Environmental Isotope (T,^{18}O) Studies of Storm Runoff in the Red Cedar Basin, Michigan

By

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ABSTRACT

ENVIRONMENTAL ISOTOPE (T, ^{18}O) STUDIES OF STORM RUNOFF IN THE RED CEDAR BASIN, MICHIGAN

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The natural tritium and oxygen-18 composition of rainwater differs from that of the groundwater in the Red Cedar basin, Michigan. This isotopic difference was used to differentiate between groundwater and rain components in storm runoff in the Red Cedar basin for the period of September 24 to October 9, 1993. Before, during, and after the storm event of September 26 to September 30, 1993 samples of stream water, groundwater, and rain were analyzed for tritium and oxygen-18.

Initial tritium and oxygen-18 results indicate that 69 % to 79 % of the storm runoff must have been groundwater during the storm runoff event which is somewhat greater than that obtained using a graphical technique (63 %) of streamflow separation. However, statistical analysis of the data shows that analysing tritium concentration in streamflow is not appropriate to separate flow components and that analysing oxygen-18 concentration in streamflow can be used to separate flow components.

The results from these studies indicate that groundwater is an extremely important contributor to storm runoff events in the humid headwater catchment such as the Red Cedar basin.

For the memory of my little brother, Cheol Woo ...

ACKNOWLEDGMENTS

Sincere appreciation and thanks to my advisor, Dr. Grahame J. Larson, for his thoughtful insight, intense interest, and willingness to offer guidance relating to both this thesis and to my education in general. I am grateful to my committee members Dr. David T Long and Dr. Nathaniel E. Ostrom for helpful suggestions and advice.

I would like to thank Myeounghee Oh as my friend who was always willing to encourage me. Finally, special thanks go to my parents for their endless encouragement and support.

Thank God.

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I. INTRODUCTION

General Introduction

The term 'hydrograph separation' is normally associated with graphical hydrograph separation techniques which have been used for decades in predicting runoff components. For example, the graphical separation technique is commonly applied to storm hydrographs from forested catchments to separate 'quick flow' and 'delayed flow' contributions (Sklash, 1990).

Another type of hydrograph separation, based on natural chemical tracers in water, attempts to be more physically based than the graphical technique in separating the rapid and slow delivery of water to the stream (Sklash, 1990). This separation technique apportions the storm hydrograph into contributing components based on the distinctive chemical signatures (TDS, electrical conductivity, and Cl) carried by each of the contributing components. The distinctive signature of each component is developed as the water passing through the catchment takes different flow paths and has different residence times.

The tracer-based hydrograph separation technique normally involves a two-component mixing model for the stream. The model assumes that water in the stream at any time during a storm runoff event is a mixture of two components: 'new water', which is water from the current rain event, and 'old water', which is the subsurface water that existed in the catchment prior to the current rain event. This simple two-component mixing model approach allows the hydrologist to evaluate the importance of given conversion processes in a catchment. For example, if a rapid conversion mechanism (partial-area overland flow, saturation overland flow or subsurface flow through macropores) is the dominant conversion process contributing to a storm runoff hydrograph, the tracer study should detect mostly 'new water' in the stream. Conversely, if a slow conversion mechanism (Darcian subsurface flow) is dominant in producing the storm runoff, the tracer study should find mostly 'old water' in the stream.

There are some problems with separating hydrographs on the basis of chemical parameters such as TDS, electrical conductivity, and Cl because such parameters may have various sources or be affected by geochemical reactions (Sklash, 1990). For example, Nakamura (1971), Pilgrim *et al.* (1979) and others have shown that the chemistry of the 'new' water may vary as the rain water interacts with the catchment materials on the way to the stream. However, natural isotope tracers such as tritium, deuterium, and oxygen-18 may overcome these applied tracer problems mostly by the nature of their application.

Statement of Purposes

The purposes of this research are to analyze and understand the temporal variation of tritium and oxygen-18 in discharge of the Red Cedar River in southern lower Michigan and to test whether the concentration of tritium and oxygen-18 in discharge can be used to separate flow components, for example surface runoff and groundwater flow.

Study Area

The Red Cedar basin is located in Ingham County and western Livingston County, Michigan, and covers an area of 355 mi^2 (Figure 1). The principal river in the basin is the Red Cedar River which is 42.2 miles long and has an average gradient of 2.7 ft/mi.

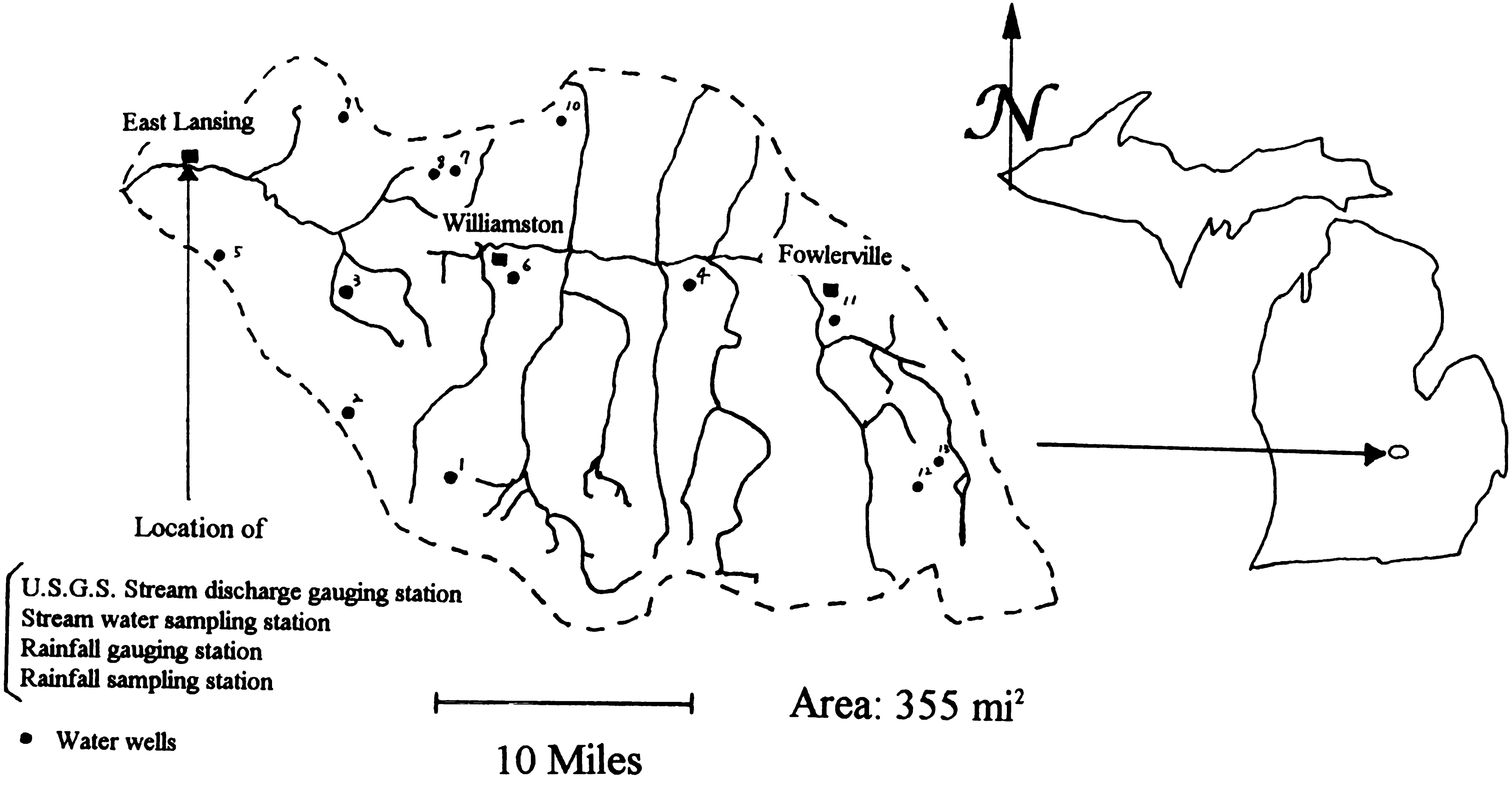

Figure 1. The Red Cedar Basin in Michigan.

The basin is underlain by drift and bedrock. The drift is only a few feet thick in some areas, but is about 60 feet thick over most of the basin. It is composed mostly of till, but includes some fairly extensive beds of sand and gravel (Humphrys and Bradford, 1958). The bedrock includes the Saginaw Formation which is Paleozoic in age and consists mainly of sandstone and shale but includes some thin beds of limestone and coal (Humphrys and Bradford, 1958). The Saginaw Formation is a major source of groundwater for the municipal, industrial, and institutional water supplies in the basin (Humphrys and Bradford, 1958).

