfall at the British sites from that at

*[1] The root constant, which is related to the soil moisture deficit at which actual evaporation rates fall below potential, for the soil—plant system concerned.

*[2] Because of a systematic difference in laboratory calibration, all the British values quoted in this paper should be multiplied by a factor of 0.89 to conform with international standards; this factor was taken into account when undertaking statistical comparisons with the Valentia data.

TABLE IV

Results of statistical analyses of data on tritium in post-1965 rainfall

Stations compared			Valentia/Orfordness	Valentia/Milford Haven	Milford Haven/Orfordness
TU	monthly values*1	t	11.42 (S)	5.90 (S)	7.27 (S)
		r^2	0.78	0.80	—
TUm	monthly values*1	t	0.01 (NS)	0.35 (NS)	1.78 (NS)
		r^2	0.23	0.29	—
TUm	yearly totals*2	t	0.82 (NS)	0.48 (NS)	1.40 (NS)
		r^2	0.82	0.87	—

Calculated t is compared with tabulated t-values of 1.98 and 2.20 for monthly and yearly time base, respectively, for 95% level of significance; S indicates significant difference between sites and NS indicates no significant difference.
*1 For months where TU available for all sites.
*2 TU interpolated for months when not available.

Valentia, the accuracy of any data generated will be uncertain and subject to wide confidence limits. The regression equations obtained:

$$TU_{Orfordness} = 1.89\ TU_{Valentia} - 4.26$$

and

$$TU_{Milford\ Haven} = 1.47\ TU_{Valentia} - 10.22$$

appear to give greater values for the 1963 rainfall maximum than those published as the British "average".

It was considered that the total TUm fallout in rainfall might be more constant spatially, TU varying inversely with rainfall. Statistical analyses showed that, although monthly TUm did not appear to be significantly different, high scatter in the data caused extremely low correlation coefficients (Table IV), and no useful regression equations could be produced. The correlation between sites increases dramatically, however, when longer periods of analysis are considered. Thus on a yearly time base the TUm in fallout is spatially quite uniform, any temporal variations in local TU distribution and rainfall incidence being averaged out. However, yearly totals of TUm are only of limited use for the present purpose.

In conclusion, the average values for TU in British rainfall (Fig.4) are subject to serious limitations and must only be treated as a general indication of the scale of temporal variations that occurred. Amongst the sites under consideration, it is likely that both Berkshire and Norfolk would have experienced above "average" TU values, although no simple relationship can be anticipated. There is substantial uncertainty over the TU and TUm in rainfall during the critical period 1962—1964, although it remains absolutely certain that the bulk of the TUm in infiltration must have been derived from rainfall during this period. The subsequent variations in TU and TUm in rainfall are better understood and will be useful for future studies of temporal change in porewater tritium profiles.

