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Tritium hydrology of the Mississippi River basin

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Abstract:

In the early 1960s, the US Geological Survey began routinely analysing river water samples for tritium concentrations at locations within the Mississippi River basin. The sites included the main stem of the Mississippi River (at Luling Ferry, Louisiana), and three of its major tributaries, the Ohio River (at Markland Dam, Kentucky), the upper Missouri River (at Nebraska City, Nebraska) and the Arkansas River (near Van Buren, Arkansas). The measurements cover the period during the peak of the bomb-produced tritium transient when tritium concentrations in precipitation rose above natural levels by two to three orders of magnitude. Using measurements of tritium concentrations in precipitation, a tritium input function was established for the river basins above the Ohio River, Missouri River and Arkansas River sampling locations. Owing to the extent of the basin above the Luling Ferry site, no input function was developed for that location. The input functions for the Ohio and Missouri Rivers were then used in a two-component mixing model to estimate residence times of water within these two basins. (The Arkansas River was not modelled because of extremely large yearly variations in flow during the peak of the tritium transient.) The two components used were: (i) recent precipitation (prompt outflow) and (ii) waters derived from the long-term groundwater reservoir of the basin. The tritium concentration of the second component is a function of the atmospheric input and the residence times of the groundwaters within the basin. Using yearly time periods, the parameters of the model were varied until a best fit was obtained between modelled and measured tritium data. The results from the model indicate that about 40% of the flow in the Ohio River was from prompt outflow, as compared with 10% for the Missouri River. Mean residence times of 10 years were calculated for the groundwater component of the Ohio River versus 4 years for the Missouri River. The mass flux of tritium through the Mississippi Basin and its tributaries was calculated during the years that tritium measurements were made. The cumulative fluxes, calculated in grams of ^{3}H were: (i) 160 g for the Ohio (1961–1986), (ii) 98 g for the upper Missouri (1963–1997), (iii) 30 g for the Arkansas (1961–1997) and (iv) 780 g for the Mississippi (1961–1997). Published in 2004 by John Wiley & Sons, Ltd.

KEY WORDS Mississippi River; tritium; isotopes; surface water; radioactivity; residence time

INTRODUCTION

Studies over the past decades have demonstrated the value of isotopic monitoring of the water flowing out of river basins (Rank *et al.*, 1998; Kendall and Coplen, 2001). Isotopes provide a method of obtaining information on physical parameters and responses of the basin that are not easily obtained by other approaches. One of the most important isotopes for determination of time-scales is tritium. Bomb-produced tritium (a radioactive isotope of hydrogen with a half-life of 12·41 years) has been used extensively as a tracer of hydrological processes in the environment for the past five decades. Being a part of the water molecule as HTO, tritium provides an excellent tracer for the physical movement of water. It follows the pathway of water through hydrological systems with no changes except for decay and a slight fractionation during phase transitions. This fractionation is small and can be ignored in most tritium hydrological studies.

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Before the beginning of the nuclear era, about 3–4 k of tritium were present on Earth's surface through production by cosmic-ray spallation in the atmosphere (Lal and Peters, 1967). The tritium concentrations in the various hydrological reservoirs reflected the steady-state achieved between cosmogenic production, radioactive decay, and the rates of mixing and exchange between various hydrological systems (Buttlar and Libby, 1955; Giletti *et al*., 1958). With the beginning of atmospheric nuclear testing, large amounts of radioactivity were released into the atmosphere with major peaks in tritium production occurring in the late 1950s and early 1960s (Miskel, 1973; Carter and Moghissi, 1977). The increases in tritium concentrations in precipitation following the 1962 weapons tests were two to three orders of magnitude above natural concentrations at most locations in the Northern Hemisphere (Eriksson, 1965; Taylor, 1966; IAEA, 1981) with highest concentrations found at mid-continental locations that were removed from the influence of oceanic water vapour with its lower tritium concentration. The value of bomb-produced tritium as a tracer in the world's water cycle was quickly recognized (Suess, 1969), and beginning in the 1960s, tritium was widely applied to the study of physical mixing processes occurring in the world oceans (Dockins *et al*., 1967; Michel and Suess, 1975; Ostlund and Brescher, 1982).

Tritium has also received wide use in the study of continental hydrological systems (Plummer *et al*., 1993; Clark and Fritz, 1997), including studies of surface water systems, such as lakes, streams and rivers. For streams and rivers, tritium measurements can provide information on the average residence time of water within the basins (Brown, 1961; Kennedy *et al*., 1986; Rose, 1993, 1996). To obtain time-scales for waters in stream catchments and river basins, it is best to have a time-series of tritium data for both the outflow and precipitation. When tritium measurements are available on a decadal time-scale, models can be developed that simulate the response of the system to the tritium transient (Yurtsever and Payne, 1986). Tritium data from rivers are also useful in studying hydrological systems where a river is the major source of incoming water. Using long-term data and residence times obtained from models, estimates of tritium concentrations in river water can be obtained for years when tritium data are unavailable, typically prior to about 1962. The reconstructed tritium concentrations for river waters furnish a tritium source function to study hydrological processes in systems where water from these rivers have been used for municipal or agricultural purposes. Examples of the use of reconstructed tritium transients for river water are found in the work of Michel and Schroeder (1994) in the Imperial Valley and Hussein *et al*. (1998) in the Nile Valley. In both studies, the river water represented the main input of water into agricultural systems. Time-scales for processes occurring within the irrigation systems required an understanding of the tritium input function obtained from the river data. The above studies demonstrated that long-term records of tritium in river water can be used both to study hydrological parameters of the river system, and furnish a source function for studies in hydrological systems where river water is the main source of water.

