The Possible Use of Tritium for Estimating Groundwater Storage

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Abstract

In view of a recent work by BEGEMANN & LIBBY (1957) their postulate on rapid mixing inside a groundwater body is examined. It is found that there are no possible processes which can accomplish such a mixing. Their observations can, however, be readily explained from a simple model of groundwater flow, assuming no mixing. Possible methods of using tracers like tritium for estimating groundwater storage are also discussed.

I. Introduction

BEGEMANN & LIBBY (1957) recently reported figures on the tritium content of Mississippi river water after the Operation Castle. The first sampled listed was taken nine months after the explosions and from that time to the beginning of October the following year the concentration in the Mississippi River was remarkably constant. This led Begemann & Libby to postulate a very rapid mixing of the fallout tritium with the groundwater body and were thus able to calculate the amount of groundwater from the average increase in concentration of tritium in the Mississippi River and the estimated fallout of bomb produced tritium. The figure they arrived at, 7.7 m, may not be unreasonably high, yet the way it was arrived at may be critisized. The purpose of the present paper is therefore to discuss possible mixing mechanisms for water in the ground and evaluate their importance and to find some alternative ways of computing groundwater storage from river water data on tritium.

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II. Mixing processes in the ground and ground water models

a) *The water in the ground*

When water enters as precipitation it is generally held up for some time in the upper part of the ground, i.e. in the soil proper, before it enters the region where all available pore space is filled with water, i.e. the groundwater region proper. The storage capacity of the soil may amount to 100 mm of precipitation or more and while in the soil part of the water is taken up by the plants and brought back to the atmosphere in the transpiration of plants which is the most important evaporation process over the land surfaces. The tritium precipitated will consequently also follow the same fate by and large except for a small fractionation effect. As no mixing between soil water and groundwater can be expected—the transport is rather one way – the tritium lost in evaporation will be about that contained in the same amount of precipitation. In the Mississippi Valley where evaporation amounts to two thirds of the precipitation, only one third of the estimated fallout from the Castle tritium can have reached the groundwater.

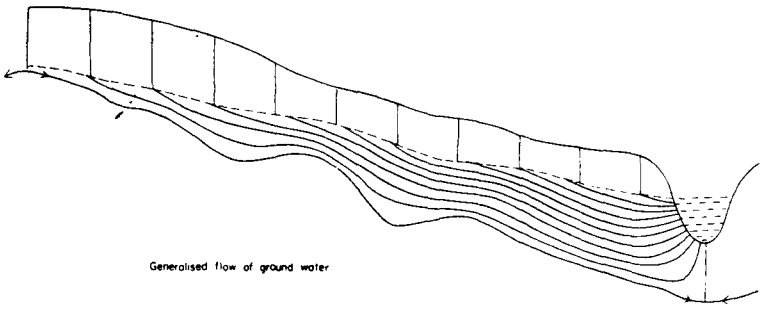

Fig. 1. Generalized streamline pattern in the groundwater region.

This will, of course, reduce the groundwater storage calculated by Begemann & Libby to one third or 2.6 m, provided their postulate of rapid mixing within the groundwater body is correct. We will see later that other data support this lower figure.

b. *Groundwater flow and mixing processes*

It is well known that water flow in porous media under normal circumstances is non-turbulent or laminar as it is frequently called. This is so because frictional forces dominate completely over inertia forces. Streamlines in a non-turbulent flow can, of course, never cross and as to streamsurfaces they never cut except along streamlines. From these simple rules and continuity considerations the streamline pattern in groundwater flow can be easily predicted. The general arrangement of streamlines in a groundwater body can be pictured as in fig. 1. The streamline originating on the water divide branches at some depth and forms the bottom of the groundwater body. The upper boundary is, of course, the groundwater surface, or water table, where streamlines originate.

It is apparent from fig. 1 that unless great dispersive forces are at work normal to the streamlines a chemical stratification of groundwater will occur when the composition along the water table changes with the distance from the water divide. Dispersive forces normal to the streamlines will tend to smooth this stratification. A chemical stratification can also be arrived at if the composition of groundwater at the water table changes with time as in the case of tritium fallout. In this case dispersive forces acting along streamlines tend to smooth this stratification. It is well worth to consider both types of dispersions.

