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THE CHALK GROUNDWATER TRITIUM ANOMALY — A POSSIBLE EXPLANATION

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ABSTRACT

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Attention is drawn to a mechanism which could profoundly complicate the interpretation of tritium determinations in investigations of the rate of groundwater movement in the British Chalk and other physically-comparable formations. It could explain the anomalously low levels of thermonuclear tritium currently observed in the saturated zone of the Chalk aquifer, with important implications for pollution control.

BACKGROUND

The low level of thermonuclear tritium in groundwater from the *saturated zone* of the Chalk aquifer throughout much of its intake area has been recognised as a major anomaly in British hydrogeology in recent years. The tritium profile of pore-water from the *unsaturated zone* at a Berkshire site in October 1968 led Smith et al. (1970) to suggest that about 85% of the total flow of vadose groundwater was by intergranular seepage at a mean rate of less than 0.9 m/year, contradicting the widely-held concept that fissure-flow dominated downward movement. A similar profile was determined in September 1970 for a site in Dorset (Smith, 1973).

This work had serious implications for resources management and pollution protection in this important aquifer, from which about 15% of all national water-supplies are derived. In the case of nitrate pollution resulting from arable farming for example, a critical question was the potentially high nitrate concentration of vadose pore-waters, by implication, in slow transit through a thick unsaturated zone to the water-table (Foster and Crease, 1974).

The unquestionable advantages of tritium (HTO) as a tracer in studies of groundwater movement (e.g. Libby, 1961; Smith, 1973) give considerable strength to the interpretation, but there are significant hydraulic objections. While the physical properties of Chalk are not such as to preclude significant intergranular seepage in the unsaturated zone, in the absence of a major fissure-flow component, it is difficult to see why surface run-off does not develop particularly after prolonged or high-intensity rainfall.

The purpose of the present note is to draw attention to a possible process which could explain the present low levels of HTO in the *saturated zone* and at the same time would be compatible with relatively-rapid flow down joints and fissures in the *unsaturated zone.*

HYDRAULIC CHARACTERISTICS OF CHALK

The physical characteristics of the Chalk are such as to make it a most unusual porous medium. The rock matrix has very low permeability (10^{-3}—10^{-4} m/d) but moderate to high porosity (0.15—0.40), very high specific retention (specific yield less than 0.01), exceedingly small pore diameters (mostly less than 1 μm) and an exceptional specific interstitial surface area (Edmunds et al., 1973; Foster and Crease, 1974). It is generally a very-pure fine-grained carbonate (Hancock and Kennedy, 1967) but at some horizons there are significant proportions of clay minerals and at others occasional thin marl bands.

The jointing of the rock-mass varies with depositional province, stratigraphical zone, tectonic and morphological setting, but the Chalk is normally traversed by frequent high-angle joints and numerous horizontal discontinuities associated with bedding and secondary structures (Fig.1), the latter group being most commonly associated with major permeability development in the saturated zone. In the unsaturated zone the opening on some joints may be relatively large (> 5 mm), particularly where the rock-mass is in overall tension as on escarpments and where they have been enlarged by solution, but more typically is small or even microscopic. Nevertheless it is likely that *in situ* every metre of Chalk is traversed by at least one high-angle joint with an effective opening of 0.1 mm. Such a system alone would impart an overall permeability to the rock-mass 50—500 times greater than the intergranular value. It is thus evident that the Chalk aquifer possesses two distinct physical components each with highly-contrasting permeability and porosity; one of these components, the intergranular pore-space, will be almost always fully saturated, even in the *unsaturated* zone, except perhaps very close to the land surface.

EVALUATION OF HTO DIFFUSION PROCESS

Self-diffusion of HTO in Chalk pore-water was considered by Smith et al. (1970) as one process which would "necessarily lower and broaden" the main peak of the tritium profile (in a vertical sense), causing significant changes in concentration over distances of perhaps 0.3—0.5 m after periods of numbers of years. Implicit are the assumptions that the profile was not varying laterally on any scale, that the input was areally uniform and that no lateral diffusion was occurring, despite the probability of the Chalk being traversed by frequent high-angle joints.

