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Investigating surface water–well interaction using stable isotope ratios of water[☆]

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Abstract

Because surface water can be a source of undesirable water quality in a drinking water well, an understanding of the amount of surface water and its travel time to the well is needed to assess a well's vulnerability. Stable isotope ratios of oxygen in river water at the City of La Crosse, Wisconsin, show peak-to-peak seasonal variation greater than 4‰ in 2001 and 2002. This seasonal signal was identified in 7 of 13 city municipal wells, indicating that these 7 wells have appreciable surface water contributions and are potentially vulnerable to contaminants in the surface water. When looking at wells with more than 6 sampling events, a larger variation in $\delta^{18}O$ compositions correlated with a larger fraction of surface water, suggesting that samples collected for oxygen isotopic composition over time may be useful for identifying the vulnerability to surface water influence even if a local meteoric water line is not available.

A time series of $\delta^{18}O$ from one of the municipal wells and from a piezometer located between the river and the municipal well showed that the travel time of flood water to the municipal well was approximately 2 months; non-flood arrival times were on the order of 9 months. Four independent methods were also used to assess time of travel. Three methods (groundwater temperature arrival times at the intermediate piezometer, virus-culture results, and particle tracking using a numerical groundwater-flow model) yielded flood and non-flood travel times of less than 1 year for this site. Age dating of one groundwater sample using ^3H–^3He methods estimated an age longer than 1 year, but was likely confounded by deviations from piston flow as noted by others. Chlorofluorocarbons and SF_6 analyses were not useful at this site due to degradation and contamination, respectively. This work illustrates the utility of stable hydrogen and oxygen isotope ratios of water to determine the contribution and travel time of surface water in groundwater, and demonstrates the importance of using multiple methods to improve estimates for time of travel of 1 year or less.
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1. Introduction

Many communities use groundwater that is under the influence of surface water, but surface water can be a source of undesirable water quality. The City of La Crosse, Wisconsin, is located adjacent to the Mississippi River, but its drinking water source is groundwater from the alluvial sand-gravel aquifer underlying the city and the river. Numerical groundwater-flow modeling (Hunt et al., 2003; Chapel et al., 2003a) suggests that some municipal wells are inducing surface water infiltration. Simulated capture areas can be uncertain, however, because of model parameter uncertainty and solution non-uniqueness (Evers and Lerner, 1998). Independent methods of identifying water sources can reduce the uncertainty in the model, and the predictions that are premised on modeling (Hunt et al., 2001).

Although the source of water is of interest when assessing water-supply vulnerability, the time of travel from the surface water source to the well also is important. This information is critical for deciding the response time for intervention, and is necessary for assessing whether particular microbiological contaminants are viable/infectious when the surface water reaches the well. For example, viruses are thought to survive in the subsurface for times on the order of 6–12 months (Yates et al., 1985; Yates and Yates, 1988; DeBorde et al., 1998); groundwater travel times often are appreciably longer than 1 year. However, large gradients and hydraulically conductive sediments (as might be found near a municipal wellfield near a surface water source) could result in travel times of less than 1 year (e.g. Maloszewski et al., 1990; Hötzl et al., 1989; Sheets et al., 2002). Thus, much could be gained if simple methods could be used to assess time of travel to the supply well in addition to identifying the source of water.

Stable hydrogen, oxygen, carbon, nitrogen, and sulfur isotope ratios can be valuable tools for investigating hydrologic systems (Mazor, 1997; Clark and Fritz, 1997). Of these, stable hydrogen (δ^2H) and oxygen isotope (primarily δ^{18}O) ratios in water are ideal conservative tracers of water sources, because they are part of the water molecule itself. Stable isotope ratios of water are conservative in aquifers at low temperature, but water can be isotopically fractionated on the surface at less than 100% humidity (Gat, 1970). Because the vapor pressure and diffusivity of H_2^{16}O is greater than that of H_2^{18}O, the residual liquid is characterized by a higher H_2^{18}O content after evaporation and rain or snow falling from clouds is enriched in H_2^{18}O, preferentially depleting air masses in H_2^{18}O as they move across continents. Protium (^{1}H) and deuterium (^{2}H) can also fractionate, but to a greater extent due to larger relative mass difference. ^{2}H is also enriched in precipitation falling from clouds, which caused air masses to become preferentially depleted in ^{2}H as they become colder and lose their moisture. Additionally, evaporation preferentially enriches surface water in ^{18}O relative to ^{2}H. These processes create a seasonal cycle in surface water such that water is depleted in ^{18}O and ^{2}H in snowmelt in the winter and early spring, and water is enriched in ^{18}O and ^{2}H during summer and early fall. As a result, ^{18}O/^{16}O and ^{2}H/^{1}H ratios can be used to identify the source and timing of groundwater flow (e.g. Fritz, 1981; Maloszewski et al., 1990; Krabbenhoft et al., 1990).

Whereas discrete physical measurements represent the system at the point in time the sample was taken, stable isotope compositions reflect the initial isotopic composition of waters entering the system, subsequent additions and withdrawals, and processes acting within the system. Consequently, transient hydrologic events have isotopic effects proportional to their physical importance. Periodic monitoring of hydraulic gradients only show 'snapshots' of the flow field, but cannot relay the importance of gradient changes (i.e. the amount of movement caused by a reversal) without a continuous data set and rigorous analysis. Given a sufficient understanding of the underlying flow system and distinction between sources, stable hydrogen and oxygen isotope ratios of water can give similar information with reduced sampling and physical measurement (Hunt et al., 1998). However, approaches using stable isotopes of water are not widely used in wellhead protection studies and have only infrequently been applied to drinking water supplies (for example, Stichler et al., 1986; Maloszewski et al., 1990; Hötzl et al., 1989; McCarthy et al., 1992; Coplen et al., 1999).

In this study, stable hydrogen and oxygen isotope ratios of water are used to identify sources of water for 13 municipal wells in the City of La Crosse, Wisconsin, and to assess the time of travel from surface water to one of the municipal wells. The time of travel was also evaluated using four independent

methods including: (1) commonly used age-dating tracers, (2) virus-culture results for Hepatitis A virus (HAV), (3) a groundwater temperature time series, and (4) a numerical groundwater-flow model. This study utilized relatively simple analyses that would be readily accessible to others; it also provides insights into potential methods for hydrologic settings where wells are near surface water sources.