Environmental Isotopes (T, ^{18}O) in Runoff Studies

Tritium (T) and oxygen-18 are ideal tracers for runoff studies because of two attributes of these isotopes. Since tritium and oxygen-18 are constituent parts of some natural water molecules (e.g. $HT^{16}O$, $H_2{}^{18}O$ respectively), they travel at the same rate through the catchment as 'average' water ($H_2{}^{16}O$). Also, tritium and oxygen-18 are chemically conservative at low temperatures associated with most small watershed systems (Fritz *et al.*, 1976; Kennedy *et al.*, 1986; and others). This means that their concentrations in a volume of water do not change by reactions with catchment materials.

Tritium

Tritium is a radiogenic isotope of hydrogen whose half-life is in the order of 12.4 years. Tritium atoms represent an extremely small proportion of terrestrial hydrogen, about 10^{-14} - 10^{-16} % of all hydrogen atoms. Concentrations of tritium are expressed in tritium units (TU), where 1 TU equals $1T/10^{18}$ atoms of protium (Fritz and Fontes, 1980).

Tritium is produced naturally in the atmosphere by bombardment of nitrogen by solar radiation (Faure, 1986). It is also produced anthropogenically. Since the advent of atmospheric testing of thermonuclear devices in 1952, tritium as a by-product of thermonuclear testing ('bomb tritium') has been the dominant source of tritium in precipitation. After 1963, the year in which the atmospheric test ban treaty was signed, the tritium levels in precipitation began to decline gradually because of the cessation of atmospheric testing and radioactive decay (Gat, 1980).

In addition to the order-of-magnitude variations in tritium in precipitation over the past few decades, tritium input also varies seasonally. For example, Chen (1993) reports that the tritium concentration of precipitation in East Lansing, Michigan is greatest during the months of June and July and least during the month of November due to the seasonal transference of tritium from the stratosphere to the troposphere.

Distinct 'old' and 'new' water T values are required for storm runoff hydrograph separation. The required difference is possible because of the gradual decline in precipitation T values since 1963 and the even more gradual fall in groundwater T values.

Oxygen-18

The important requirement in storm runoff hydrograph separation using oxygen-18 is that 'old' and 'new' water have distinct isotope values, like tritium. The 'new' water oxygen isotope values may vary considerably from event to event while the 'old' water oxygen isotope value remains fairly constant.

Once rain passes into the saturated zone of shallow flow systems, the oxygen isotope values of subsurface water are changed only by mixing with waters with different isotopic contents. The homogenizing effects of recharge and dispersive processes produce groundwater with isotope values which approach uniformity in time and space and which approximate a damped reflection of the precipitation over a period of years (Brinkmann *et al.*, 1963). Evaporation and molecular exchange with ambient water vapor on the oxygen isotope content of water which infiltrates can lead to an enrichment in oxygen isotopes of the recharge as compared to precipitation (Gat and Tzur, 1967).

II. METHODS

Sampling

Stream and Rain Samples

The Red Cedar River was sampled on a daily basis for the months of August, September, and October of 1993 from under the Farm Lane Bridge located on the campus of Michigan State University, East Lansing (Figure 1). The apparatus for collecting the samples was 250 ml high-density polyethylene bottles. A subset of 16 samples (Figure 2) representing a single storm event (Sep. 24 ˉ Oct. 9) was selected based on 1) size of storm, 2) simplicity of hydrograph, and 3) clear definition of baseflow recession. This subset was then analyzed for T and ^{18}O and used to separate 'new' and 'old' water for the storm event. Red Cedar River discharge data for the months of August, September, and October of 1993 were obtained from the U. S. Geological Survey gauging station located under the Farm Lane Bridge (Figure 1).

Whole rain was also sampled for the months of August, September, and October of 1993 from behind the Natural Science Building on the campus of Michigan State University (Figure 1). From these samples, a subset of 4 samples associated with storm precipitation from September 26 to September 30 was also analyzed for T and^{18}O (Figure 3). Precipitation data of the Red Cedar basin were obtained from the Michigan Meteorological Resources Station located at the Horticulture Research Center, on the campus of Michigan State University (Figure 1).

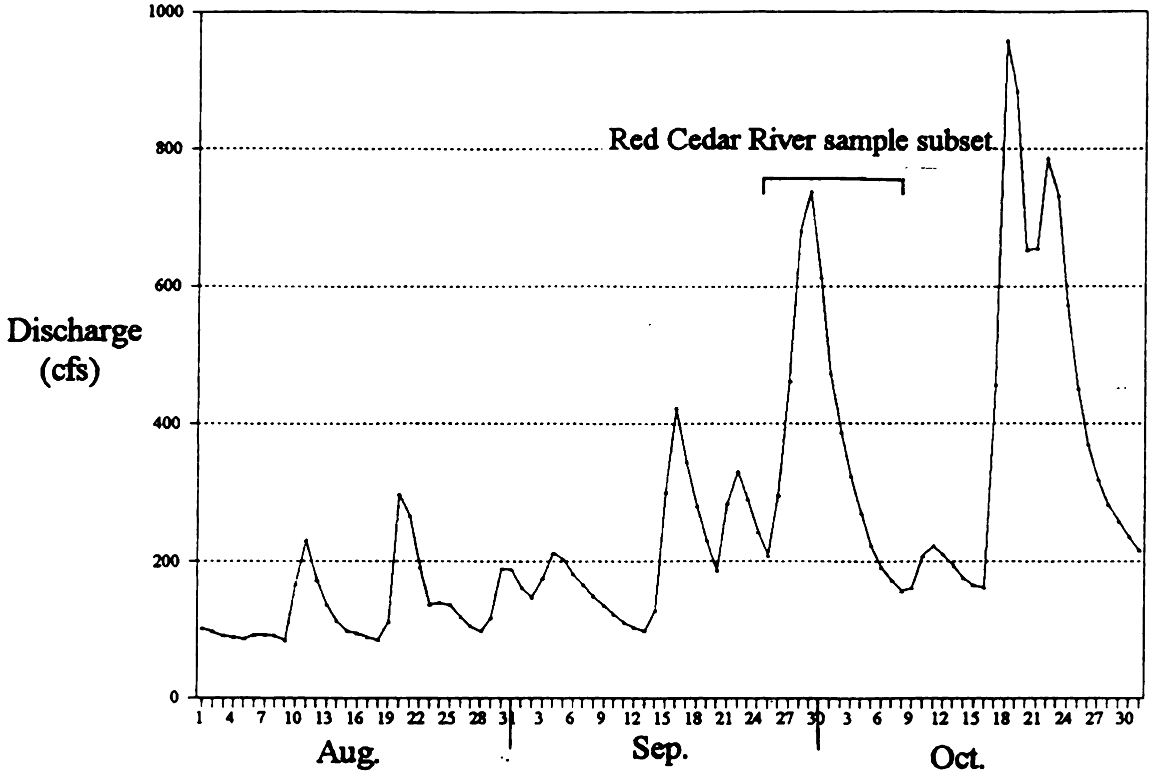

Figure 2. The hydrograph of the Red Cedar River during Aug., Sep., and Oct. 1993.

