9000 years indicates rather stable atmospheric circulation patterns for this part of North America. If there had been any significant change during this period one would not expect a nearly constant oxygen isotope ratio. There remains the possibility that two or more variables cancel each other, but such a mechanism seems unlikely.

A drop in O^{18} and O^{16} content of about 1.8 per mil for the precipitated carbonate (somewhat less for the mollusks) is encountered between depth of 390 and 440 cm. The reduction in O^{18} content indicates colder conditions, that is, if one assumes the most likely cause to be a change in evaporation rate associated with a change in average summer temperature. A change in temperature around this time is also indicated by pollen studies of the same Pretty Lake core (*15*). This core, as well as other published pollen profiles for Indiana localities, shows a disappearance of spruce pollen (A-zone) followed by a sharp pine maximum (B-zone), which in turn is replaced by an oak and elm maximum (C-zone). The replacement of conifers by deciduous trees in the Great Lakes region is generally associated with a change in climate. For the Pretty Lake core the only possible important change in climate indicated by the oxygen ratios is between 440 and 390 cm of depth. The pine maximum in this core is between 470 and 400 cm, and the subsequent decline in pine and replacement by oak between depth of 400 and 350 cm seems to be a response to the change in climate, as indicated by the oxygen isotope ratios. In this instance, evidently about 500 years were needed by the forest vegetation to establish a new equilibrium.

The replacement of spruce by pine at around 480 cm depth does not seem to be correlative with any important change in ratio of O^{18} to O^{16}. There remains the possibility that such a change would be noticeable in a longer core.

In view of the many factors causing possible oxygen isotope composition changes in small freshwater reservoirs, it is not feasible to attach much significance to the small variations encountered in the Pretty Lake core over the last 11,000 years. However, the variations are surprisingly small and restrict the extent of possible atmospheric circulation pattern changes.

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Uranium Disequilibrium in Groundwater: An Isotope Dilution Approach in Hydrologic Investigations

Abstract. *The distribution and environmental disequilibrium patterns of naturally occurring uranium isotopes (U^{234} and U^{238}) in waters of the Floridan aquifer suggest that variations in the ratios of isotopic activity and concentrations can be used quantitatively to evaluate mixing proportions of waters from differing sources. Uranium is probably unique in its potential for this approach, which seems to have general usefulness in hydrologic investigations.*

In closed geological systems older than about 10^6 years, U^{234} will have achieved radioactive equilibrium with its parent, U^{238}; that is, their alpha activity ratio is 1.00. However, in open systems exposed to weathering and the circulation of groundwater, separation of these two isotopes can occur, giving rise to a state of radioactive disequilibrium (*1–3*).

The observed U^{234}/U^{238} disequilibrium is the result of the formation of U^{234} from the alpha and beta decay of U^{238}. Suggested physicochemical mechanisms include nuclear recoil-induced bond breakage, displacement of the U^{234} daughter within the crystal structure, and preferential attainment of the +6 valence for U^{234}, resulting in the increased mobility and preferential leaching of U^{234} with respect to U^{238} (*1, 4*). The ratio of U^{234} to U^{238} in many natural waters, including most rivers, is greater than 1.00, with the oceans having a 15 percent excess of U^{234} (*3, 5*). However, waters with an activity ratio less than 1.00 may occur when the source of the uranium is previously weathered rock.

A water-saturated, slightly oxidizing environment appears to be the primary medium for this observed disequilibrium (*4, 6*). As a consequence, the hydrologic system exerts a major control on disequilibrium patterns; frequently the result is that the waters of a region have differing activity ratios and concentrations. Such differences have been used to estimate the absolute ages of closed drainage basins (*7*).