In a non-turbulent flow the only dispersive force normal to the streamlines is molecular diffusion and it is well known from experiments where colored liquids have been used to trace streamlines that this type of dispersion is very slow. The effect can be visualized by considering the characteristic length of diffusion $\sqrt{Dt}$ where D is the diffusion coefficient and t the time. In water solutions D is around 1 $cm^2 \times day^{-1}$ so for different times the following values of $\sqrt{Dt}$ can be anticipated:

t in days	1	4	16	64	256	1 024	4 096
$\sqrt{Dt}$ in cm	1	2	4	8	16	32	64

It should be noted that in the diffusion from a surface source the concentration will form a normal distribution perpendicular to the source. Therefore one can anticipate that going along a streamline practically all molecules considered at $t = 0$ will be found within a width of $6\sigma = 8.4 \cdot \sqrt{Dt}$ at the time t. In a year a streamline will have "spread" about 100 cm but streamlines lying 100 cm apart would still be recognizable if they originally had different chemical properties. The effect of diffusion normal to streamlines are nicely demonstrated in a field experiment by GUSTAFSSON (1946). A line of sodium chloride was put into the soil at 2.0 and 5.0 m distance from a tile drain and one year later soil samples were taken at different points in the soil and analysed for chloride. The result is shown in fig. 2 and as seen the "spread" of the streamlines in a year is about the same as predicted above.

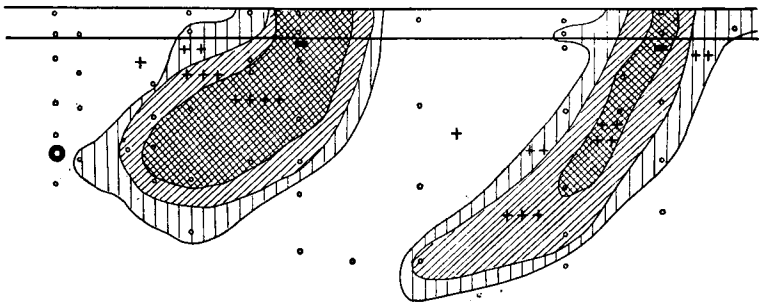

Fig. 2. Effect of diffusion normal to streamlines. Large circle, position of tile drain. Black rectangels, position of sodium chloride lines (at 2 and 5 m distance from the tile drain respectively). Shaded areas: chloride ion concentrations in qualitative degrees found in the soil one year after application of sodium chloride. Note: this soil has a large capillary effect so the water table is practically at the surface all year round.

It is obvious that molecular diffusion along streamlines cannot exceed that normal to streamlines and is therefore negligible. But there are other dispersive forces to consider along streamlines due to the nature of laminar flow. These have recently been discussed by the author (1958) and the following discussion is mainly based on that paper.

It is clear that on a microscale in a soil the velocity along a streamline will vary from point to point depending on at which distance from a soil particle the streamline passes. The velocity distribution in a pore will be something like that in a capillary and often capillaries have been used as models for water flow through porous media. As to soils two cases can be distinguished. The arrangement of particles may be completely at random and this will give a complete random arrangement of pores. The soil will in other words show isotropic properties with respect to water flow. Streamlines would have no preferred direction and the average velocity along any streamline would be the same. However, due to the varying velocities along the streamlines an initially plane front would develop into a topographically very rough surface of ever changing pattern but important is that the topographical variation would be limited to some value determined by the particle size and it would be independent on the length of travel of the front. The originally plane front can be regarded as a highly improbable configuration of this changing surface. Under such circumstances the mixing along streamlines would have but small effect in a groundwater body.

The conditions would be different if the soil behaved anisotropically with respect to water flow. One can easily imagine a highly anisotropic system by considering pores being arranged as parallel capillary tubes. In this case the permeability of the soil to water in any other direction than along the capillaries would be zero. The deformation of an originally plane front would increase linearly with the length of travel. As the maximum velocity in a capillary tube is twice the average a considerable bulk mixing could take place. But even so, it could not complete the mixing of the Mississippi groundwater within a few weeks if the residence time of this water is to be measured in years.

It is, however, possible to conceive of a mixing process on a larger scale in a soil that is made up of strata of different permeability. But this does not really mix the water inside the groundwater body. The mixing can take place only in the water course. It merely means that the time it takes for a water parcel to reach the water course is not always a simple function of the way of travel.