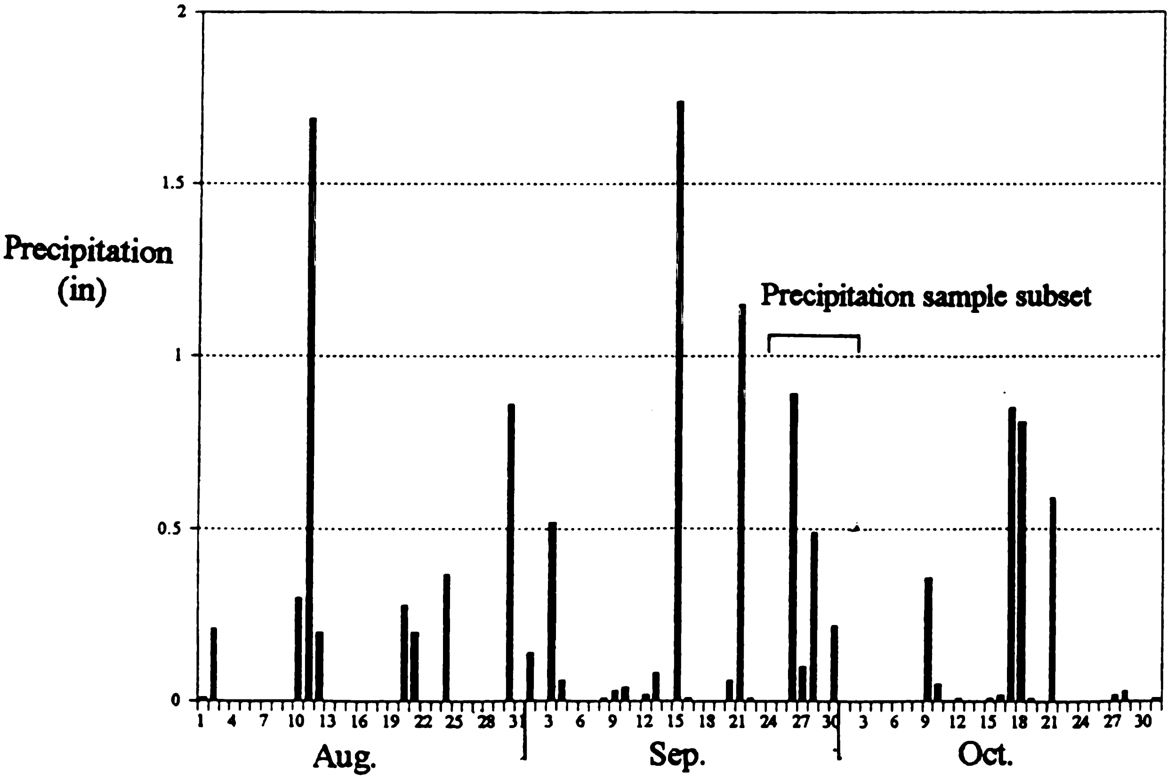

Figure 3. Precipitation in the Red Cedar Basin during Aug., Sep., and Oct. 1993.

Analytical Methods

Analyses of Water Samples for T and ^{18}O

Tritium analyses for the samples collected were done at the Michigan State University Tritium Laboratory and included electrolytic enrichment and scintillation counting (Ostlund and Werner, 1961, Taylor, 1981, and Wyerman, 1976, see Appendices). Results of the analyses are accurate to the ±1.0 TU and are presented in Table 1.

The ^{18}O analyses for the samples were done at the University of Michigan Stable Isotopes Laboratory using the CO_2 equilibration method (Roether, 1970) and mass spectrometry. The results of the analyses are shown in Table 2 and are reported as the relative ratio of ^{18}O to ^{16}O in the water sample expressed in parts per mil (‰). This value, $\delta^{18}O$, is defined by:

$$\delta^{18}O = [(R_x - R_{SMOW}) / R_{SMOW}] \times 1000$$

where R is the ratio of the heavy to light isotope ($R = {}^{18}O/{}^{16}O$), x is the unknown sample and SMOW (Standard Mean Ocean Water) is an international standard used for oxygen-18 analysis of water (Craig, 1961 a).

Isotopic Hydrograph Separation

Between storm events, stream flow reflects the isotopic composition mainly of 'old' water because mostly groundwater contributes to stream flow (Pearce *et al.*, 1986). During storm runoff events, however, the isotopic character of the stream may be altered by the addition of 'new' water from rainfall. The 'old' and 'new' water contributions can be calculated by solving the mass balance equations for the water and isotopic fluxes in the stream. These equations (Pearce *et al.*, 1986) can be expressed as:

$$Q_s = Q_o + Q_n \qquad (1)$$

$$C_sQ_s = C_oQ_o + C_nQ_n \qquad (2)$$

These equations can be reduced to:

$$Q_o = [(C_s - C_n) / (C_o - C_n)]\, Q_s \qquad (3)$$

$$Q_n = Q_s - Q_o \qquad (4)$$

where Q is discharge, C refers to tracer (isotope) concentration of a component, and the subscripts s, o, and n indicate stream, 'old' water component and 'new' water component, respectively.

In order to test the validity of the above method of flow separation, each component of Q_n and Q_o derived from tritium and oxygen-18 analyses of stream flow is compared to components of surface runoff and groundwater flow derived from hydrograph separation using graphical techniques.

Graphical Hydrograph Separation

Barnes' graphical method (Barnes, 1939) of hydrograph separation was used to separate the storm hydrograph of Sep. 24 ~ Oct. 9, 1993. The Red Cedar River discharge (Q) vs. time were plotted on a semi-log graph, the log axis for Q, (Figure 4). A straight line of the baseflow recession was extended from point 'C' back to point 'B' under point 'D', the inflection point. And then, a straight line 'A-B' was connected. The line 'A-B-C' represents baseflow during the storm event, likewise the area under the total hydrograph and above 'A-B-C' represents direct runoff during the event. Both the total hydrograph and the baseflow hydrograph are replotted on a arithmetic graph in Figure 5.

According to graphical hydrograph separation, the mean discharge of the baseflow during the period of September 24 to October 9, 1993 was 230.52 cfs or 63 % of total runoff, and the mean discharge of the surface runoff was 133.08 cfs or 37 % of total runoff (Figure 4, Figure 5).

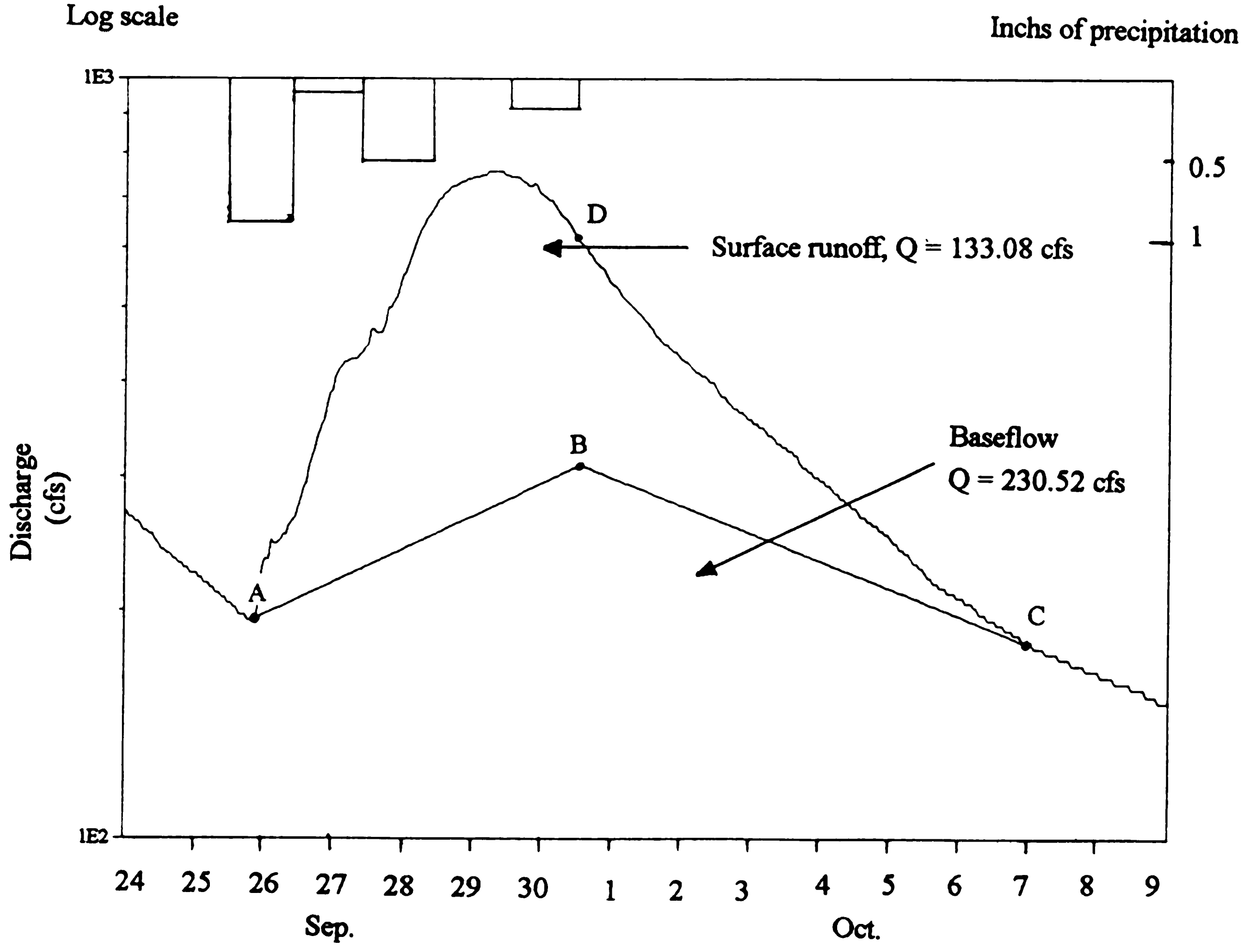

Figure 4. Hydrograph separation using graphical method (semi-log scale).

