

Article

Stable Isotopic Evidence of Paleorecharge in the Northern Gulf Coastal Plain (USA)

Estifanos Haile ¹, Benjamin J. Currens ² and Alan E. Fryar ^{3,*}¹ Department of Physics, Geosciences, and Astronomy, Eastern Kentucky University, Richmond, KY 40475, USA; estifanos.haile@eku.edu² Division of Water, Kentucky Department for Environmental Protection, Frankfort, KY 40601, USA; benjamin.currens@ky.gov³ Department of Earth and Environmental Sciences, University of Kentucky, Lexington, KY 40506, USA

* Correspondence: alan.fryar@uky.edu; Tel.: +1-859-257-4392

Abstract: Stable isotope abundances ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) in regional aquifers can provide important paleoclimate information. However, identifying paleoclimate signals can be complicated by cross-formational mixing and, potentially, by isotopic diffusion between aquifers and confining units. We examine controls on $\delta^{18}\text{O}$ and $\delta^2\text{H}$ distributions in the Wilcox aquifer of the northern Gulf Coastal Plain (USA). We sampled groundwater for $\delta^{18}\text{O}$, $\delta^2\text{H}$, Cl^- , and ^{36}Cl along a ~300 km downgradient transect. We developed a simplified, 1D numerical model of groundwater flow and ^{18}O transport to assess the possible importance of isotopic diffusion between the aquifer and its confining units. Along the inferred flowpath, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were depleted by as much as 1.3 and 8.2‰, respectively, as the Wilcox aquifer transitioned from unconfined to confined. However, they then gradually rose farther downgradient by up to 1.1 and 8.6‰. Chlorine-36 analyses and ^{14}C analyses (from other studies) indicate that groundwater ages range from $\sim 10^3$ yr to $\sim 8 \times 10^5$ yr. Modeling results indicate that the effect of diffusion on isotopic abundances is limited, whereas Cl^- data indicate that cross-formational flow is limited. Therefore, we posit that confined groundwater in our study reflects a Pleistocene paleorecharge signal.

Keywords: paleoclimate; Mississippi Embayment; oxygen-18; deuterium; groundwater; recharge; confined aquifer



Citation: Haile, E.; Currens, B.J.; Fryar, A.E. Stable Isotopic Evidence of Paleorecharge in the Northern Gulf Coastal Plain (USA). *Hydrology* **2024**, *11*, 118. <https://doi.org/10.3390/hydrology11080118>

Academic Editors: Ulrich Ofterdinger and James E. Landmeyer

Received: 9 June 2024

Revised: 31 July 2024

Accepted: 6 August 2024

Published: 10 August 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

In regional aquifers with flowpath lengths on the order of 10^2 – 10^3 km, groundwater residence times can be as long as 10^5 – 10^6 yr, as indicated by radiogenic and radioactive isotopes (^4He , ^{36}Cl , ^{81}Kr) [1–4]. The stable isotopes (^{18}O , ^2H) and noble gases (Ne, Ar, Kr, Xe) present in groundwater can preserve the evidence of timing, sources, and the temperature of recharge for these aquifers [4]. In the continental USA, aquifers exhibit regional variability in contemporaneous values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ [5], where the δ notation refers to $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ abundances relative to a standard of 0‰ [6,7]. Interpretations of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ variability within aquifers can be complicated by cross-formational mixing [8–10], which results in groundwater having an ensemble of ages and compositions [11,12]. Isotopic diffusion between an aquifer and adjoining low-permeability units can also alter $\delta^{18}\text{O}$ along groundwater flowpaths [13,14], but that process has received relatively little attention.

In this paper, we examine controls on $\delta^{18}\text{O}$ and $\delta^2\text{H}$ within a large, understudied regional aquifer in the south-central USA within the Mississippi Embayment in the northern Gulf Coastal Plain (Figure 1). The clastic Wilcox aquifer is less exploited than shallower units [15]. West of the Mississippi River, the aquifer transitions in the downdip and down-valley directions from unconfined to confined conditions, with wells extending to >500 m below land surface. Few studies have examined isotope hydrology in the Wilcox aquifer in this region [16]. We sampled wells in the Wilcox aquifer and the adjoining aquifers for

Cl^- , $\delta^{18}\text{O}$, $\delta^2\text{H}$, and (for a subset of wells) ^{36}Cl along a ~300 km downgradient transect, coinciding with the hydrogeochemical study of [17]. We developed a simple 1D numerical groundwater flow and ^{18}O transport model, which included diffusion between the aquifer and the confining units. Together with published data, this approach enabled us to assess the possible effects of cross-formational flow and diffusion on $\delta^{18}\text{O}$ and $\delta^2\text{H}$ distributions in the Wilcox aquifer. We argue that these $\delta^{18}\text{O}$ and $\delta^2\text{H}$ distributions represent a record of Pleistocene recharge in a region where paleoclimate data are lacking.

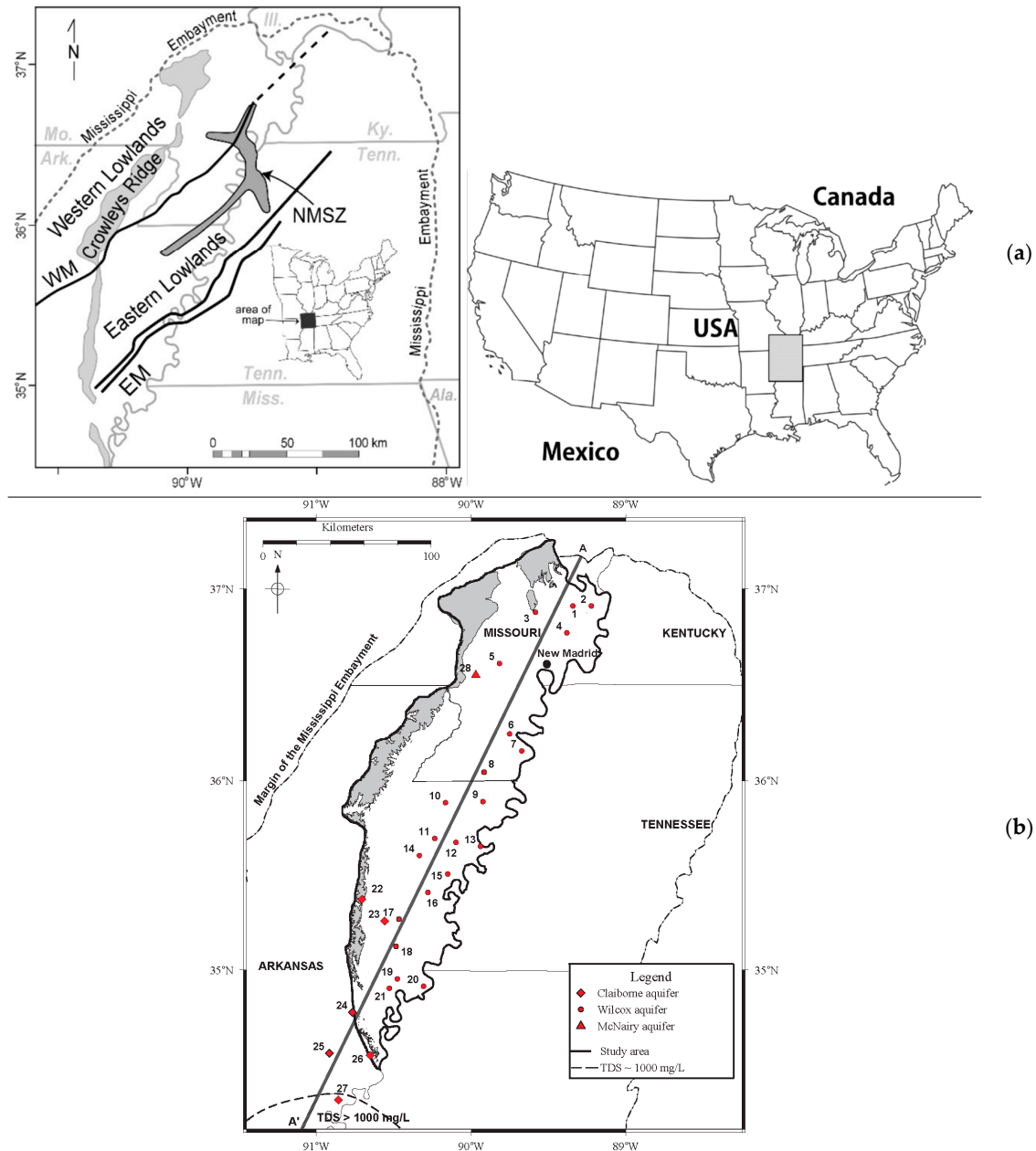


Figure 1. (a) Map view of the seismotectonic and physiographic settings of the study area (modified from [18]). NMSZ is the New Madrid Seismic Zone; EM and WM represent the eastern and western rift margin faults, respectively. (b) Map of sample locations, the approximate line of the cross section (Figure 2), and the extent of fresh water in the lower Wilcox aquifer west of the Mississippi River. The gray region indicates Crowley's Ridge. The area south of the hatched line represents groundwater TDS concentrations ≥ 1000 mg/L. The figure is modified from [17], Haile, E.; Fryar, A.E., Chemical evolution of groundwater in the Wilcox aquifer of the northern Gulf Coastal Plain, USA. Hydrogeology Journal, 2017, v. 25, p. 2403–2418, reproduced with permission from Springer Nature.

