Use of geochemical and mathematical models for the determination of mixing ratios in groundwater from municipal wells, Madison, Wisconsin, USA

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ABSTRACT: Geochemical and mathematical methods are presented, which include NETPATH model and the Moore-Penrose pseudo-inverse (MPPI) to quantify the contributions of water from distinct recharge areas and aquifers to public supply wells in the city of Madison, Wisconsin. Previous studies investigated the hydraulic connectivity between different aquifers in the study area and proved the impact of the shallower aquifers as well as the surface water on some of the deep wells, but did not address the percentages of the contributions of such sources. The MPPI, executed by MATLAB code, in conjunction with the inverse-based NETPATH model was used to estimate the mixing proportions of four end members ("initials") in some of the deep groundwater wells. The quantitative estimation of the contribution of the different water resources (reference waters) on the water extracted from the deep municipal wells is considered as the main ultimate goal of this manuscript. Therefore, in this paper, many tools including WATEQ program, NETPATH and MPPI codes, were applied to verify the influence of such reference waters as well as to assess their ratios in the deep municipal wells. Datasets including major ion chemistry and stable isotopes (such as $\delta^{18}O$ and δD) data were manipulated to determine similarities and differences between the samples and reference waters. These data provided a basis for selecting and grouping of the samples that are believed to be affected by mixing. The results showed that there are two groups of wells; one group was mainly affected by the deeper Mount Simon water (about 70%), while the second group showed a slight increase in the shallower Tunnel City water (up to 15%) and a significant increase in the Wonewoc Formation water (up to 40%) with a decrease in the ratio of the deeper Mount Simon water. The contribution of lake waters was almost around 20% in all of the studied groundwater wells. It is worth mentioning that it is not easy to choose the most appropriate models that express the mixing ratios if the necessary data are not available, as well as the appropriate programs used to adapt these data correctly. Therefore, the MPPI mathematical program was adapted along with other geochemical programs in order to constrain the models computed by such programs as well as to verify that the outputs of these programs will be as close to reality as possible. Generally, quantification of the contribution of different sources of recharge to groundwater sheds light on the vulnerability of a certain aquifer or well to pollution. Such analysis may also highlight the need for additional characterization of aquifer heterogeneity at a given location.

Key words: geochemical, mathematical, modeling, recharge, mixing ratios, groundwater, Madison, Wisconsin

1. INTRODUCTION

1.1. General Outline

Groundwater chemistry is a result of multiple factors including the interaction between the groundwater and the mineral composition of the aquifer materials through which it moves. Hydrogeochemical processes, including dissolution, precipitation, ion-exchange, sorption, and desorption, together with the residence time occurring along the flow path, control the evolution in chemical composition of groundwater (Apodaca et al., 2002).

Variations in groundwater chemistry are also affected by variations in sources of recharge. Groundwater is recharged naturally by rain and snow melt and may also result from infiltration of surface water from rivers and lakes. Recharge may be altered by human activities including paving, urban development, logging, or agriculture. These activities can result in loss of topsoil, resulting in reduced water infiltration, enhanced surface runoff and reduction in recharge. Reductions in infiltration can increase surface runoff, which in turn diverts water to a drainage system (Vazquez-Sune, 2010). In addition, new sources of recharge may arise such as losses from sewage or water distribution systems (Kim et al., 2001; Wolf et al., 2004; Blackwood et al., 2005). Municipal pumping can affect hydraulic gradients, causing changes in natural groundwater flow paths. In some cases, pumping induces recharge from surface water bodies and movement of water from shallow to deeper aquifers. This can result in mixing of water from several sources, with associated changes in groundwater chemistry.