2. Site description

The municipal water supply for the City of La Crosse is supplied by 13 high capacity wells located in the uppermost, unconfined fluvial sediments of the Mississippi River system (Fig. 1, Table 1). The fluvial sediments consist of relatively coarse unlithified glacial and alluvial materials that overlie Paleozoic
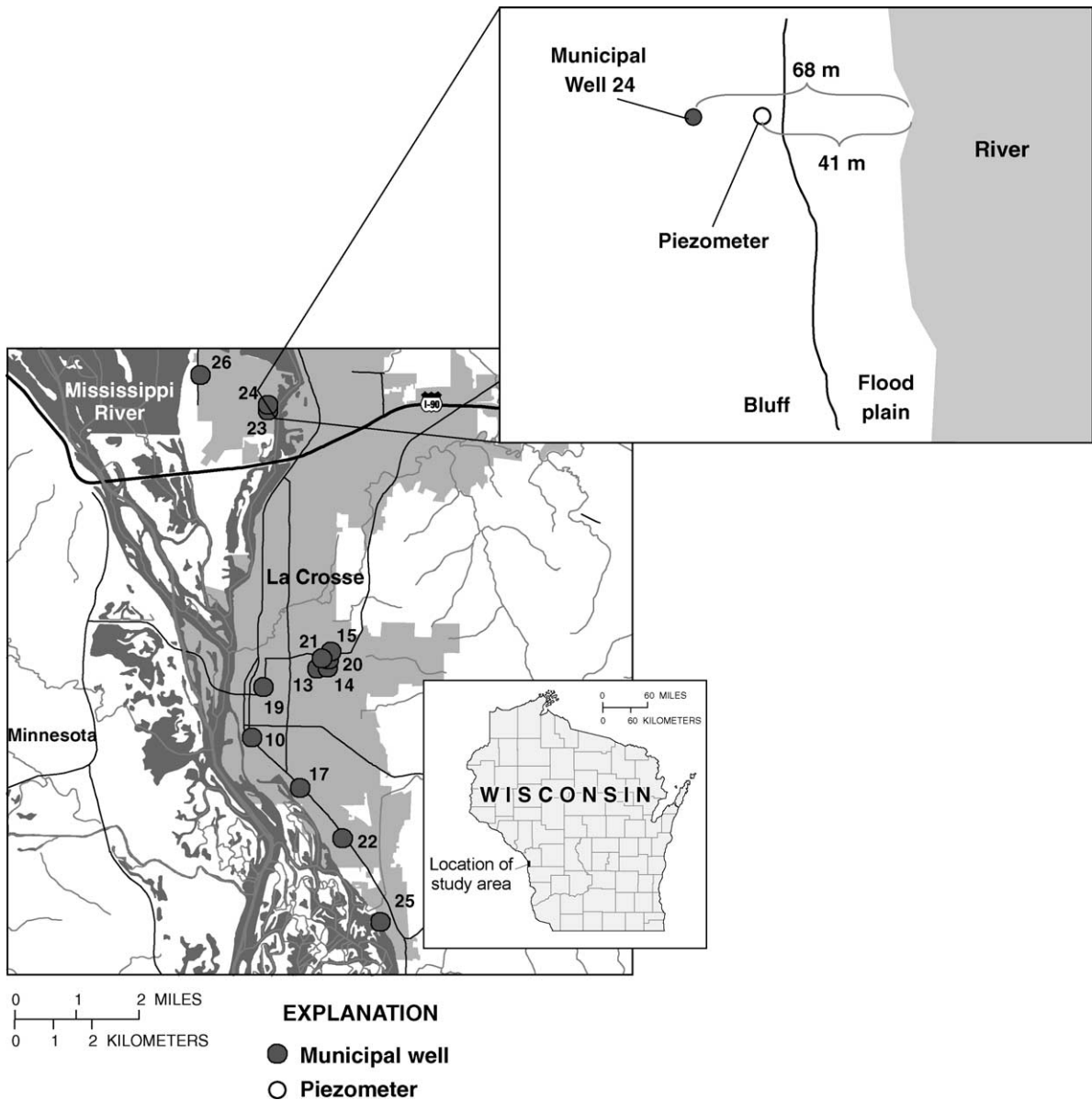

Fig. 1. Site map showing area hydrography and locations of municipal wells.

Table 1
Construction and pumping data for La Crosse, Wisconsin, municipal well

Well no.	Construction date	Well depth (m)	Well casing depth (m)	Static water level (m)	Study period[a] average pumping rate (m³/s)	Study period[a] high/low avg. monthly pumping rate (m³/s)
10	1936	45.7	15.2	11.6	0.02	0.04/0.0
13	1952	46.0	30.8	11.0	0.07	0.17/0.0
14	1952	44.2	29.0	4.3	0.05	0.07/0.01
15	1952	45.7	30.5	NA	0.04	0.09/0.01
17	1955	48.8	33.5	7.9	0.05	0.09/0.003
19	1964	49.7	34.4	14.3	0.06	0.16/0.02
20	1968	48.8	32.9	14.0	0.05	0.12/0.02
21	1968	48.8	32.9	14.0	0.05	0.13/0.02
22	1972	45.4	29.6	9.4	0.06	0.11/0.02
23	1976	30.5	19.2	4.9	0.05	0.06/0.03
24	1980	33.2	21.6	7.6	0.05	0.06/0.02
25	1984	29.9	19.2	3.0	0.05	0.06/0.02
26	1988	28.3	19.2	5.5	0.06	0.20/0.0

[a] Measured during the study period, March 2001–September 2002.

bedrock. The sediments are thickest in the Mississippi River valley; they are thin or absent in the highlands outside the river valleys. Two bedrock aquifers underlie the sediments and are separated by a shale confining unit (the Eau Claire Formation), which is partially absent in the La Crosse area (Chapel et al., 2003b). The upper bedrock aquifer is made up of Paleozoic sandstone and dolomite. The lower bedrock aquifer consists of a relatively thick Cambrian sandstone unit (Young, 1992). The fluvial sediments have high conductivity estimated to be on the order of tens to hundreds of meters per day; the bedrock aquifers, on the other hand, have hydraulic conductivity values on the order of 3–4 m/d (Hunt et al., 2003).

3. Methods

Groundwater and surface water were monitored for water level, temperature, and stable hydrogen and oxygen isotopic composition. Unfiltered water samples were collected from the municipal well discharge via the sampling port prior to chlorination and analyzed for stable hydrogen and oxygen isotopic composition. These samples were collected unfiltered in clean, dry, 20-ml glass vials and sealed with a Polyseal cap. Paraffin film was used to secure the cap after sample collection and prevent evaporation that can alter $^{18}O/^{16}O$ and $^{2}H/^{1}H$ ratios. In November 2001,

a piezometer was installed on land between the surface water source and Well 24 (Fig. 1) to characterize groundwater recharged from the surface water. The piezometer was installed using hydraulic push equipment and consisted of a 2.5-cm diameter PVC well riser and a 0.3-m PVC well screen placed approximately 12 m below land surface. The screen was placed approximately 7 m below the water table to ensure that local terrestrial recharge was not included in the groundwater sampling. Samples for isotopic composition were collected from the piezometer using a peristaltic or check-valve pump. Groundwater level and temperature data from the piezometer were collected hourly by a pressure transducer/temperature datalogger (Solinst Leveloggers) placed in the screened interval. Surface water elevation data were obtained from the US Corps of Engineers. Similar to groundwater samples, sampling of surface water for isotopic composition used unfiltered water in clean, dry, 20-ml glass vials sealed with a Polyseal cap and paraffin film. The samples were collected from approximately 10 cm below the water surface by peristaltic pump or as a grab sample. Hourly surface water temperature data were collected just above the sediment–water interface at a shallow water location adjacent to the piezometer using a self-contained temperature datalogger (Hobo Tidbit).

Initial sampling for stable hydrogen and oxygen isotopic composition of 4 of the 13 wells and a surface

water site was conducted monthly from March 2001–February 2002. Based upon the results of this preliminary sampling, isotope sampling was extended to include the piezometer, one additional surface water site near the piezometer, and the entire municipal well system. These additional samples were collected periodically during November 2001–September 2002.

Oxygen isotope ratios were measured using CO_2–H_2O equilibration (Epstein and Mayeda, 1953). Stable hydrogen isotope ratios were determined by H_2–H_2O equilibration (Coplen et al., 1991). Oxygen and hydrogen isotopic results are reported in per mill (‰) relative to VSMOW (Vienna Standard Mean Ocean Water) and normalized (Coplen, 1994) on scales such that the oxygen and hydrogen isotopic values of SLAP (Standard Light Antarctic Precipitation) are -55.5 and $-428‰$, respectively. Analytical error (2σ) is estimated at ±0.2 and $\pm2.0‰$ for $\delta^{18}O$ and δ^2H, respectively.

Water samples were collected for sulfur hexafluoride (SF_6) analysis from municipal wells (2 samplings) and the piezometer (1 sampling) using procedures outlined by the USGS (2003a). Water samples collected from the piezometer also were analyzed for chlorofluorocarbons (CFCs) and tritium–helium (^3H–^3He) to determine an age of the water. Water samples from the surface water source were also analyzed for CFCs (1 sampling). CFC samples were flame sealed in borosilicate-glass ampules using equipment and procedures described by Busenberg and Plummer (1992). Sampling protocol for ^3H–^3He are detailed by USGS (2003b). Dissolved gas samples were used to estimate recharge temperature. All age-dating and dissolved gas samples from locations other than municipal wells were collected using a stainless steel and Teflon bladder pump with sample lines constructed of copper and Viton (trademark).

SF_6 and CFC samples were analyzed at the USGS CFC laboratory in Reston, Virginia. SF_6 concentrations were measured by gas chromatography using an electron capture detector (Busenberg and Plummer, 2000). CFC concentrations were determined in the laboratory using a purge-and-trap gas chromatographic procedure and an electron capture detector. Details of the analytical procedure for CFCs are given by Busenberg and Plummer (1992). CFC samples were collected in sets of five; replicate samples were analyzed for all sites sampled and the average value was used. ^3H–^3He samples were collected in duplicate

and were analyzed using a mass spectrometer (Ludin et al., 1997) at the Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY.