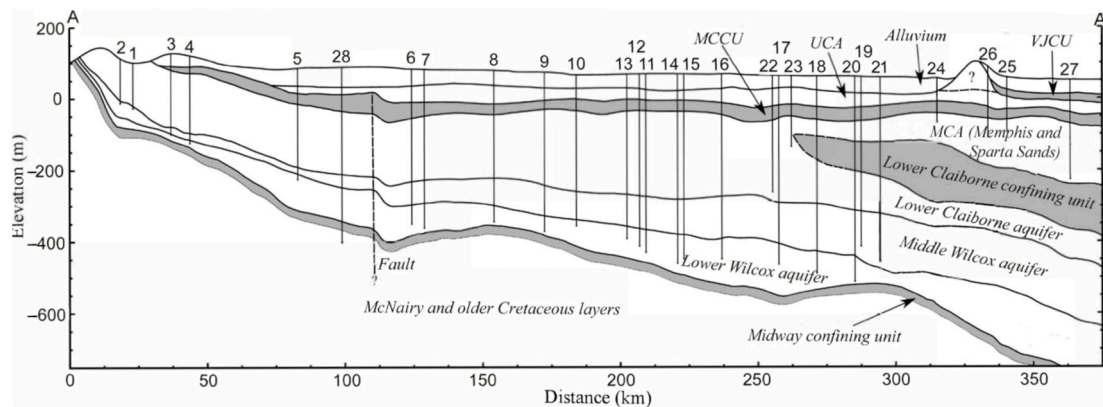


Figure 2. NNE-SSW cross section through the Mississippi Embayment aquifer system derived from individual aquifer structural contour maps [19]. MCA is Middle Claiborne aquifer; MCCU is Middle Claiborne confining unit; UCA is Upper Claiborne aquifer; VJCU is Vicksburg-Jackson confining unit. Sampled wells (1–28) are projected to the cross section for illustration purposes. The figure is modified from [17], Haile, E.; Fryar, A.E., Chemical evolution of groundwater in the Wilcox aquifer of the northern Gulf Coastal Plain, USA. *Hydrogeology Journal*, 2017, v. 25, p. 2403–2418, reproduced with permission from Springer Nature.

2. Materials and Methods

2.1. Isotope Systematics

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ signatures of water at near-surface temperatures result from isotopic fractionation due to physical processes such as evaporation, condensation, melting, and diffusion [20]. As condensation and precipitation occur, the residual water vapor becomes isotopically lighter. Rainfall becomes progressively depleted with distance from the ocean, which occurs as a result of the rainout of heavier isotopes (the continental effect), and with elevation as air masses move upward and temperature decreases (the altitude effect) [21]. The partial evaporation of water at the land surface and within the soil zone can result in the differential enrichment of ^{18}O relative to ^2H in water. Below the soil zone, the stable isotopic composition of water is considered conservative at near-ambient temperatures [22]. Consequently, the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ compositions of dated groundwaters are used as indicators of the Holocene and Pleistocene paleoclimates.

In the midcontinental USA, regional variability in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of groundwater, which was recharged during the last glacial maximum (LGM; c. 21 ka), has been attributed to factors including differences in moisture sources by area, proximity to ice sheets, the seasonality of recharge, and atmospheric circulation patterns [5,8,23,24]. Contemporaneous $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are more depleted than modern values in some areas (e.g., the Madison aquifer in the northern Great Plains [25]) and more enriched in others (e.g., the Cambro-Ordovician aquifer in Iowa [26]). The lack of consistent spatiotemporal shifts in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ probably reflects the combined effects of temperature and atmospheric circulation (e.g., isotopically depleted Pacific-sourced moisture versus enriched Gulf of Mexico-sourced moisture) [27].

The observed ^{36}Cl levels in groundwater reflect the levels of atmospheric and in situ production, mixing with other sources of chloride and radioactive decay [28]. The primary atmospheric source is proton-induced spallation of ^{40}Ar [29], although neutron activation of ^{35}Cl as a result of atmospheric nuclear testing also contributes ^{36}Cl [30]. The spallation of ^{39}K and ^{40}Ca on rock outcrops and subcrops by atmospheric neutron flux contributes about 2% of the total ^{36}Cl [31]. About 10% of the ^{36}Cl produced is from the decay of U and Th in sediments, which releases neutrons that collide with ^{35}Cl atoms in groundwater [29]. This process can contribute a significant amount of ^{36}Cl when the aquifer of interest has high dissolved Cl^- concentrations (e.g., because of the presence of connate waters or evaporite layers). The half-life of ^{36}Cl is $3.01 \times 10^5 \pm 4 \times 10^3$ years [31]. Groundwater dating using ^{36}Cl (reported as $^{36}\text{Cl}/\text{Cl}$) is dependent on the assumption of the initial value (which varies

with time and latitude) and its source [28]. The approaches to estimating the initial value include using long-term records from ice cores [28] and the long-term average of modern atmospheric ^{36}Cl [32,33].

2.2. Study Area Setting

2.2.1. Physiography, Climate, and Hydrogeology

The study area is located in southeast Missouri (MO) and eastern Arkansas (AR), and is bounded by the Mississippi River to the east and Crowley's Ridge to the west-northwest (Figure 1a). Land surface elevation decreases gradually from ~120 m above sea level (asl) at the northern limit of the study area to ~60 m asl near the southern limit [34]. The climate is humid-temperate (Köppen–Geiger classification Cfa [35,36]). Annual precipitation varies from ~123 to 136 cm (1981–2010 averages for Sikeston, MO; Jonesboro, AR; and Memphis, Tennessee) [37]. Potential evapotranspiration, as estimated from pan evaporation, increases from 89–114 cm/yr in the north to 127 cm/yr in the south [34].

The major aquifers within the study area are part of the Mississippi Embayment Aquifer System (MEAS), which consists of a Paleocene to Holocene fluviodeltaic sedimentary sequence (Figure 2). This sequence is underlain by the Midway Group (Paleocene), which separates the Wilcox Group (Paleocene) from the deeper McNairy Formation (Cretaceous) [34]. The Wilcox Group transitions upward from massive, laterally continuous sands to thin, laterally discontinuous sand, silt, and clay beds [38]. The study area overlaps the New Madrid Seismic Zone (NMSZ), which was the locus of the largest historic earthquakes in eastern North America (three events in the winter of 1811–1812, with estimated moment magnitudes as high as 7.5 [39]). Faulting within the NMSZ may result in some displacement of Wilcox strata [17]. The lower Wilcox aquifer thickens from ~25 m near the outcrop to ~200 m along the axis of the embayment and becomes more clayey downward in eastern Arkansas. The lower and middle Wilcox aquifers (collectively referred to here as the Wilcox aquifer) are overlain by the lower and middle aquifers of the Claiborne Group (Eocene). The middle Claiborne is referred to as the Memphis Sand in northeast Arkansas and the Sparta Sand in southeast Arkansas. The upper Wilcox Group sediments are classified as part of the lower Claiborne aquifer. Confining units separate the lower and middle Claiborne aquifers in the southern part of the study area, and otherwise separate the middle and upper Claiborne aquifers, except near the margins of the embayment. In the Mississippi River floodplain, the surficial aquifer consists of Quaternary alluvium (the Mississippi River Valley alluvial [MRVA] aquifer).

The Wilcox and Claiborne aquifers are recharged when those units occur at or near the land surface along the margins of the embayment. Regional groundwater flow follows topographic and stratigraphic dips toward the south and southeast in the study area. We compared pairs of wells, located within ~10 km, which were measured during the same year. We found that hydraulic heads in the Wilcox aquifer were lower than heads in the underlying McNairy aquifer in southeast Missouri by 11.9–16.8 m [40], and lower than heads in the overlying middle Claiborne aquifer in northeast Arkansas by 6.7–28.3 m [41,42]. Natural discharge from the Wilcox aquifer occurs via upward cross-formational flow [43], which may be facilitated by faulting in southeast Arkansas [44]. Although the MRVA aquifer is heavily pumped for irrigation, and the middle Claiborne aquifer supplies water to Memphis (the largest city in the region) and other communities [15], the Wilcox aquifer is generally only used for the water supplies of small communities, with the largest withdrawals for Blytheville and West Memphis, AR [45].

2.2.2. Paleoclimate

There is a dearth of data on Pleistocene precipitation and its isotopic signature for the study area. Using paired values of calcite $\delta^{18}\text{O}$ and inclusion-water $\delta^2\text{H}$ while using U/Th dating of speleothems, Harmon and Schwarcz [46] calculated the paleotemperature at six sites across the Caribbean and North America. The closest site to our study area was a cave in Kentucky, from which a speleothem dated from 106 to 217 ka was analyzed. Because

the temperatures calculated using the dependence of ^{18}O fractionation between calcite and water were unrealistically low, Harmon and Schwarcz [46] suggested that the modern global meteoric water line (GMWL; $\delta^2\text{H} = 8\delta^{18}\text{O} + 10$ [6]) does not accurately represent the $\delta^2\text{H}$ – $\delta^{18}\text{O}$ relationship during the growth of these speleothems. Paleo-water $\delta^{18}\text{O}$ values were calculated by inferring a paleo-GMWL of $\delta^2\text{H} = 8\delta^{18}\text{O}$ [46]. The decreasing trend in calculated values (from -5.6 to -7.7‰) between 171 and 127 ka agrees with other lines of evidence for Illinoian glaciation between 175 and 130 ka [47–49]. The pronounced increase in $\delta^{18}\text{O}$ at 122 ka (-5.3‰), followed by similar values at 112 ka (-5.7‰) and 106 ka (-5.5‰), is consistent with a transition to a warmer climate, as marked by the formation of the Sangamon paleosol [47–49].

Coinciding with the onset of the Wisconsinian period, the aeolian deposition of Roxana silt within the region occurred between 60 and 26 ka [48]. The sea level was 5–8 m above present values by 25 ka [50], but fell to a low of ~ 120 m below present values around 22 ka. Proximity to the Laurentide ice sheet [51,52] and topographic forcing along its southern margin [53] may have affected both annual precipitation and seasonal variability. The juxtaposition of cold air near the ice sheet and warmer, moist air from the Gulf Coast during the LGM likely caused increased summer precipitation in the area immediately adjacent to the ice sheet and decreased precipitation further south [53].