The idea of applying isotope dilution analysis to the natural variations in uranium disequilibrium arose from an investigation of uranium isotopes in the Floridan aquifer and related natural waters of north Florida (*8, 9*). The artesian Floridan aquifer is part of the principal aquifer system in the southeastern United States consisting of tertiary limestone. This aquifer is the major source of groundwater and the most important hydrologic unit within the area of study (Fig. 1) (*10*). The karstic nature of the topography results in a well-developed, subterranean drainage system and, toward the south, several springs of the first magnitude. Wakulla Spring, one of the largest in Florida, has an average discharge of 10.3 m^3/sec (365 ft^3/sec) (*11*). Hydrologic data, including large seasonal fluctuations of spring discharge correlated with local precipitation, suggest that the source of water is local recharge in the karst area (*8*). An alternative explanation is that the source of part of the water is to the north, with flow down the gradient of the piezometric surface.

Table 1. Additions of uranium and water between aquifer sampling points. The first row refers to the aquifer between Havana and Tallahassee, in which A_1 and C_1 are the activity ratio and concentration, respectively, of the aquifer water at Havana, and A_3 and C_3 are the corresponding values at Tallahassee; A_2 is the estimated range of possible values for the activity ratio of uranium added between these two points. Values for M_2, V_2, and C_2 are calculated from Eqs. 5 and 6; M_2 is the amount of uranium added, V_2 is the volume of water added (the range of possible V_2 values is given, corresponding to the listed A_2 ranges), and C_2 is the resulting concentration of uranium if M_2 and V_2 describe a mixing water. The quantities ΔM and ΔV refer to the proportions M_2/C_1 and V_2/V_1, respectively. The last column follows from the various V_2 values calculated with respect to the flow model (Fig. 1).

Aquifer interval (see Fig. 1)	Results of analysis				Deduced values		Computed values						
	A_1 ratio	C_1 (μg/liter)	A_3 ratio	C_3 (μg/liter)	A_2 ratio	A_2 ratio range	M_2 (μg)	V_2 (liter)	V_2 range (liter)	C_2 (μg/liter)	ΔM (percent)	ΔV (percent)	Contribution to Wakulla (percent)
H to T	1.02	1.14	0.95	0.51	0.90	0.85–0.93	1.60	4.37	2.8–9.1	0.37	140	440	8
T to B	0.95	0.51	.69	2.63	.65	.63– .68	3.31	0.45	$<$ 0.1–4.2	7.35	650	45	32
B to W	.69	2.63	.85	.60	.90	.87– .95	8.42	17.4	10.–38.	.48	320	1740	60
T to W	.95	.51	.85	.60	.80	.75– .83	1.02	1.55	0.7–4.1	.66	200	155	

