Atmospheric tritium as a tool for the study of certain hydrologic aspects of river basins

By ERIK ERIKSSON, *International Metrological Institute in Stockholm*

(Manuscript received February 12, 1963)

ABSTRACT

In this paper a method is demonstrated by which the hydrological characteristics of a river basin are computed from a knowledge of added bomb-produced tritium in precipitation and tritium in run-off. It is also demonstrated that the hydrological characteristics thus computed agree well with the physiography and geology of the basin.

1. Introduction

BEGEMANN & LIBBY (1957) published a paper on continental water balance, groundwater inventory etc. as revealed by studies of atmospheric tritium in precipitation and river water. Their paper aroused considerable interest and discussion, and although some of the assumptions they made can be questioned—and were questioned—the paper is nevertheless important as it focuses the attention on the possibilities for study of certain hydrologic aspects of river basins. Inspired by their paper, ERIKSSON (1958) discussed this possibility further and in a later paper (1961) the theory for using atmospheric tritium for the study of river basin characteristics was outlined. BROWN (1961), realizing the possibilities of atmospheric tritium in this respect, made a study of the tritium in the Ottawa Valley catchment area. Aware of the criticism raised against Begemann and Libby's approach, he developed an equation which describes the behaviour of tritium in river water as a function of the added atmospheric tritium and the turnover time of water in the basin. This is an interesting application, although it involves an assumption of a well-mixed reservoir. Such an assumption can be justified as a first approach, realizing that mixing mainly takes place in the rivers. In the case of the Ottawa study, there are, however, enough data available to make less rigorous assumptions about the reservoir and, in fact, to describe the water reservoir on the basis of the collected data. Since this is of basic scientific interest it is well worth carrying out.

2. Available data

Brown (l.c.) has listed his data on tritium in Ottawa precipitation and Ottawa river water up to the end of 1959. Since then more data have been collected and from the distribution sheets of data issued by the International Atomic Energy Agency in Vienna, the period 1960 to the middle of 1961 can also be covered. From the available data it is thus possible to work out half-yearly averages up to the middle of 1961. These are listed in Table 1 in columns 2 and 3.

It is well known that in 1954 the first large test series involving hydrogen bombs were carried out, releasing large amounts of tritium and subsequent test series have added more. This represents a transient imposed on the previous steady state of the tritium circulation in nature and can thus be utilized for the present purpose. It is, however, necessary to correct the data for the steady state distribution. There were no regular analyses made earlier, but from Brown's data on water in chemical reagents collected well before 1953, it looks as if the river water had a concentration of about 15 TU.[1] If the turnover of water in the basin is of the order of 3 years, as found by Brown, then the concentration of tritium in precipitation should be about 18 TU. Consequently, these values will be used to correct the rest of the data which are then assumed to represent the transient concentration. The results of these corrections are also shown in Table 1, columns 4 and 5, and are the data to be used in subsequent computations.

[1] TU = tritium unit equal to 10^{-18} T/H.

TABLE 1. *Original and corrected half-yearly averages for precipitation in river water.* Concentrations in TU ($= 10^{-18}$T/H).

Period in half-years	Averages		Correction for steady state		Computed river water conc. (corr. for steady rate)
	Prec.	River	Prec.	River	
1948–52	(18)	15	—		
1953 : 2	27	—	9		
1954 : 1	358	—	340		18.8
1954 : 2	86	—	68		49.6
1955 : 1	55	—	37		60.5
1955 : 2	30	—	12		44.5
1956 : 1	130	63	112	48	47.9
1956 : 2	162	87	144	72	70.7
1957 : 1	126	93	108	78	77.2
1957 : 2	118	95	100	80	80.0
1958 : 1	433	100	415	85	86.6
1958 : 2	596	154	578	139	142.6
1959 : 1	868	214	850	199	230.4
1959 : 2	215	302	197	287	287.7
1960 : 1	144	288	129	273	272.8
1960 : 2	163	256	145	241	239.0
1961 : 1	184	252	166	237	239.9

3. Theory and methods of computations

The theory, on which the computations are founded, is simple and has been given earlier, but will be recapitulated in a form suitable for the present purpose.