A well sample (from Well 24) that tested positive for HAV by reverse transcription polymerase chain reaction (RT-PCR) was analyzed by cell culture to determine HAV infectivity (Borchardt et al., 2004). This result is useful for determining water age because infectious viruses in the subsurface represent travel times on the order of 1 year or less (Yates et al., 1985; Yates and Yates, 1988; DeBorde et al., 1998). Negative control and positive controls were cultured and processed simultaneously with the samples. Positive cultures were further confirmed to contain HAV by RT-PCR and Southern hybridization. The reader is referred to Borchardt et al. (2004) for a detailed description of the culture methods used.

Time of travel evaluations through groundwater-flow modeling used the model described by Chapel et al. (2003a). The groundwater-flow modeling code was MODFLOW (McDonald and Harbaugh, 1988), and the advective particle tracking code was MOD-PATH (Pollock, 1994).

4. Results and discussion

4.1. Identifying surface water in municipal wells

Kendall and Coplen (2000) published $\delta^{18}O$ and δ^2H of river samples collected at selected US Geological Survey water-quality monitoring sites; this dataset used river water to provide baseline data on the spatial distribution of $\delta^{18}O$ and δ^2H of meteoric waters for local hydrologic investigations and regional paleoclimate assessments (Kendall and Coplen, 2001). Surface water analyses were available for a site located approximately 16 miles north of La Crosse at the Black River at Galesville, Wisconsin (Coplen and Kendall, 2000). For this study, the Black River surface water site was used to construct a local meteoric water line (LMWL, Fig. 2a) instead of collecting precipitation or surface water sampled during this study. Surface water sampled downstream of the Mississippi River impoundment Pool 7 had stable isotope ratios of oxygen that showed peak-to-peak seasonal variation greater than 4‰ in 2001 and 2002 (Fig. 2; Appendix A) and annual mean $\delta^{18}O$
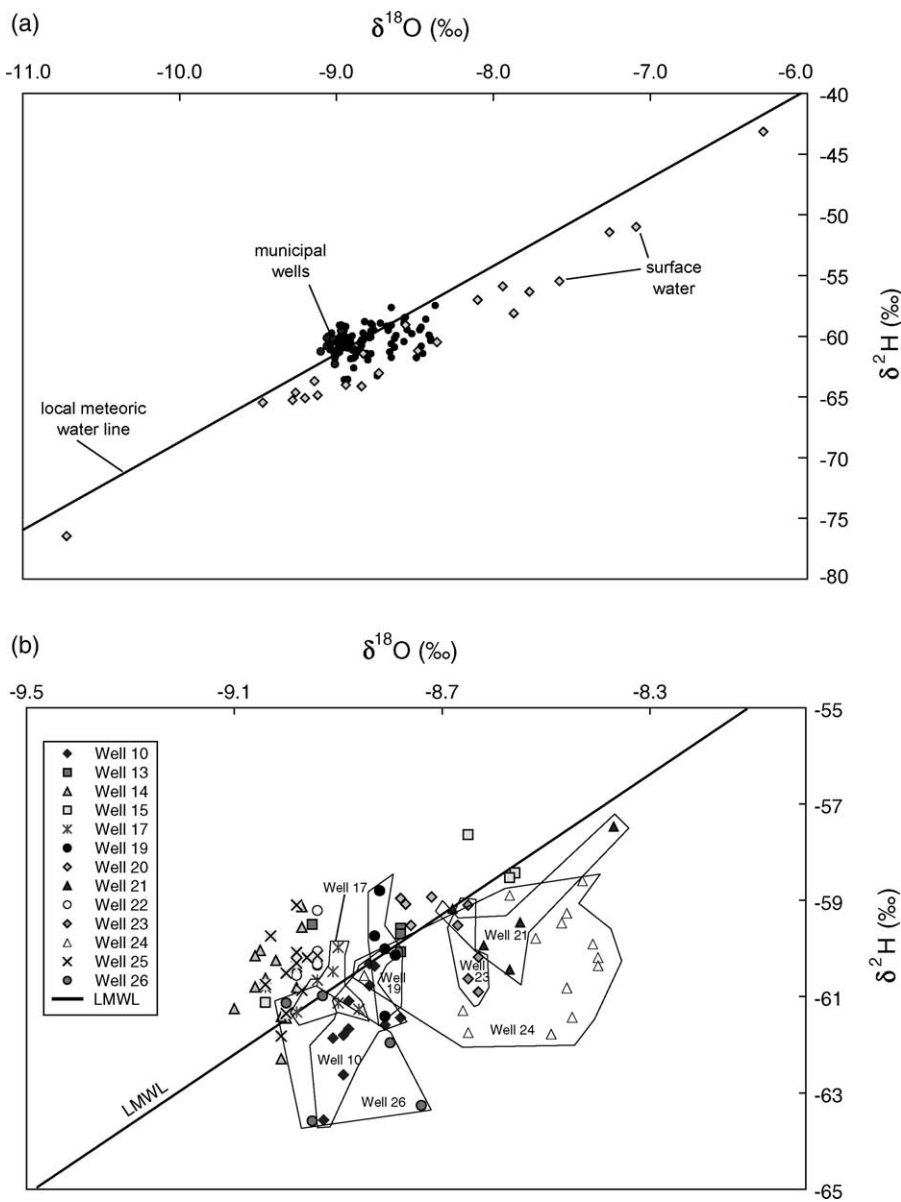
Fig. 2. Plot of $\delta^{18}O$ versus δ^2H of samples collected from the La Crosse Municipal wells and surface water during this study. The local terrestrial water line was determined using isotopic data from the Black River at Galesville, Wisconsin (Coplen and Kendall, 2000). Municipal wells with appreciable surface water contributions are grouped in (b).

composition ($-8.5‰$) near that of groundwater. The isotopic compositions show effects of evaporation in the pool and lie to the right of the LMWL on a plot of δ^2H versus $\delta^{18}O$ (Fig. 2a).

Using the LMWL calculated by the Galesville data, the municipal well data can be characterized into

two qualitative groups: one group (6 of 13 wells) that plots more tightly near or to the left-hand side of the LMWL, and another group (7 of 13 wells) that resides to the right of the LMWL (Fig. 2b). The first group is typical of meteoric groundwater recharge. Groundwater isotopic compositions are characterized by $\delta^{18}O$

values around -8.5‰ in the lower elevations (i.e. groundwater recharged on islands in the river) to around -8.8 to -9.0‰ for water recharged on the valley bluffs. The second group shows temporal variability in isotopic composition and effects of evaporative isotopic fractionation, indicating the presence of surface water. The 7 wells that show the influence of surface water illustrate an important point—a single sampling event may not identify the surface water source because the isotopic composition of groundwater is between the extremes of the surface water end members. That is, a single sample from a well may have surface water present that has the same composition as the groundwater thus be indistinguishable. Although analytic error bars are not included in Fig. 2 for clarity, it should also be noted that the groups are less sharply defined than shown in the figure.