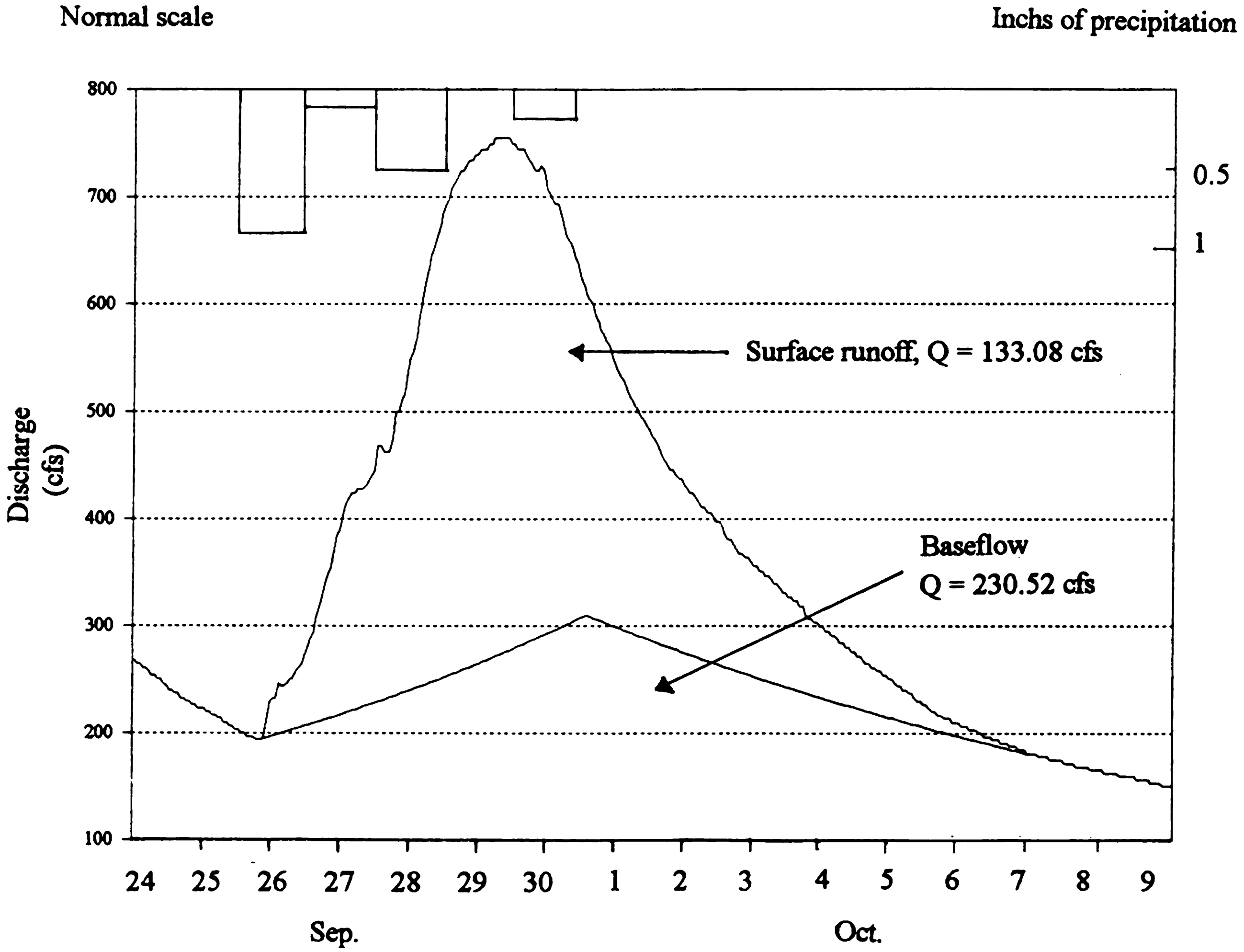

Figure 5. Hydrograph separation using graphical method (arithmetic scale).

III. RESULTS

Tritium

The tritium data in Table 1 and Figure 6 indicate a high concentration of 19.45 TU in stream discharge before the storm of September 26 to September 30, 1993 and a low concentration of 14.94 TU during highest stream discharge associated with the storm event. The data do not show a smooth change in tritium concentration with time, however a smoothed curve for each data point can be approximated considering an error of ±1 TU (Figure 6). The amount of tritium in precipitation during the storm period ranged from 14.99 TU to 16.70 TU (Figure 6).

Oxygen

The $\delta^{18}O$ data in Table 2 and Figure 7 indicate a high concentration of -8.43 ‰ in stream discharge before the storm of September 26 to September 30, 1993 and a low concentration of -11.20 ‰ during highest stream discharge associated with the storm event. The error bars of each data point were not constructed in Figure 7 because the amount of errors was too small to show in the figure. The amount of oxygen-18 in precipitation during the storm period ranged from -12.76 ‰ to -12.87 ‰. In Table 2 and Figure 7, sample number 18 and 19 of rain indicate -5.17 ‰ and -10.69 ‰, respectively, but these values were excluded from further consideration because the standard deviations of these values were excessively high (±1.12 and ±1.35, respectively) due to lack of sample volume.

Table 1. Tritium results.

SAMPLE	CPM	CE	β	EE	DPM	TU
STD1	60.1	0.27	7.57	0.67	1.3623	191.87
BKG1	3.81	0.27				
1	9.44	0.27		0.67	0.1381	19.45
2	9.1	0.27		0.67	0.1262	17.77
3	8.01	0.27		0.67	0.1002	14.11(17.58[1])
4	8.48	0.27		0.67	0.1155	16.27
5	8.77	0.27		0.67	0.1202	16.93
6	9.17	0.27		0.67	0.1228	17.3
8	8.48	0.27		0.67	0.113	15.92
9	9.14	0.27		0.67	0.1221	17.2
10	9.1	0.27		0.67	0.121	17.04
STD2	49.02	0.26	6.85	0.66	1.3763	193.85
BKG2	4.22	0.26				
11	8.08	0.26		0.66	0.1124	15.84
12	7.47	0.26		0.67	0.1119	15.77
13	7.79	0.26		0.67	0.1158	16.32
14	8.66	0.26		0.64	0.115	16.2
15	8.04	0.26		0.66	0.1207	17.01
16	8.05	0.26		0.67	0.1248	17.58
rain 17	7.69	0.26		0.66	0.1097	15.45
rain 18	5.69	0.26		0.65	0.0423	5.96(15.08[1])
rain19	8.23	0.26		0.65	0.1186	16.7
rain 20	6.32	0.26		0.66	0.0668	9.41(14.99[1])
STD1	56.43	0.2	18.66	0.85	1.3528	190.54
BKG1	3.9	0.2				
7[2]	8.1	0.2		0.85	0.1061	14.94

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[1] These numbers are from re-calculation considering the amount of dead distilled water (no tritium in it) added due to lack of sample volume.

[2] This sample was re-counted.