First, net precipitation is defined to be the part of the precipitation which runs off and it is supposed that this part remains constant from year to year. This assumption is necessary as there are no flow-rate data available for the different years. It would have been better to work with amounts of precipitation tritium and with amounts of tritium in run-off, but lacking adequate information, concentrations will now be used.

Of the net precipitation which is added to the basin during half a year, a certain fraction, ϕ_1 is transported out of the basin by the river water during this half-year. Another fraction, ϕ_2, is leaving the basin the next half-year and so on. Thus we divide each half-year's precipitation into fractions according to the time the water stays in the basin.

Let the concentration of tritium in precipitation during the first half-year be C_1 during the second half-year C_2 and so on and define the concentrations in river water for the same periods by γ_1, γ_2 etc. We can accordingly formulate conditions of continuity by a set of equations:

$$\gamma_1 = C_1\phi_1 q_1,$$
$$\gamma_2 = C_1\phi_2 q_2 + C_2\phi_1 q_1,$$
$$\gamma_n = C_1\phi_n q_n + C_2\phi_{n-1}q_{n-1} + \dots + C_{n-1}\phi_2 q_2 + C_n\phi_1 q_1,$$

where q_1, q_2 etc. are factors accounting both for the decay of tritium in water while in the basin, and for fractionation effects which may operate when part of the precipitation evaporates. It is convenient to write $\phi_n q_n = \phi_n'$ so the sets of equation are:

$$\gamma_1 = C_1\phi_1',$$
$$\gamma_2 = C_1\phi_2' + C_2\phi_1',$$
$$\gamma_n = C_1\phi_n' + C_2\phi_{n-1}' + \dots C_{n-1}\phi_2' + C_n\phi_2'.$$

The physical meaning of these equations is quite obvious. As an example, during the fourth half-year period the river-water tritium will be made up by a fraction ϕ_4' from the first half-year's precipitation, by the fraction ϕ_3' from the second half-year's precipitation, by the fraction ϕ_2' from the third half-year's precipitation and by the fraction ϕ_1' from the fourth half-year. We are, of course, assuming that these fractions always remain the same, i.e., we assume a steady state of water flow.

If all data existed, one would start by solving the first equation for ϕ_1', use this to solve for ϕ_2' in the second, use both, ϕ_1' and ϕ_2' to solve for ϕ_3' in the third and so on. Unfortunately, there are four periods of data missing for river water, so this straightforward method cannot be applied. We can, however, solve the system of equations by imposing certain conditions on the series ϕ which can be regarded as a function of time. In Brown's treatment ϕ was supposed to be of the form $k \cdot e^{-k\tau}$, where τ is the time which is equivalent to assuming apparent rapid mixing of water in the reservoir. In such a case one really needs only one equation to obtain k, which is the inverse of the turn-over time of water in the basin. If several equations exist, one can solve all of them for k and work out an average k-value.

The function $k \cdot e^{-k\tau}$ imposes rather rigid conditions as it implies that the basin characteristics can be described by one parametre only, the turn-over time. We could at present, as there are 11 equations available, assume that ϕ can be represented by a power function of time (or of the indices n) and could in this way determine 11 coefficients for this function. We could also choose a lesser number of coefficients and apply the least-square method for the best fit, thereby allowing some smoothing of the data. However, such procedures are time-consuming unless one has a computer of suitable design for the purpose. It is, of course, not necessary to use a power function; a Fourier series could also be used if the interval is fixed.