The Mississippi River is the main drainage basin for the central USA. The main stem of the Mississippi River begins in northern Minnesota and travels over 3500 km to its mouth in Louisiana, where it empties into the Gulf of Mexico. Among the major rivers that flow into the Mississippi River are the Ohio River, the Missouri River and the Arkansas River. Of these, the Ohio River provides the largest input, accounting for the largest fraction of the Mississippi River's flow. The land drained by the Mississippi River includes some of the most productive agricultural areas in the USA. The quality of the river water in the agricultural areas of the basin has been affected by the increasing use of fertilizers, herbicides and pesticides (Meade, 1995; Goolsby and Battaglin, 2000). There are concerns about potential impacts of the increased loading of these chemicals on areas downstream in the Mississippi River and in the Gulf of Mexico. There is particular concern about the increase in nutrient fluxes from the basin on to the continental shelf, with a resultant increase in productivity in the seawater (Rabalais *et al*., 1999). It is suspected that the increase in nitrate loading in the river is one of the causes of an increase in the occurrence of hypoxia in shelf waters in the Gulf of Mexico. There have been discussions about changing agricultural practices to try to lessen this problem, but the time-scale required to obtain an impact in river water quality is not well understood. Thus, there is a need to understand the basic physical responses of the Mississippi Basin to non-point-source pollution. Below, the long-term tritium data

sets of the Mississippi River and three of its main tributaries are analysed and the implications for basin responses to changes in chemical loading are discussed.

SAMPLING PROGRAMME

Beginning in the 1960s, tritium samples were collected at five sites within the Mississippi Basin. Tritium data from one of these sites, the upper Mississippi River at Anoka, Minnesota, has been discussed in a previous report (Michel, 1992). Sampling locations discussed in this report are: A, the upper Ohio River at Markland Dam, Kentucky; B, the upper Missouri River at Nebraska City, Nebraska; C, the Arkansas River at Lock and Dam 13 near Van Buren, Arkansas; D, the Mississippi River at Luling Ferry, Louisiana (Figure 1). The Mississippi River station at Luling Ferry, Louisiana is located 28 km west of New Orleans and the basin area above the station is approximately 3 200 000 km^2. The location of this station is on the main stem of the Mississippi River and samples collected here can be considered as representative of waters that flow out of the basin into the Gulf of Mexico. The Ohio River station at Markland Dam is located about 5 km west of Warsaw, Kentucky and has a basin area of approximately 215 400 km^2. The station is located above the confluence of the Cumberland and Tennessee Rivers, and thus does not include water from these rivers. The source for the water at this location is primarily from Ohio and the Appalachians. The site on the Arkansas River has a basin of about 389 800 km^2, and is located below a dam about 280 km upstream from Little Rock, Arkansas. The largest sub-basin sampled in this programme is the upper Missouri River, with a drainage area of about 1 073 300 km^2. Unlike the Ohio and Arkansas Rivers, no major dams are located immediately upstream. However, the site is below the six major dams on the main stem of the river, which contain the equivalent of about 1 year of flow in their reservoirs. The total flow at the three tributary sites represents about 35% of the flow of the Mississippi River at the Luling Ferry site.

Samples initially were collected from daily composites during the 1960s. Beginning in the late 1960s, as tritium concentrations started to decline and variations became smaller, sampling was reduced to approximately once a month. As tritium concentrations continued to decline during the following decades, sampling frequency was further reduced. Sampling continued on the Ohio River into the mid-1980s and at the other sites until the 1990s. After collection, samples were returned to the US Geological Survey Tritium Laboratory for electrolytic enrichment and analysis by liquid scintillation counting (Thatcher *et al*., 1977). Typical analytical uncertainties are about $\pm 3\%$.

TRITIUM DISTRIBUTIONS IN RIVER WATER

Table I gives discharge-weighted yearly tritium concentrations in tritium units (1 TU = 1 tritium atom/10^{18} hydrogen atoms) for river water collected at the four sampling locations. The tritium concentrations in these river waters show the same pattern seen in other North American rivers. The highest tritium concentrations occur in 1963 at all sites (Figure 2), coinciding with the peak tritium concentrations found in precipitation produced by the large atmospheric nuclear bomb tests of 1962. Owing to its high-latitude mid-continental location, the highest tritium concentrations occur in Missouri River water throughout the post-bomb period, reaching a peak of over 1200 TU for 1963. The lowest concentrations are found in the Arkansas River where tritium concentrations never exceed 850 TU and fall to less than 10 TU in the mid-1980s. The low concentrations are the result of low concentrations in areal precipitation produced by water vapour advected north from the Gulf of Mexico. Tritium concentrations in the Ohio River, whose basin has a mid-continent location at a lower latitude than the Missouri Basin, are almost identical to those of the Mississippi River at Luling Ferry. Because of the large volume of water in the river basin, and the relatively long times water reside within the basin as opposed to the atmosphere, the response of the river basin waters to the tritium transient is different from that of precipitation. Figure 3 shows the tritium concentration of upper Missouri River water compared with that of precipitation within the river basin during the tritium transient. Precipitation

Figure 1. Location of sampling sites: (A) upper Ohio River, (B) upper Missouri River, (C) Arkansas River and (D) Mississippi River

data are derived from data collected at Omaha, Nebraska and Bismarck, North Dakota, with estimates for years where no data are available derived from the Ottawa correlation (Michel, 1989). Tritium concentrations in the river water are approximately one-third of the tritium concentration in precipitation during the bomb deposition peak. However, the decline in tritium concentrations in river water is much slower than the decline in precipitation, and tritium concentrations in river water exceed those in precipitation by 1966. The reason for the different response of the river water to the tritium transient is that the water in the river is composed of a mixture of recent precipitation and water from various hydrological systems within the basin with differing tritium concentrations. The tritium concentrations of the water in these systems are a function of the residence time of the water within various aquifers of the river basin (Rose, 1996). These reservoirs store high tritium concentrations for a series of years, producing a memory effect reflected in the higher tritium concentrations in river water.