2.3. Sampling and Laboratory Analyses

Groundwater samples were collected in July 2006 and May–June 2007 from 21 public water-supply wells in the Wilcox aquifer, six wells in the middle Claiborne aquifer, and one well in the McNairy aquifer (Table 1). All samples were taken directly from the wellhead. Approximate locations and distances along the down-valley transect are projected onto a cross section in Figure 2. Sampling locations were selected to ensure detailed coverage (along-transect spacing < 30 km); where Wilcox wells were not available, wells in the overlying or underlying aquifers were sampled. The well-completion depths shown in Table 1 represent the bottom of the screened interval, where known, and the reported total depth otherwise. Data were taken from the U.S. Geological Survey’s National Water Information System database [54], the Missouri Source Water Protection and Assessment database [55], and the Arkansas Water Well Construction Commission database [56].

After our measurements of pH, temperature, Eh, and electrical conductivity had stabilized [17], samples were collected through in-line, disposable $0.45\ \mu\text{m}$ capsule filters. Chloride samples were collected in 125 mL HDPE bottles. Samples for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ were collected in 40 mL amber glass vials with solid caps; care was taken to exclude air bubbles. Chloride was analyzed at the University of Kentucky using an ion chromatograph (Dionex ICS-2000) with an AS18 column. The detection limit was $0.1\ \text{mg/L}$ and the analytical error was generally $< 6\%$. Water isotopes were analyzed at the Isotope Geochemistry Laboratory at the University of Arizona using a continuous-flow isotope-ratio mass spectrometer (ThermoQuest Finnigan DeltaPlusXL). Analytical precision (1σ) was $\pm 0.08\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.9\text{‰}$ for $\delta^2\text{H}$.

Four wells in the confined Wilcox aquifer were sampled for ^{36}Cl analysis using 20 L polyethylene carboys. Chloride was extracted in the laboratory using a chromatographic column (10 mm internal diameter, 75 cm length) packed with AG 1-X8 analytical-grade anion-exchange resin (Bio-Rad, Hercules, CA, USA), which was pre-conditioned with $1.5\ \text{M HNO}_3$ to remove any residual Cl^- . Because the Cl^- concentration was $< 10\ \text{mg/L}$, the entire sample volume was eluted by gravity through the column to concentrate a sufficient mass of Cl^- . A $1\% \text{HNO}_3$ solution was used to extract the concentrated Cl^- from the resin, and AgNO_3 was added in excess to the extract to precipitate AgCl . Chlorine-36 was analyzed using an accelerator mass spectrometer in the Purdue Rare Isotope Measurement Laboratory (PRIME Lab) at Purdue University. The analytical error was $\leq 7\%$.

Table 1. Locations and depths of sampled wells. State: MO = Missouri, AR = Arkansas. Distances were estimated from the upgradient end of regional flowpath. Latitude and longitude for well 3 were corrected from [55] based on field observations. The total depth for well 18 was taken from [56]. The table is modified from [17], Haile, E.; Fryar, A.E., Chemical evolution of groundwater in the Wilcox aquifer of the northern Gulf Coastal Plain, USA. Hydrogeology Journal, 2017, v. 25, p. 2403–2418, reproduced with permission from Springer Nature.

Well	USGS ID	Location	County/State	Date Sampled (mm/dd/yy)	Longitude	Latitude	Altitude (masl)	Depth (m)	Distance (km)
Unconfined Wilcox									
1	365444089203001	Charleston	Mississippi/MO	7/7/2006	−89.34156	36.91213	97.5	116.7	23
2	365445089132001	Wyatt	Mississippi/MO	7/7/2006	−89.22258	36.91185	96.6	139.3	18
3	365242089350601	Sikeston	Scott/MO	7/9/2006	−89.58469	36.87838	99.7	118.0	37
4	364618089224901	East Prairie	Mississippi/MO	7/8/2006	−89.38017	36.77157	93.0	179.8	44
5	363644089490501	Parma	New Madrid/MO	7/9/2006	−89.81567	36.61279	85.3	141.4	83
Confined Wilcox									
6	361415089445801	Hayti	Pemiscot/MO	7/10/2006	−89.74945	36.23741	82.3	395.6	124
7	360923089401901	Caruthersville	Pemiscot/MO	5/29/2007	−89.67190	36.15632	80.8	420.6	129
8	360239089545501	Pemiscot Co.	Pemiscot/MO	7/10/2006	−89.91523	36.04436	76.2	410.0	154
9	355323089552101	Dogwood	Mississippi/AR	7/11/2006	−89.92259	35.88980	76.2	426.7	173
10	355252090095701	Manila	Mississippi/AR	7/11/2006	−90.16432	35.88488	73.2	353.0	184
11	354133090135001	Little River	Mississippi/AR	7/13/2006	−90.23085	35.69225	69.2	408.4	209
12	354033090055201	Keiser	Mississippi/AR	7/13/2006	−90.09675	35.67577	70.1	442.6	207
13	353917089561501	Osceola	Mississippi/AR	5/30/2007	−89.93832	35.65468	74.7	457.2	202
14	353630090194501	Lepanto	Poinsett/AR	7/12/2006	−90.33063	35.60584	68.3	439.8	221
15	353029090085801	Joiner	Mississippi/AR	7/15/2006	−90.15000	35.50833	70.7	461.2	223
16	352450090165201	Gilmore	Crittenden/AR	7/15/2006	−90.27889	35.41083	67.7	460.6	237
17	351614090275401	Earle	Crittenden/AR	7/14/2006	−90.46458	35.27069	65.5	533.4	258
18	350734090290101	Shell Lake	St Francis/AR	5/31/2007	−90.48389	35.12528	60.7	483.1	271
19	345710090283002	Hughes	St Francis/AR	7/14/2006	−90.47493	34.95326	60.7	493.5	288
20	345448090182701	Horseshoe Lake	Crittenden/AR	6/1/2007	−90.30775	34.91349	61.3	499.3	285
21	345416090313801	Brickeys	Lee/AR	6/1/2007	−90.52663	34.90369	59.7	518.8	294
Claiborne (Memphis Sand)									
22	352231090421501	Birdeye	Cross/AR	5/30/2007	−90.70514	35.37552	130.9	345.0	255
23	351544090334101	Parkin	Cross/AR	5/31/2007	−90.55829	35.26059	62.5	140.8	262
Claiborne (Sparta Sand)									
24	344629090455803	Marianna	Lee/AR	6/4/2007	−90.76611	34.77472	70.4	149.0	315
25	343324090544601	Marvell	Phillips/AR	6/5/2007	−90.91539	34.55676	64.0	210.0	340
26	343242090390201	West Helena	Phillips/AR	6/4/2007	−90.65194	34.54524	76.2	180.1	334
27	341822090512401	Elaine	Phillips/AR	6/5/2007	−90.85669	34.30724	50.6	283.5	363
McNairy									
28	363442089580901	Malden	Dunklin/MO	5/29/2007	−89.96927	36.57825	89.6	278.9	99

2.4. Modeling

To examine the possible effect of diffusion on distributions of $\delta^{18}\text{O}$ and $\delta^2\text{H}$, a simplified model of oxygen-18 transport along the regional flowpath and between the aquifer and confining units was developed using COMSOL Multiphysics software (COMSOL, Inc., Burlington, MA, USA). The model domain was limited to the confined section of the Wilcox aquifer, which is assumed to span ~175 km down dip from near New Madrid, MO. The model assumed that (1) the aquifer was isotropic and well mixed in the transverse direction to the flow; (2) the aquifer was fully confined along the modeled flowpath; (3) the confining unit was well mixed in transverse and longitudinal directions; (4) fluid flow was negligible across the contact between the aquifer and confining unit; and (5) the confining unit was enriched in ^{18}O relative to the aquifer. Both the upgradient and downgradient boundaries were open to water masses and isotope fluxes, and diffusion could occur either into or out of the confining unit, depending on the concentration gradient. The values of aquifer and confining-unit parameters were taken from prior studies of the Mississippi Embay-

ment, where available [41,57]; otherwise, representative values for the medium lithology were used [58] (Table 2). Because no spatial trend was apparent in terms of hydraulic conductivity (K), an arithmetic mean was calculated. The value of K was of the same order of magnitude as that used by [59] and the values compiled by [60], which ranged from 1×10^{-5} to 4.5×10^{-4} m/s. Because advection was not simulated between the Wilcox aquifer and the adjoining confining units, no K value was needed for the confining units. A value of the ^{18}O diffusion coefficient in a clay-rich medium [61] was used to represent the Midway Group. Confining-unit porosity was determined based on grain size [58], which was described as that of silty clay and clayey silt [57].

Table 2. Model parameters and sources.

Parameter	Value	Units	Source
Model mesh	250	m	
Time tolerance	0.1		
Aquifer hydraulic conductivity	0.00003	m/s	Arithmetic mean [41,57]
Aquifer thickness	20–400	m	Arbitrary
Aquifer porosity	0.15–0.225		[58]
Confining-unit porosity	0.35		[58]
^{18}O diffusion coefficient	2.27×10^{-9}	m/s	[62]
^{18}O diffusion coefficient in clay	1.7×10^{-10}	m/s	[61]
Longitudinal dispersion	$0.83 \times \log(L^*)^{2.414}$	m	[63]

* L = flowpath length.

The upgradient boundary consisted of a steady-state recharge flux and a time-dependent isotope flux. Steady-state recharge was used because varying precipitation by 25% (the difference between reconstructed LGM and modern averages) over 60,000 yr periods caused hydraulic heads to vary by only ~1.6% within the modeled region of the aquifer. A zero-head condition was chosen for the downgradient boundary, and the observed hydraulic heads compiled by [60] were shifted for comparison with the model's output. The recharge flux was initially set at 0.151 m/yr based on the present-day effective recharge value (=precipitation—evapotranspiration) [34]. It was then adjusted to approximate the observed hydraulic gradient and ^{36}Cl -derived groundwater velocity (10^{-8} m/s). Recharge fluxes of 0.14 and 0.1395 m/yr were selected for aquifer porosity values of 0.15 and 0.225, respectively (equating to velocities of 3.0×10^{-8} and 2.0×10^{-8} m/s). The calculated hydraulic gradient varied from the observed linear best fit by 0.01 m/km (RMSE = 2.94 and 2.92, Figure S1). With the selected aquifer parameters (hydraulic conductivity and porosity), groundwater velocity varied from the average modeled lower Wilcox value by 1.95×10^{-9} and 8×10^{-9} m/s for the different recharge fluxes.