The municipal well-water isotopic results also suggest that sampling municipal wells over time can qualitatively identify the presence of surface water even without detailed knowledge of the LMWL. This approach is of interest because determining a LMWL is often logistically difficult and expensive due to the extensive sampling of precipitation required, which varies substantially in isotopic composition over time. Thus, a large data set of precipitation samples is needed to improve define the meteoric water line (Clark and Fritz, 1997). When examining municipal wells with six or more samples collected over the study period, the median and standard deviation of the time series form a direct relation (Fig. 3), because the isotopic composition of groundwater has no measurable evaporation and is less variable than surface water (measured range of 23 surface water samples $=4.4$‰, standard deviation $=1.0$‰; Appendix A). The pumping history of the well of interest, and surrounding wells, needs also to be known, however. For example, Well 14 has a slightly larger standard deviation than what would have been expected given the median isotopic composition (Fig. 3). The well is located in a group of five closely spaced wells (Fig. 1) that interfere with each other (Chapel et al., 2003a) and have adjacent capture zones. One nearby well (Well 13) was being pumped at rates ranging from 0 to over 122 million gallons per month (0.17 m^3/s, Table 1) during the study period (Berendes, 2002). Therefore, the capture zone of Well 14 was likely changing over time, resulting in more
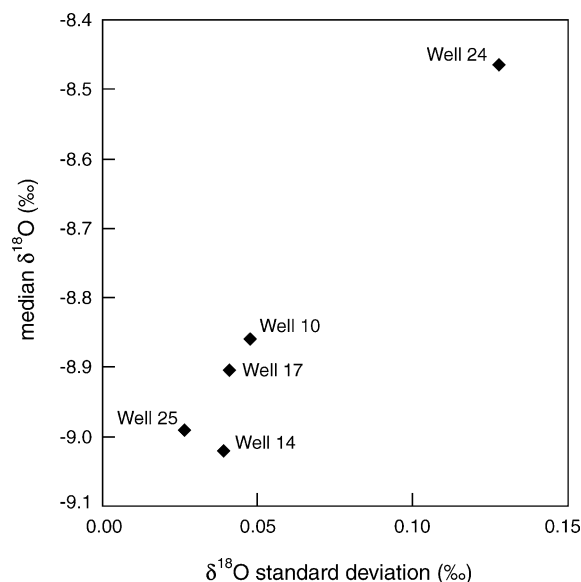

Fig. 3. Plot of median $\delta^{18}O$ versus standard deviation of all wells with more than 6 sampling events. For reference, $\delta^{18}O$ standard deviation of 23 surface water samples was equal to 1.0‰.

variation than would have been expected given its substantial groundwater signal.

The most comprehensive dataset is from Well 24 and an associated Piezometer (Fig. 1). These data provide an opportunity to assess if quantitative estimates of surface water can be obtained from isotope-ratio mass-balance techniques. Well 24 is relatively well suited for such an approach as the pumping regime was relatively constant during the study period (Berendes, 2002), and the variation in isotopic composition of surface water with season was substantial (Fig. 2b; Appendix A). The study funding was not sufficient to install and sample piezometers at all municipal well locations; thus, the feasibility of the approach is demonstrated using Well 24 site data.

Using the approach of Maloszewski et al. (1990), the amount of surface water in the well can be estimated using a simple binary mixing calculation and annual average values of well discharge, groundwater, and river isotopic composition (Table 2). In addition, the mass-balance approach can be extended to use the representative value of groundwater isotopic composition and the measured extremes of surface water composition (Table 2). Unlike the use of annual average isotope-ratio values, the mass balance in the latter approach was calculated using extreme

Table 2
Binary mixing calculations of percent surface water in Well 24

Well 24 summer 2001 maximum		Well 24 winter 2001 minimum	
−8.53	Composition groundwater	−8.53	Composition groundwater
−7.09	Composition surface water	−10.72	Composition surface water
91%	%Groundwater	86%	%Groundwater
−8.40	Calculated well value	−8.85	Calculated well value
−8.40	Measured well value 2/26/2002	−8.85	Measured well value 6/25/2001

Using Maloszewki et al. (1990) method of isotope averages

Mean 3/01–2/02, $\delta^{18}O$ well	Mean 3/01–2/02, $\delta^{18}O$ river	Assumed, $\delta^{18}O$ GW
−8.52	−8.46	−8.53
%Groundwater=86%		

values of the isotopic composition of surface water as they can be identified in the groundwater time series shown in Fig. 4. This method is attractive as it is less sensitive to uncertainties in groundwater isotopic composition than annual average isotopic calculations, an important consideration at Well 24 as surface water contributions are a minority component in the well discharge. The result must still be considered approximate, however, as the mass-balance calculation assumes that surface water will arrive at the well at the same composition at which it left the river (i.e. piston flow); this is not the case as shown by the reduced variation in the piezometer located between the river and Well 24 (Fig. 4). It should also be noted that the fraction of surface water could be calculated for each monthly sample if the river water isotopic composition and the corresponding lag of river water arrival in the well were known perfectly for each sample. However, the flow in the subsurface is appreciably confounded by river stage transience (Fig. 4) such that the lags for intermediate surface water compositions are not well constrained.
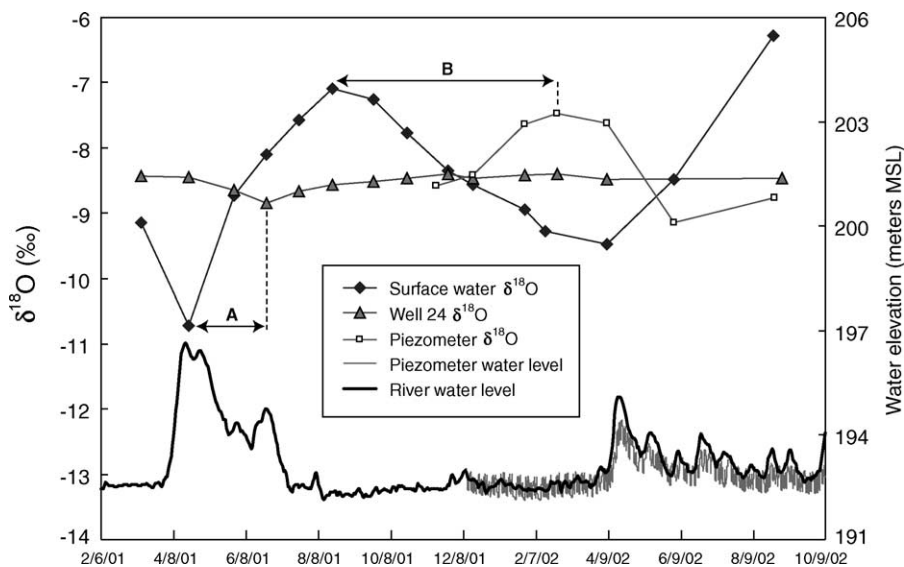
Fig. 4. Plot of the $\delta^{18}O$ time series from the municipal well, river, and piezometer installed between the river and the municipal well. Two periods are labeled in the figure: A, time required for floodwater depleted in ^{18}O to appear at the municipal well; B, time for surface water enriched in ^{18}O to appear at piezometer. River stages estimated from US Army Corps of Engineers' Pool 7 tailwater elevation data are also shown.

The simple mass balance results suggest that 9–14% of Well 24's discharge was captured from the river; this compares well to an estimated 14% (USGS, unpublished data) calculated using the numerical groundwater-flow model of Chapel et al. (2003a). It should be noted that the uncertainty on the oxygen-isotope ratio measurements is 0.07‰ or more; thus, it may be fortuitous that the agreement with the binary mixing model is as good as shown. The small range of surface water contribution for Well 24 (Table 2) is consistent with a regional stress from a constantly pumping high capacity well. That is, the stress on the system is sufficiently large to overcome the effects of surface water transience and other potential confounding factors. Moreover, Well 24 is the ultimate sink in the local site area. Thus, small variations in flowpath to Well 24 are not important; all water within the zone of contribution eventually makes it to the well.

It is important to note that although the surface water contribution to Well 24 was relatively small, it was sufficient to deliver infectious HAV particles at a concentration that could be detected by cell culture (see results below). Except for the river, no other fecal source containing HAV was present in the Well 24 capture zone. The HAV concentration was not measured, but given the limit of detection of the cell culture methods the ambient HAV concentration in the well water would have presented a health risk if the water is not chlorinated.

4.2. Estimating time of travel of surface water to the well

Use of stable hydrogen and oxygen isotope ratios. As noted by Stichler and Moser (1979), seasonal variation in the surface water system and the tracing abilities of stable hydrogen and oxygen isotope ratios of water allow surface water to be tracked into the subsurface by looking at the data as a time series (as shown in Fig. 4). A seasonal cycle is observed in the data that includes water depleted in ^{18}O and ^{2}H from snowmelt in the winter and early spring and water that is enriched in ^{18}O and ^{2}H during the late summer and early fall. The stable hydrogen and oxygen isotopic composition of groundwater collected from the municipal well and the piezometer also follow this cycle, though they are lagged. Moreover, the temporal

signal is muted in the municipal well as a result of mixing with terrestrial recharge; the range observed in the piezometer data is more similar to that seen in the surface water, indicating that it is intercepting groundwater derived from the surface water (Fig. 4).