ANALYSIS OF RESERVOIR CHARACTERISTICS

The tritium concentrations measured in these rivers reflect a complex interaction of processes within the reservoir, including direct runoff and outflow of water from a series of groundwater reservoirs. The fact that the tritium concentrations in the river water are different from those in precipitation indicates that a component of water with residence times of more than 1 year is present within the outflowing waters of the basin (Figure 3). There have been a series of models developed that estimate tritium concentrations of water flowing out of groundwater reservoirs into streams and rivers (Przewlocki and Yurtsever, 1974; Maloszewski and Zuber, 1982; Amin and Campana, 1996). The approaches vary from a piston-flow system where the water proceeds through the reservoir without mixing to a completely mixed reservoir system (Revelle and Suess,

Table I. Yearly tritium concentrations weighted by flow for the four sampling locations on the Mississippi River and its tributaries. Concentrations given in (tritium units (Tu))

Year	Arkansas	Ohio	Missouri	Mississippi
1963	830	918	1294	928
1964	614	898	1162	723
1965	381	588	1025	500
1966	270	373	981	353
1967	208	256	700	261
1968	128	199	565	179
1969	124	190	437	174
1970	98	179	369	138
1971	81	144	305	143
1972	58	108	233	101
1973	37	83	161	73
1974	38	71	155	65
1975	37	62	143	62
1976	35	64	119	63
1977	33	51	100	54
1978	37	61	87	55
1979	29	41	81	40
1980	22	40	69	36
1981	22	38	64	30
1982	17	38	61	28
1983	13	42	44	28
1984	12	33	40	28
1985	11	23	35	33
1986	9	28	35	25
1987	9	—	29	23
1988	9	—	32	20
1989	8	—	26	18
1990	8	—	24	18
1991	7	—	25	15
1992	8	—	16	18
1993	7	—	16	15
1994	6	—	17	15
1995	7	—	15	15
1996	7	—	14	14
1997	7	—	13	13

1957) and several variations of these approaches. These techniques can be applied to attempt to model the response of the river basins to the tritium transient. The parameters used in the model can give information about time-scales of physical processes within the basin. It is clear that by introducing enough reservoirs with different time-scales, it would be possible to reproduce the measured data almost exactly. However, as noted by Kirchner *et al*. (1996), the physical meaning of the parameters within the model start to lose significance as more parameters are added.

The two simplest models are the piston-flow approach and the well-mixed reservoir approach. Neither approach can reproduce the tritium concentrations measured in the river waters. The failure of the piston-flow approach is evident in Figure 3, where the tritium pulse appears immediately in river water, but at a concentration below that found in rain water. The system can be treated as a well-mixed reservoir with the outflowing concentration dependent on the residence time of water within the basin (Revelle and Suess, 1957). However, this approach cannot produce both the high concentrations found in the river water in the

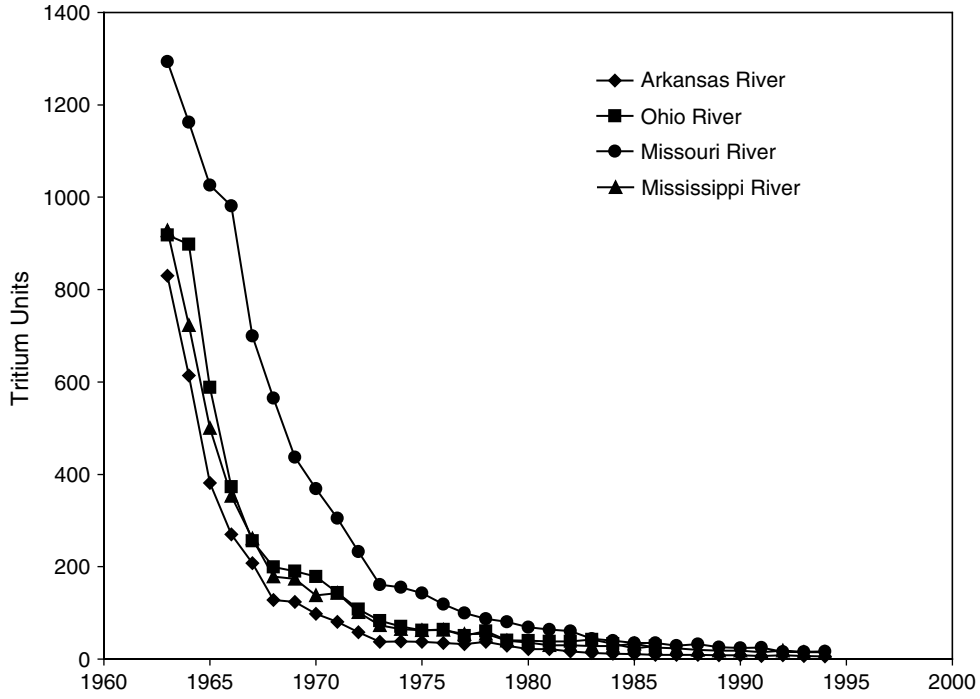

Figure 2. Yearly discharge-weighted tritium concentrations for the four Mississippi River sampling sites in tritium units