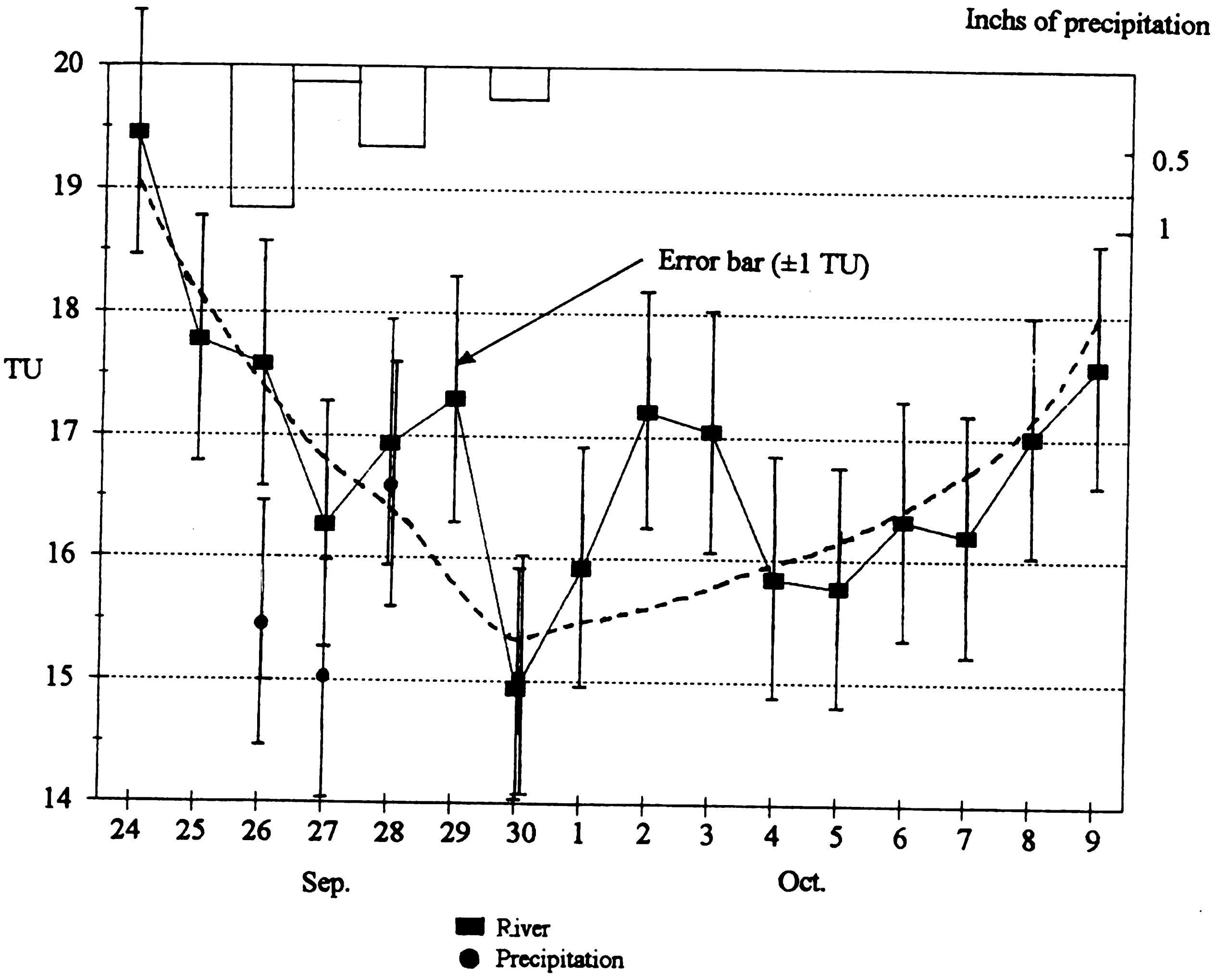

Figure 6. Variation of tritium in the Red Cedar River.

Table 2. Oxygen-18 results.

SAMPLE	Date run	δ18O,CO2	δ18O,CO2	δ18O,H2O	std dev
	on Δ S	17O corr	(SMOW)	(SMOW)	±
#1	24-Oct	-1.579	33.424	**-8.47**	0.08
#2	24-Oct	-1.538	33.484	**-8.43**	0.08
#3	24-Oct	3.158	38.299	**-2.95**	**1.92**
#4	24-Oct	-1.629	33.344	**-8.52**	0.04
#5	24-Oct	-2.436	32.509	**-9.32**	0.04
#6	24-Oct	-2.415	32.531	**-9.3**	0.07
#7	24-Oct	-4.316	30.467	**-11.2**	0.05
#8	24-Oct	-3.905	30.988	**-10.78**	0.08
#15	24-Oct	-2.198	32.726	**-9.08**	0.02
#19 rain	24-Oct	-4.627	30.241	**-10.69**	**1.35**
MDIW3	24-Oct	-2.754	32.18	**-8.82**	0.06
MDIW3	24-Oct	-2.691	32.245	**-8.76**	0.03
#9	25-Oct	-3.724	30.776	**-10.99**	0.04
#10	25-Oct	-3.905	30.988	**-10.78**	0.03
#11	25-Oct	-2.771	32.162	**-9.66**	0.04
#12	25-Oct	-2.75	32.141	**-9.68**	0.02
#13	25-Oct	-2.598	32.302	**-9.53**	0.02
#14	25-Oct	-2.426	32.517	**-9.31**	0.05
#16	25-Oct	-2.215	32.703	**-9.12**	0.03
#17 rain	25-Oct	-5.991	28.829	**-12.87**	0.03
#18 rain	25-Oct	1.758	36.849	**-5.17**	**1.12**
#20 rain	25-Oct	-5.892	28.931	**-12.76**	0.01
MDIW3	25-Oct	-1.809	33.157	**-8.7**	0.1
MDIW3	25-Oct	-2.093	32.864	**-8.98**	0.03

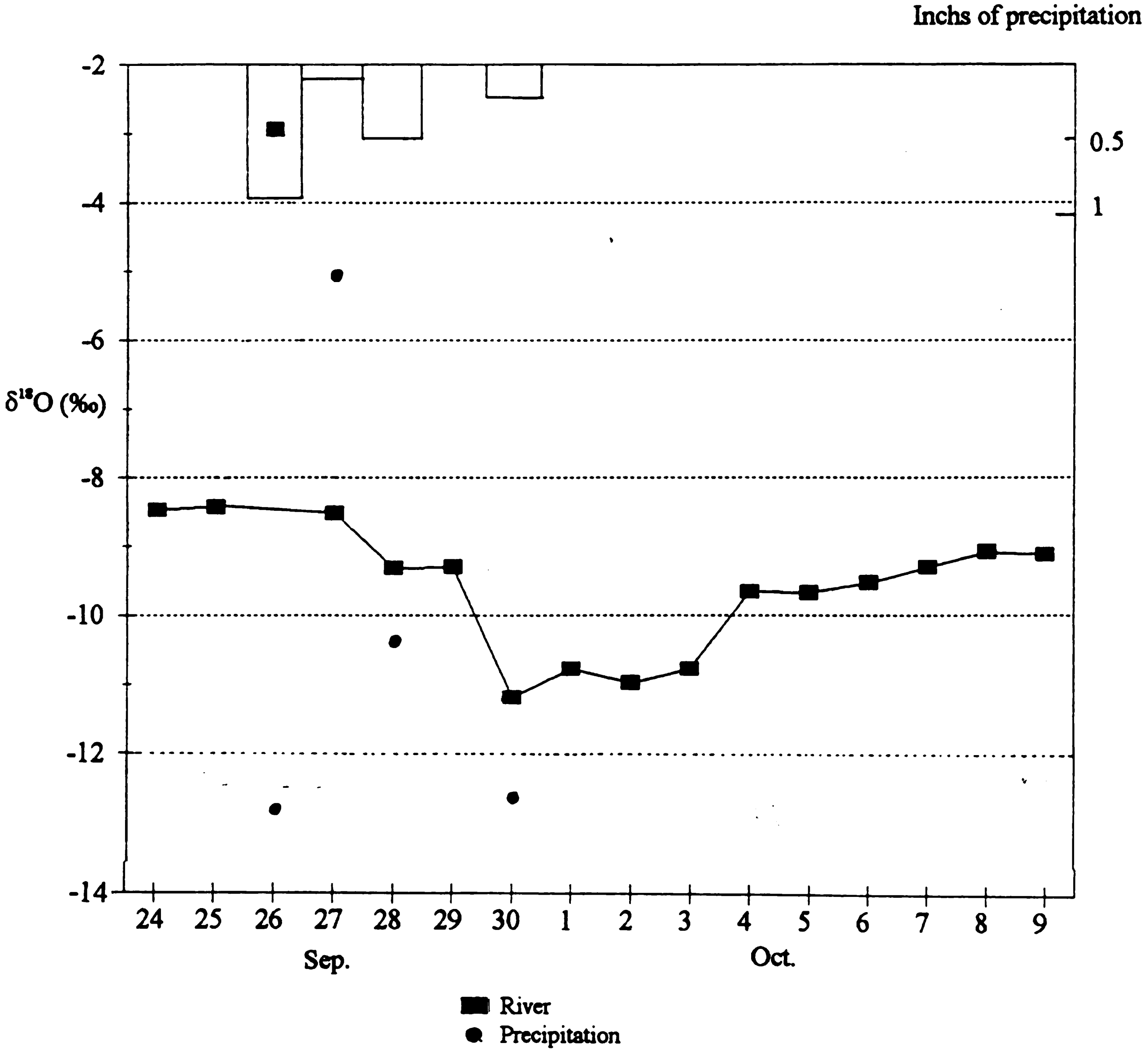

Figure 7. Variation of oxygen-18 in the Red Cedar River.