Isotope transport was solved using a combined advection–dispersion and diffusion equation with an additional cross-contact diffusive flux:

$$\theta_s \frac{\partial C_x}{\partial t} = (-D_{D,x} + \theta \tau_{L,i} D_{L,x}) \frac{\partial^2 C_i}{\partial x^2} - v_x \frac{\partial C_i}{\partial x} \pm \text{diffusive flux} \quad (1)$$

The first product on the right-hand side is the dispersion–diffusion term, the second product is the advection term, θ_s is aquifer porosity, D_D is the species diffusion coefficient, θ is liquid volume fraction (equal to porosity under saturated conditions), τ_L is tortuosity ($\sim \theta^{1/3}$ for saturated porous media), D_L is longitudinal dispersivity, and x is distance along the flowpath. The diffusive flux was calculated as follows:

$$\frac{\partial C_t}{\partial t} = \frac{-D}{\Delta y \phi_t b_t} (C_{t_i} - C_{f_i}) \quad (2)$$

where D is the species diffusion coefficient, Δy is the confining-unit interaction thickness (nodal spacing), ϕ_t is confining-unit porosity, b_t is aquifer thickness, C_{t_i} is the confining-unit isotope concentration, and C_{f_i} is the aquifer isotope concentration. Initial $\delta^{18}\text{O}$ was

specified as the median of the calculated paleo-water values of [46] (-5.9‰) for the aquifer and the mean of those values (-5.6‰) for the confining unit, assuming fluxes both out of and into the aquifer.

A sensitivity analysis was conducted to determine the influences of groundwater velocity and isotope abundance gradient on the distribution of $\delta^{18}\text{O}$ in the aquifer. The initial aquifer and confining-unit $\delta^{18}\text{O}$ values were -6‰ and -4‰ , respectively. The velocity was varied from 1.82×10^{-9} to 2.81×10^{-7} m/s. Confining-unit thickness was varied from 40 to 400 m, while aquifer thickness was maintained at 40 m. Confining-unit isotope abundance was varied between the aquifer value and $100\times$ that value.

The effects of varying groundwater velocity and confining-unit interaction thickness (cell-centered vs. full-unit thickness) were also examined in terms of variable isotope input. The calculated paleo-water $\delta^{18}\text{O}$ values from [46] were input across a 175 kyr runtime. For time periods lacking $\delta^{18}\text{O}$ data, input values were calculated using linear interpolation. Except where noted, a mass flux of 0.151 m/yr was maintained. The ^{18}O isotope flux was calculated as a piecewise function of 5000 yr intervals across the study period.

3. Results

3.1. Water Analyses

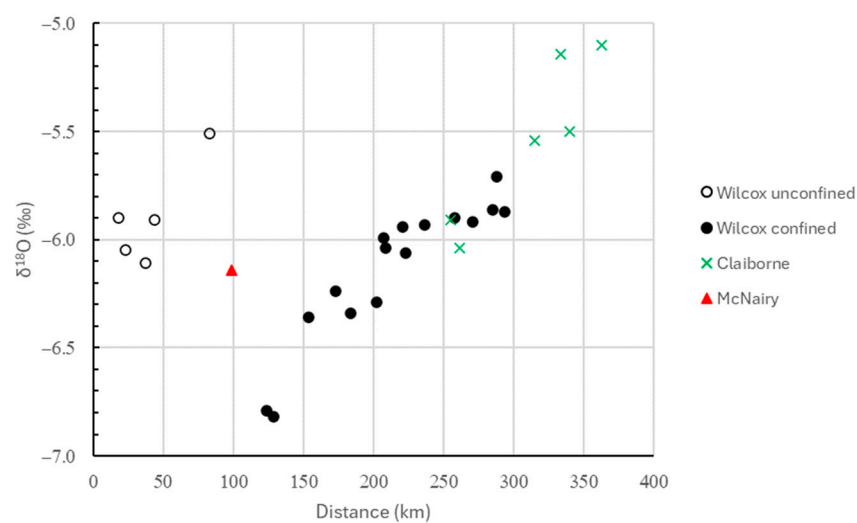
Chloride concentrations tended to be markedly lower in the Wilcox (median 1.5 mg/L) than in the Claiborne and McNairy aquifers (Table 3). Except for well 3 (9.0 mg/L), Cl^- in the Wilcox ranged from 0.78 to 7.1 mg/L and increased gradually downgradient. Chloride values were similarly low for Claiborne wells located in the Memphis Sand (2.9 and 2.3 mg/L for samples 22 and 23, respectively), but Claiborne wells located in the Sparta Sand farther south (samples 24–27) had Cl^- values ranging from 39.0 to 311.2 mg/L. The chloride level for the McNairy well (sample 28) was 157.2 mg/L.

The values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of groundwater from the unconfined Wilcox aquifer ranged from -6.11 to -5.51‰ and -36.97 to -33.13‰ , respectively (Table 3). The isotopic abundances became depleted between the farthest downgradient unconfined well (Parma, MO [well 5]: $\delta^{18}\text{O} -5.51\text{‰}$, $\delta^2\text{H} -33.13\text{‰}$) and the farthest upgradient confined well (Hayti, MO [well 6]: $\delta^{18}\text{O} -6.79\text{‰}$, $\delta^2\text{H} -41.31\text{‰}$). Isotopic abundances in the confined Wilcox aquifer ranged from -6.82 to -5.71‰ for $\delta^{18}\text{O}$ and from -41.31 to -32.74‰ for $\delta^2\text{H}$, and tended to become enriched with the distance downgradient (Figure 3). For the Claiborne aquifer, $\delta^{18}\text{O}$ ranged from -6.04 to -5.10‰ and $\delta^2\text{H}$ from -34.57 to -28.07‰ , with the values of the Sparta Sand following the confined Wilcox trend of progressive enrichment down-valley (Table 3; Figure 3). The values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for the McNairy well at Malden, MO (-6.14 and -32.45‰ , respectively) were more similar to those of the unconfined Wilcox aquifer than the confined Wilcox aquifer. On a plot of $\delta^2\text{H}$ versus $\delta^{18}\text{O}$ (Figure 4), trendlines for various groups of samples fall subparallel to the local meteoric water line (LMWL) for McCracken County, Kentucky ($\delta^2\text{H} = 7.5\delta^{18}\text{O} + 10.6$; [60]), with slopes of 6.08 for the unconfined Wilcox aquifer, 6.71 for the confined Wilcox aquifer, and 6.42 for the Claiborne aquifer.

The measured $^{36}\text{Cl}/\text{Cl}$ ratios decreased with the distance downgradient in the confined Wilcox aquifer, falling from 212×10^{-15} at Osceola, AR (well 13) to 41×10^{-15} at Brickeys, AR (well 21; Table 3). Assuming an initial $^{36}\text{Cl}/\text{Cl}$ of 272×10^{-15} (the value from a well at Bloomfield, MO near the upgradient limit of the study area [27]) gives ages of 108–822 kyr for confined Wilcox samples. Given the inferred distances along the regional flowpath, the resulting velocity values progressively decrease from 5.91×10^{-8} to 1.13×10^{-8} m/s (1.86 to 0.358 m/yr) (Table 4). If the initial $^{36}\text{Cl}/\text{Cl}$ value is decreased to 225×10^{-15} , which is plausible given the regional patterns in groundwater shown by [28,64], the calculated age range decreases to 26.0–739 kyr, and the range of velocity values ranges from 2.46×10^{-7} to 1.26×10^{-8} m/s (7.75 to 0.398 m/yr) (Table 4).

Table 3. Chloride concentrations and stable isotope abundances in groundwater samples.

Well	Cl [−]	δ ¹⁸ O	δ ² H
	(mg/L)	‰ VSMOW	‰ VSMOW
Unconfined Wilcox			
1	0.9	−6.05	−36.18
2	1.5	−5.90	−35.94
3	9.0	−6.11	−36.97
4	0.43	−5.91	−35.15
5	1.3	−5.51	−33.13
Confined Wilcox			
6	1.1	−6.79	−41.31
7	1.2	−6.82	−39.41
8	2.0	−6.36	−37.82
9	0.78	−6.24	−36.94
10	1.5	−6.34	−35.70
11	3.5	−6.04	−34.90
12	1.3	−5.99	−35.18
13	1.1	−6.29	−35.33
14	1.7	−5.94	−34.16
15	0.58	−6.06	−35.49
16	1.7	−5.93	−34.12
17	2.2	−5.90	−33.74
18	2.2	−5.92	−33.60
19	5.1	−5.71	−33.06
20	2.8	−5.86	−32.74
21	7.1	−5.87	−35.15
Claiborne (Memphis Sand)			
22	2.9	−5.91	−33.15
23	2.3	−6.04	−34.57
Claiborne (Sparta Sand)			
24	310	−5.54	−31.45
25	39	−5.50	−31.15
26	83	−5.14	−28.07
27	160	−5.10	−28.69
McNairy			
28	160	−6.14	−32.45

**Figure 3.** Variation in the $\delta^{18}\text{O}$ present in groundwater along the inferred regional flowpath; analytical precision (1σ) for the samples in this study was $\pm 0.08\text{‰}$.