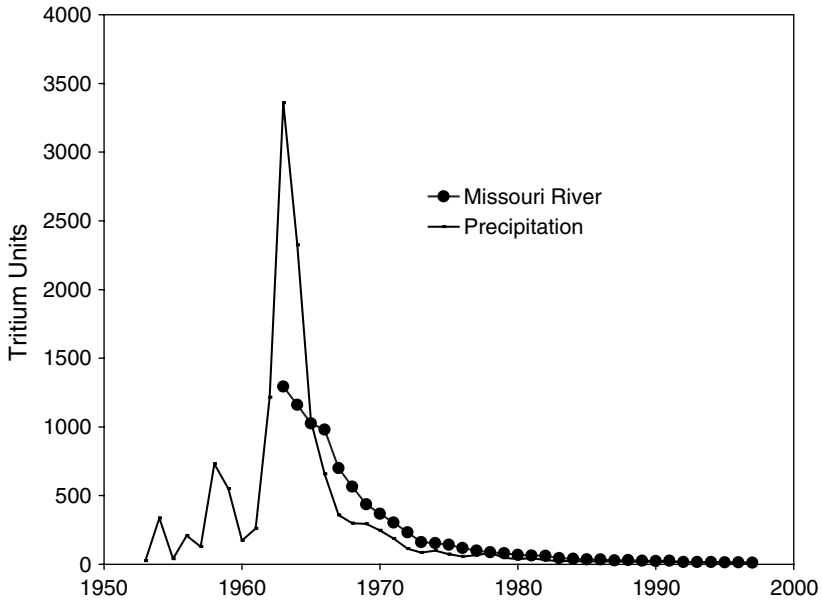

Figure 3. Comparison of tritium concentrations in precipitation versus tritium concentrations in the Missouri River. Tritium concentrations in precipitation were derived from stations at Lincoln, Nebraska and Bismarck, North Dakota. The Ottawa correlation was used to generate tritium concentrations in precipitation for years when data were not available

1963–64 period and the tailing effect of the tritium concentrations seen in later years, no matter what time-scale parameters are used. Other approaches, including piston flow with perfect or partial mixing, also fail to produce the peak concentrations at the same time as the precipitation bomb-peak.

One strategy to overcome these shortcomings is to use a two-member mixing model, as used by Michel (1992). In this approach, the outflow in the river is considered to be composed of two components, one of which is a prompt-flow component that is composed of recent precipitation. This fraction effectively can be considered as a piston-flow component with no time lag. Another fraction is composed of waters that reside in the basin for longer than 1 year and is treated as a well-mixed reservoir. The concentration of water flowing out of the basin (C_o) can be expressed as a combination of these two components

$$C_o = nC_p + mC_r \tag{1}$$

where C_p is the tritium concentration in precipitation and C_r is the measured tritium concentration of the water flowing out of the reservoirs within the basin, n is the fraction of flow that is from the prompt runoff and m is the fraction that is composed of flows from waters that have resided in the basin for more than 1 year. These last two factors are related by

$$n + m = 1 \tag{2}$$

The model treats the water in the river basin above the sampling location as a well-mixed reservoir and C_r is taken to be representative of the tritium concentration of the waters within the basin. The basin tritium concentration, C_r, is a function of the residence times of the waters within the basin, any sinks and/or sources of tritium within the system, and the input function. The only sink for tritium will be radioactive decay, and production of tritium occurs only in very small amounts in certain mineral formations (Andrews and Kay, 1982), which are too small to influence tritium concentrations of river basin systems. The input concentration is determined from the tritium concentrations in precipitation within the basin. The changing tritium concentrations of the long-term component of the water flowing out of the basin reservoirs during the tritium transient is treated numerically on a yearly basis

$$dC_r / dt = -\lambda C_r - kC_r + kC_p \tag{3}$$

where λ is the decay constant of tritium (0·0557 year^{-1}) and k(year^{-1}) represents the time-scale on which water in the basin is replaced by precipitation. This number can vary from year to year, depending on inflow and outflow.

The values of λ and C_r are known and the value of C_p is estimated from precipitation data. Although the concentrations of precipitation within each basin vary according to latitude and longitude, estimates of the average concentration can be derived from stations located in or near the basin. In the late 1950s and early 1960s, a series of tritium sampling stations were established on the North American continent (IAEA, 1981). Only the station at Ottawa, Canada has a complete set of data for tritium concentrations in wetfall from 1953 through the bomb transient to the present time. The International Atomic Energy Agency (IAEA), however, has developed the Ottawa correlation to estimate tritium concentrations in precipitation for stations where partial records are available (IAEA, 1981). Michel (1989) used this correlation to estimate tritium concentrations in precipitation for tritium sampling stations in the continental USA for these periods, typically prior to 1962. The precipitation stations used to estimate the tritium concentrations in wetfall within the river basins are: (i) Ohio River basin—Chicago, Illinois and St Louis, Missouri; (ii) Missouri River basin—Bismarck, North Dakota and Omaha, Nebraska; (iii) Arkansas River basin—Waco, Texas and St Louis, Missouri. In each case, an average of the two stations was used. Owing to the extent of the Mississippi River basin, which covers a wide range of latitudes and longitudes with large variations in tritium concentrations in precipitation, no effort was made to estimate the average tritium concentrations in precipitation for the basin above the Luling Ferry site. The tritium concentrations in precipitation for the other three basins are given in Figure 4. As found