In summarizing it seems safe to conclude that mixing of groundwater is highly unlikely and that the observed constancy of tritium in the Mississippi river water must be explained in a different way. A possible mechanism will be given below.

c. *Stationary flow in an idealized model*

The general model in fig. 1 can be idealized by assuming the groundwater body to be wedge like with streamlines running parallel

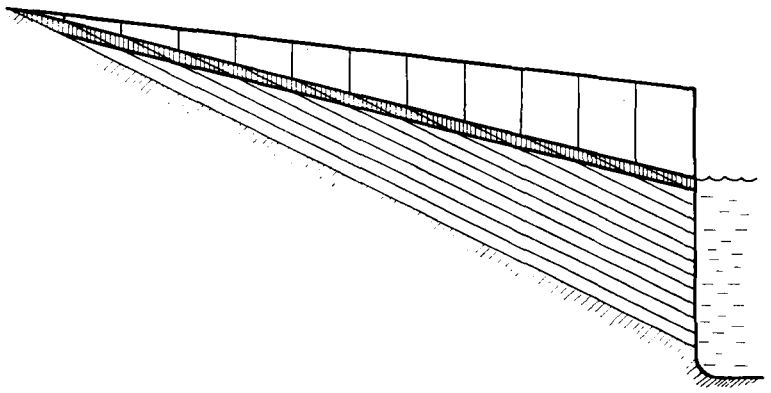

Fig. 3. Idealized model of groundwater flow with constant permeability. The heavy shaded area pictures the position of a tritium rich layer immediately after applications.

as in fig. 3. Further it is assumed that the permeability of the soil is the same everywhere inside the groundwater body and that mixing processes can be neglected. During a certain time interval, water with a much higher tritium content is added to the groundwater surface, forming a stratum as indicated in fig. 3. This stratum will obviously move in the direction of the streamlines with constant velocity but will not show any deformation like bending. Consequently, the excess tritium will be fed into the water course at a constant rate as long as there is any left of the stratum. The concentration of excess tritium in the river water will therefore remain constant. Thus, already the simplest possible model of groundwater flow will give the constancy of tritium actually observed. It can, further, be derived from this model that the average groundwater storage is only half of that derived in the way Begemann & Libby did.

The idealized model in fig. 3 can, however, be improved, still giving a reasonable constancy of tritium in river water during a shorter interval. It is likely that the permeability of the water-bearing strata decreases with depth. This would lead to very long travel times for groundwater originating near the water divide. A tritium stratum like that in fig. 3 would then no longer move with the same velocity in its different parts but will be deformed so that the rate of tritium delivery to the water course decreases with time. Consequently, the tritium concentration in the river water will also decrease with time. It is quite conceivable that the actual tritium concentration will fall off exponentially with time or, at least, its variation with time can be approximated by an exponential function. This is of considerable interest because this effect is exactly that of very rapid mixing.

It is thus seen that in the case of interpreting tritium data from river waters, the postulate of rapid mixing though unsatisfactory from a physical point of view may be a good approximation to conditions in the field. In the case of well waters, however, the postulate of rapid mixing may lead completely astray. This is very obvious from Begemann and Libby's discussion on well and spring water tritium.

III. Possible methods of estimating ground water storage by means of tracers

In the preceding section we concluded that rapid mixing in groundwater most unlikely takes place. The nature, however, of the groundwater flow can be such that when groundwater from various strata are mixed in the water courses, it behaves chemically as if the mixing had taken place in the groundwater body. Two idealized models of groundwater flow have been presented and their merits will be discussed further in this section. It seems, however, possible to reconstruct the groundwater flow from empirical data and basing upon such a reconstruction to make a much more satisfactory estimate of the groundwater storage. This is, however, limited to

cases where the addition of a tracer is instantaneous.

a. *Continuity considerations in groundwater flow*

Consider a drainage area of any size with any number of branches of a common outlet water course. Suppose further that the travel times of water in the water courses inside the area are short compared to the travel times for water in the groundwater region.

Under stationary conditions a water parcel starting from a surface element dS of the groundwater surface will spend a certain time T in the groundwater before it reaches a water course. If the rate of run-off from this area dS is R per unit area the continuity requires that the storage of water along the path of the water parcel (a streamline) is

$$dW = R \cdot T\, dS \tag{1}$$

where dW is the amount of water stored. Within the whole area S_0 the total storage will consequently be

$$W = \int_0^{S_0} RT\, dS \tag{2}$$

The travel times T from various surface elements can be arranged after increasing values as to form a monotonic function of S which then can be looked upon as the surface area where travel times are equal to or less than the value T. In this way T can be represented as a function of S and for $S = S_0$ we will have $T = T_0$. Fig. 4, curve A, gives a generalized picture of such a function T of S. If R in eq. (2) should happen to be constant it is seen that the total groundwater storage is equal to R, the rate of run-off per unit area, times the surface area below curve A in fig. 4 between $S = 0$ and $S = S_0$.