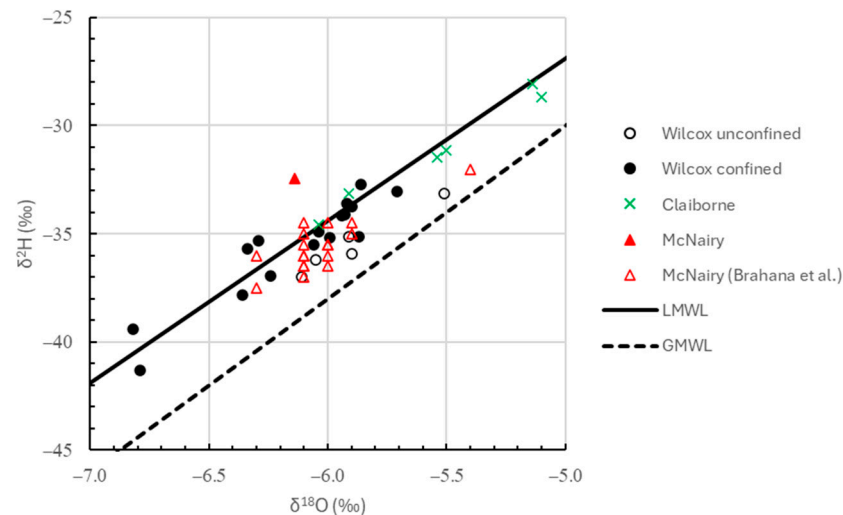


Figure 4. Groundwater values of $\delta^2\text{H}$ plotted vs. $\delta^{18}\text{O}$ from this study and Brahana et al. (1985) [16]. Analytical precision (1σ) for samples in this study was $\pm 0.08\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 0.9\text{‰}$ for $\delta^2\text{H}$. LMWL and GMWL refer to local [60] and global [6] meteoric water lines, respectively.

Table 4. The estimated ages and values of groundwater velocity (v) based on ^{36}Cl analyses from this study and from [28] (denoted by *) and ^{14}C analyses from [12,65], assuming flowpath distances measured from the northern end of the transect shown in Figure 2. Low- and high-bound v values reflect initial $^{36}\text{Cl}/\text{Cl}$ ratios of 272×10^{-15} and 225×10^{-15} , respectively. LPM = lumped parameter model. State: AR = Arkansas; MO = Missouri.

Location	Aquifer	$^{36}\text{Cl}/\text{Cl} \times 10^{-15}$	^{14}C (pmc)	Low Age (yr)	High Age (yr)	LPM Age (yr)	Distance (km)	Low v (m/s)	High v (m/s)	LPM v (m/s)
Osceola, AR	Wilcox	211.9		2.60×10^4	1.08×10^5		202	5.91×10^{-8}	2.46×10^{-7}	
Shell Lake, AR	Wilcox	89.6		4.00×10^5	4.82×10^5		271	1.78×10^{-8}	2.15×10^{-8}	
Horseshoe Lake, AR	Wilcox	59.9		5.75×10^5	6.57×10^5		285	1.38×10^{-8}	1.57×10^{-8}	
Brickeys, AR	Wilcox	41.0		7.39×10^5	8.22×10^5		294	1.13×10^{-8}	1.26×10^{-8}	
Birdeye, AR *	Claiborne	205		4.04×10^4	1.23×10^5		255	6.58×10^{-8}	2.00×10^{-7}	
Parkin, AR *	Claiborne	70		5.07×10^5	5.89×10^5		262	1.41×10^{-8}	1.64×10^{-8}	
Parma, MO	Wilcox		86.5			1090	83			2.41×10^{-6}
Malden, MO	McNairy		83.8			1340	99			2.34×10^{-6}
Caruthersville, MO	Wilcox		19.2			16,000	129			2.56×10^{-7}

3.2. Model Simulations

In sensitivity analyses, the mid-flowpath $\delta^{18}\text{O}$ value was maintained as groundwater velocity increased from the minimum to 1.96×10^{-8} m/s (0.618 m/yr). It then became depleted by almost 1‰ as velocity approached 2×10^{-7} m/s (6 m/yr). The diffusive flux increased with increasing ^{18}O gradient and approached an asymptotic value once confining-unit $\delta^{18}\text{O}$ reached $4 \times$ the value of aquifer $\delta^{18}\text{O}$. The diffusive flux was greater for interaction with the full confining-unit thickness, as shown by the greater variation in the surface signal isotope values (Figure 5). Increasing the diffusive flux by altering interaction thickness increased the dispersive mixing (Figure 6), while increasing velocity increased both the dispersive mixing and the penetration of the surface isotope signal (Figure 6). We performed simulations using a velocity of 3.2×10^{-8} m/s (0.151 m/yr recharge flux; porosity of 0.15) with the paleo-water data from [46]. These indicated that changes in the confining-unit thickness and interaction thickness only slightly altered the amplitude of the $\delta^{18}\text{O}$ pattern (Figures 5 and 6).

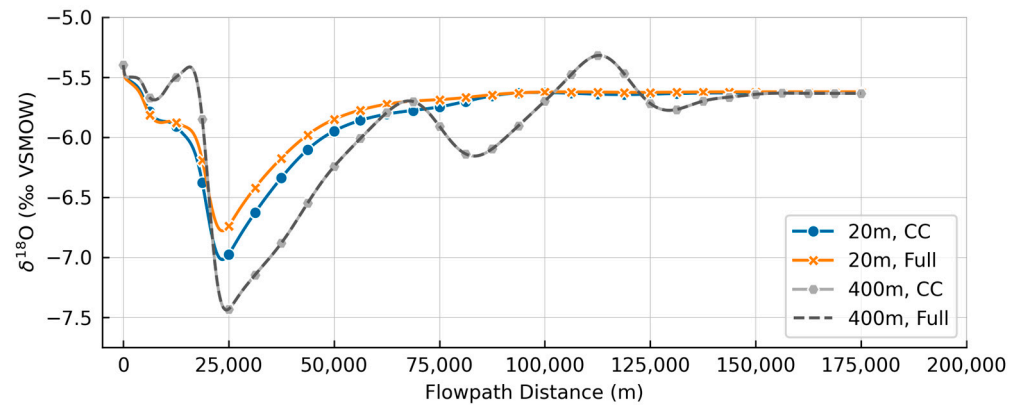


Figure 5. Aquifer $\delta^{18}\text{O}$ vs. flowpath distance for varying confining-unit thickness with cell-centered (CC) and full-thickness diffusive interaction given a 0.151 m/yr mass flux.

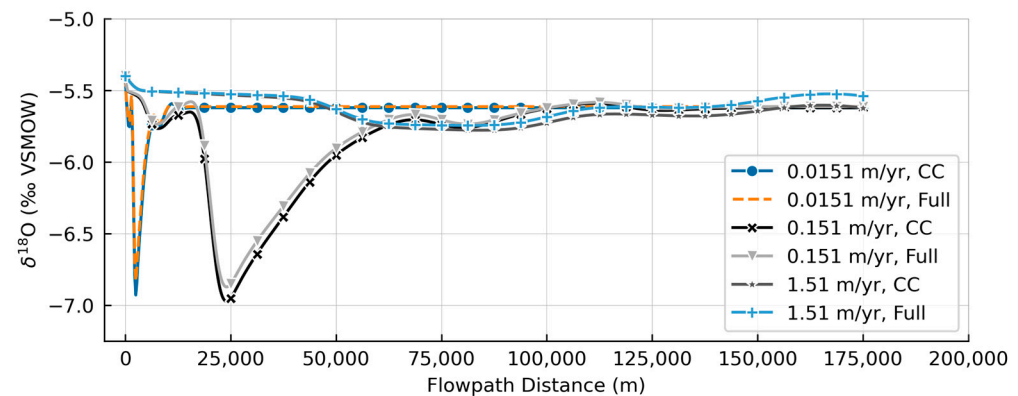


Figure 6. Aquifer $\delta^{18}\text{O}$ vs. flowpath distance for a 40 m thick confining unit with cell-centered (CC) and full-thickness diffusive interaction given a range of mass fluxes of two orders of magnitude.

4. Discussion

Several possible explanations exist for the spatial distribution of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in groundwater in this study, including the diffusion of stable isotopes between the Wilcox aquifer and adjoining confining units, cross-formational flow from adjoining aquifers, anthropogenic activities, and temporal variability in the isotopic signature of recharge. We examine each of these possible explanations below in light of modeling results, hydros-tratigraphy, Cl^- concentrations, and radioisotopes. The progressive enrichment of $\delta^{18}\text{O}$ (and $\delta^2\text{H}$) with the distance downgradient in the confined Wilcox aquifer resembled the $\delta^{18}\text{O}$ pattern observed in the clastic Milk River aquifer of Montana and Alberta, which [13] argued was altered by ^{18}O diffusion from an adjoining confining unit. Without data on the isotopic composition of porewater in MEAS confining units, we cannot fully judge the extent to which diffusion affects $\delta^{18}\text{O}$ or $\delta^2\text{H}$ values in the Wilcox aquifer. However, $\delta^{18}\text{O}$ values in the aquifer appear to be relatively insensitive to confining-unit thickness and interaction thickness for the modeled velocity of 3.2×10^{-8} m/s. Moreover, our modeling results indicate that, above a velocity of $\sim 10^{-7}$ m/s, water is advected through the aquifer faster than diffusive exchange with the confining unit is capable of altering $\delta^{18}\text{O}$ (or $\delta^2\text{H}$) values, which is consistent with findings of [14].

The progressive downgradient enrichment in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ is also suggestive of the continental effect and, therefore, of downward cross-formational flow. In the midcontinental USA, the $\delta^{18}\text{O}$ of modern precipitation increases with decreasing latitude (LAT), reflecting proximity to the Gulf of Mexico, following the relationship $\delta^{18}\text{O} = -0.0057 \text{ LAT}^2 + 0.1078 \text{ LAT} - 1.6544$ for the land surface < 200 m asl [66]. However, the polynomial best-fit trend of our data for the confined Wilcox aquifer is markedly steeper ($\delta^{18}\text{O} = -0.681 \text{ LAT}^2 + 47.736 \text{ LAT} - 842.4$), which indicates that $\delta^{18}\text{O}$ values do

not reflect modern meteoric recharge. Notwithstanding the downward hydraulic gradient between the Claiborne and Wilcox aquifers in northeast Arkansas, the lower Claiborne confining unit appears to limit the downward cross-formational flow in the southern part of the study area: the cone of depression in the Wilcox aquifer around West Memphis, AR is not evident in the middle Claiborne aquifer [41,42]. The relatively low $^{36}\text{Cl}/\text{Cl}$ ratios in that area (41×10^{-15} to 90×10^{-15}) are consistent with a lack of modern recharge in the Wilcox aquifer.