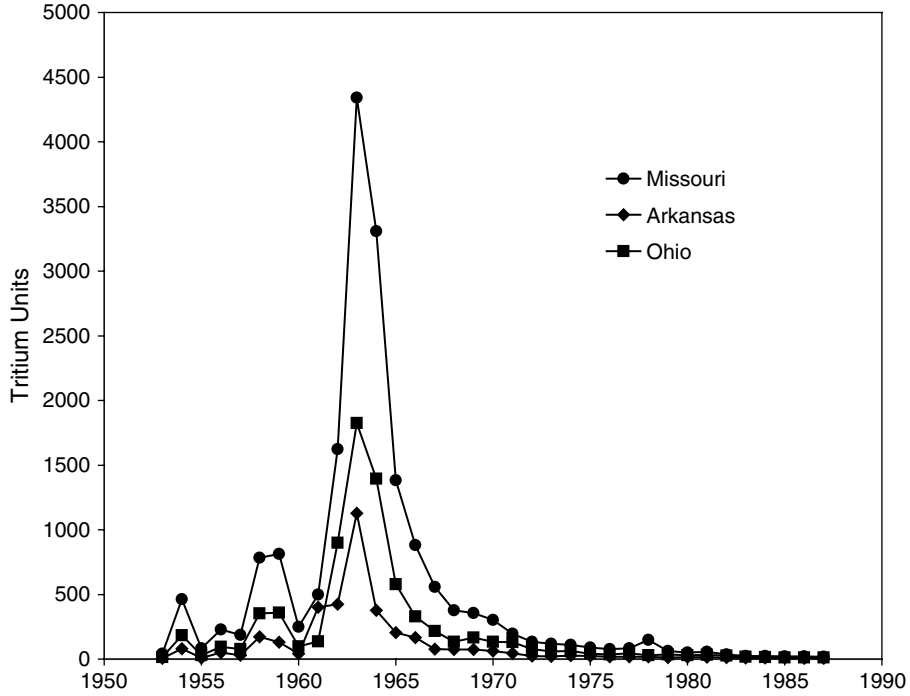

Figure 4. Tritium concentrations used for the input function for the three river basins of the Mississippi River. Tritium concentrations were derived from: (i) St Louis, Missouri and Chicago, Illinois (upper Ohio River); (ii) Lincoln, Nebraska and Bismarck, North Dakota (upper Missouri River); (iii) St Louis, Missouri and Waco, Texas (Arkansas River). The Ottawa correlation was used to generate tritium concentrations in precipitation for years when data were not available

for the rivers, highest concentrations for precipitation occur in the Missouri Basin and lowest concentrations occur in the Arkansas Basin. The value for dC_r/dt is obtained from Table I, so the only unknown quantity in Equation (3) is k.

The value $1/k$ is representative of an average residence time (τ) for waters within the basin. It is a function of the residence times for all the hydrological systems within the basin, which can have residence times varying from a couple of years to thousands of years. The value of k has no exact physical meaning, but it represents a useful parameter when looking at the overall response of river basins. Tritium can be considered an atmospherically derived, non-point-source conservative pollutant deposited in the basin. It is a conservative tracer, save for the loss through radioactive decay, so $1/k$ can be considered the time-scale for removal of a conservative area-wide pollutant from the basin (i.e. the fundamental physical rate for a non-point-source pollutant to be flushed from the river basin). For most pollutants there will be interactions, such as absorption or degradation, which will modify the rate of the removal, but the value derived from tritium data represents the underlying flushing rate for the basin. Any attempts to change nutrient and pollutant loads within the various river basins by land-use changes will have to take this rate into account. This rate is also a factor that has to be considered when studying climatic or land-use changes within the basin. Recent studies have suggested that stable isotopic data may be of value when studying the effect of climatic fluctuations within river basins (Rank *et al*., 1998; Kendall and Coplen, 2001). However, the delay of water leaving the basin modifies the signal from the stable isotopes so the values of k, m and n need to be considered when trying to derive a climatic signal for the basin.

As noted, there is some variation in k from year to year, but in the long term it should be approximately constant unless there have been major changes in the hydrological system such as the construction of dams that impound a significant fraction of the flow in one year. Mean yearly variations in flow rates from the

average are within about 20% for the Missouri and Ohio River during the decades when tritium samples were collected (Figure 5). These variations are taken into account when running the model by multiplying the average k by a flow factor for each year. The yearly correction factor is the flow for a given year divided by the average flow measured over the period of the sampling programme. Flow variations within the Arkansas River range over an order of magnitude, with very low flow rates in the mid-1960s and large flow rates for 1971–1974. These periods are the times when tritium variations were largest, and represent the most sensitive period for the model. The changes of flow rate within the basin are not a function of normal inflow and outflow but of anthropogenic factors. Because of the extreme variations in the flow for the Arkansas River during this time, the model cannot be applied reliably.

Using the tritium concentrations in precipitation from Figure 4 and the yearly weighted tritium concentrations in river water from Figure 2, the model was run by manually varying values of m, n and k to obtain a best fit between measured and modelled data. A simple linear correlation of the form

$$C_r = aC_o + b \tag{4}$$

is used, where C_o is the modelled concentration, C_r is the measured concentration, and a and b are constants. As we are trying to estimate basin parameters, and also determine tritium concentrations for periods when no data are available, it is necessary to obtain an exact match between the modelled and real data. To do this, the model is run with b set equal to zero (Taylor, 1982). Values of m, n and k are varied manually both to maximize r^2 and make the value of a as close to 1 as possible. This process has been carried out for the upper Ohio River and upper Missouri River sites and the results are given in Table II with the values of r^2 and a obtained. Using the values of m, n and k obtained from the model, estimates of tritium concentrations in the river water for years when no data were available were also calculated. Estimates for tritium concentrations for pre-bomb precipitation were obtained from Thatcher (1962) and are approximately 8 TU for the Missouri River and 6 TU for the Ohio River.