The other possibility is to work numerically with the 11 existing equations, imposing certain conditions which have to be fulfilled and then adjusting $\phi_1', \phi_2', \phi_3'$ and ϕ_4' so that these conditions are fulfilled. As to these conditions, some can be based on physical arguments. One condition is that no ϕ_n can be negative as this is a physical impossibility. Water cannot run upstream into the basin. The second condition to be imposed is that the sum of the ϕ's cannot exceed unity when no fractionation effects are considered, and if such effects are considered, the sum should not exceed unity by, say, more than 5 per cent. Finally, we can impose a rather vague condition that the series of ϕ's should be reasonably smooth. It must be admitted that in this condition a certain subjectivity enters.

One thing which cannot be avoided by any assumptions is error in the data, especially in the river-water concentrations because these are not weighted according to discharge rate. Finally, the assumption of constant ϕ's is dubious in the case of ϕ_1 which more or less represents the surface run-off from the basin. Especially on a half-yearly basis ϕ_1 can be expected to oscillate and the effect of such oscillations will be strongest during a year when new tritium is injected into the atmosphere. Looking at Table 1 starting our series with 1954:1 the effect of such fluctuations in ϕ_1 would be most strongly felt in 1958:1 and 2 and in 1959:1 because of the high precipitation concentrations during this period. This would affect ϕ_9, ϕ_{10} and ϕ_{11} and in fact, during the operations carried out to arrive at a likely series of ϕ's it was found that ϕ_{11} turned out abnormal, being negative after all the others were adjusted to proper values. This indicates that the value for river water 199 TU is too low because the fractional run-off during the first half of 1959 was below the average, maybe due to lower than normal precipitation. In such a case one has to adjust the ϕ in question to a reasonable value, adjusting subsequent ones accordingly, as they are also affected, although to a minor degree.

4. Computational procedure

In the present case the procedure adopted was the following: Firstly, some likely arbitrary values are chosen for $\phi_1', \phi_2', \phi_3'$ and ϕ_4' after which the computations of subsequent ϕ's are made from the system of equations starting with

$$48 = 340\phi_5' + 68\phi_4' + 37\phi_3' + 12\phi_2' + 112\phi_1'$$

and ending with

$$\begin{aligned} 237 = {} & 340\phi_{15}' + 68\phi_{14}' + 37\phi_{13}' + 12\phi_{12}' + 112\phi_{11}' \\ & + 144\phi_{10}' + 108\phi_9' + 100\phi_8' + 415\phi_7' + 578\phi_6' \\ & + 850\phi_5' + 197\phi_4' + 129\phi_3' + 145\phi_2' + 166\phi_1'. \end{aligned}$$

The 1953:2 figure 9 TU for precipitation has been ignored starting the series with 1954:1. The resulting set of ϕ's is listed in Table 2, column 2. It is seen that the series is rather irregular and there are also negative values. Adjustments in the first four ϕ's have to be made to

TABLE 2. *First approximation and adjustment factors for the ϕ series.*

	First appoxi-mation	Adjustment factors for $\Delta\phi_1' =$ 0.100	$\Delta\phi_2' =$ 0.100	$\Delta\phi_3' =$ 0.100	$\Delta\phi_4' =$ 0.100	Final series	Correc-tion for decay	ϕ_n	ϕ_n smoothed
ϕ_1	0.100	0.100	0.000	0.000	0.000	0.055	1.014	0.056	0.056
ϕ_2	0.100	0.000	0.100	0.000	0.000	0.135	1.043	0.141	0.141
ϕ_3	0.100	0.000	0.000	0.100	0.000	0.145	1.072	0.155	0.155
ϕ_4	0.100	0.000	0.000	0.000	0.100	0.085	1.102	0.094	0.094
ϕ_5	0.074	−0.033	−0.004	−0.011	−0.020	0.085	1.133	0.096	0.096
ϕ_6	0.107	−0.036	−0.032	−0.001	−0.007	0.109	1.166	0.127	0.127
ϕ_7	0.089	−0.021	−0.036	−0.032	0.000	0.071	1.198	0.085	0.085
ϕ_8	0.067	−0.020	−0.021	−0.036	−0.032	0.058	1.232	0.071	0.071
ϕ_9	−0.027	−0.104	−0.019	−0.018	−0.029	0.011	1.266	0.014	0.019
ϕ_{10}	−0.016	−0.121	−0.103	−0.016	−0.012	0.005	1.303	0.006	0.010
ϕ_{11}	−0.081	−0.181	−0.120	−0.101	−0.014	0.004	1.340	0.005	0.009
ϕ_{12}	0.147	0.032	−0.181	−0.119	−0.099	0.015	1.378	0.021	0.008
ϕ_{13}	0.097	0.081	0.035	−0.170	−0.099	0.004	1.415	0.006	0.007
ϕ_{14}	0.001	0.140	0.084	0.046	−0.150	0.012	1.455	0.017	0.006
ϕ_{15}	0.040	0.232	0.146	0.101	0.076	−0.009	1.498		0.005
$\Sigma\phi_n$									0.889