In southeast Missouri and northeast Arkansas, the Midway confining unit appears to limit the upward cross-formational flow from the McNairy aquifer to the Wilcox aquifer. Whereas $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in the McNairy aquifer and stratigraphically equivalent wells sampled by [16] were similar to our unconfined Wilcox values (Figure 4), Cl^- concentrations in those McNairy wells (range 5–1200 mg/L, median 45 mg/L) were generally much higher than our Wilcox values. Conversely, near the southern limit of our study area, upward cross-formational flow was apparent. In the Grand Prairie region of east-central Arkansas, the middle Claiborne aquifer receives a small amount of modeled inflow from the lower Claiborne confining unit (5.5% for pre-development conditions and 3.8% for post-development conditions) [15]. Salinity anomalies in the MRVA aquifer in southeast Arkansas appear to result from small amounts of brine (<1% by volume) moving upward from the Smackover Formation (Jurassic) and mixing with Wilcox groundwater along faults [44]. We do not expect salinity impacts associated with petroleum production in our study area, given the lack of natural gas and oil wells [67,68].

Given the apparently limited effects of isotopic diffusion between the Wilcox and adjoining confining units, the lack of evidence for cross-formational flow into the Wilcox in our study area, and the absence of anthropogenic impacts, we conclude that the observed fluctuations in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ along the down-valley flowpath reflect a Pleistocene paleoclimate record. The observation that the slopes of $\delta^2\text{H}$ – $\delta^{18}\text{O}$ plots fall subparallel to the LMWL suggests partial evaporation during recharge. However, the likelihood that $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values from the confined Wilcox aquifer span glacial and interglacial periods limits our ability to infer changes in evaporation over time by comparing $\delta^2\text{H}$ – $\delta^{18}\text{O}$ slopes. The estimated velocity values in Table 4 decrease by about two orders of magnitude, from $\sim 10^{-6}$ m/s in the unconfined part of the Wilcox aquifer to $\sim 10^{-7}$ m/s in the upgradient part of the confined aquifer and $\sim 10^{-8}$ m/s farther downgradient. Velocity values are limited by assumptions regarding the geometry of the flow system (i.e., the sampled wells lie on a linear flowpath), the source of ^{36}Cl , and the initial $^{36}\text{Cl}/\text{Cl}$ value. Subsurface contributions to ^{36}Cl in the monitored portion of the Wilcox aquifer are probably minimal, given the low Cl^- concentrations. The modeled velocity of 3.2×10^{-8} m/s is intermediate relative to the values obtained for Osceola, AR and for Wilcox wells farther downgradient using either the high- or low-bound initial $^{36}\text{Cl}/\text{Cl}$ value (Table 4).

Our finding that velocity decreases with distance from the presumed recharge area builds on other studies that sampled the same or nearby wells. Using ^{14}C dating with lumped parameter models (LPMs), Jurgens et al. [12,65] obtained ages of 1090 yr for a Wilcox well at Parma, MO, and 1340 yr for a McNairy well at Malden, MO, corresponding to inferred velocities of ~ 2.3 – 2.4×10^{-6} m/s, and an age of 16,000 yr for a Wilcox well at Caruthersville, MO, corresponding to an inferred velocity of 2.56×10^{-7} m/s (Table 4). Davis et al. [28] reported $^{36}\text{Cl}/\text{Cl}$ values of 205×10^{-15} and 70×10^{-15} for Claiborne wells at Birdseye and Parkin, AR, respectively. These values corresponded to ages of 40.4–590 kyr, given the estimated initial $^{36}\text{Cl}/\text{Cl}$ range of 225 – 272×10^{-15} , and to inferred velocities of $\sim 2.0 \times 10^{-7}$ – 1.4×10^{-8} m/s (Table 4). The recharge of the last two wells could have been more local (i.e., along the northwest margin of the embayment [59]), shortening flowpaths and giving velocities higher than those inferred from the distances observed along our down-valley transect (Table 1).

The decrease in velocities between the unconfined and confined portions of the Wilcox aquifer could result at least in part from faulting in the NMSZ. Between Parma and Hayti, MO (~ 40 km), the depth of Wilcox wells increases by ~ 250 m. In the intervening area,

Wilcox wells are generally absent, perhaps because of the reduced horizontal hydraulic conductivity associated with stratigraphic offset. Faults may both impede lateral flow of groundwater and locally facilitate vertical flow and mixing [69], as inferred for the MRVA aquifer in southeast Arkansas [44]. The 424 m deep Wilcox well at Caruthersville, MO analyzed by [12], was inferred to contain a mixture of 1.7% Holocene-aged water and 98.3% Pleistocene-aged water (reflecting ^{14}C content of 19.2% modern C). The Wilcox well that [16] sampled at Hayti contained similarly low levels of ^{14}C (8.1% modern) and a detectable level of ^3H (2.0 pCi/L), which likewise indicates the downward leakage of a small amount of modern recharge mixing with much older groundwater. However, the depletion in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ observed at Hayti and Caruthersville is unlikely to be explained by upward or downward flow along faults. As noted above, McNairy groundwater is isotopically similar to unconfined Wilcox groundwater in southeast Missouri. Isotopically depleted meltwater pulses, moving down the Mississippi River valley from the Laurentide Ice Sheet [70], are recorded in Gulf of Mexico seafloor sediments at 14, ~120, and 210 ka [71]. Assuming mixing between upgradient groundwater with $\delta^{18}\text{O}$ of -5.8‰ and meltwater with $\delta^{18}\text{O}$ of -10‰ [70], meltwater would have to comprise an unrealistically high proportion (24%) of downgradient groundwater to explain the observed $\delta^{18}\text{O}$ values.

5. Conclusions

Stable isotope patterns in the Wilcox and the adjoining aquifers of the Mississippi Embayment appeared to reflect a regional paleoclimatic signal. Along the inferred flowpath down the Mississippi River valley in Missouri and Arkansas, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values became depleted as the Wilcox aquifer transitioned from unconfined to confined. Then, values gradually became enriched farther downgradient. Chlorine-36 analyses from four Wilcox wells in this study and three wells in other studies, as well as ^{14}C analyses of wells in another study, indicated that groundwater ages in the studied aquifers ranged from $\sim 10^3$ yr to as much as $\sim 8 \times 10^5$ yr. Inferred velocity values in the Wilcox aquifer decreased downgradient by about two orders of magnitude, from $\sim 10^{-6}$ to 10^{-8} m/s. Velocity calculations depended upon the initial $^{36}\text{Cl}/\text{Cl}$ value chosen and assumed that the sampled wells lay on a linear flowpath.

Diffusion between the Wilcox aquifer and bounding confining units may smooth isotope signals, particularly at velocities $\lesssim 10^{-8}$ m/s, but a simplified numerical model suggests that diffusion does not fully explain the observed isotopic enrichment with distance. Likewise, neither latitudinal enrichment in rainfall proximal to the Gulf of Mexico (i.e., meteoric recharge along the regional flowpath) nor the upward movement of water from underlying units appear to explain the isotopic trends seen in confined groundwater, because cross-formational flow is limited. The depletion in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ coincides with the NMSZ, but pulses of meltwater recharge from the Laurentide Ice Sheet along faults are unlikely to have been volumetrically sufficient to explain those offsets. We posit that confined groundwater in our study reflects a paleorecharge signal spanning multiple glacial and interglacial periods. To test this conclusion and refine our understanding of regional climate during the Pleistocene, we recommend additional sampling of wells in the Wilcox and adjoining aquifers to assess noble gases and radioisotopes (e.g., ^4He), and using the data obtained to calibrate a more sophisticated numerical model of groundwater flow and solute transport that includes faults in the MEAS. Such a model would be useful for assessing the sustainability of the Wilcox aquifer under scenarios of expanded water supply pumping, given the current stresses on the MRVA and middle Claiborne aquifer.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/hydrology11080118/s1>, Figure S1: Calculated fit to observed hydraulic heads for range of recharge fluxes considered.

Author Contributions: Conceptualization, A.E.F., E.H. and B.J.C.; methodology, A.E.F., E.H. and B.J.C.; software, B.J.C.; validation, B.J.C.; formal analysis, A.E.F., E.H. and B.J.C.; investigation, A.E.F., E.H. and B.J.C.; resources, A.E.F., E.H. and B.J.C.; data curation, A.E.F., E.H. and B.J.C.; writing—original draft preparation, A.E.F.; writing—review and editing, A.E.F., E.H. and B.J.C.; visualization, E.H., B.J.C. and A.E.F.; supervision, A.E.F.; project administration, A.E.F.; funding acquisition, A.E.F., E.H. and B.J.C. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by U.S. Geological Survey grant no. 06HQGR0087 to A.E.F. and E.H. through the University of Kentucky; by a National Science Foundation Graduate Research Fellowship under grant no. 3048109801 to B.J.C.; by a student research grant to E.H. from the Gulf Coast Association of Geological Societies; and by a seed grant from the PRIME Lab at Purdue University to A.E.F. The views and conclusions contained herein are those of the authors and should not be interpreted as representing the opinions or policies of the U.S. Geological Survey.

Data Availability Statement: Unpublished data and results of analyses presented herein are available upon request from the corresponding author.