Computations using meteorological data

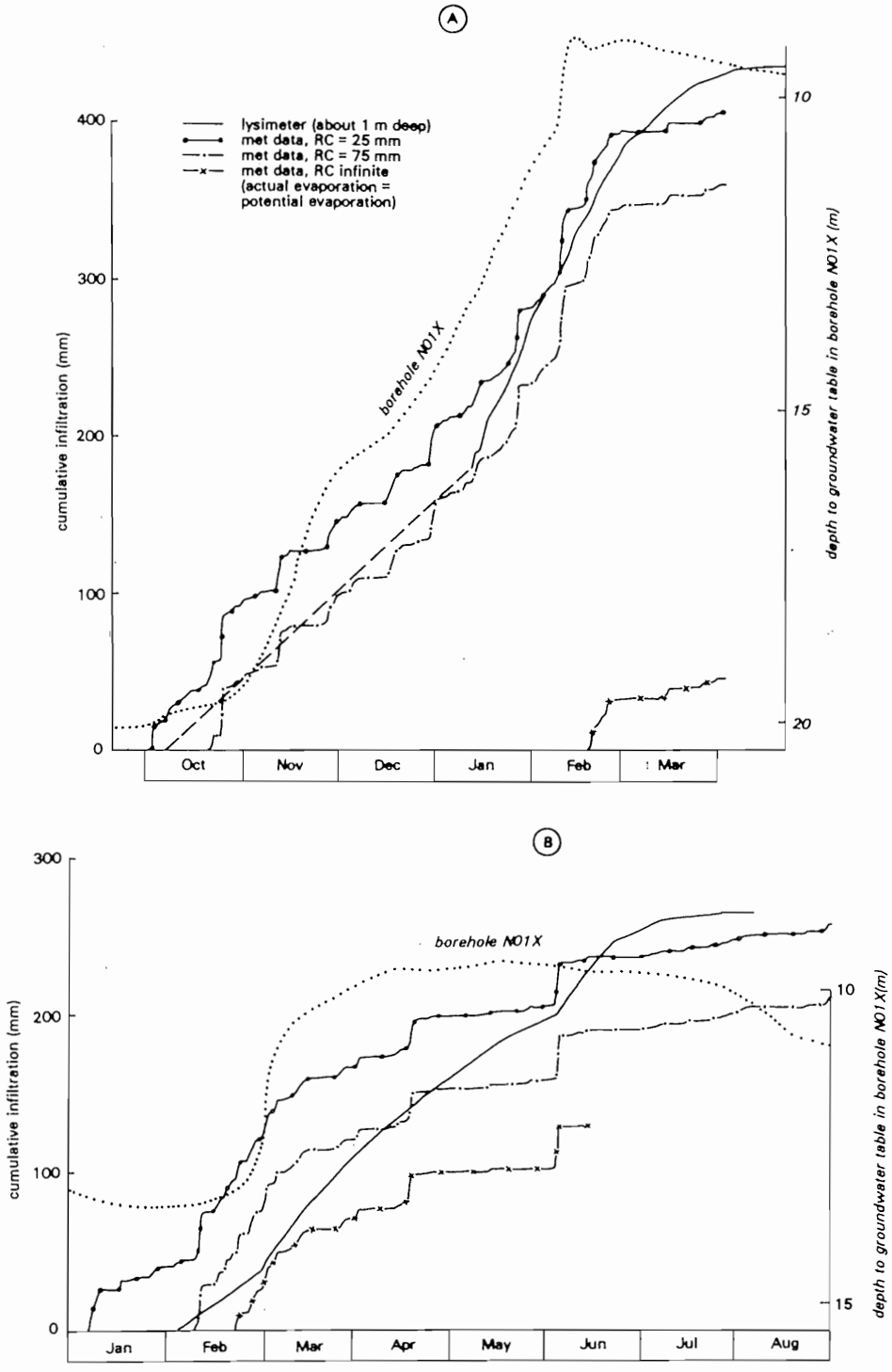
There will be errors in the measurement and computation of the basic meteorological data (rainfall and potential evaporation), and it is also accepted that rainfall may be subject to some spatial variation between the investigation site and the nearest gauging station. However, their effect on the computation of long-term infiltration is likely to be small.

Lysimeter experiments (R. Kitching, pers. commun., 1978) and water balance studies (e.g., Headworth, 1970) suggest that the RC for short-rooted vegetation could be reduced from 75 mm to perhaps as low as 25 mm. However, the use of a single root constant for arable farmland may not adequately represent the change in the regime of evaporation after harvest. Some lysimeter measurements and the monitoring of the shallow groundwater table at one of the Norfolk sites during 1976—1978* (Fig.5A and B) supports the hypothesis that the RC certainly does not exceed, and is probably substantially less than, 75 mm. The reduction of RC to 25 mm would have the effects of reducing the computed soil moisture deficit to zero earlier each year, increasing the infiltration by about 10—20% allowing larger displacement of the main tritium peak and producing a significant increase in the TUm in infiltration, particularly in 1963 when maximum concentrations in rainfall occurred [Table II, (*B*)]. However, this factor alone cannot nearly account for the apparent deficit in TUm estimated in infiltration against that measured in pore-water profiles, except in Dorset.

There is some evidence from groundwater level hydrographs for infiltration of summer rainfall to the Chalk, following certain intense storms. On occasions such infiltration appears to occur without the soil moisture deficit being satisfied (and therefore is not taken into account by classical calculations based on meteorological data). Such events are likely to be associated with the highest TU in the yearly rainfall cycle (Fig.4), but in recent years at least, the associated rises in groundwater level in Norfolk (Fig.6) and Dorset have never exceeded 0.05 m and may include a component of barometric fluctuation, known to occur in unconfined Chalk observation boreholes during storms. Even assuming a high value for Chalk specific yield (2%), the amount of infiltration involved would only produce an additional input of 3—4 TUm in Norfolk during the period 1964—1977. It is believed that summer infiltration occurs because of the cracking of the clay soil cover, but it only results in recharge of the Chalk aquifer in the very *small* percentage of the land surface underlain *directly* by solution pipes or exceptionally large fissures. Elsewhere

*It should be noted that the period 1976—1978, included a sequence of rather unusual meteorological conditions — the end of the worst British drought of the 20th century in October 1976, followed by the extremely wet winter of 1976—1977, and the wettest spring—summer for many years in 1978.