Hydrograph Separation Using Tritium and Oxygen-18

The relationship between tritium and oxygen-18 of the stream water samples analyzed is presented in Figure 8 and shows a general linear relationship between both values. The correlation coefficient for this relationship is 0.5293 and is statistically significant at confidence level 95 %. There is one anomalous point (-2.95 ‰) which is discounted because it has a high standard deviation of±1.92 due to lack of sample volume.

Tritium

The weighted average tritium value of the rain water for the storm event of September 26 to September 30, 1993 is 15.73 TU with a range from 14.99 TU to 16.70 TU (Table 1). The tritium concentration in prestorm water (groundwater) mixing with, or displaced by, the rainfall, however, is unknown since tritium data is generally not available for wells in the basin. Also, because mixing of groundwater has not been extensive since the introduction of "bomb" derived tritium, individual samples of groundwater from wells would not be representative for the entire basin. Information about tritium in prestorm water (groundwater), however, can be obtained from baseflow in the Red Cedar River on October 8 and October 9, 1993 and shows a range from 17.01 TU to 17.58 TU (Table 1 and Figure 6) and a weighted average of 17.30 TU which presumably represents an average of the water entering tributary channels from adjacent saturated zones.

When the weighted average tritium content of rainfall is taken as Tn = 15.73 TU, displaced prestorm water (groundwater) as To = 17.30 TU, and the tritium content for storm runoff (Ts) as in Table 1, application of equations (1) ~ (4) show that 69 % of the storm runoff during the period of September 24 to October 9, 1993 was prestorm water or groundwater and that 31 % of the storm runoff was surface runoff (Table 3, Table 6, and Figure 9). The subscripts n, o, and s indicate the 'new' water component, 'old' water component, and the stream, respectively.

Oxygen-18

The weighted average of the $\delta^{18}O$ values for the rain samples from the storm event of September 26 to September 30, 1993 is -12.85 ‰ with a range from -12.76 ‰ to -12.87 ‰ (Table 2), whereas that for baseflow is -9.09 ‰ with a range from -9.08 ‰ to -9.12 ‰. It is interesting to note that the baseflow values tend to match the $\delta^{18}O$ values of groundwater samples collected from wells by the U. S. Geological Survey in the basin (Table 4).

When the weighted average $\delta^{18}O$ value of rainfall is taken as $\delta^{18}O_n = -12.85$ ‰, displaced prestorm water (groundwater) as $\delta^{18}O_o = -9.09$ ‰, and the $\delta^{18}O$ values for storm runoff ($\delta^{18}O_s$) as in Table 2, application of equations (1) ~ (4) show that 79 % of the storm runoff during the period of September 24 to October 9, 1993 was prestorm water or groundwater and that 21 % of the storm runoff was surface runoff (Table 5, Table 6, and Figure 9).

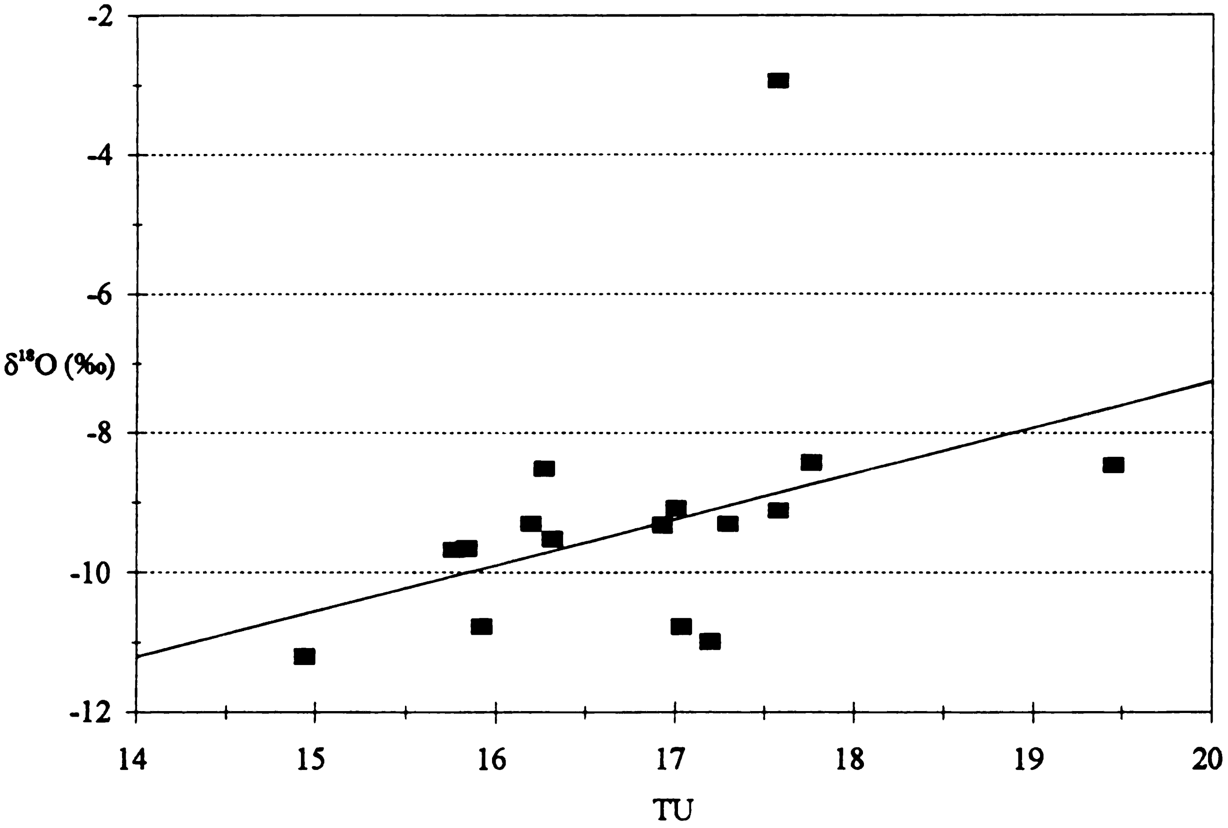

Figure 8. Relationship between tritium and oxygen-18.

Table 3. Storm hydrograph separation using tritium.

SAMPLE	$\frac{Ts - Tn}{To - Tn}$	Qs	$Qo = \left(\frac{Ts - Tn}{To - Tn}\right) Qs$	$Qn = Qs - Qo$
1	1[2]	243	243	0
2	1[2]	208	208	0
3	0.78	296	230.88	65.12
4	0.65	463	300.95	162.05
5	0.59	682	402.38	279.62
6	0.59	739	436.01	302.99
7	——	614	355[1]	259
8	0.55	473	260.15	212.85
9	0.56	387	216.72	170.28
10	0.64	323	206.72	116.28
11	0.66	269	177.54	91.46
12	0.77	223	171.71	51.29
13	0.86	192	165.12	26.88
14	0.95	172	163.4	8.6
15	1[2]	161	161	0
16	1[2]	157	157	0
Total		350.12	240.97	109.15

---

[1] This number is not from the calculation, it is from the hydrograph separation curve, because the data are not valid for the calculation.

[2] These number are slightly greater or less than 1, but they are adjusted to 1 in order to get a smoothed hydrograph separation curve.

Table 4. Oxygen-18 data of groundwater in the Red Cedar Basin (Dannemiller *et al.*, 1990).

Well number	$\delta^{18}O$ (‰)
1	-8.35
2	-8.80
3	-9.10
4	-9.70
5	-9.20
6	-9.30
7	-9.10
8	-8.90
9	-9.80
10	-9.95
11	-8.60
12	-9.10
13	-9.00

Table 5. Storm hydrograph separation using oxygen-18.

SAMPLE	$\frac{\delta^{18}Os - \delta^{18}On}{\delta^{18}Oo - \delta^{18}On}$	Qs	$Qo = \left(\frac{\delta^{18}Os - \delta^{18}On}{\delta^{18}Oo - \delta^{18}On}\right)Qs$	Qn = Qs - Qo
1	1[2]	243	243	0
2	1[2]	208	208	0
3	——	296	296[1]	0
4	0.95	463	439.85	23.15
5	0.86	682	586.52	95.48
6	0.81	739	598.6	140.4
7	0.51	614	313.14	300.86
8	0.54	473	255.42	217.58
9	0.64	387	247.68	139.32
10	0.7	323	226.1	96.9
11	0.74	269	199.06	69.94
12	0.82	223	182.86	40.14
13	0.9	192	172.8	19.2
14	0.96	172	165.12	6.88
15	1[2]	161	161	0
16	1[2]	157	157	0
Total		350.12	278.26	71.86

---

[1] This number is not from the calculation, it is from the hydrograph separation curve, because the data are not valid for the calculation.