Acknowledgments: The authors thank operators of municipal wells for facilitating sampling; Audrey Sawyer for providing guidance and feedback on development of the mathematical model; Edward Woolery for providing Figure 1a; and the two reviewers and academic editor for their constructive recommendations.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Torgersen, T.; Habermehl, M.A.; Phillips, F.M.; Elmore, D.; Kubik, P.; Jones, G.B.; Hemmick, T.; Gove, H.E. Chlorine 36 dating of very old groundwater: 3. Further studies in the Great Artesian Basin, Australia. *Water Resour. Res.* **1991**, *27*, 3201–3213. [\[CrossRef\]](#)
2. Marty, B.; Torgersen, T.; Meynier, V.; O’Nions, R.K.; de Marsily, G. Helium isotope fluxes and groundwater ages in the Dogger aquifer, Paris Basin. *Water Resour. Res.* **1993**, *29*, 1025–1035. [\[CrossRef\]](#)
3. Sturchio, N.C.; Du, X.; Purtschert, R.; Lehmann, B.E.; Sultan, M.; Patterson, L.J.; Lu, Z.-T.; Müller, P.; Bigler, T.; Bailey, K.; et al. One million year old groundwater in the Sahara revealed by krypton-81 and chlorine-36. *Geophys. Res. Lett.* **2004**, *31*, L05503. [\[CrossRef\]](#)
4. Plummer, L.N.; Eggleston, J.R.; Andreasen, D.C.; Raffensperger, J.P.; Hunt, A.G.; Casile, G.C. Old groundwater in parts of the Upper Patapsco aquifer, Atlantic Coastal Plain, Maryland, USA: Evidence from radiocarbon, chlorine-36 and helium-4. *Hydrogeol. J.* **2012**, *20*, 1269–1294. [\[CrossRef\]](#)
5. Jasechko, S.; Lechler, A.; Pausata, F.S.R.; Fawcett, P.J.; Gleeson, T.; Cendón, D.I.; Galewsky, J.; LeGrande, A.N.; Risi, C.; Sharp, Z.D.; et al. Late-glacial to late-Holocene shifts in global precipitation $\delta^{18}\text{O}$. *Clim. Past* **2015**, *11*, 1375–1393. [\[CrossRef\]](#)
6. Craig, H. Isotopic variations in meteoric waters. *Science* **1961**, *133*, 1702–1703. [\[CrossRef\]](#) [\[PubMed\]](#)
7. Kendall, C.; Caldwell, E.A. Chapter 2—Fundamentals of isotope geochemistry. In *Isotope Tracers in Catchment Hydrology*; Kendall, C., McDonnell, J.J., Eds.; Elsevier: Amsterdam, The Netherlands, 1998; pp. 51–86.
8. Dutton, A.R. Groundwater isotopic evidence for paleorecharge in U.S. High Plains aquifers. *Quat. Res.* **1995**, *43*, 221–231. [\[CrossRef\]](#)
9. Clark, J.F.; Davisson, M.L.; Hudson, G.B.; Macfarlane, P.A. Noble gases, stable isotopes, and radiocarbon as tracers of flow in the Dakota aquifer, Colorado and Kansas. *J. Hydrol.* **1998**, *211*, 151–167. [\[CrossRef\]](#)
10. Stotler, R.; Harvey, F.E.; Gosselin, D.C. A Black Hills-Madison aquifer origin for Dakota aquifer groundwater in northeastern Nebraska. *Groundwater* **2010**, *48*, 448–464. [\[CrossRef\]](#) [\[PubMed\]](#)
11. Jasechko, S. Partitioning young and old groundwater with geochemical tracers. *Chem. Geol.* **2016**, *427*, 35–42. [\[CrossRef\]](#)
12. Jurgens, B.C.; Faulkner, K.; McMahon, P.B.; Hunt, A.G.; Casile, G.; Young, M.B.; Belitz, K. Over a third of groundwater in USA public-supply aquifers is Anthropocene-age and susceptible to surface contamination. *Commun. Earth Environ.* **2022**, *3*, 153. [\[CrossRef\]](#)
13. Hendry, M.J.; Schwartz, F.W. An alternative view on the origin of chemical and isotopic patterns in groundwater from the Milk River aquifer, Canada. *Water Resour. Res.* **1988**, *24*, 1747–1763. [\[CrossRef\]](#)
14. LaBolle, E.M.; Fogg, G.E.; Eweis, J.B.; Gravner, J.; Leaist, D.G. Isotopic fractionation by diffusion in groundwater. *Water Resour. Res.* **2008**, *44*, W07405. [\[CrossRef\]](#)
15. Clark, B.R.; Hart, R.M.; Gurdak, J.J. *Groundwater Availability of the Mississippi Embayment*; Professional Paper 1785; U.S. Geological Survey: Reston, VA, USA, 2011. [\[CrossRef\]](#)

16. Brahana, J.V.; Mesko, T.O.; Busby, J.F.; Kraemer, T.F. *Ground-Water Quality Data from the Northern Mississippi Embayment; Arkansas, Missouri, Kentucky, Tennessee, and Mississippi*; Open-File Report 85-683; U.S. Geological Survey: Nashville, TN, USA, 1985. [\[CrossRef\]](#)
17. Haile, E.; Fryar, A.E. Chemical evolution of groundwater in the Wilcox aquifer of the northern Gulf Coastal Plain, USA. *Hydrogeol. J.* **2017**, *25*, 2403–2418. [\[CrossRef\]](#)
18. Woolery, E.W.; Wang, Z.; Carpenter, N.S.; Street, R.; Brengman, C. The Central United States Seismic Observatory: Site characterization, instrumentation, and recordings. *Seismol. Res. Lett.* **2016**, *87*, 215–228. [\[CrossRef\]](#)
19. Hart, R.M.; Clark, B.R.; Bolyard, S.E. *Digital Surfaces and Thicknesses of Selected Hydrogeologic Units within the Mississippi Embayment Regional Aquifer Study (MERAS)*; Scientific Investigations Report 2008-5098; U.S. Geological Survey: Reston, VA, USA, 2008. [\[CrossRef\]](#)
20. Geyh, M. Groundwater: Saturated and unsaturated zone. In *Environmental Isotopes in the Hydrological Cycle: Principles and Applications*; UNESCO/IAEA: Vienna, Austria, 2001; Volume IV.
21. Darling, G.W.; Bath, A.H.; Gibson, J.J.; Rozanski, K. Isotopes in water. In *Isotopes in Palaeoenvironmental Research*; Leng, M.J., Ed.; Springer: Dordrecht, The Netherlands, 2006; pp. 1–66.
22. Gat, J.R. Oxygen and hydrogen isotopes in the hydrologic cycle. *Annu. Rev. Earth Planet. Sci.* **1996**, *24*, 225–262. [\[CrossRef\]](#)
23. Plummer, L.N. Stable isotope enrichment in paleowaters of the southeast Atlantic Coastal Plain, United States. *Science* **1993**, *262*, 2016–2020. [\[CrossRef\]](#)
24. Kennedy, C.D.; Genereux, D.P. ^{14}C groundwater age and the importance of chemical fluxes across aquifer boundaries in confined Cretaceous aquifers of North Carolina, USA. *Radiocarbon* **2007**, *49*, 1181–1203. [\[CrossRef\]](#)
25. Plummer, L.N.; Busby, J.F.; Lee, R.W.; Hanshaw, B.B. Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota. *Water Resour. Res.* **1990**, *26*, 1981–2014. [\[CrossRef\]](#)
26. Siegel, D.I. Evidence for dilution of deep, confined ground water by vertical recharge of isotopically heavy Pleistocene water. *Geology* **1991**, *19*, 433–436. [\[CrossRef\]](#)
27. Ma, L.; Castro, M.C.; Hall, C.M. A late Pleistocene–Holocene noble gas paleotemperature record in southern Michigan. *Geophys. Res. Lett.* **2004**, *31*, L23204. [\[CrossRef\]](#)
28. Davis, S.N.; Cecil, D.; Zreda, M.; Sharma, P. Chlorine-36 and the initial value problem. *Hydrogeol. J.* **1998**, *6*, 104–114. [\[CrossRef\]](#)
29. Andrews, J.N.; Fontes, J.-C.; Michelot, J.-L.; Elmore, D. In-situ neutron flux, ^{36}Cl production and groundwater evolution in crystalline rocks at Stripa, Sweden. *Earth Planet. Sci. Lett.* **1986**, *77*, 49–58. [\[CrossRef\]](#)
30. Fontes, J.C.; Brissaud, I.; Michelot, J.L. Hydrological implications of deep production of chlorine-36. *Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At.* **1984**, *5*, 303–307. [\[CrossRef\]](#)
31. Bentley, H.W.; Phillips, F.M.; Davis, S.N.; Habermehl, M.A.; Airey, P.L.; Calf, G.E.; Elmore, D.; Gove, H.E.; Torgersen, T. Chlorine 36 dating of very old groundwater: 1. The Great Artesian Basin, Australia. *Water Resour. Res.* **1986**, *22*, 1991–2001. [\[CrossRef\]](#)
32. Purdy, C.B.; Helz, G.R.; Mignerey, A.C.; Kubik, P.W.; Elmore, D.; Sharma, P.; Hemmick, T. Aquia aquifer dissolved Cl^- and $^{36}\text{Cl}/\text{Cl}$: Implications for flow velocities. *Water Resour. Res.* **1996**, *32*, 1163–1171. [\[CrossRef\]](#)
33. Lee, M.-K.; Griffin, J.; Saunders, J.; Wang, Y.; Jean, J.-S. Reactive transport of trace elements and isotopes in the Eutaw Coastal Plain aquifer, Alabama. *J. Geophys. Res. Biogeosci.* **2007**, *112*, G02026. [\[CrossRef\]](#)
34. Williamson, A.K.; Grubb, H.F. *Ground-Water Flow in the Gulf Coast Aquifer Systems, South-Central United States*; Professional Paper 1416-F; U.S. Geological Survey: Reston, VA, USA, 2001. [\[CrossRef\]](#)
35. Kottke, M.; Grieser, J.; Beck, C.; Rudolf, B.; Rubel, F. World map of the Köppen-Geiger climate classification updated. *Meteorol. Z.* **2006**, *15*, 259–263. [\[CrossRef\]](#) [\[PubMed\]](#)
36. Brugger, K. World Map of the Köppen-Geiger Climate Classification Updated Map for the United States of America. Available online: <http://koeppen-geiger.vu-wien.ac.at/usa.htm> (accessed on 7 June 2024).
37. U.S. Climate Data—Monthly Averages. Available online: <https://www.usclimatedata.com/> (accessed on 6 June 2024).
38. Hosman, R.L. *Regional Stratigraphy and Subsurface Geology of Cenozoic Deposits, Gulf Coastal Plain, South-Central United States*; Professional Paper 1416-G; U.S. Government Printing Office: Washington, DC, USA, 1996. [\[CrossRef\]](#)
39. U.S. Geological Survey Earthquake Hazards Program. Summary of 1811–1812 New Madrid Earthquakes Sequence. Available online: <https://www.usgs.gov/programs/earthquake-hazards/science/summary-1811-1812-new-madrid-earthquakes-sequence> (accessed on 13 July 2024).
40. Brahana, J.V.; Mesko, T.O. *Hydrogeology and Preliminary Assessment of Regional Flow in the Upper Cretaceous and Adjacent Aquifers in the Northern Mississippi Embayment*; Water-Resources Investigations Report 87-4000; U.S. Geological Survey: Nashville, TN, USA, 1988. [\[CrossRef\]](#)
41. Pugh, A.L. *Potentiometric Surfaces and Water-Level Trends in the Cockfield (Upper Claiborne) and Wilcox (Lower Wilcox) Aquifers of Southern and Northeastern Arkansas*, 2009; Scientific Investigations Report 2010-5014; U.S. Geological Survey: Reston, VA, USA, 2010. [\[CrossRef\]](#)
42. Schrader, T.P. *Water Levels and Water Quality in the Sparta-Memphis Aquifer (Middle Claiborne Aquifer) in Arkansas, Spring–Summer 2009*; Scientific Investigations Report 2013-5100; U.S. Geological Survey: Reston, VA, USA, 2013. [\[CrossRef\]](#)