Fig.5. Comparison of computed and observed infiltration in Norfolk during: (A) 1966—1977; and (B) 1977—1978.


A
lysimeter (about 1 m deep)
met data, RC = 25 mm
met data, RC = 75 mm
met data, RC infinite
(actual evaporation =
potential evaporation)
borehole NO1X
cumulative infiltration (mm)
depth to groundwater table in borehole NO1X (m)
0
100
200
300
400
10
15
20
Oct
Nov
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cumulative infiltration (mm)
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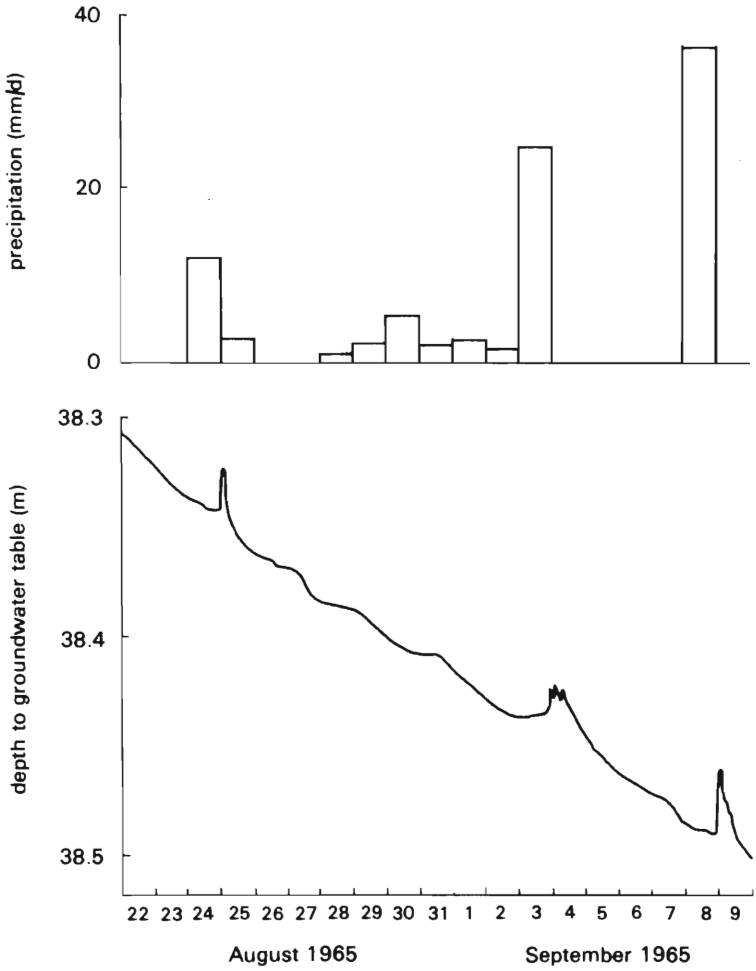

Fig.6. Minor recharge to Norfolk Chalk from summer rainfall.

there would be no potential for any short-term excess rainfall to be drawn laterally into such features, because of the prevailing high pore-water suctions; thus averaged over the entire land area this phenomenon results in almost negligible infiltration.

Some other factors which might affect the TU of rainfall, evaporation and infiltration, should also be mentioned. While there is no isotopic enrichment of water during transpiration through plants (Zimmermann et al., 1966), a degree of fractionation (preferential evaporation of non-tritiated water) occurs during evaporation from bare soil. Although this condition arises on arable land for up to eight months each year, the overall enrichment of TU in the soil water is unlikely to be more than 2%. This is negligible, bearing in mind that the total evaporation during the non-growing season is unlikely to exceed

150 mm. The actual TU in rainfall incident at soil level may be modified by plant interception and by recycling of water vapour in the microclimate. The presence of any deeper root development in the soil—rock profile could lead to a disproportionate loss of TUm by evapotranspiration.