It is also obvious from fig. 4 that S can be regarded as a function of T and be formulated $S = F(T)$. In the case of the idealized models discussed previously $F(T)$ can be explicitly formulated. When the travel times are linearly proportional to the distance to the water course and the water courses are regularly spaced, this function is simply

$$S = S_0 \cdot \frac{T}{T_0} \tag{4}$$

whereas in the second case the relation would read

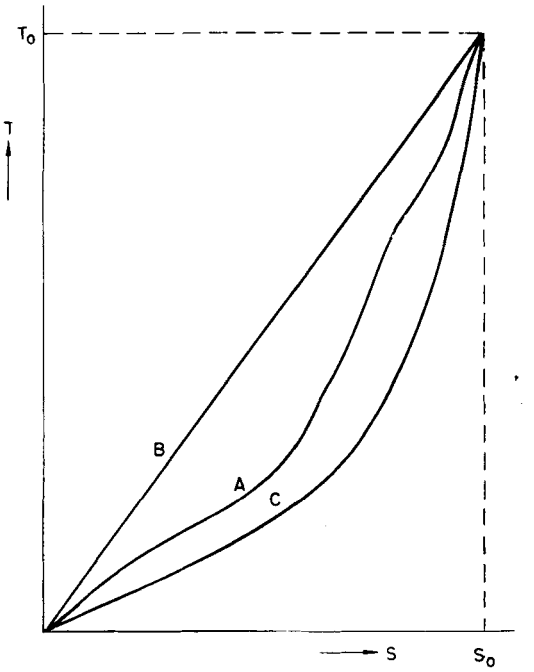

Fig. 4. The relation between T and S for different cases. Curve A: Generalized relation. Curve B: Idealized model with constant permeability. Curve C: Idealized model with exponential relation between S and T.

$$S = S_0 \left(1 - e^{-kT}\right) \tag{5}$$

In fig. 4 the relation in eq. (4) is represented by the straight line B and eq. (5) by the curve C. We have thus two idealized cases and a generalized case represented in fig. 4, and we will next investigate how they can be used.

b) *Stationary flow and steady-rate addition of non-conservative tracers*

By non-conservative is meant substances that either are added or subtracted in the groundwater region. Tritium belongs to this category as it disintegrates radioactively. Any other radioactive substance added at a constant rate to the groundwater surface could be used as a tracer in this connection. Also radioactive substances added inside the groundwater region could be used if the rate of addition was known. Other non-conservative compounds are oxygen and carbon dioxide but also here the rate of consumption or addition has to be known. It is thus seen that there are many possibilities to be explored

but at present only the addition of radioactive substances produced naturally in the atmosphere will be considered.

If the concentration of the tracer at the groundwater surface is denoted by C and the travel time from a surface element dS is T, then the concentration in the same water parcel when arriving at the water course is

$$C_r = C \cdot e^{-\lambda T} \tag{6}$$

where λ is the decay constant of the tracer. The average value of C_R will consequently be

$$\overline{C_r} = \frac{C}{S_0} \int_0^{T_0} e^{-\lambda t} \frac{\partial S}{\partial T} dT \tag{7}$$

when R is regarded as constant. It is seen that it is not possible to reconstruct the function $S = F(T)$ but if its general form is postulated, it is at least possible to determine a parameter of the function. Chosing the idealized models in fig. 5, the "linear" model eq. (4) gives upon integration

$$\frac{2\lambda w}{R} \frac{\overline{C_r}}{C} = 1 - e^{-\frac{2\lambda w}{R}} \tag{8}$$

where w is the average groundwater storage per unit surface.

In the case of the "exponential" model (eq. 5) we get

$$w = \frac{(C - \overline{C_r})}{\lambda \overline{C_r}} \tag{9}$$

which, of course, is the same as if rapid mixing of the groundwater was postulated.

It may be of interest to compare these two models. The ratio w/R can be calculated for different $\overline{C_r}/C$ using $1/\lambda = 18$ (as for tritium). The result is shown below

$\overline{C_r}/C$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0·8	0.9
w/R (eq. 8)	90	45	28.6	20.2	14.2	10.3	7.0	4.5	2.0
w/R (eq. 9)	162	72	42	27	18	12.0	7.7	4.5	2.0

w/R can be interpreted as the turnover time for the groundwater. It is seen that the two models do not give too different results for turnover times up to the half life of tritium but for larger values the differences become appreciable. Thus, as long as $\overline{C_r}/C$ is greater than 0.6, it does not really matter which model is chosen.