43. Arthur, J.K.; Taylor, R.E. Mississippi Embayment aquifer system in Mississippi: Geohydrologic data compilation for flow model simulation. *JAWRA J. Am. Water Resour. Assoc.* **1986**, *22*, 1021–1029. [\[CrossRef\]](#)
44. Larsen, D.; Paul, J.; Cox, R. Geochemical and isotopic evidence for upward flow of saline fluid to the Mississippi River Valley alluvial aquifer, southeastern Arkansas, USA. *Hydrogeol. J.* **2021**, *29*, 1421–1444. [\[CrossRef\]](#)
45. Kresse, T.M.; Hays, P.D.; Merriman, K.R.; Gillip, J.A.; Fugitt, D.T.; Spellman, J.L.; Nottmeier, A.M.; Westerman, D.A.; Blackstock, J.M.; Battreal, J.L. *Aquifers of Arkansas: Protection, Management, and Hydrologic and Geochemical Characteristics of Groundwater Resources in Arkansas*; Scientific Investigations Report 2014-5149; U.S. Geological Survey: Reston, VA, USA, 2014. [\[CrossRef\]](#)
46. Harmon, R.S.; Schwarcz, H.P. Changes of ^2H and ^{18}O enrichment of meteoric water and Pleistocene glaciation. *Nature* **1981**, *290*, 125–128. [\[CrossRef\]](#)
47. Rodbell, D.T.; Forman, S.L.; Pierson, J.; Lynn, W.C. Stratigraphy and chronology of Mississippi Valley loess in western Tennessee. *GSA Bull.* **1997**, *109*, 1134–1148. [\[CrossRef\]](#)
48. Markewich, H.W.; Wysocki, D.A.; Pavich, M.J.; Rutledge, E.M.; Millard, H.T.; Rich, F.J.; Maat, P.B.; Rubin, M.; McGeehin, J.P. Paleopedology plus TL, ^{10}Be , and ^{14}C dating as tools in stratigraphic and paleoclimatic investigations, Mississippi River Valley, U.S.A. *Quat. Int.* **1998**, *51–52*, 143–167. [\[CrossRef\]](#)
49. Forman, S.L.; Pierson, J. Late Pleistocene luminescence chronology of loess deposition in the Missouri and Mississippi River valleys, United States. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **2002**, *186*, 25–46. [\[CrossRef\]](#)
50. Muhs, D.R.; Wehmiller, J.F.; Simmons, K.R.; York, L.L. Quaternary sea-level history of the United States. In *Developments in Quaternary Sciences*; Elsevier: Amsterdam, The Netherlands, 2003; Volume 1, pp. 147–183.
51. Williams, J.W.; Shuman, B.N.; Webb III, T. Dissimilarity analyses of late-Quaternary vegetation and climate in eastern North America. *Ecology* **2001**, *82*, 3346–3362. [\[CrossRef\]](#)
52. Rovey, C.W.; Balco, G. Chapter 43—Summary of early and middle Pleistocene glaciations in northern Missouri, USA. In *Developments in Quaternary Sciences*; Ehlers, J., Gibbard, P.L., Hughes, P.D., Eds.; Elsevier: Amsterdam, The Netherlands, 2011; Volume 15, pp. 553–561.
53. Bromwich, D.H.; Toracinta, E.R.; Oglesby, R.J.; Fastook, J.L.; Hughes, T.J. LGM summer climate on the southern margin of the Laurentide Ice Sheet: Wet or dry? *J. Clim.* **2005**, *18*, 3317–3338. [\[CrossRef\]](#)
54. USGS Water Data for the Nation. Available online: <https://waterdata.usgs.gov/nwis> (accessed on 6 June 2024).
55. Center for Applied Research and Engagement Systems, University of Missouri. Missouri Source Water Protection and Assessment. Available online: <https://drinkingwater.missouri.edu/> (accessed on 13 July 2024).
56. Johnston, J. (Arkansas Water Well Construction Commission, Little Rock, AR, USA). Personal communication, 2006.
57. Brahana, J.V.; Broshears, R.E. *Hydrogeology and Ground-Water Flow in the Memphis and Fort Pillow Aquifers in the Memphis Area, Tennessee*; Water-Resources Investigations Report 89-4131; U.S. Geological Survey: Nashville, TN, USA, 2001. [\[CrossRef\]](#)
58. Castany, G. *Traité Pratique des Eaux Souterraines*; Dunod: Paris, France, 1967.
59. Clark, B.R.; Hart, R.M. *The Mississippi Embayment Regional Aquifer Study (MERAS): Documentation of a Groundwater-Flow Model Constructed to Assess Water Availability in the Mississippi Embayment*; Scientific Investigations Report 2009-5172; U.S. Geological Survey: Reston, VA, USA, 2009. [\[CrossRef\]](#)
60. Haile, E. Chemical Evolution and Residence Time of Groundwater in the Wilcox Aquifer of the Northern Gulf Coastal Plain. Ph.D. Dissertation, University of Kentucky, Lexington, KY, USA, 2011.
61. Hendry, M.J.; Wassenaar, L.I. Implications of the distribution of δD in pore waters for groundwater flow and the timing of geologic events in a thick aquitard system. *Water Resour. Res.* **1999**, *35*, 1751–1760. [\[CrossRef\]](#)
62. Tanaka, K. Measurements of self-diffusion coefficients of water in pure water and in aqueous electrolyte solutions. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **1975**, *71*, 1127–1131. [\[CrossRef\]](#)
63. Xu, M.; Eckstein, Y. Use of weighted least-squares method in evaluation of the relationship between dispersivity and field scale. *Groundwater* **1995**, *33*, 905–908. [\[CrossRef\]](#)
64. Davis, S.N.; Moysey, S.; Cecil, D.L.; Zreda, M. Chlorine-36 in groundwater of the United States: Empirical data. *Hydrogeol. J.* **2003**, *11*, 217–227. [\[CrossRef\]](#)
65. Jurgens, B.C.; Musgrove, M.; McAdoo, M.A.; Faulkner, K.E. Data for Distribution of Groundwater Age in Aquifers Used for Public Supply in the Continental United States, 2004–2017 (Version 1.1: June 2022). U.S. Geological Survey Data Release. Available online: <https://doi.org/10.5066/P9W7T0DN> (accessed on 6 August 2024).
66. Dutton, A.; Wilkinson, B.H.; Welker, J.M.; Bowen, G.J.; Lohmann, K.C. Spatial distribution and seasonal variation in $^{18}\text{O}/^{16}\text{O}$ of modern precipitation and river water across the conterminous USA. *Hydrol. Processes* **2005**, *19*, 4121–4146. [\[CrossRef\]](#)
67. Arkansas Oil and Gas Commission. Wells, Fields, and Pipelines Maps. Available online: <https://www.aogc.state.ar.us/maps/googleEarth.aspx> (accessed on 13 July 2024).
68. Missouri Department of Natural Resources. Oil and Gas Wells List, March 4, 2024. Available online: <https://dnr.mo.gov/media/file/oil-gas-well-list-march-4-2024> (accessed on 15 July 2024).
69. Bense, V.F.; Person, M.A. Faults as conduit-barrier systems to fluid flow in siliciclastic sedimentary aquifers. *Water Resour. Res.* **2006**, *42*, W05421. [\[CrossRef\]](#)

70. Clayton, R.N.; Friedman, I.; Graf, D.L.; Mayeda, T.K.; Meents, W.F.; Shimp, N.F. The origin of saline formation waters: 1. Isotopic composition. *J. Geophys. Res.* **1966**, *71*, 3869–3882. [[CrossRef](#)]
71. Joyce, J.E.; Tjaisma, L.R.C.; Prutzman, J.M. North American glacial meltwater history for the past 2.3 m.y.: Oxygen isotope evidence from the Gulf of Mexico. *Geology* **1993**, *21*, 483–486. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.