Other factors

Rainfall may not be the only source of TU input; tritium may be taken up directly from the atmosphere by soil micro-organisms and then oxidised to become part of the soil water (Ehhalt, 1973; McFarlane et al., 1978), but this process seems unlikely to be particularly significant in British field conditions. The TU in the water of crystallization of fertiliser compounds (applied in large quantities to arable land) is also considered to be negligible. There is also no record to suggest that any of the sites investigated have ever been subjected to agricultural irrigation. Tritium may be retained to some degree on clay minerals and organic material (Stewart, 1967), but other than in the soil zone, their proportion is minimal and such effects are likely to be unimportant in chalk itself.

Revised model of soil-moisture behaviour

While each of the above-mentioned factors imposed some limitation on the accuracy of evaluation of the tritium input from infiltration, they did not appear sufficient to make up for the larger of the deficits on this side of the mass balance calculation. Some important factor seemed to have been overlooked; the modelling of the physical behaviour of the uppermost metre or so of the soil—rock profile (the zone of plant influence) was, in particular, regarded as oversimplistic. Only a proportion of the soil moisture in this zone is available to short-rooted plants*, but this moisture is intimately associated with that retained permanently in the finer pore space. Given the relatively low evapotranspiration rates generally experienced in Britain, it is highly probable that much of the *summer* rainfall resides in the soil zone for sufficient time to allow TU equilibration with the soil moisture, by vertical hydraulic dispersion and lateral molecular diffusion.

Thus a revised soil moisture model was introduced in which the TU of the soil moisture at the end of each month is given by:

$$T_s = [T_{s-1}(S_0 - S_{s-1}) + T_R R]/(S_0 - S_{s-1} + R)$$

where S_0 is the limiting size of the soil moisture store (i.e. the field capacity); S_{s-1} and T_{s-1} are the antecedent soil moisture deficit and TU in the store, respectively; R is the rainfall; and T_R its average TU. The evaporation and any

*The low values of RC, which appear appropriate, suggest that short-rooted vegetation cannot draw water from Chalk pores of much less than about 0.6 μm, that is against suctions of more than 5 atm. (50 m of water).

infiltration occurring during the month in question are assumed to have a TU equal to T_s. The TUm input is $T_s I$, where I is the infiltration.

For the calculation of infiltration the classical Penman—Grindley method, applied to the *daily* meteorological data is retained. It is recognised that, ideally, values of T_s should also have been computed on a daily basis, but because of the afore-mentioned uncertainties over the precise values of T_R, the additional computation hardly seemed justified.

The physical character of the soil—rock profile will control S_0 and it is estimated, from physical properties (Table III), that the top metre has a moisture content at field capacity of 300—350 mm at the Dorset sites and 150—200 mm at the Norfolk sites. The Berkshire site is similar to those in Dorset. If the next 0.5 m of the profile could be included it would increase the above values to 500—550 and 300—350 mm, respectively, and thus values for S_0 of 100, 300 and 500 mm must be considered.

A somewhat similar model to that developed here was suggested by Andersen and Sevel (1974), but it only allowed the *monthly excess* of rainfall over actual evaporation to enter and mix with the soil moisture storage; this seems less realistic, at least under British conditions. Even the proposed model departs from physical reality because:

(a) it fails to take account of interception, that is the water stored on the wetted surface of plants and evapotranspired directly from them during and immediately following rainfall;

(b) it neglects the effect of any small upward water flux from below the soil zone (which may occur under certain conditions in drier summers) on the TU in the soil moisture store;

(c) the depth of penetration and residence time of summer rainfall in the soil zone will vary widely and the assumption of total equilibration throughout this zone will not always hold.

A number of different combinations of S_0 and RC have been evaluated, using meteorological data for each of the three sites under consideration and the average TU in British rainfall decayed to the appropriate date. The computation was started in September 1960 with the initial T_s in the soil moisture store set at 160 TU before decay. The revised model produces very much larger tritium inputs in infiltration (Table II, (*C*)] because some of the tritium in summer rainfall, which possesses the highest TU each year (Fig.4), is retained in the soil moisture and enters infiltration in the subsequent autumn—winter. The store acts as a buffer, and the fluctuations of TU in the soil moisture, and therefore in infiltration, are much more subdued and lag behind the widely-varying concentrations in rainfall (Fig.7). The increased autumn inputs (when T_s is greater than T_R) tend to be partially counteracted by reduced inputs in spring (when T_s is less than T_R), but once a high TU has built up in the store a long time is required for it to dissipate. The behaviour of the store thus also explains the fact that the TU at shallow depth in pore-water profiles is commonly observed to be higher than the TU in the winter rainfall of the immediately preceding years.