c) *Stationary flow and instantaneous addition*

Suppose a tracer, not necessarily radioactive, is added to the groundwater surface uniformly, at time $t = 0$. At time T from the addition a surface $S = F(T)$ has delivered its tracer already to the outlet whereas the surface $S_0 - S$ has not delivered any. If the amount of tracer added per unit area at time $t = 0$ is M then the rate of discharge in the run-off, m, of the tracer per unit area at time $t = T$ can be derived from fig. 4, curve A, and becomes

$$m = \frac{M}{S_0} \frac{dS}{dT} \tag{10}$$

From this

$$dS = \frac{S_0}{M} \cdot m \, dT \tag{11}$$

and

$$S = \frac{S_0}{M} \int_0^T m dT \tag{12}$$

By determining m at regular intervals the integral $\int_0^T m dT$ can be constructed as a function of T and consequently, $S = F(T)$ can be reconstructed. If T is plotted as a function of S like that in fig. 4 and R, the rate of run-off, is assumed to be constant, then, of course, the total groundwater storage can be estimated from eq. 2.

It is thus seen that this method makes it unnecessary to postulate any property of the function $S = F(T)$ and gives actually a good insight into the drainage conditions in any area where the method is applied.

A question arizes how long time is needed to complete such an investigation. Apparently it has to be continued until the zero level of the tracer is approached and this will depend upon the actual storage or turnover time as well as on the nature of the function $S = F(T)$. If the turnover time of the groundwater is say 10 years, then at least 20 years of observation are needed, perhaps more. If a radioactive tracer is used, a correction for the decay has, of course, to be done.

A practical question in connection with

instantaneous addition of a tracer is how absorption of the tracer by the soil material will affect the results. Due to absorption a front of a tracer will move at a lower velocity than the velocity of the water, a phenomena well known and taken advantage of in chromatography. KAUFMAN and ORLOB (1956) have investigated this effect for a number of substances. In the case of tritium the absorption will be proportional to the amount of hygroscopic water in a soil and the retardation of the front will be proportional to the ratio of hygroscopic to total water. The effect can normally hardly exceed 10 per cent and it is doubtful whether the estimate of groundwater can be made with this accuracy anyway so the error would not be too pronounced.

d) *Discussion*

In all derivations done in this section, stationary conditions of groundwater flow have been postulated. This is, of course, an approximation to actual conditions though probably not serious. The main mass of ground water is probably but little effected by seasonal variations in rainfall and evaporation and normally, the soil through which the water has to move before reaching the groundwater surface acts as a buffer, smoothing the irregular addition of water to the ground. Even if the water table shows variations in depth, one would not expect the streamlines to be much affected in their course, and it is always possible to imagine an average travel time from each surface element. Actually the areas with the shortest travel times will be most affected by periodic variations in the rate of supply of water to the groundwater surface but on the other hand these contributes least to the groundwater storage. Seasonal variations in rainfall can therefore not be expected to invalidate the derivations made.

More serious are secular variations. In humid regions, however, they are normally small but in arid regions with very irregular annual rainfalls, they may invalidate the equations derived.

There are very few data available yet to demonstrate the applicability of the equations derived. There are, however, some pre-Castle tritium data on rain and Mississippi river water published by VON BUTTLAR and LIBBY (1955) which can be used in equations (8) and (9). They give average values for Chicago rainwater and Mississippi river water collected at Rock Island and at St Louis. As a check on the rainwater value they calculate the average tritium in rainwater from the tritium concentration in Lake Michigan knowing the volume of this lake. The averages are:

Chicago rainwater, weighted average
$8.2 \cdot 10^{-18}\ T/H$

Calculated from Lake Michigan tritium
$7.4 \cdot 10^{-18}\ T/H$

Mississippi river water: Rock Island
$4.7 \cdot 10^{-18}\ T/H$

Mississippi river water: St Louis
$6.0 \cdot 10^{-18}\ T/H$

Average for rainwater	$7.8 \cdot 10^{-18}\ T/H$
Average for river water	$5.3 \cdot 10^{-18}\ T/H$

Using eq. (8) with $R = 24$ cm · year^{-1} and $1/\lambda = 18$ years, gives $w = 184$ cm. With eq. (9) and the same R and λ, $w = 204$ cm. It seems therefore not too unreasonable to believe that the average groundwater storage in the Mississippi Valley is about 2 m. This is somewhat less than $^1/_3$ of the estimate by Begemann and Libby, the discrepancy being largely due to their postulate of rapid mixing of groundwater before evaporation and possibly also due to an overestimate of the total fallout as discussed recently by BOLIN (1958).

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