make the series more realistic. This can be done in a rather simple way. If we vary the ϕ's in the relation

$$\gamma_n = C_1\phi_n' + C_2\phi_{n-1}' + \dots C_{n-1}\phi_2' + C_2\phi_1'$$

we obtain the relation

$$0 = C_1\Delta\phi_n' + C_2\Delta\phi_{n-1}' + \dots C_{n-1}\Delta\phi_2' + C_n\Delta\phi_1'.$$

where $\Delta\phi'$ is the change in ϕ'. Thus, if we allow ϕ_1' to vary, keeping ϕ_2', ϕ_3' and ϕ_4' constant we can compute what changes take place in ϕ_5' and subsequent members. The same can be done varying ϕ_2' keeping ϕ_1', ϕ_3' and ϕ_4' constant and so on. In this way we arrive at the four series for $\Delta\phi$ also given in Table 2 which shows the change taking place in ϕ_5' and subsequent ϕ's when either of $\phi_1', \phi_2', \phi_3'$ and ϕ_4' is varied by 0.100 units. We have then to change one of these in turn by suitable amounts and change the ϕ_5' and subsequent ϕ's accordingly so that a reasonable series is obtained. As was mentioned earlier, it was found that ϕ_{11}' needed to be corrected for reasons which are physically probable—actually it was increased by 0.090 units—and the subsequent ϕ's were adjusted accordingly so that they would still conform to original river-water concentration. The final result, or better, a reasonable series, after a series of such adjustments of $\phi_1', \phi_2', \phi_3'$ and ϕ_4' is also given in Table 2, column 7. There are still minor fluctuations in the tail of the series but they can hardly be removed and are not unreasonable in view of the possibility of fluctuations in ϕ, discussed earlier. The best we can do is to smooth the series as a last procedure. Correcting for the decay of tritium is done through the factors in column 8. Columns 9 and 10 give the corrected series, the latter smoothed in its tail end. The sum of smoothed ϕ's becomes 0.889, indicating that nearly 90 per cent of the half-yearly addition has been accounted for. The remaining 10 per cent would accordingly spend more than 7.5 years in the basin and form deeper parts of groundwater. Possible fractionation effects would perhaps increase this part slightly. It is possible that such a large fraction exists, judging from Brown's analyses of water from a well which gave an age for the water of about 50 years.

The river-water concentrations can now be computed and compared to those found. The result is found in Table 1, the last column and shows good agreement except, as expected, in 1959:1 when the discrepancy is about 30 TU.