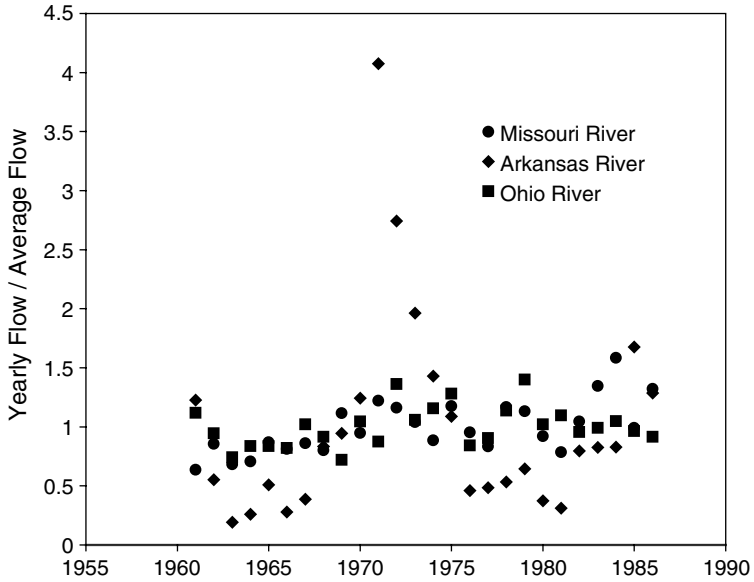

Figure 5. Deviation of yearly flow rates from the average flow rates measured during the sampling programs for the three tributary river basins

Table II. Basin parameters obtained from long-term tritium data

River	a	r^2	k	m	n
Ohio (1963–1986)	1·00	0·97	0·1	0·6	0·4
Missouri (1963–1997)	1·02	0·99	0·25	0·9	0·1

DISCUSSION

Good fits were obtained between the modelled and measured concentrations for the years when data were available (Table II). The slope value, a, was within 2% of 1 for both rivers, with r^2 values of 0·97 and 0·99 for the upper Ohio and upper Missouri Rivers respectively. Thus, the numbers given for n, m and k in Table II result in a close match to the actual response of the river basin to the tritium transient.

The modelled results versus measured concentrations are shown for the upper Ohio River in Figure 6. They match very well during the height of the tritium transient in the 1960s. The model results deviate most from the measured concentrations during the early 1970s, possibly as the result of the precipitation input function being too high. The input function for the Ohio River site was derived from measurements at Chicago, IL and St Louis, MO, which are the closest available stations for this basin. The tritium concentrations in upper Ohio basin precipitation may be lower owing to the seasonal influence of water vapour with a lower tritium concentration moving up from the Gulf of Mexico. The value of k obtained for the upper Ohio basin is 0·1 year^{-1}, and the tritium data indicate that about 40% of the flow at the sampling site of the upper Ohio River is water that has resided in the basin less than 1 year. The 10 year residence time calculated for waters within the upper Ohio basin indicate that flushing of pollutants out of the groundwaters of the basin will take place on a decadal time-scale. It is evident that pollutants within the groundwater from the Ohio Basin will continue to enter the Ohio River in the future, regardless of any changes in nutrient loading or land use. This is similar to a study by Bohlke and Denver (1995) in Maryland, which indicated that even if nitrate pollution was to cease entirely, residual nitrate from groundwater entering streams would continue to cause problems for areas such as the Chesapeake Bay for many more years. Of course, remediation for many of these pollutants will occur within the basin (Alley, 1993), so their release into the river system will frequently decrease faster than the decrease found for a conservative pollutant such as tritium. For some pollutants there will be adsorption to soils and sediments and a delayed release of these chemicals, resulting in a tailing effect in their concentrations in the rivers. However, all these effects will be overlain on the basic response of the basin to non-point-source pollutants as determined by the tritium records.

The tritium data for the upper Missouri River is very closely matched by the model results (Figure 7). The modelled results match the measured data almost exactly during the 1960s and early 1970s, and are only slightly lower during the late 1970s and early 1980s. The basin characteristics found for the upper Missouri River differ significantly from the results found for the upper Ohio River and other river basins. The fraction of outflow composed of water deposited in the basin for one year or less is very small (*c*. 10%) compared with most other basins (Michel, 1992). Furthermore, the value of k is large relative to most large rivers where long-term tritium data are available. Both of these results are undoubtedly the result of the impoundment of waters in the dams upstream from the sampling location. As noted above, the dams impound the equivalent of about 1 year of total flow for the river at this location. The dams limit the amount of prompt flow that can reach the sampling site from the basin, thus lowering the value of n. Without the dam system, the value of n would undoubtably be much larger. This retention of what would normally compose the prompt flow also results in an increase in the value of k. The prompt outflow is initially held up in the dam system but will leave the basin system within 1–2 years. Thus, instead of being part of the prompt flow (n), it becomes part of the long-term water of the basin (m). It will have a residence time in the basin of 1–2 years and will result in an increase in the value for k, decreasing the apparent residence time of water within the basin. Thus, the values obtained in Table II are representative of the modified Missouri Basin, as opposed to the