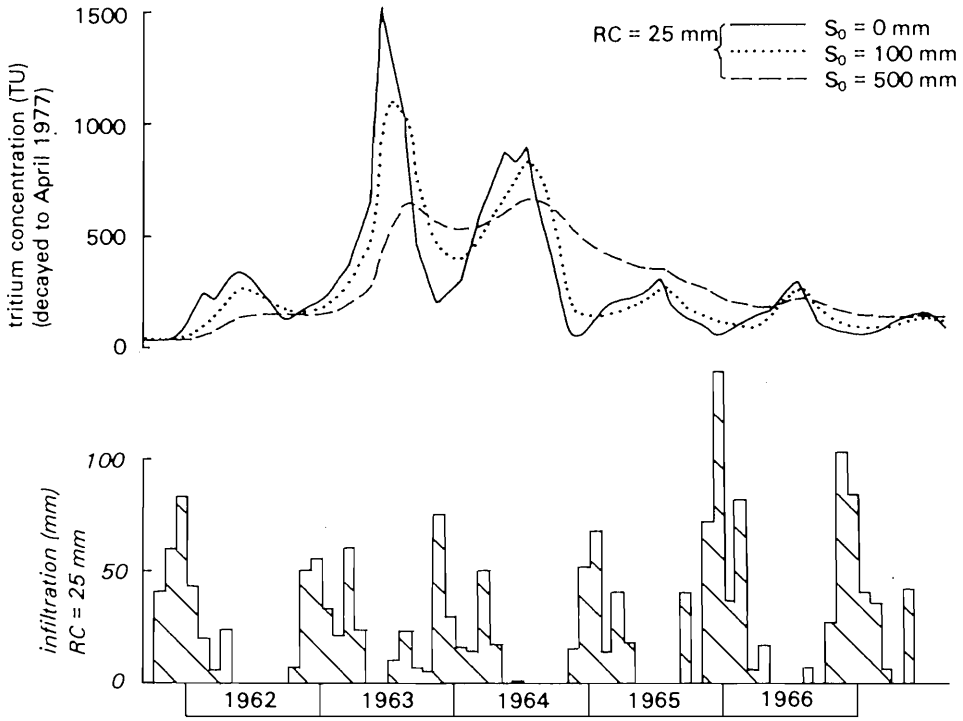

Fig.7. The effect of soil moisture mixing on tritium concentration in infiltration (Norfolk sites). The TUm input is the production infiltration is the product of tritium concentration and infiltration.

INTERPRETATION OF TRITIUM PROFILES

The combination of S_0 and RC selected to model a given Chalk site must be capable of producing the time distribution of TU and TUm in infiltration apparently implied by its tritium profiles (after allowing for the effects of radioactive decay and of minor vertical diffusion) and, in particular, account for the magnitude and width of the main tritium peak.

In general terms, the larger the S_0, the greater is the total TUm in infiltration but the less peaked is the distribution of TU with time. However, the timing of the last infiltration in 1962—1963 and the first in 1963—1964 (Fig.7) is the critical factor in determining which model produces the highest peak TU in infiltration [Table II, (*B*) and (*C*)]. In the presence of a soil moisture store, the effect of variation in RC is also not straightforward, because it influences not only the timing and magnitude of autumn infiltration but also the size of the summer soil moisture deficits.

The uncertainty about the distribution of TUm in rainfall, especially during 1962—1964, preclude the confident selection of a single combination of S_0 and RC as the best-fit model for any given site. The significant difference in the

original mass balance anomaly between Dorset and Berkshire or Norfolk is, in all probability, essentially a reflection of differing degrees of departure of the actual TU in rainfall from the "average" British value. On the balance of the available data, the most appropriate model for all sites would appear to have an S_0 of 100—300 mm and RC of 25—50 mm.