Numerous studies focused on different approaches to identify and estimate sources of groundwater recharge. Among these methods are: The use of chemical tracers to study the effect of human-induced alteration of groundwater flow (Ayotte et al., 2011); Application of major ions, nutrients, chlorofluorocarbons, tritium (^{3}H), helium-3 as well as noble gases as tracers to better understand the groundwater flow patterns (Toth and Katz, 2006), Assessment of the vulnerability of production wells to non-point contaminant inputs by comparing age distributions groundwater-flow models to particle-tracking models (Eberts et al., 2012). Studying the effect of the hydrological differences as well as similarities of wells, well- construction practices and land-use settings on contaminant movement to wells (Landon et al., 2010). Identification of the main causes of the degradation of the groundwater quality using multivariate statistical analysis (Houria et al., 2020). Additionally, naturally-occurring environmental tracers including common dissolved constituents, such as major cations and anions, stable isotopes of oxygen (δ^{18}O) and hydrogen (δD) are useful tools used to track the movement of water through watersheds (Winter et al., 1998). In order to understand the hydrological systems and the resulting groundwater quality, there are some important aspects that must be recognized, such as the origin of water, mixing processes and reactive geochemical processes. In this paper, major ion chemistry (such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, CO_3^{2-}, HCO_3^{-}, SO_4^{2-}, Cl^{-} and Si) and stable isotope tracers (δ^{18}O and δD) were used to track groundwater quality change with the emphasis on how to compute the proportion of each recognized recharge source pumped from public-supply wells (PSWs). Interpretation of groundwater chemical data to infer processes associated with chemical evolution along flow paths and mixing can be aided by statistical models and by

models that account for geochemical mass balances and reactions. Statistical models for evaluating groundwater chemistry in a rock formation may reveal patterns that are not readily apparent from a simple tabulation of analytical results. Techniques range from simple x-y plots, in which variations in concentration of one species are compared with those of another, to complex diagrammatic or statistical methods depicting the data so that sources of dissolved salts, groundwater residence time, water-rock interactions and mixing of different water types, can be identified (Laaksoharju et al., 2008).

Mixing calculations are based on the proportions of two or more end members, or sources of origin, that contribute to a specific mixture pumped from a well (Huntoon, 1981). In hydrology, mixing proportions can be estimated on the basis of hydrochemical data such as major ion chemistry and stable isotopes (Fritz et al., 1976; Christopherson and Hooper, 1992; Doctor et al., 2006). One approach has been developed that, in part, uses mixing models to supplement geochemical reactions when accounting for observed groundwater compositions. For instance, the standard code NETPATH (Plummer et al., 1991, 1994) can be used to interpret net geochemical mass-balance reactions between initial (or multiple initial waters that mix) and final waters along flow paths in aquifers or other hydrologic systems. The program uses inverse geochemical modeling techniques (Plummer et al., 1983; Plummer, 1985; Parkhurst and Plummer, 1993; Glynn and Brown, 1996; Nordstrom and Campbell, 2014) to construct geochemical reaction models by using chemical and isotopic data for waters from the hydrochemical system.

The Cambrian–Ordovician sandstones and carbonates underlying Madison, Wisconsin, are one system in which mixing of water from several recharge sources and among aquifers is likely to be occurring. An areally extensive, composite cone of depression in the potentiometric surface of the deeper sandstone units results from many decades of pumping. Hunt et al. (2005) identified variations in the pumping history as a potential mechanism that can affect the variability in water composition. Bradbury et al. (2010) and Gellasch et al. (2013) documented connections between shallow sources of contamination and the deep aquifer, especially in municipal wells that are close to the lakes. Bradbury et al. (2010) reported also that the vulnerability of some wells to contamination from near surface sources is likely to increase with increasing proportion of lake water, shallow groundwater, and recently recharged groundwater that reaches the well. This vulnerability can be magnified in the presence of preferential flow paths connecting the shallow and deeper aquifers. For example, Swanson et al. (2006a) provided evidence for the lateral hydraulic continuity of high-permeability zones in the shallow Tunnel city group aquifer over tens of kilometers