The travel time of surface water to the municipal well is shorter during high water conditions, as demonstrated by the surface water (depleted in ^{18}O and ^{2}H) of the April 2001 flood appearing at the municipal well approximately 2 ± 1 months later (label 'A' in Fig. 4). The floodwater signature was sufficient to cause a measurable change in the isotopic composition of the municipal well discharge. The floodwater not only subjects the aquifer to higher gradients, but also 'short circuits' distance that is traveled because the increased elevation of floodwater inundates the floodplain that separates the river from the well during non-flood conditions. Using the 2001 flood stage, the distance between infiltrating surface water and the municipal well decreased by about 50%.

Using the time lag measured between the surface water most enriched in ^{18}O and ^{2}H (summer) and the groundwater most enriched in ^{18}O and ^{2}H sampled from the piezometer, the estimated non-flood time of travel to the piezometer is approximately 6 ± 1 months (Fig. 4; duration labeled 'B'). The piezometer is located approximately two-thirds of the distance between the municipal well and the surface water. Using a simple linear scaling, estimated travel time for surface water to reach the municipal well would be on order of 9 months. Because the horizontal hydraulic gradient and associated velocities will increase near the pumping well, the actual time of travel to the well would be expected to be less than 9 months. Non-flood conditions are characterized by changes in isotopic conditions that affect a smaller part of the municipal well discharge (that is, a smaller portion of the well's zone of contribution is covered by surface water); thus, surface water contributions can be observed isotopically in the piezometer, but they are not sufficiently distinct to be observed in the municipal well (Fig. 4). It should be noted that the gradient between the river and the well is stable due to the relatively stable river levels (Fig. 4) and the constant pumping schedule maintained during this period (Berendes, 2002). Because this period of time encompassed the conditions of smallest hydraulic

gradient, it can be considered among the longest expected travel times.

It is conceivable that the isotopic time series reflects seasonal changes in isotopic composition that occurred in previous years (if travel times to the monitoring points were more than 1 year). A longer time series of groundwater and surface water might allow the use of the amplitude of the seasonal signal to distinguish between years. Alternatively, higher spatial resolution along the transect between the well and the river, such as used by Sheets et al. (2002), would also help distinguish between a single and multiple-year seasonal signal (Coplen et al., 1999). Neither approach was available for this study. For this work, groundwater velocities calculated using other methods and a positive result for virus culturing (see below) excluded travel times longer than 1 year.

Age dating using traditional tracers. Traditional tracers such as CFCs and SF_6 were not useful in this study (Table 3) primarily due to degradation of the tracer signal in the groundwater (CFCs) and contamination from additional non-atmospheric sources (SF_6). CFC concentrations measured in samples from the surface water source (Table 3) essentially represented water at equilibrium with atmospheric concentrations (CFC-12 was slightly contaminated, but CFC-11 and CFC-113 were at equilibrium). Concentrations of all CFCs in groundwater samples appear to be degraded from anaerobic conditions (Busenberg and Plummer, 1992; Oster et al., 1996)—an artifact noted in lake-derived groundwater recharge in northern Wisconsin (USGS, unpublished data).

Thus, the CFC degradation is likely a result of exposure to anoxic zones in river sediments as the surface water infiltrates the aquifer.

The contamination of SF_6 has been noted elsewhere in Wisconsin (USGS, unpublished data), though the source of the contamination (natural versus anthropogenic) is not well understood. Busenberg and Plummer (2000) indicated that SF_6 concentrations in groundwater samples that exceeded the mean North American SF_6 air curve by more than 10% probably represent pollution events near the sampling location. In addition, Paleozoic dolomitic rock might also be a source of contamination (Busenberg and Plummer, 2000, Table 1). This rock is part of the suite of bedrock in the La Crosse area. The age-dating artifacts notwithstanding, these methods are best suited for measuring groundwater ages greater than 1 year, which is greater than the survival time of some pathogen contaminants such as viruses.

One water sample for tritium–helium (^3H–^3He) age dating was collected from a piezometer; if groundwater flow occurred without mixing (e.g. piston flow), the calculated age of the groundwater would be 7.4 years (Table 3). However, this groundwater sampled from the piezometer likely contains water with a range of different ages (discussed below), thus deviates from piston flow. Because the quantity and ages of the water sampled from the piezometer are poorly constrained, age dating of this sample is inherently uncertain.

HAV cell culture results. The Well 24 sample that tested positive for HAV by RT-PCR was also positive for infectious HAV by cell culture (Borchardt et al., 2004).

Table 3
Results of age dating using CFCs, SF_6, and $^3H/^3He$, La Crosse, Wisconsin

Site	Calculated CFC atmospheric partial pressure, pptv			CFC-modeled recharge age	Calculated SF_6 partial pressure, pptv	SF_6-modeled recharge age	Tritium (^3H) concentration, TU	$^3He_{trit}$ concentration, TU	Tritium–He modeled recharge age[a]
	CFC-11	CFC-12	CFC-113						
Well 24	NS	NS	NS	NS	5.6 (Mar 2001), 6.0 (Apr 2001)	Contam., Contam.	NS	NS	NS
Piezo-meter	50.4	132.4	18.3	CFCs degraded	7.8 (Nov 2001)	Contam.	10.99	5.30	7.4 years
Surface water source	286.5	621.0	88.9	Modern (2001)	NS	NS	NS	NS	NS

NS, not sampled.
[a] Corrected for terrigenic He; reported age assumes piston flow in the subsurface.

Because enteric viruses in groundwater tend to become completely inactivated and lose their infectivity within 1 year, this finding suggests that the virus and associated water had a travel time from the source to the well of less than 1 year. Unlike other wells in the La Crosse system near sanitary sewer lines, Well 24 does not have any other known source of HAV other than the river. Thus, we conclude that Well 24 does have a component of water with an associated travel time of less than 1 year.

Age dating using a temperature time series. The temperature signal of the surface water source can often be tracked in the groundwater system, especially where production wells induce infiltration. Using the simplest analysis, inflection points in a time series of the temperature in the groundwater system represent the seasonal changes of infiltrating water. This method could not be applied to the flood event of April 2001 as the surface water temperature probe and piezometer were installed in November 2001. However, surface water and groundwater temperatures were monitored before, during, and after the high-water conditions of 2002 (Fig. 5). The surface water temperatures started to increase on February 18, 2002; the monitoring-well temperature low occurred around May 31, 2002, after which groundwater temperatures increased. However,

surface water temperatures did not exceed the lowest groundwater temperature (8.4 °C) until April 10, 2002. If advection dominates, infiltrating surface water colder than 8.4 °C cannot be responsible for the post-June 4th temperature increase in the groundwater. Therefore, April 10, 2002 was used to calculate the warm-water arrival. Assuming simple advective transport of heat (i.e. the heat travels at the same rate as the groundwater), the travel time from the river to the piezometer during the larger gradients of the high-water conditions is on the order of 2 months (51 days). Similar to the isotopic time series, the travel to the piezometer represents approximately two-thirds the distance to the municipal well; therefore, the time to the municipal well is estimated to be approximately 3 months. The 2002 temperature estimate is about 1 month longer than the isotopic time series estimated for the April 2001 flood, but the 2001 flood was a record high-water event (196.65 m above MSL) and the 2002 flood was not as extreme (195.11 m above MSL). However, the agreement between these two travel time estimates is quite good, and provides additional confidence in the estimates.