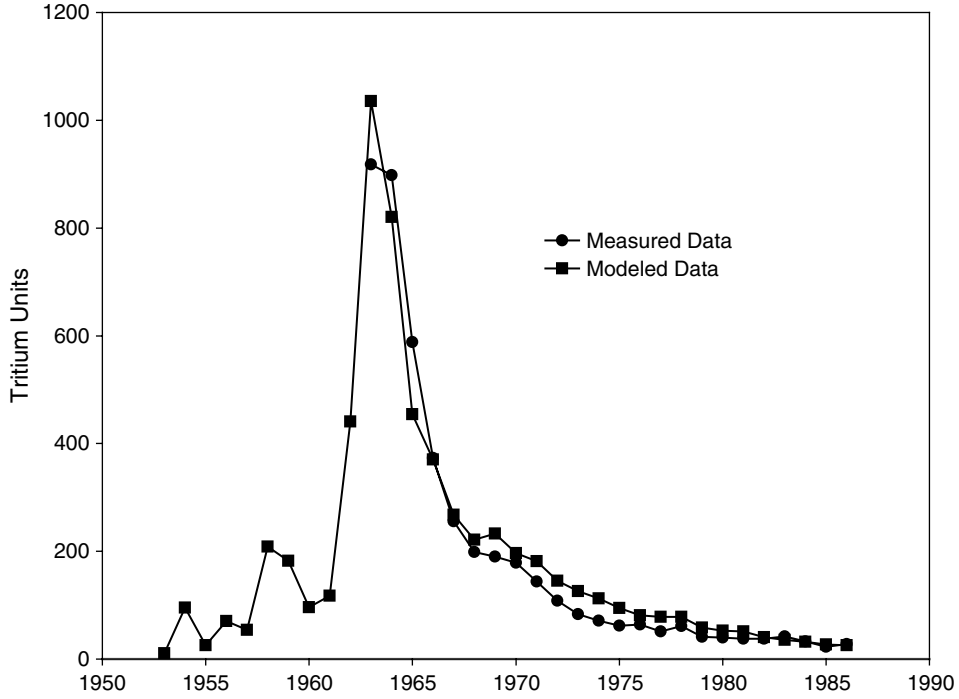

Figure 6. Modelled tritium concentrations versus measured concentrations for the upper Ohio River

unaltered basin. However, in determining how basin time-scales have an impact on the rate of removal of non-point-source pollutants from the watershed, the values in Table II are representative of the response of the basin as now composed.

Figure 8, using the results from Table II, shows the response of both the upper Missouri and Ohio Rivers to a 50% decrease in the input of a conservative pollutant into the basin. In the Ohio basin, the response is initially very rapid because of the large prompt-flow component, decreasing to almost 75% of the original concentrations in the first year. After the first year, the decrease slows and approaches the 50% reduction in about 20–25 years. The Missouri basin responds much more slowly and does not decrease to 75% until about 5–6 years later. However, owing to the much larger value for k, it also approaches 50% in about 20–25 years.

TRITIUM FLUX ESTIMATES

Using the measured tritium data and flow records of the US Geological Survey, the mass flux of tritium through the main stem of the Mississippi River into the Gulf of Mexico can be estimated. Table III gives the flux of tritium in grams during the period of measurements at each of the four sampling sites. This is calculated by using the yearly tritium concentrations and flow rates for that year to calculate yearly tritium fluxes. The data indicate that about 780 g of tritium has flowed out of the Mississippi River into the Gulf of Mexico between 1961 and 1997. Assuming that the Mississippi River had tritium concentrations similar to concentrations calculated for the Ohio River for the period from 1953 to 1960, approximately 1 k of tritium has flowed into the Gulf of Mexico from the Mississippi River during the bomb-tritium transient. Current fluxes of tritium through the Mississippi River are of the order of 1–2 g of tritium per year. Pre-bomb fluxes were probably of the order of 0·4 g/year or less. Owing to the volume of flow in the Mississippi River, this is undoubtably the largest flux of tritium off the continental USA.

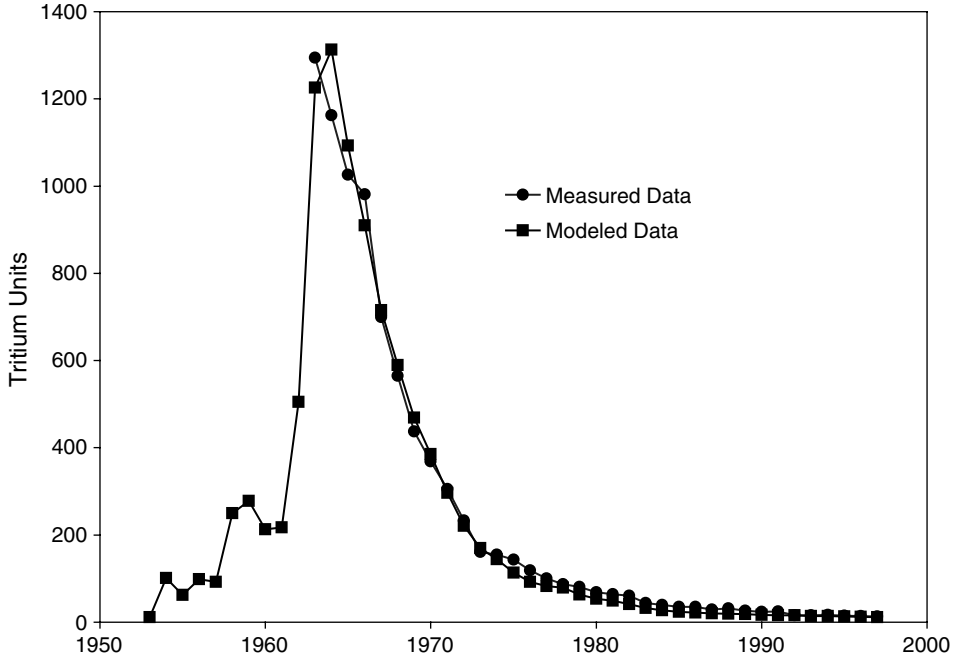

Figure 7. Modelled tritium concentrations versus measured concentrations for the upper Missouri River