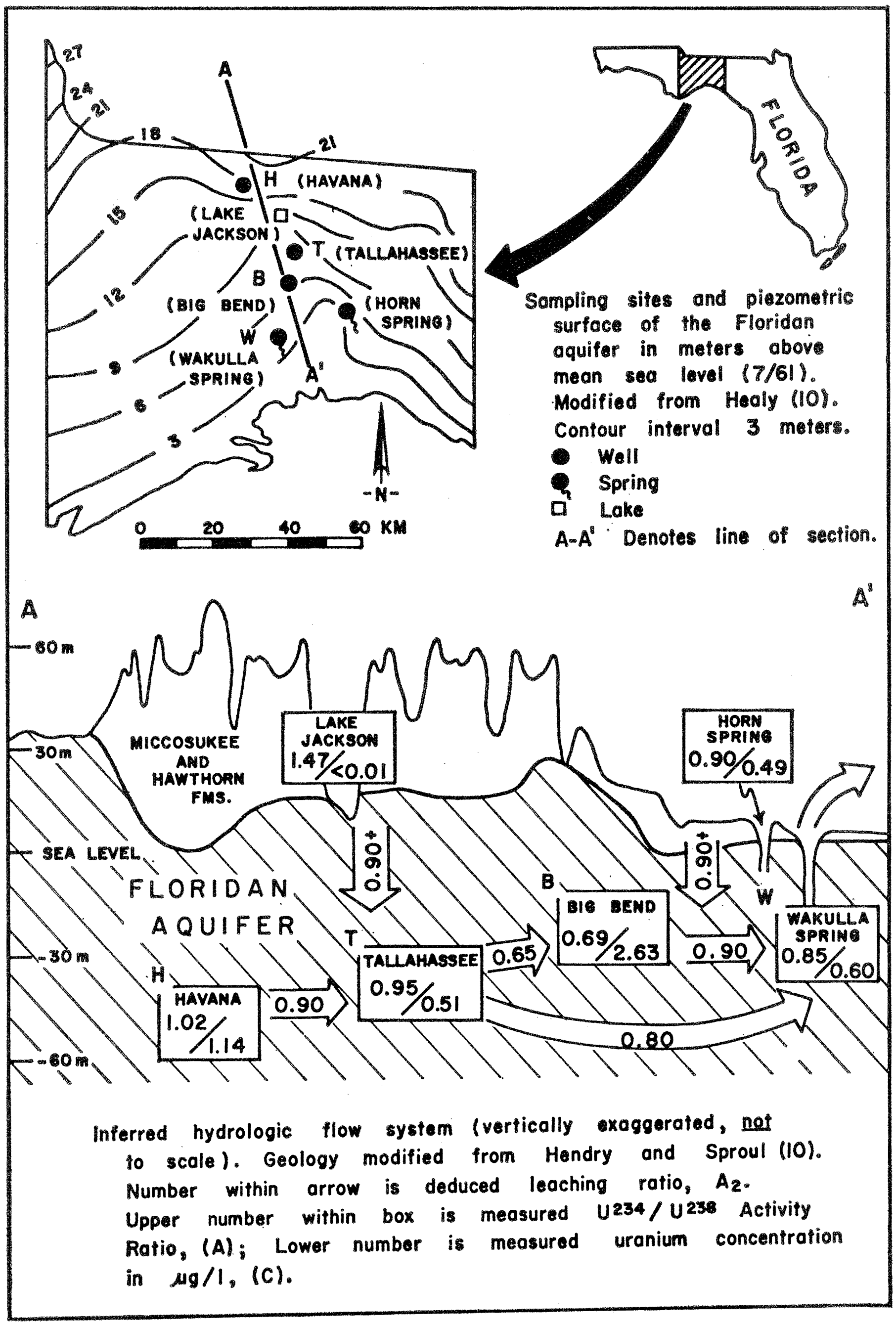

Fig. 1. Map and diagrammatic section portraying the inferred hydrologic flow system. Each box represents a sampling site showing activity ratio above and uranium concentration (in micrograms per liter) below. The numbers within the arrows refer to inferred activity ratio of the uranium added to the water (leached from the rock) between sampling sites. All A and C values correspond to those used in Table 1.

Water samples from wells and springs were collected in duplicate, acidified, spiked with U^{232} tracer, and analyzed along with suitable blanks. Uranium was separated from the other elements by coprecipitation, solvent extraction, ion exchange, and electrodeposition prior to radiometric determination of the uranium content and the ratio of isotopic activity by pulse-height analysis (*8*). Average errors for uranium content and activity ratio at the .05 level of significance were 5 percent and 3 percent respectively, for water having a uranium content greater than 0.1 μg/liter.

The data for the Floridan aquifer suggest that variations in the activity ratio and concentration of the uranium isotopes may be used, in conjunction with equations similar to those for isotopic dilution analysis, to delineate major source areas and to permit quantitative estimates of mixing volumes to be made.

Natural waters may be considered an isotope dilution system inasmuch as variations in the activity ratio of U^{234} to U^{238} can occur only when uranium is added to the system through leaching of the enclosing rock or by mixing with other uranium-bearing waters; once uranium is in solution, the activity ratio is unaffected by dilution, precipitation, or changes in chemical state.

If water 1 is mixed with water 2 to produce a mixture, water 3 (each with its dissolved uranium), the following relations hold:

$$V_1 + V_2 = V_3 \qquad (1)$$

$$M_1 + M_2 = M_3 \qquad (2)$$

$$M_1A_1 + M_2A_2 = M_3A_3 \qquad (3)$$

$$M_1 = C_1V_1 \qquad (4)$$

where V is the volume in liters; M is the amount of uranium in micrograms; C is the concentration in micrograms per liter; and A is the activity ratio, U^{234}/U^{238}. If V_1 is unity, the following equations are derived:

$$M_2 = C_1 (A_1 - A_3)/(A_3 - A_2) \quad (5)$$

$$V_2 = [(C_1 + M_2)/C_3] - 1 \quad (6)$$

These expressions can be used in two ways: (i) in calculating the relative mixing volumes of two waters when C and A values for the two source waters (1 and 2) and the resultant mixed water (3) have been determined, and (ii) in deducing the amount of uranium and water (2) that have been added to an initial water (1) to produce a resultant water (3). In the latter case, there are three unknowns, M_2, A_2, and V_2, in Eqs. 5 and 6; one of these variables must be estimated.