The non-flood conditions have a more subtle temperature regime. Surface water temperatures
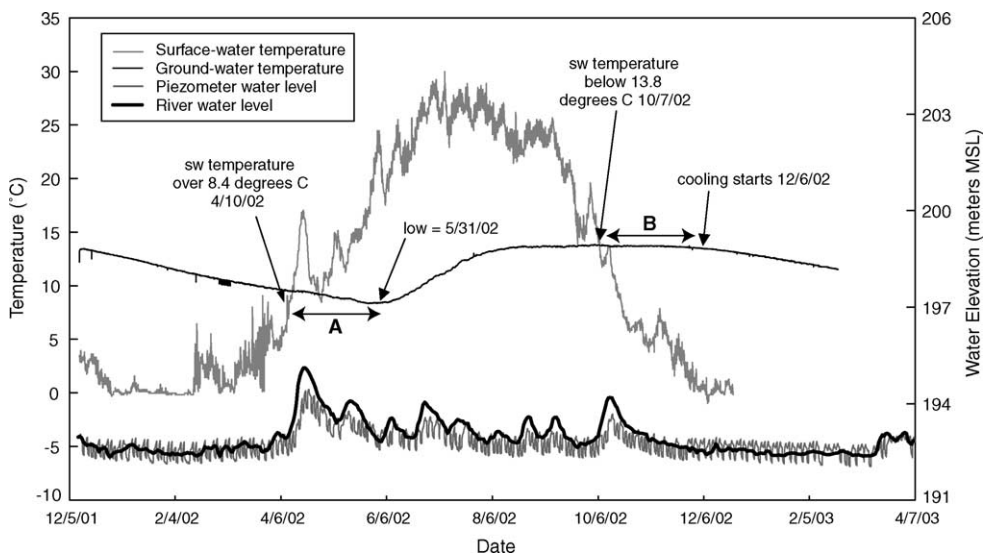

Fig. 5. Plot of temperature versus time in the river and at a piezometer located between the municipal well and the river. Two periods are labeled in the figure: A, time required for warmer surface water to appear at the piezometer; B, time for cooled surface water to appear at piezometer. US Army Corps of Engineers' Pool 7 tailwater elevation and piezometer groundwater elevation data are also shown.

climb relatively steadily until around June 30, 2002, then fluctuated between 22 and 30 °C until mid-September (77 days). The signal in the groundwater system was more muted and did not have a sharp inflection point at higher temperatures. After the May 31, 2002, low groundwater temperatures climbed until mid-August, and then remained relatively constant (around 13.5–13.8 °C) until cooling in December 2002. Similar to the arrival of warmer water discussed above, the surface water has to be below 13.5 °C (assuming only advective transport of heat) in order for cooling at the piezometer to occur; this occurred on October 7, 2002. Using October 7th, the length of time for cooler water to arrive at the piezometer is on the order of 2 months (60 days), and is on the order of 3 months for the municipal well. This yields a non-flood travel time that is comparable to the 2002 flood travel time and appreciably shorter than the 2001 non-flood times calculated by the isotope time series (about 9 months). This could be a result of a series of relatively high river stages observed in 2002 that did not occur in 2001 (Fig. 4). Higher river stages will increase the hydraulic gradient and advective transport between the river and the piezometer (Fig. 5). Regardless, the temperature time-series estimates being on the order of months is consistent with the isotopic time series.

This temperature analysis uses the following simplifying assumptions: (1) heat moves through the subsurface primarily through groundwater advection, (2) water moves through the aquifer at the same rate as heat. Although aquifer sediments can also conduct heat, advection is expected to dominate heat transport in sediments with high hydraulic conductivity and appreciable hydraulic gradients such as are found in high-capacity wellfields. The second assumption is not as easily addressed; the fact that the range of temperature fluctuations in the piezometer is smaller than those in the surface water demonstrates that heat transport is not fully conservative. However, surface water heat signals were found over 43 times the distance observed at Well 24 (albeit, with a smaller range of temperature fluctuation and longer time lag) at another location in La Crosse, Wisconsin (USGS, unpublished data). Thus, heat transport can be considered sufficiently conservative to investigate how reasonable a sub-year travel-time estimate is at the Well 24 site.

Similar to the isotopic time series analysis, the temperature time series may also reflect seasonality that occurred in previous years. Unlike stable isotope ratios, however, temperature is not conserved; thus, the amplitude of the annual temperature deflection decreases over time and distance traveled. In some settings, the signal decline could complicate the use of longer time-series data or higher spatial resolution data collected at distances far from the surface water source.

Evaluation of age using a groundwater-flow model. Chapel et al. (2003a) used a steady-state local numerical groundwater-flow model (Fig. 6) to delineate 5-year capture zones for the City of La Crosse municipal wells. The model consisted of three layers that encompassed the basal bedrock aquifer and the overlying sand-and-gravel aquifer. The municipal wells were located in layer 1, and simulated using the average annual pumping rate. The river was simulated using the MODFLOW river package (head dependent flux boundary) and was assigned to layer 1 only. Values for parameters used in the model are a leakance of the river sediments equal to 1 m/d/m, a hydraulic conductivity of alluvial sediments equal to 128 m/d (420 ft/d), and an aquifer porosity of 0.25. The local model was extracted from a regional groundwater-flow model for La Crosse County (Hunt et al., 2003) and refined. Model refinement was limited to a smaller grid size; thus, additional detail to the surface water feature and model calibration was not performed (Chapel et al., 2003a). As a result of this limited refinement, the model retains some of the coarse river discretization of the regional model. However, the model is well suited for evaluating how reasonable a sub-year travel time estimate is for this system.

Hypothetical particles were added to the river (top of layer 1) and tracked to the municipal well (Fig. 7); these results demonstrated that travel times to the municipal well are around 4.5 months using the unmodified local model. Moreover, travel times to the well were less than 1 year for ranges of model parameters that could be considered extreme for this system (river leakance = 1 order of magnitude lower, hydraulic conductivity = 50% lower, and porosity = 0.4). Thus, we conclude that the sub-year non-flood travel times estimated by the isotopic data and temperature are reasonable for this system.
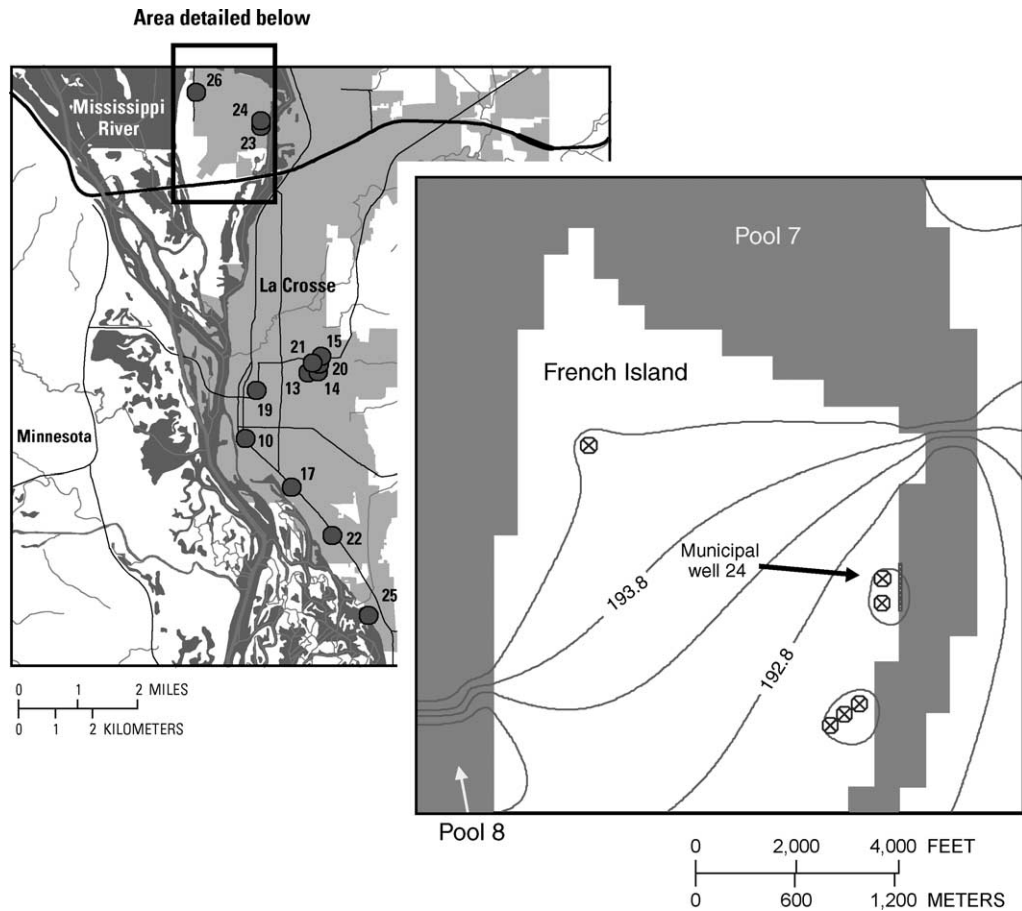
Fig. 6. Map showing the groundwater model extent of wellhead protection model of Chapel et al. (2003a). Contour lines represent simulated groundwater head; contour interval is 0.5 m.