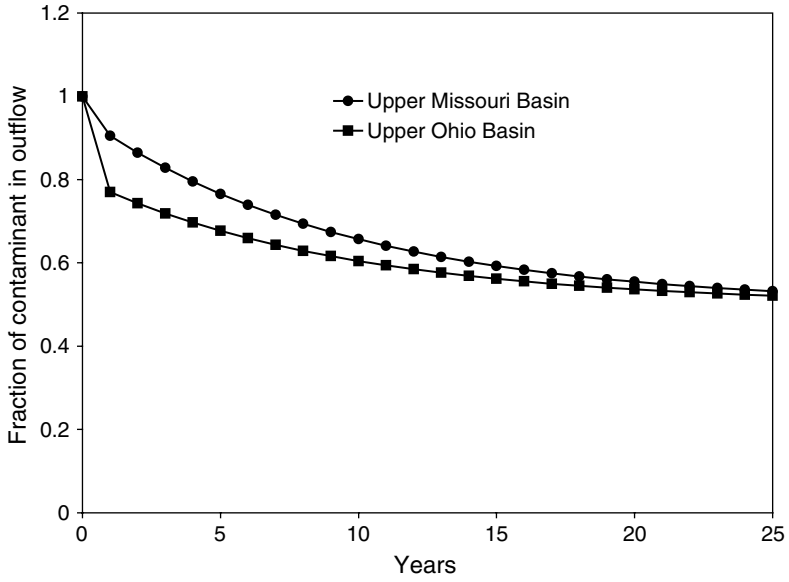

Figure 8. Response of the upper Missouri and Ohio Rivers to a 50% reduction to the input of a conservative pollutant. Responses were calculated using the values for the river basins in Table II

The values calculated here can be compared with estimated global inventories of tritium. Prior to the advent of nuclear testing, it was estimated that the global inventory of tritium was 3·5–4 kg (Lal and Peters, 1967; O'Brien *et al.*, 1992). Testing of nuclear weapons raised the tritium inventories by more than two orders of

Table III. Flux of tritium through the sampling sites for the period when measurements were made

River	Total tritium flux (g)
Mississippi River (1961–1997)	780
Ohio River (1961–1986)	160
Missouri River (1963–1997)	100
Arkansas River (1961–1997)	30

magnitude and approximately 550–800 kg of tritium were produced during this period (Miskel, 1973). Michel (1976) estimated that approximately 300 kg were present on Earth's surface in 1970, with 80–90% of that amount stored in the world oceans, about 120 kg of which was stored in the Atlantic Ocean in 1970. That would result in a global inventory in 2000 of about 55 kg with about 22 kg of that amount in the waters of the Atlantic Ocean. Of the 780 g of tritium that have flowed into the Atlantic Ocean from the Mississippi River in 1961–1997, approximately 200 g are still present in the environment, with most of that amount probably still within the Atlantic Ocean. Thus, although the tritium flux of the Mississippi River is important by continental standards, it is not important by global standards, or relative to the Atlantic Ocean tritium inventory. The main input of tritium to the Atlantic Ocean is via molecular exchange and direct precipitation, with influx of surface waters from the North American continent being a minor component.

CONCLUSIONS

The long-term tritium databases have been analysed at four sites in the Mississippi River basin, three sites on tributaries and one on the Mississippi main stem in Louisiana. Tritium concentrations were highest in the upper Missouri River, owing to its high-latitude and mid-continental location. Lowest tritium concentrations were found in the Arkansas River, owing to the influence of water vapour with low tritium concentrations from the Gulf of Mexico on tritium concentrations in precipitation in the basin. At all sites, tritium concentrations peaked during 1963–64, and dropped immediately following the cessation of major atmospheric testing. Tritium concentrations in the rivers continued to be at or above the concentrations in incoming precipitation in the years following 1966 owing to the time it takes to flush the bomb-tritium out of ground and surface water reservoirs within the basins. Using a two-component mixing model, an estimate was made of the residence time of the active portion of the waters in two of the three tributary basins. For the Ohio River above Markland Dam, it was estimated from the tritium data that about 40% of the flow was composed of precipitation that had resided in the basin for less than 1 year (the prompt flow component). The effective residence time for the older waters in the basin was calculated to be 10 years. The residence time for waters in the Missouri River basin above Nebraska City, Nebraska was found to be 4 years, and the prompt flow component was calculated to be 10%. The low percentage of prompt flow and the relatively short residence time of waters within the Missouri basin are probably due to a series of dams, which retain water equal to about 1 year's flow in the main stem of the Missouri River above the sampling location. The results obtained represent the rate at which a conservative non-point-source pollutant will be removed from the two river basins.

The mass flux of tritium flowing through the main stem of the Mississippi Basin into the Gulf of Mexico from 1961 to 1997 was calculated to be 780 g. This represents about 0·1–0·2% of the tritium produced by atmospheric nuclear weapons testing.

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