Adoption of such a model implies that the TUm observed in the Chalk pore-water profiles down to the base of the thermonuclear tritium peak may represent a smaller proportion of the total input in post-1962 infiltration than has been previously estimated. The balance of the available data could be interpreted as suggesting that up to 20% of the *tritium* is transported by a preferential (more-rapid) flow of water, involving some type of "by-pass" of the slow route of downward movement.

Temporal changes in profiles

Reliable interpretation of tritium in the Chalk unsaturated zone also requires study of the temporal changes in profiles at the same sites, particularly with respect to the movement of tritium peaks.

Redrilling and sampling at the Dorset site in 1977 showed that the main tritium peak had moved downwards through the unsaturated zone by 3.5—4.0 m since 1970 (Fig.8), but detailed analysis of the new profiles poses certain complications. The total TUm in the 1977 profiles is some 10—15% *less* than the appropriately decayed 1970 profile, despite the input of significant quantities of tritium during the period 1970—1977. In the case of the original (lower) site, groundwater levels in recent years have occasionally risen above 10 m b.g.l. (below ground level) and could have washed some tritium out of the unsaturated zone profile but this *certainly* could not have occurred at the adjacent upper site, where, because of the higher elevation, groundwater levels have never risen above 15 m b.g.l. During September 1970—July 1977 the infiltration in the area is estimated to be 2780—3130 mm (depending on the root constant employed). If an apparent piston displacement of the tritium peak was occurring as a result of *all* infiltration, the peak would have been expected to move down by 6.5—7.3 m; the observed movement was *less than* 60% of that expected. The proportion of infiltration associated with the slow mode of downward movement* (by whatever physicochemical process) is thus further questioned.

In the analysis of the Berkshire profile, Smith et al. (1970) interpreted the proportion of the total TUm that had penetrated in advance of the main peaks to depths of more than 12 m as being a measure of the component of preferential rapid fissure movement. This approach is questionable since it is

*It would be valuable if unsaturated zone pore-water chemical profiles (perhaps Cl or Na) beneath untreated non-agricultural land could be used for a complementary analysis of this proportion, but sensitivity of this method to small errors in the estimation of mean solute concentration in rainfall appear to preclude its confident application.

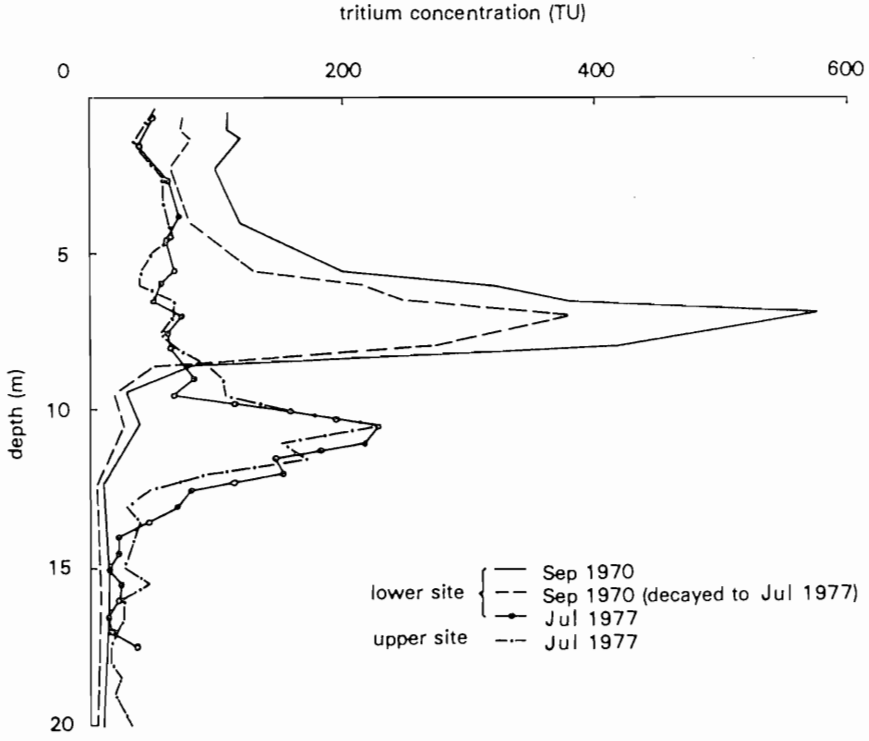

Fig.8. Temporal variation of tritium profiles in Dorset.

highly probable that some part of any rapid component will have passed down fissures not intersected by the investigation borehole and/or have reached the water table.