4.3. Implications for water supply investigations and vulnerability

Surface water can contain many constituents unsuitable for drinking water such as human pathogenic viruses, endocrine disrupters, and other anthropogenic chemicals (Kolpin et al., 2002). Characterizing the amount of surface water in a drinking water well facilitates an assessment of a well's vulnerability, and is critical for maintaining a safe water supply. For some microbiological pathogens (e.g. viruses), time of travel is paramount to assessing the susceptibility of the well. Therefore, methods are needed that are able to discern the presence of very recent water. Moreover, information

about the associated pathways of transport (overland versus subsurface) is required in order to develop a conceptual model of how surface water travels through the aquifer, as well as to develop a pumping schedule that can best protect the quality of the water pumped.

Similar to river-wellfield lag times reported by others (e.g. Maloszewski et al., 1990; Hötzl et al., 1989; Sheets et al., 2002), four methods used to assess the travel time from the river to municipal Well 24 are less than 1 year (on the order of 2–9 months). If piston-flow is assumed for groundwater flow, ^3H–^3He dating estimates approximately 11–12 years (Table 4). Although the representativeness and repeatability of the ^3H–^3He age was not evaluated due to high analytical cost, recent work in the literature
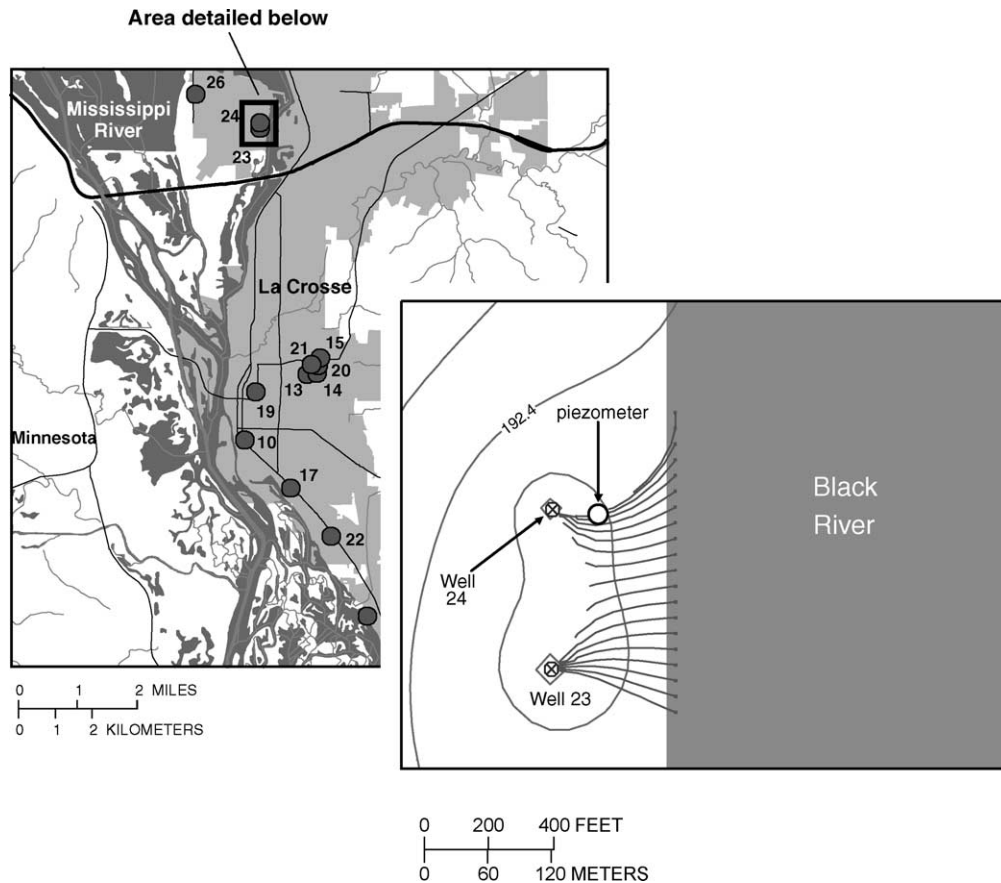
Fig. 7. Map showing modeled area near the municipal well and river; particle-tracking results for time=135 days are also shown. Contour interval is 0.2 m.

suggests that groundwater age determined from sampling wells may deviate from ages calculated using a simple piston-flow model (e.g. Goode, 1996; Bethke and Johnson, 2002a,b; Weissmann et al., 2002). That is, rather than the screened interval sampling a water with a single homogeneous age, the sample is a complex mixture of water of various ages, comparable to water samples analyzed for solute concentrations. The deviation from piston flow has been related to the degree of aquifer heterogeneity, including heterogeneity caused by the presence of confining layers (Bethke and Johnson, 2002b), large hydraulic conductivity contrasts within a heterogeneous aquifer (for example, 5 orders of magnitude

Table 4
Summary of time of travel estimates (river to municipal Well 24)

	Isotope time series	^3H–^3He age dating	HAV cell culture	Temperature time series	Groundwater model
Flood conditions	2 Months (2001)	NA	NA	3 Months (2002)	NA
Non-flood conditions	9 Months (2001)	11–12 Years	<1 Year	3 Months (2002)	4.5 Months

NA, not analyzed.

in Fogg et al., 1999; Weissmann et al., 2002), or large difference in types of source water (e.g. lake recharge versus terrestrial recharge reported by Pint et al., 2003). Of these possible mechanisms for causing deviation from piston flow, aquifer heterogeneity and transience appears most likely given the fluvial sediments of the Mississippi River valley and the proximity of the river. Additional support for the shorter travel times calculated by the isotope/temperature/model approaches is observed in the literature; Sheets et al. (2002) used a transect of piezometers between a river and a municipal well to quantify sub-year travel times in a setting similar to the La Crosse study site.

If mixing artifacts are the underlying reason for the conflicting travel-time estimates, why was not the isotopic time series affected to the same degree as the tritium–helium sample? The range of $\delta^{18}O$ variation in the water sample from the piezometer (with a sampling point 7 m below the water table) was smaller than that of the surface water source (Fig. 4), indicating that a mixture of surface water age was sampled. The effect of the mixing may not have been as discernible because the old water (having an appreciably different age) was derived from the same range of possible surface water isotopic compositions; thus, the old water would have expected range of isotopic composition similar to that of the new water.

Time series of stable hydrogen and oxygen isotope ratios in well-water discharge can be an effective tool—not only can the amount of surface water in the well discharge be characterized, information about travel times can be gained as well. There are, however, some considerations for successful application. First, the end-member isotopic compositions and their variability should be properly characterized. In our example, we had available the results of a national database that guide the sampling frequency and total number of samples for the study. Second, the sampling plan is most effective if it has both the insight of fixed interval sampling and the flexibility of event sampling that can be performed to capture the isotopic composition of hydrologically important events. Thirdly, while the flood event was easily seen in the isotopic composition of the pumping well discharge, the non-flood time of travel was better observed using a piezometer installed between the river and the municipal well. The use of a piezometer simplifies

the interpretation as it is sampling a single flow direction, unlike the municipal well itself, which is dominated by radial flow. Finally, the use of isotopic abundances alone is often non-unique. At the site discussed here, the stable hydrogen and oxygen isotopic compositions were complimented with physical measurements (groundwater level, river stage, surface water, and groundwater temperature), as well as a site-specific groundwater-flow model (Chapel et al., 2003a). While using one method, such as a stable isotope time series, can give insight into the vulnerability of the well, the use of multiple methods is critical for ensuring this insight is representative of the system.

5. Conclusions

There are four primary conclusions of this work.