It seems more probable that the input to the unsaturated zone (after infil-

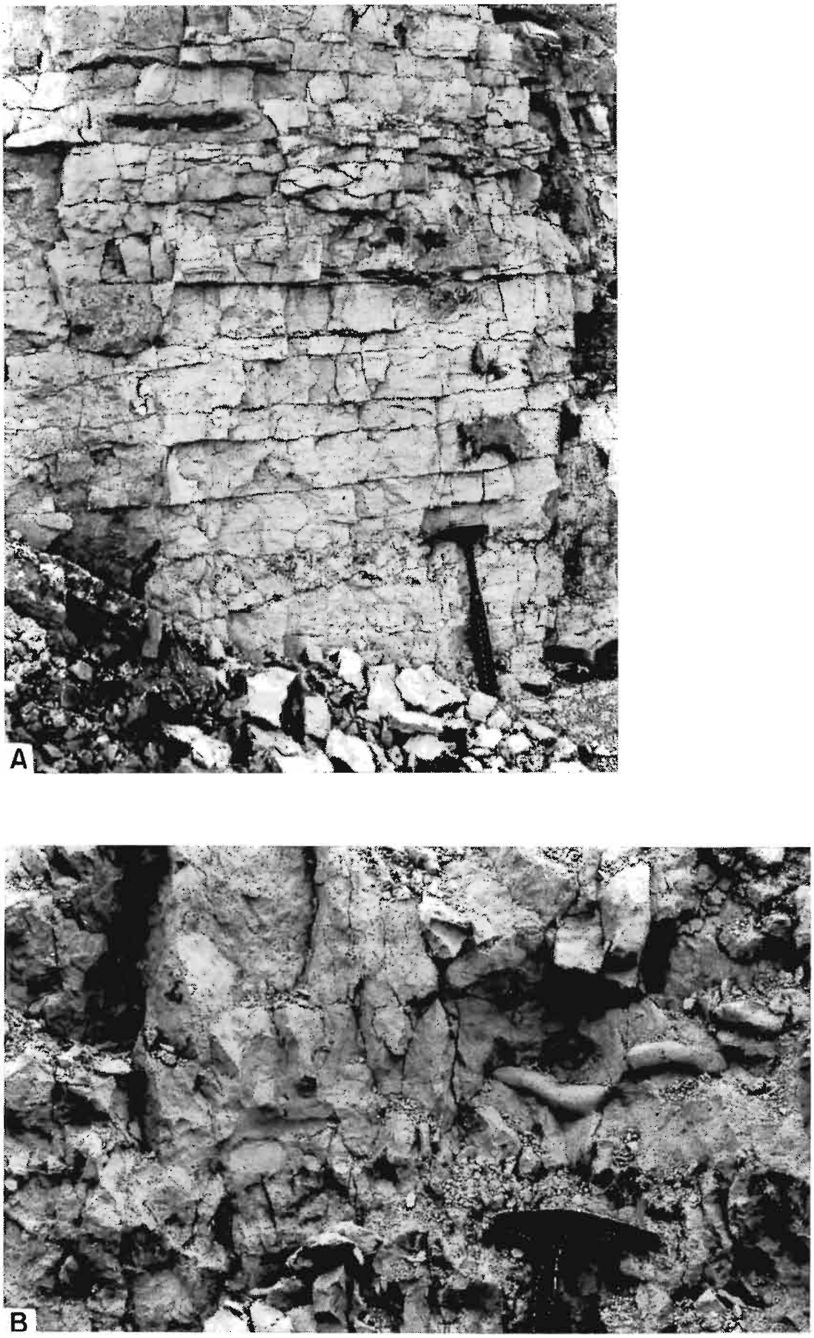

Fig.1. Examples of jointing in a Chalk rock-mass; (above) Turonian of Lincolnshire, "northern province" and (below) Turonian of Buckinghamshire, "southern province". (Photos by C.J. Wood.)

tration through the very thin soil cover) will be localised on joints. In the late 1950's when the first groundwater containing thermonuclear tritium entered the system, there would have been large HTO concentration gradients between the joint-water and the existing pore-water. In response to these gradients some diffusion of HTO into the pore-water would have occurred. Diffusion in the water-phase of a non-homogeneous porous medium is a complex subject; some idea of the resultant reduction in HTO levels of water passing through joints can be gained from application of the theoretical equations of non-steady state diffusion to simplified situations. The coefficient of self-diffusion (D) for HTO in water at 10° C is $1.6 \cdot 10^{-9}$ m^2/sec (Wang et al., 1953) but in water-saturated porous media will be lower and depend on the porosity (ϕ) and saturation of the media and the tortuosity of the pore-space. In the case of saturated Chalk it is unlikely to be less than 10^{-10} m^2/sec (Smith et al., 1970).

One appropriate solution of Fick's diffusion laws would appear to be that for diffusion from an infinitesimally thin layer for which boundary condition the following applies (Crank, 1956; Golubev and Garibyants, 1971):

$$\frac{(C_{xt}-C_{xo})}{(C_{bo}-C_{xo})} = \frac{b}{\sqrt{\pi D t}} \cdot \exp\left(-x^2/4Dt\right)$$

where C_{xt} is the concentration at a distance x from the joint after time t, C_{bo} and C_{xo} the initial concentrations in the joint-water and pore-water respectively and $2b$ the joint opening; the decreasing HTO concentration with time in the joint-water itself (C_{bt}) being given by $(C_{bt}-C_{xo})/(C_{bo}-C_{xo}) = b/\sqrt{\pi D t}$. The theoretical picture of diffusion from a joint of small opening, 0.2 mm for example, can thus be estimated (Fig.2); empirical corrections to allow for the effect of the matrix porosity (ϕ taken as 0.30) have been attempted by balancing the distributions so that they always hold the same amount of HTO as the initial input. It can be seen that, while the theoretical increases in HTO concentration in the matrix pore-water are very localised, the process appears capable of producing major reductions in the HTO level of the water in this size of joint by about 10,000 sec (3 h). The case of more open joints ($2b$ = 1.0 mm for example) has been evaluated (Fig.2), using a solution for diffusion from a confined finite region (Crank, 1956):

$$\frac{(C_{xt}-C_{xo})}{(C_{bo}-C_{xo})} = \frac{1}{2}\left[\operatorname{erf}\frac{(b-x)}{(2\sqrt{DT})} + \operatorname{erf}\frac{(b+x)}{(2\sqrt{DT})}\right]$$

Even here the rate of reduction in the HTO level of the joint-water is still significant but overall the effect becomes less rapid with increasing joint-opening and also with reduction in porosity and with decreasing saturation.