Probable physical mechanism for by-pass flow

Foster (1975) showed that the effectiveness of the Chalk matrix in retarding the rate of downward movement of tritium and other solutes in water-filled fissures would decrease with increasing fissure aperture, due to the larger fluid volumes involved and the faster rate of fluid movement, which would make lateral molecular diffusion less effective. However, except at very low suctions, fissures of larger aperture would remain air-filled and not be conductive.

Scotter (1978) has demonstrated that very rapid preferential movement of solutes in soils can be expected to occur in cracks and pores with a characteristic size exceeding 0.1—0.2 mm but that such voids would only conduct water in near-saturated soil (i.e. at negative potentials (water suctions) of less than about 0.2 m). It is likely, therefore, that the slow mode of downward tritium movement is associated with water transport in the microfissures and largest

pores of the Chalk, whose characteristic size are in the range 0.01—0.2 mm. Such voids are unlikely to represent more than 1% of the Chalk by volume and probably produce a saturated vertical hydraulic conductivity of up to 10^{-2} m/day.

After the most intense rainfall, the infiltration capacity of this system is likely to be exceeded, suctions will fall concomitantly and positive potentials will develop locally allowing horizontal groundwater movement to the macrofissures (of greater than 0.2 mm in aperture). The distribution of macrofissures in shallow Chalk is difficult to quantify, but in many areas they are likely to occur at a spacing of less than 1 m. Larger structures, such as pipes, although of widespread occurrence, are much less abundant. Unsaturated groundwater flow in the macrofissures is probably too rapid to allow significant lateral molecular diffusion of tritium into the Chalk matrix. Temporal variation in operative flow mechanism, according to rainfall intensity, will cause wide variation in the rate of water-table response to infiltration. Apparent rates of downward movement well in excess of 20 m/day have been recorded. The bacteriological contamination of groundwater supplies, which not infrequently occurs in areas of thick Chalk unsaturated zone after high-intensity excess rainfall, is further evidence for the existence of such a flow mechanism.

Variation in the proportion of high-intensity rainfall in Dorset between the periods 1962—1970 and 1970—1977 might be the explanation for the slower movement of the tritium peak during the latter period (Fig.8). (Any analysis of rainfall intensity in this context, however, is unavoidably subjective; spatial variation in the macrofissuring and temporal variation in antecedent meteorological conditions combine to preclude the choice of any specific rainfall intensity above which rapid by-pass flow will occur.) Another cause could be that physical properties (fissure aperture and frequency) change with depth.

The presence of a preferential rapid component of downward flow dependent on the intensity of excess rainfall would have significant implications for the interpretation of the behaviour of other solutes in the unsaturated zone. The availability of ions for leaching from agricultural soils varies with time, maximum concentrations being likely to occur in the first autumn drainage, and also in any drainage in late spring. During the main winter period, when the probability of high-intensity *excess* rainfall is greatest, the concentration of agricultural leachates is likely to be relatively low. This factor could be of considerable significance in the overall interpretation of the Chalk groundwater nitrate problem.

CONCLUSIONS

(1) The introduction of a more realistic conceptual model of the behaviour of tritium in the soil fully accounts for the large amounts of thermonuclear tritium in the Chalk unsaturated zone.

(2) At any given location, uncertainties over the limiting size of the soil store in the new model and over the TUm in rainfall during 1962—1964 com-

bine to exclude an adequate evaluation of the mass balance for tritium pore-water profiles.

(3) Individual profiles cannot be interpreted with sufficient precision to question or to qualify the standard hydrometeorological models for the calculation of excess rainfall.

(4) The TUm recovered in the pore-water profiles probably represent a smaller proportion of the total TUm input from infiltration than was previously believed. An important component of preferential rapid downward movement of tritium (and other solutes) could occur by some by-pass mechanism associated with macrofissures that only conduct water in response to high intensity excess rainfall. It is in the evaluation of these unsaturated zone processes that Chalk pore-water tritium profiling finds its most valuable application.

(5) Long-term investigation of the temporal changes in pore-water tritium profiles at individual sites will be required before unsaturated zone models to predict solute movement can be adequately calibrated.

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