- The use of the stable hydrogen and oxygen isotopic composition of water is an effective tool for describing the influence of surface water on municipal well supplies. In the City of La Crosse municipal well network, 7 of the 13 wells are thought to have appreciable amounts of surface water contributing to the well water. Multiple samples over time may be required in order to identify surface water effects because the isotopic composition of ambient groundwater is intermediate to the end members of the surface water composition. Correct application of this method will depend on properly characterizing the source isotopic composition and variability.
- In addition to identifying the source of water, analyses of stable hydrogen and oxygen isotope ratios of water over time can yield insight into the time of travel from a surface water source to the well. In the example shown here, surface water required approximately 2–3 months during flood conditions and about 9 months during non-flood conditions to reach the municipal well. The flood events reduce the travel time by overland inundation (decreasing the distance) and by increasing the gradient to the well. While the flood event was recognized by its isotopic signature in the pumping well discharge, the non-flood time of travel was better characterized using a piezometer installed between the river and the municipal well.

- Traditional age tracers (SF$_6$, CFC) were not useful at this site because of contamination (SF$_6$) and degradation (CFC) of the tracers. A tritium–helium (^{3}H–^{3}He) age in one sample collected from a piezometer was on the order of 7–8 years if simple piston flow is assumed, but other methods estimated travel times of less than 1 year. This discrepancy suggests that there are age-mass issues at this site similar to those reported by researchers in other hydrogeologic settings. Regardless, it is uncertain if common age dating techniques would be able to accurately discern travel times on the order of 1 year or less—the timeframe needed to assess a well's vulnerability to pathogens such as viruses.
- Groundwater temperature variations in a piezometer between the municipal well and the surface water source yield similar times of travel as those estimated using isotopic time series. A local groundwater-flow model also estimated a travel time of less than 1 year, even for extreme model parameters. These supporting results increase the confidence in the time of travel estimated by the isotopic time series.

As more becomes known about potential sources of contamination to our groundwater resource, new techniques will be required to assess accurately a well's vulnerability. As shown here, the use of multiple techniques increased the confidence of our characterization. Moreover, with emerging contaminants, such as viruses, accurate assessments of time of travel, in addition to water source, are needed to truly protect the public's water supply.

Acknowledgements

Appendix A. Results of stable isotope sampling in La Crosse, Wisconsin, USA

	Date	δ^{18}O (‰)	δ^2H (‰)
Surface water (Black River downstream of Pool 7 impoundment)	3/12/2001	−9.1	−63.7
	4/20/2001	−10.7	−76.5
	5/29/2001	−8.7	−63.0
	6/25/2001	−8.1	−57.0
	7/23/2001	−7.6	−55.5
	8/20/2001	−7.1	−51.0
	9/24/2001	−7.3	−51.4
	10/22/2001	−7.8	−56.3
	11/15/2001	−7.9	−58.1
	11/16/2001	−7.9	−55.9
	11/26/2001	−8.4	−60.5
	12/17/2001	−8.6	−59.1
	1/30/2002	−8.9	−64.0
	1/30/2002	−8.8	−61.4
	1/30/2002	−8.8	−64.1
	2/16/2002	−9.3	−65.3
	2/26/2002	−9.3	−64.6
	2/26/2002	−9.2	−65.1
	4/9/2002	−9.1	−64.9
	4/9/2002	−9.1	−64.9
	4/9/2002	−9.5	−65.5
	6/5/2002	−8.5	−61.2
	8/28/2002	−6.3	−43.2
Well 10	3/12/2001	−8.9	−61.8
	4/20/2001	−8.9	−63.6
	5/29/2001	−8.9	−61.9
	7/23/2001	−8.9	−61.1
	8/20/2001	−8.8	−61.4
	9/24/2001	−8.8	−60.1
	10/22/2001	−8.8	−60.8
	11/26/2001	−8.8	−60.2
	12/17/2001	−8.8	−60.4
	1/30/2002	−8.8	−61.6
	2/26/2002	−8.9	−61.7
	4/9/2002	−8.9	−62.6
	9/4/2002	−8.8	−60.3
Well 13	3/12/2001	−9.0	−59.5
	11/23/2001	−8.8	−59.6
	12/14/2001	−8.8	−60.1
	6/5/2002	−8.8	−59.7
Well 14	4/20/2001	−9.0	−61.4
	5/29/2001	−9.0	−60.3
	6/25/2001	−9.1	−60.8
	7/23/2001	−9.0	−60.8
	8/20/2001	−9.0	−59.6
	9/24/2001	−9.1	−60.0
	10/22/2001	−9.0	−60.6
	11/26/2001	−9.1	−60.2
	12/17/2001	−9.1	−61.3
	1/30/2002	−9.0	−62.3
	2/26/2002	−9.0	−59.1
	6/5/2002	−9.0	−60.8
	9/4/2002	−9.0	−61.5

Appendix

	Date	δ^{18}O (‰)	δ^2H (‰)
Well 15	11/26/2001	−8.6	−58.4
	12/17/2001	−9.0	−61.1
	6/5/2002	−8.6	−58.5
	9/5/2002	−8.7	−57.6
Well 17	6/25/2001	−9.0	−61.3
	11/25/2001	−8.9	−60.5
	12/17/2001	−8.9	−60.7
	2/5/2002	−8.9	−61.1
	6/5/2002	−8.9	−61.3
	9/4/2002	−8.9	−60.0
Well 19	11/26/2001	−8.8	−60.1
	12/15/2001	−8.8	−59.7
	3/5/2002	−8.8	−58.8
	6/5/2002	−8.8	−61.4
	9/5/2002	−8.8	−60.0
Well 20	11/26/2001	−8.7	−58.9
	12/17/2001	−8.8	−59.5
	6/5/2002	−8.8	−59.0
	9/5/2002	−8.8	−59.1
Well 21	11/26/2001	−8.6	−59.9
	12/17/2001	−8.7	−59.2
	2/7/2002	−8.6	−60.4
	6/5/2002	−8.6	−59.5
	9/5/2002	−8.4	−57.5
Well 22	11/26/2001	−8.9	−60.4
	12/15/2001	−8.9	−60.1
	2/5/2002	−9.0	−60.6
	6/5/2002	−8.9	−60.3
	9/5/2002	−8.9	−59.2
Well 23	11/25/2001	−8.6	−60.2
	12/16/2001	−8.7	−59.1
	2/5/2002	−8.6	−60.9
	6/5/2002	−8.7	−60.6
	9/4/2002	−8.7	−59.5
Well 24	3/12/2001	−8.4	−58.6
	4/20/2001	−8.5	−61.4
	5/29/2001	−8.7	−61.8
	6/25/2001	−8.9	−60.6
	7/23/2001	−8.7	−61.3
	8/20/2001	−8.6	−58.9
	9/24/2001	−8.5	−59.8
	10/22/2001	−8.5	−60.8
	11/26/2001	−8.4	−60.2
	12/17/2001	−8.5	−59.3
	1/30/2002	−8.4	−59.9
	2/26/2002	−8.4	−60.4
	4/9/2002	−8.5	−61.8
	9/4/2002	−8.5	−59.5
Piezometer at Well 24	11/16/2001	−8.6	−61.0
	12/17/2001	−8.4	−57.3
	1/30/2002	−7.6	−55.8
	2/26/2002	−7.5	−54.1

Appendix

	Date	δ^{18}O (‰)	δ^2H (‰)
	4/9/2002	−7.6	−53.2
	6/5/2002	−9.1	−63.1
	8/28/2002	−8.8	−60.2
Well 25	3/12/2001	−9.0	−59.1
	4/20/2001	−9.0	−60.8
	5/29/2001	−9.0	−60.9
	6/25/2001	−9.0	−59.7
	7/23/2001	−9.0	−60.4
	8/20/2001	−8.9	−60.2
	9/24/2001	−9.0	−60.2
	10/22/2001	−9.0	−61.2
	11/26/2001	−9.0	−61.4
	12/17/2001	−9.0	−60.3
	1/30/2002	−9.0	−61.8
	2/26/2002	−9.0	−60.5
	6/5/2002	−9.0	−61.1
	9/4/2002	−9.0	−60.1
Well 26	11/26/2001	−9.0	−63.6
	12/15/2001	−8.9	−61.0
	2/6/2002	−8.7	−63.3
	9/4/2002	−8.8	−62.0

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