The series in the last column of Table 2 can thus be taken as representative for the characteristics of the river basin in question with respect to travel times of certain parts of the water. If ϕ is represented as a continuous function of time it would look like the curve in Fig. 1. As ϕ in this figure is regarded as a derivative of a function F of time, it is computed with one year as a time unit. The shape of this curve may look somewhat peculiar, having two maxima. This is not unreasonable and from the data available it is rather unavoidable. We will see later if it can be justified physically. For comparison with the assumption of good mixing used in Brown's discussion of the data, the dotted line gives the function $k \cdot e^{-k\tau}$ for $k = 0.3$, one of the values used by Brown. It is seen that the average magnitude is about the same but the ϕ function computed here will give a more rapid response for short-term fluctuations in the precipitation tritium. Actually, Brown also points out that "in periods of rapid change in late 1958 and 1959 the river-water tritium concentration overshoots changes predicted by the model, both on downward (late 1958) and upward (mid-1959) trends". He also continues: "Evidently there is a greater proportion of rapid drainage than is provided in the model by the assumption of equivalence to a rapidly mixed water reservoir." His suggested explanation is nicely verified in Fig. 1.

From our set of ϕ values we can form a cumulative series which would tell the fraction of water leaving the basin within a prescribed time. This function which had been denoted F is shown in Fig. 2. For comparison the function $F = 1 - e^{-k\tau}$, corresponding to a well-mixed reservoir, is shown by the dotted line using 0.3 as a value for k.

As to the amount of water present in the basin, this can be partly estimated. If a fraction ϕ_n does not leave the basin until n periods have passed, the amount of water associated with this fraction must be $(n - \frac{1}{2})\phi_n$. In the present case the periods are half-years so $(n - \frac{1}{2})\phi_n$ is an amount of water in units of the half-yearly run-off amount or half-yearly net precipitation, if we prefer. We can also use yearly run-off units just by halving the value obtained from the sum $\sum(n - \frac{1}{2})\phi_n$. In Table 3 the smoothed values of ϕ_n are given as well as the products $\frac{1}{2}(n - \frac{1}{2})\phi_n$ and the cumulative series $\frac{1}{2}\sum(n - \frac{1}{2})\phi_n$.

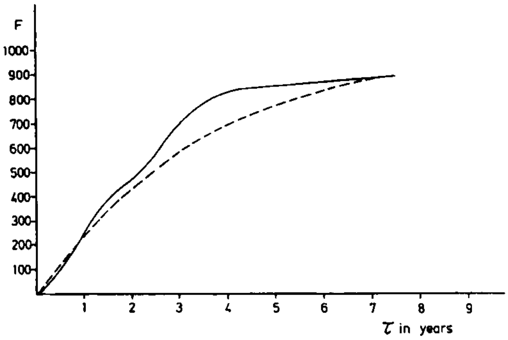

FIG. 2. The cumulative function of ϕ in per mille units. Dotted line is the function $F = 1 - e^{k\tau}$ for $k = -0.3$.

It is interesting to note that an amount equivalent to about two years' run-off stays in the basin less than 8 years. However, as we do not know how much water spends a longer time, we cannot estimate the total amount in the basin. Brown's turn-over rate of 0.3 corresponds to 3.3 years storage. If we assume that

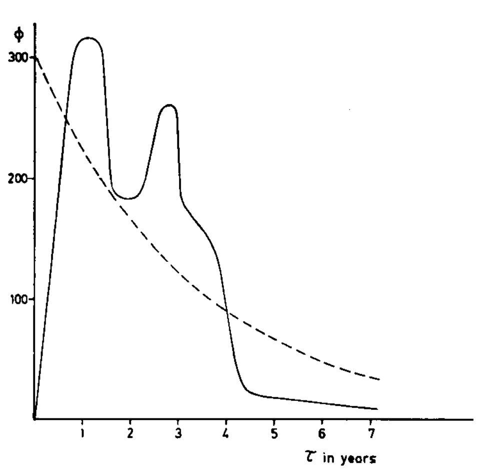

FIG. 1. ϕ as a continuous function of time in per mille. Dotted line is $\phi = k \cdot e^{-k\tau}$ for $k = -0.3$.