[2] These number are slightly greater or less than 1, but they are adjusted to 1 in order to get a smoothed hydrograph separation curve.

Table 6. Result of hydrograph separations using graphical method, tritium, and oxygen-18,

Method	Surface runoff	Baseflow	Total runoff
Graphical	133.08 cfs (37 %)	230.52 cfs (63 %)	363.60 cfs (100 %)
Tritium	109.15 cfs (31 %)	240.97 cfs (69 %)	350.12 cfs (100 %)
Oxygen-18	71.86 cfs (21 %)	278.26 cfs (79 %)	350.12 cfs (100 %)

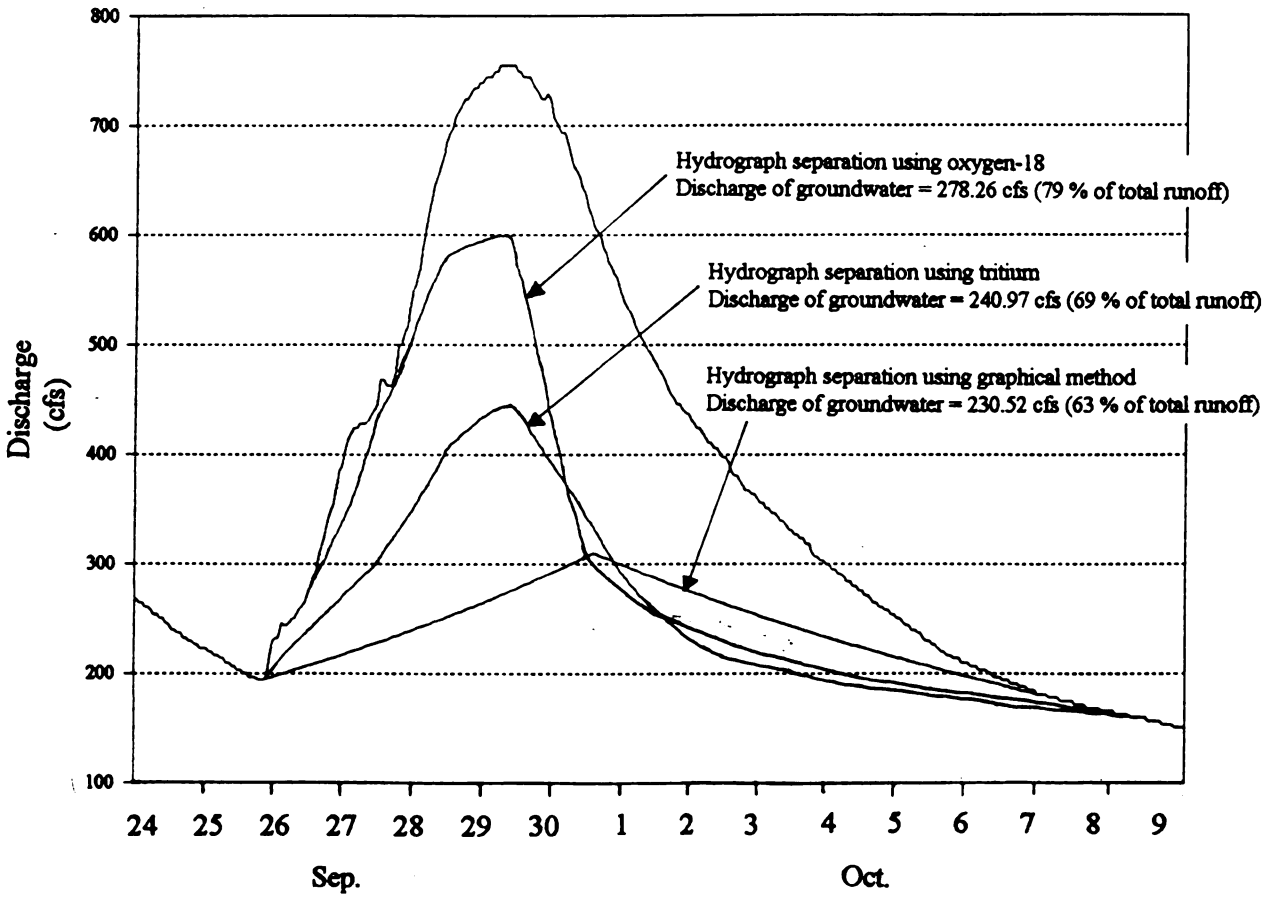

Figure 9. Hydrograph separations using tritium, oxygen-18, and graphical method.

IV. DISCUSSION

The weighted average tritium and oxygen-18 concentration of baseflow and precipitation used to separate flow components include synthetic errors. For example, the tritium data has an error of ±1 TU, and the oxygen-18 data has an error ranging from ±0.01 ‰ to±0.08 ‰ (Table 2). Also, the stream discharge and precipitation data each have errors of approximately 5 %. These errors are significant and clearly affect the analysis of flow components associated with the storm of September 26 to September 30,1993.

The following equation of Lapin (1993) is used to calculate synthetic errors of the weighted average values.

$$\alpha = 1 - \{(1 - \alpha_1)(1 - \alpha_2)(1 - \alpha_3)\cdots\}$$

where α indicates probabilities of synthetic errors, and α_1, α_2, and α_3 indicate errors probabilities of each data. The results show that the synthetic error for the weighted average tritium of baseflow (17.30 TU) and precipitation (15.73 TU) is ± 1.41 TU and ±1.38 TU respectively, and that the synthetic error for the weighted average oxygen-18 of baseflow (-9.09 ‰) and precipitation (-12.85 ‰) is±0.26 ‰ and ±0.35 ‰ respectively (Figure 10 and Figure 11).

Variation of tritium in the Red Cedar River together with the calculated synthetic error for the period September 24 to October 9, 1993 is shown in Figure 10. The data indicates an overlapping area between the weighted average tritium of baseflow with the synthetic error of ±1.41 TU and the weighted average tritium of precipitation with the synthetic error of ±1.38 TU. Clearly, the difference between the concentration of tritium in baseflow and precipitation during the period of

September 24 to October 9, 1993 is not enough to realistically separate flow components.

Figure 11 likewise shows the variation of oxygen-18 in the Red Cedar River together with the calculated synthetic error. In this case, however, the difference between the concentration of oxygen-18 in baseflow and precipitation is enough to separate flow components.

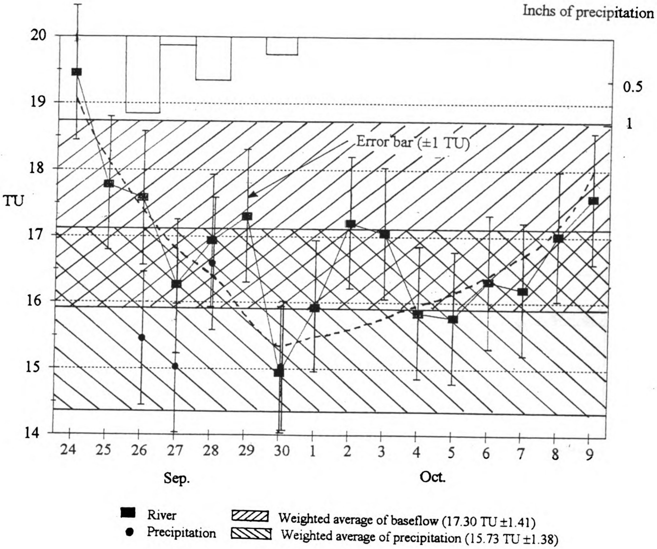

Figure 10. Variation of tritium in the Red Cedar River.