Such a process would continue to occur with each successive incident of infiltration as long as a favourable concentration gradient existed; between infiltration incidents and particularly during extended periods of soil moisture

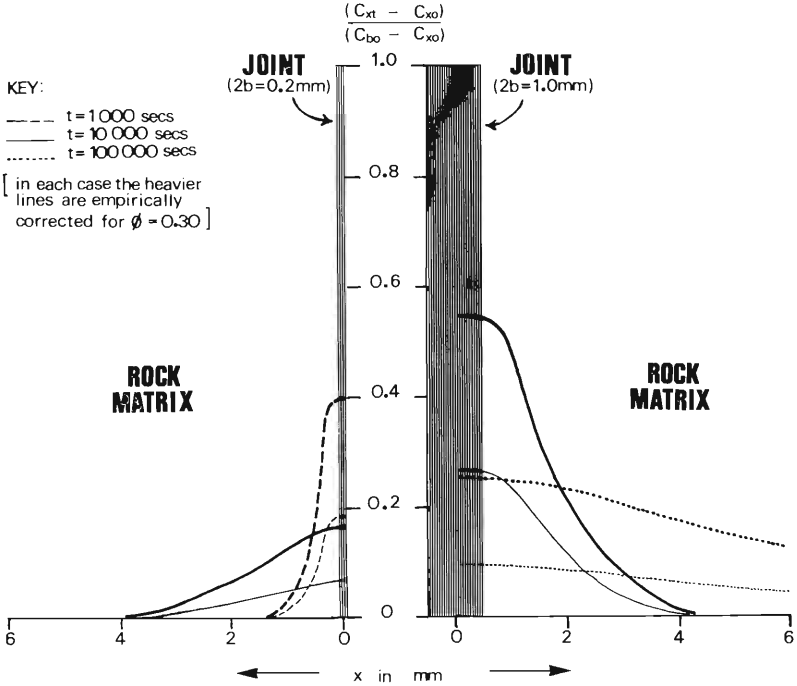

Fig. 2. Theoretical non-steady self-diffusion of HTO in water from idealised joints into the saturated pore-space of a rock matrix.

deficit, the HTO concentrations throughout the pore-water itself would tend to equilibrate. As the concentration in the unsaturated zone pore-waters built-up, HTO would tend to pass downwards to the water-table more readily. A consequence of the high porosity and specific retention of the Chalk, together with its frequently thick unsaturated zone, is that the volume of pore-water available to take part in a diffusion process will in general be a number of times greater than the total infiltration to date containing thermonuclear tritium.

It is important to establish how much time is available for diffusion to occur during downward groundwater movement in high-angle joints under field conditions. The *main* response to infiltration (as identified by rising water-table in observation boreholes) traverses the unsaturated zone of the Chalk at *average* rates of 2—10 m/day (Headworth, 1972; Foster and Crease, 1974). This response is most likely to be *directly* due to a fissure-flow infiltration front but it could alternatively be transmitted via a discontinuous air phase with slower actual rates of flow. Maximum diffusion of HTO into the Chalk pore-water would occur at any level where the passage of the infiltration front was retarded by tighter jointing and lower vertical permeability, such as immediately above marl bands, and the HTO profile might be expected to vary widely between neighbouring sites with an overall tendency for the highest concentrations to occur at shallow depth. An exception would be where highly-preferred routes of flow have developed, for example in the occasional major solution feature.

CONCLUDING REMARKS

In summary, the diffusion process appears to have considerable capacity for reducing HTO concentrations in Chalk groundwater recharge. The same process would continue to occur below the water-table with further reduction in the HTO levels of the fissure-water, which represents only 1—5% of the total volume in saturated zone storage. The role of diffusion thus needs to be further investigated before tritium determinations can be interpreted with confidence in studies of groundwater movement in the Chalk and any similar formation with two contrasting hydraulic components and thick unsaturated zones. In particular, the interpretations placed upon previous tritium "age" determinations in relation to the possible delay between the times of infiltrations and sampling, can be called in question. Carefully-controlled and appropriately-scaled laboratory experiments would be required together with field investigations involving a network of boreholes at any one site and a sequence of boreholes in time at the same site.

The diffusion process would also occur with any ions in solution, though the appropriate values of D are likely to be lower. In most cases the ion concerned would have been present in the infiltration for much longer periods and equilibrium conditions would be approached. Where concentrations of a given ion have increased or new pollutants are present, the process would influence their rate of penetration from the land surface.

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