For example, we might ask: what volume of water such as that from Horn Spring (2) must be mixed with a unit volume of water such as that from Big Bend (1) to produce water such as that flowing from Wakulla Spring (3) (Fig. 1)? From Eqs. 5 and 6, M_2 is 8.4, and V_2 is 17.4. Thus, for every liter of Big Bend water, 17.4 liters of Horn Spring water would be required to yield 18.4 liters of Wakulla Spring water. As a check on the uranium balance, we can compute the necessary concentration of Horn Spring water ($C_2 = 0.48$ μg/liter), which is almost precisely the value measured.

There are probably numerous hydrologic situations in which such "closed system" assumptions can be made, the C and A values of three waters determined, and the mixing volumes calculated with confidence and accuracy. Requirements include sufficient uranium (0.1 μg/liter or more), diverse activity ratios, and a reasonable understanding of the hydrologic system. Isotope dilution analysis cannot define a mixing model; it does, however, set limits on possible models and develops the implications of these.

As an example of the second approach, we refer to Fig. 1, in which successive aquifer points are compared, and the additions of uranium and water between points are deduced. This approach is useful because the aquifer system here is quite open; rainwater is infiltrating from the surface, and uranium is being leached from the aquifer rock. In this case the observed variations in the activity ratios of waters within the aquifer are systematic enough to permit most probable values for A_2 to be assigned (*12*) and values for M_2 and V_2 to be calculated.

The results of these calculations of successive intervals are shown in Table 1, in which the relative volumes, as well as the amounts of uranium which are added between Havana (H), Tallahassee (T), Big Bend (B), and Wakulla Spring (W) are computed. (The larger interval, Tallahassee to Wakulla Spring, is also computed for comparison.) Since each V_2 is defined relative to each initial V_1, the total volume increment to the final water can be determined (last column of Table 1). Our calculations show that, of the hypothesized sources for Wakulla Spring, the more local sources predominate, and that no more than about 8 percent could be contributed from as far away as Havana.

Although these results must be regarded as semiquantitative only, because of the openness of the hydrologic system, they support the model and provide limits for mixing proportions. The activity ratios used may also be anomalously low; nevertheless, we believe that this analysis illustrates the general applicability of studies of uranium isotopes to hydrologic investigations.

It is unlikely that any other element will be useful in just this way. Thorium (Th^{232}, Th^{230}) has a greater range of activity ratios in water, but it occurs in very low concentrations. Hydrogen, carbon, and radium also exhibit measurable isotopic variations; however, their relatively short half-lives, which make them of interest as a possible means of absolute age-dating of water, limit their usefulness as indicators of mixing proportions.

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Tyrosine Transaminase: Development of Daily Rhythm in Liver of Neonatal Rat

Abstract. *The development of the 24-hour rhythm in tyrosine transaminase activity was studied in the liver of the neonatal rat. A recognizable rhythm appears within 48 hours after birth, but it is opposite in phase to that observed in the adult rat. The reversal of the adult pattern occurs 21 to 23 days after birth and may represent a response to a change both in the eating pattern and in the amount of protein eaten.*

A daily rhythm in the activity of the liver enzyme L-tyrosine-2-oxoglutarate aminotransferase (TT) (E.C.2.6.1.5.), which is generated by intake of a diet (*1*), occurs in the adult rat (*2*). We have studied the development of this cycle in the neonatal rat.

Female CFE rats (Carworth) were obtained during the second week of pregnancy. During gestation and at all times thereafter, the animals were kept in large litter cages maintained with controlled temperature and humidity. Rats were given free access to an 18-