TABLE 3. *Computation of amounts of water stored, associated with the values ϕ_n.*

n	ϕ_n	$\frac{1}{2}(n-\frac{1}{2})\phi_n$	$\frac{1}{2}\sum(n-\frac{1}{2})\phi_n$
1	0.056	0.014	0.014
2	0.141	0.106	0.120
3	0.155	0.194	0.314
4	0.094	0.164	0.478
5	0.096	0.216	0.694
6	0.127	0.350	1.044
7	0.085	0.276	1.320
8	0.071	0.266	1.586
9	0.019	0.082	1.668
10	0.010	0.047	1.715
11	0.009	0.047	1.762
12	0.008	0.046	1.808
13	0.007	0.043	1.851
14	0.006	0.040	1.891
15	0.005	0.036	1.927

his well water which was 50 years old represents the missing part in our calculations, this would give an additional 5 years storage (as 10 % of the run-off spends more than 8 years underground). This figure is, however, extremely uncertain.

An interesting feature of Table 3 is revealed by the series in the third column. This shows a maximum storage of water of 3 to 4 years age. If this is true, it should be reflected in the geology and morphology of the basin. This will be discussed next.

5. Results in relation to the geology and morphology of the basin

In his paper Brown has given a good description of the Ottawa river basin. The area is within the Canadian shield and the rocks are therefore crystalline with granites and gneisses. Consequently, no great storage can be expected from the rocks themselves, except in fissures and fractures. Glacial drift is covering part of the area but there are also extensive outcrops of rocks. The valleys are filled with glacial drift debris and can provide appreciable storage. The material is probably coarse, except where lake sediments have been deposited.

The length of the river above the sampling point is 400 miles. In its upper parts it passes through a number of fairly large lakes and reservoirs. 6–8 % of the area is covered by lakes.

Looking at Fig. 1, it seems as if a certain part of the net precipitation runs off fairly quickly, within one and a half years, while there is a considerable hold-up of around 3 years in some parts of the basin. The latter could very well correspond to the extensive lake system in the upper part of the basin while the first peak would correspond to superficial drainage in the lower part of the basin. Thus, Fig. 2 can be considered to agree with the physiography of the basin. Table 3 gives further support to this, if the storage figures are inspected. About half of the stored water accounted for in the present calculation has a travel time of 3 to 4 years. As the average run-off is about 35 cm per year, the storage in the upper part of the basin should be at least 100 cm. If this was stored in the lakes only, which in this area probably cover more than 10 per cent of the area, it would give a mean depth of water in the lake of around 10 m. This is not unreasonable. Supposing one year's run-off is stored in the ground and the rest, 2.5 years in the lakes, would reduce the average depth somewhat but not very much. So on the whole the values computed seem to agree well with the topography and geology of the basin.

We may ask where the water which is older than 8 years, is stored. Part may be stored in fissures and fractures in the rocks while part of it may be stored in the deeper parts of the glacial drift material in the valleys. Only a survey of tritium in deeper groundwater would answer this question properly.

6. Conclusions

It seems as if the present situation with respect to atmospheric tritium could be taken advantage of in order to obtain certain features of river basins, Although some years have been lost since the appearance of the first bomb tritium, there have been many later and stronger additions which can facilitate such studies. Especially for large river basins such a study could be of great interest and could be carried out with yearly averages. However, if a survey of tritium in river waters started now, it would have to be continued for at least 10 years. One could probably start computations using 1958 as the base year, ignoring earlier additions, since the rate of injection into the atmosphere has increased enormously during the last years.

REFERENCES

Begemann, F., and W. F. Libby., 1957, Continental water balance groundwater inventory and storage time, surface Ocean mixing rates and worldwide water circulation patterns from cosmic-ray and bomb tritium. *Geochim. & Cosmochim. Acta*, 12, 277–296.

Brown, R. M., 1961, Hydrology of tritium in the Ottawa Valley. *Geochim. & Cosmochim. Acta*, 21, 199–216.

Eriksson, E., 1958, The possible use of tritium for estimating groundwater storage. *Tellus*, 10, 472–478.

Eriksson, E., 1961, Natural reservoirs and their characteristics. *Geofisica International*, I (2), 27–43, Mexico.