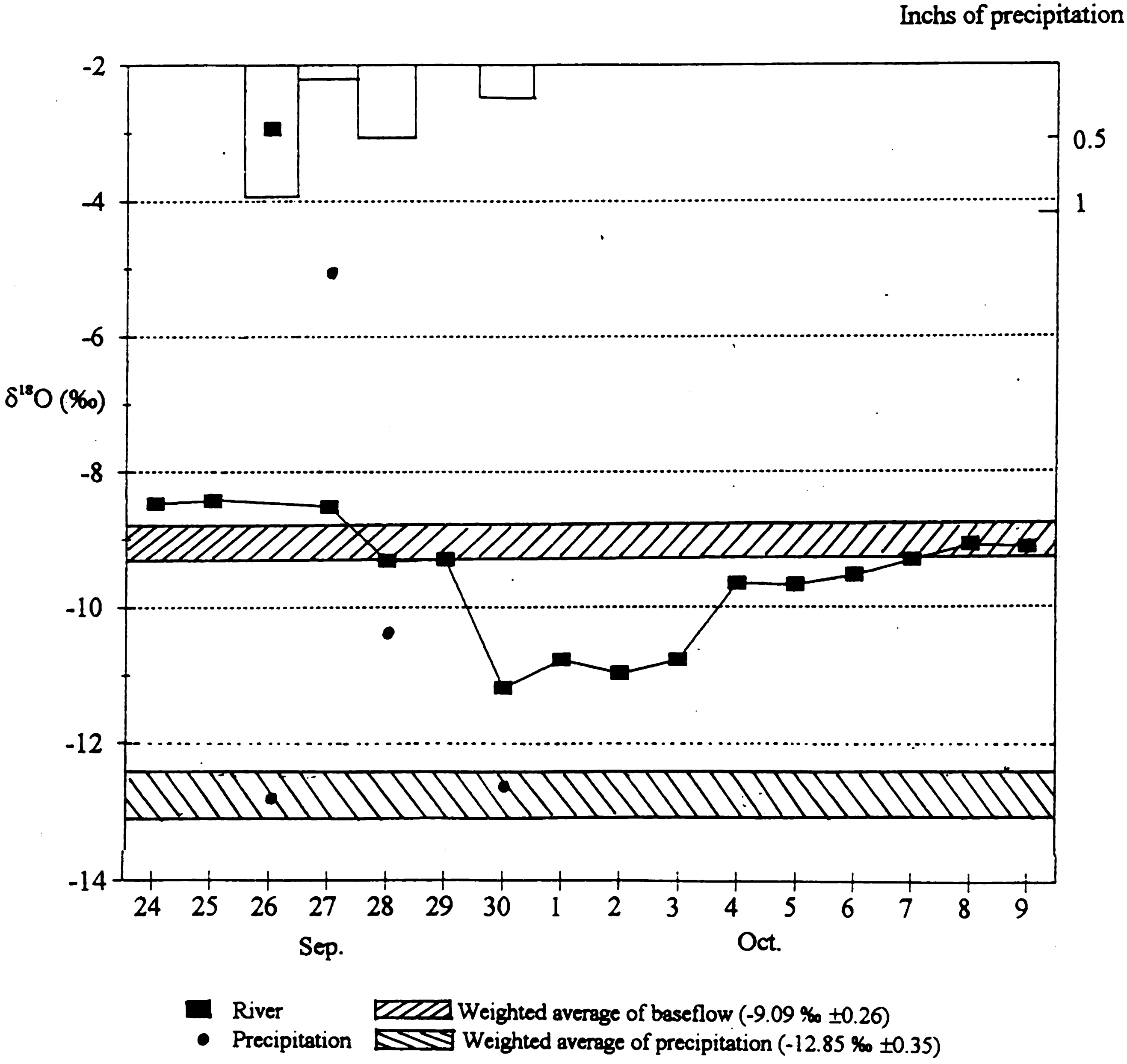

Figure 11. Variation of oxygen-18 in the Red Cedar River.

V. CONCLUSIONS

The natural isotope T and $\delta^{18}O$ were tested as practical tools for storm hydrograph separations in the Red Cedar basin and were used to separate the storm hydrograph of September 24 to October 9, 1993 into two component: rainwater contributed to the basin during the storm; and groundwater that was present in subsurface storage before the storm.

Initial tritium and oxygen-18 results indicate that 69 % to 79 % of the storm runoff must have been groundwater during the storm runoff event which is somewhat greater than that obtained using a graphical technique (63 %) of streamflow separation. However, statistical analysis of the data shows that analysing tritium concentration in streamflow is not appropriate to separate flow components and that analysing oxygen-18 concentration in streamflow can be used to separate flow components.

The results from these studies indicate that groundwater is an extremely important contributor to storm runoff events in the humid headwater catchment such as the Red Cedar basin.

APPENDICES

APPENDIX A

Sample Preparation

Distillation

In order to remove impurities from the water samples distillation was carried out before electrolysis. The system for distillation consists of flasks encased in heating coils, cooling apparatuses, and vacuum devices.

All water samples were transferred to the flasks. Vacuum was then applied to ensure that the distillation system was airtight. Heat was applied to the flasks until dryness, which takes approximately 3-4 hours.

Electrolysis

Today, tritium concentrations in natural waters are relatively low. For this reason water samples for tritium analysis were enriched by the process of electrolysis. The electrolysis system used in this study consists of 12 iron/nickel cells a freezer with 12 holes to accommodate the cells, fan to ensure even circulation of air, power supply, and gas exhaust lines. The cells were fitted with gas outlets to allow H_2 and O_2 produced during the process to be released via the exhaust lines. The reactions which occur at the electrodes are:

Anode : $2H_2O \text{ --> } 4H^+ + O_2 + 4e^-$

Cathode : $2H^+ + 2e^- \text{ --> } H_2$ (Hoffman and Stewart, 1966)

where H may be protium (H^1), deuterium (H^2), or tritium (H^3).

During each electrolysis run, ten of the electrolysis cells were used for unknown samples, the remaining two cells however contained standards: one a known tritium standard and the other a blank. The blank is 'dead' or 'pre-bomb' distilled water which serves as a measure of background radiation. One g of sodium peroxide (N_2O_2, electrolyte) was added to the cells. The cells were then connected electrically in series to the power supply and placed in the freezer at -9°C. A current of 5.8 A was maintained for approximately 110 hours or when a residual volume of 12-16 ml remained in each cell. The reasons for maintaining the freezer at cold temperature are:

a) Evaporation loss is reduced. Evaporation can lower the recovery yield of the tritium during electrolysis (Ostlund and Werner, 1962).

b) Warm N_2O_2 electrolyte can attack the anodes (Taylor, 1981).

C) The cold temperature increases the separation efficiency of the hydrogen isotopes (Hoffman and Stewart, 1966).

Post-Distillation

In order to separate the electrolyte from the electrolyzed sample post-distillation was carried out after electrolysis was completed. The system for post-distillation consists of glass test tubes capped by modified distillation heads and encased in heating coils.

All electrolyzed samples between 12-16 ml were transferred to the glass test tubes. Heat then was applied to the test tubes until dryness, which takes approximately 2-3 hours. Eleven ml of distillate was then pipetted into a plastic vial for liquid scintillation analysis.

APPENDIX B

Tritium Activity Calculations

The Packard Tri-Carb 1050 LS counter was used for scintillation counting. Prior to counting, 14 ml of cocktail was added to 11 ml of sample.

The tritium activities of unknown samples were determined using the following equation (Wyerman 1975):

$$\mathrm{DPM\ (s) / ml} = \frac{[\mathrm{CPM\ (s) / ml - CPM\ (b) / ml}]}{[\{V_o\ (s) / V_f\ (s)\} * \mathrm{CE} * \mathrm{EE\ (s)}]}$$

where

V_o (s) -------------------------- initial volume (ml) of sample

V_f (s) --------------------------- final volume (ml) of sample

CPM (s) / ml ------------------ counts per minute of sample

CPM (b) / ml ------------------ counts per minute of background

CE ------------------------------ counting efficiency

EE ------------------------------ electrolytic efficiency of sample

These values must also be known for the electrolytic standard (es). Conversion of DPM to tritium units is based on the relationship that 1 TU = 0.0071 DPM / ml. 1 TU = 1 tritium atom per 10^{18} hydrogen atoms (Faure, 1986).

The counting efficiency of a standard is defined as:

$$\mathrm{CE} = \frac{[\mathrm{CPM / ml - CPM\ (b) / ml}]}{[\mathrm{DPM_o / ml}]}$$

where

DPM_o -------------------------- initial activity of standard

Next the electrolytic efficiency of the standard, EE (es), is calculated from the equation:

$$EE\,(es) = \frac{[CPM\,(es) / ml - CPM\,(b) / ml]}{[\{V_o\,(es) / V_f\,(es)\} * CE * DPM_o\,(es) / ml]}$$

This is used to obtain a fractionation factor β which relates the T / H ratio to that of the evolved hydrogen (Taylor, 1981). The equation for beta is:

$$\beta = \frac{-\ln\,[V_o\,(es) / V_f\,(es)]}{\ln EE\,(es)}$$

β is then substituted into the following equation to determine the electrolytic efficiency of the samples, EE (s).

$$EE\,(s) = [V_o\,(s) / V_f\,(s)]^{-1/\beta}$$

The final activity of the unknown samples is then determined:

$$DPM\,(s) / ml = \frac{[CPM\,(s) / ml - CPM\,(b) / ml]}{[\{V_o\,(s) / V_f\,(s)\} * CE * EE\,(s)]}$$

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