although the heterogeneity of this aquifer in some localities might influence the groundwater flow. Additionally, Gellasch et al. (2013) suggested that bedrock fractures may serve as a preferential pathway for horizontal and vertical contaminant transport from the surface to the deep aquifer. This study comes as a continuation to what has been accomplished previously by Swanson et al. (2006a) and Gellasch et al. (2013). Therefore, it was important to shed light on the properties of a certain aquifer or well, such as its vulnerability to contamination, by estimating the percentage of the contribution of the different water resources to some wells. It is worth mentioning here that the application of the NETPATH geochemical program requires knowledge of surface and subsurface geology, as well as a good understanding of the geochemical processes that account for the interaction between water and rocks. The selection of a set of parameters to be used in a study depends on the goal for which the subject of this study was chosen, as well as on the tools and/or programs that are employed to reach that goal. Therefore, it was important for this study to focus on using the results of the analyses and measurements of some parameters, such as the major ions and stable isotopes, as inputs to the NETPATH program. The most appropriate models computed by such a program are selected by comparing the state of the predominant minerals in each model (whether dissolved or precipitated) with those that were calculated using the WATEQ program. An inverse mathematical model, namely Moore-Penrose pseudo inverse of matrix (MPPI), implemented in MATLAB program has been adapted to be used as a complementary tool or an aid method in choosing the most appropriate models that express or simulate what is happening in reality. This study has two main objectives, the first is the characterization of the types of water present in different aquifers based on their chemical composition, and the second is learning about the geochemical evolution and stable isotopic composition of groundwater pumped from deep municipal wells in Madison. As a result, a set of possible reactions will be identified based on changes in the composition of groundwater. For example, Si-TDS and δ^{18}O-δD relationships were used for grouping groundwaters and to identify the various recharging sources that affect its quality. Additionally, some outputs of the WATEQ program, such as the partial pressure of carbon dioxide (P_{CO2}) and saturation index (SI) were used to identify the different minerals and the other processes that affect their state. The use of MPPI code along with NETPATH is considered as a novel tool to clearly identify the compositions and proportions of recharge sources that mix and result in the groundwater chemistry pumped from wells completed in a complexly layered groundwater system. An improved quantification of mixing of shallow and deeper groundwater in this hydrogeological system can enhance understanding of pumping

impacts and vulnerability of the water supply to contamination. The chemical data presented in this paper were obtained from the annual report prepared by Madison water utility in June 2013. These data were supplemented with water samples collected from the studied wells for silica analyses which were performed by the first author in May 2014.

1.2. Location and Climate

The study area encompasses the city of Madison, Dane County, Wisconsin, USA (Fig. 1). The average annual precipitation in Dane County, as measured at the Madison airport, is 30.9 in. The mean annual air temperature is 45.2 °F, with an average maximum of 82.4 °F in July and an average minimum of 7.2 °F in January. Sixty percent of annual precipitation falls in the five months of May through September.

1.3. Regional Hydrogeology

The bedrock geology of Dane County consists of a series of dolomite and sandstone units overlying crystalline rock (Fig. 2). Figure 3 shows the general arrangement and approximate relative thicknesses of bedrock geologic units across the county. As described by Bradbury et al. (1999), the regional hydrogeologic system is underlain by crystalline rocks of Precambrian age are generally considered an impermeable lower boundary. Four primary hydrostratigraphic units overlie the basement: three aquifers and one aquitard. The deepest aquifer, the Mount Simon, is an important source of water to high capacity wells. The Mount Simon aquifer consists of sandstones of the Mount Simon and lower Eau Claire Formations.

An important leaky confining unit, here called the Eau Claire aquitard, extends across much of Dane County and, where it occurs, impedes the exchange of water between the Mount Simon aquifer and overlying aquifers. The Eau Claire aquitard consists of shale and siltstone facies of the upper part of the Eau Claire Formation. The aquitard appears to be thin and partially absent in the central Yahara lakes area, where the preglacial bedrock surface is believed to have been eroded deeply into the underlying Mount Simon Formation. The upper Paleozoic aquifer consists of all saturated Paleozoic rocks from the bedrock surface down to the top of the Eau Claire aquitard. These include the Wonewoc Formation and the Tunnel City Group, both of which are included in the open interval of some municipal wells. The uppermost aquifer in Dane County is the unlithified aquifer, consisting of saturated sediments primarily of Quaternary age. These materials range in lithology from clayey lake sediment to sand and gravel.

Groundwater in Dane County is mainly recharged from
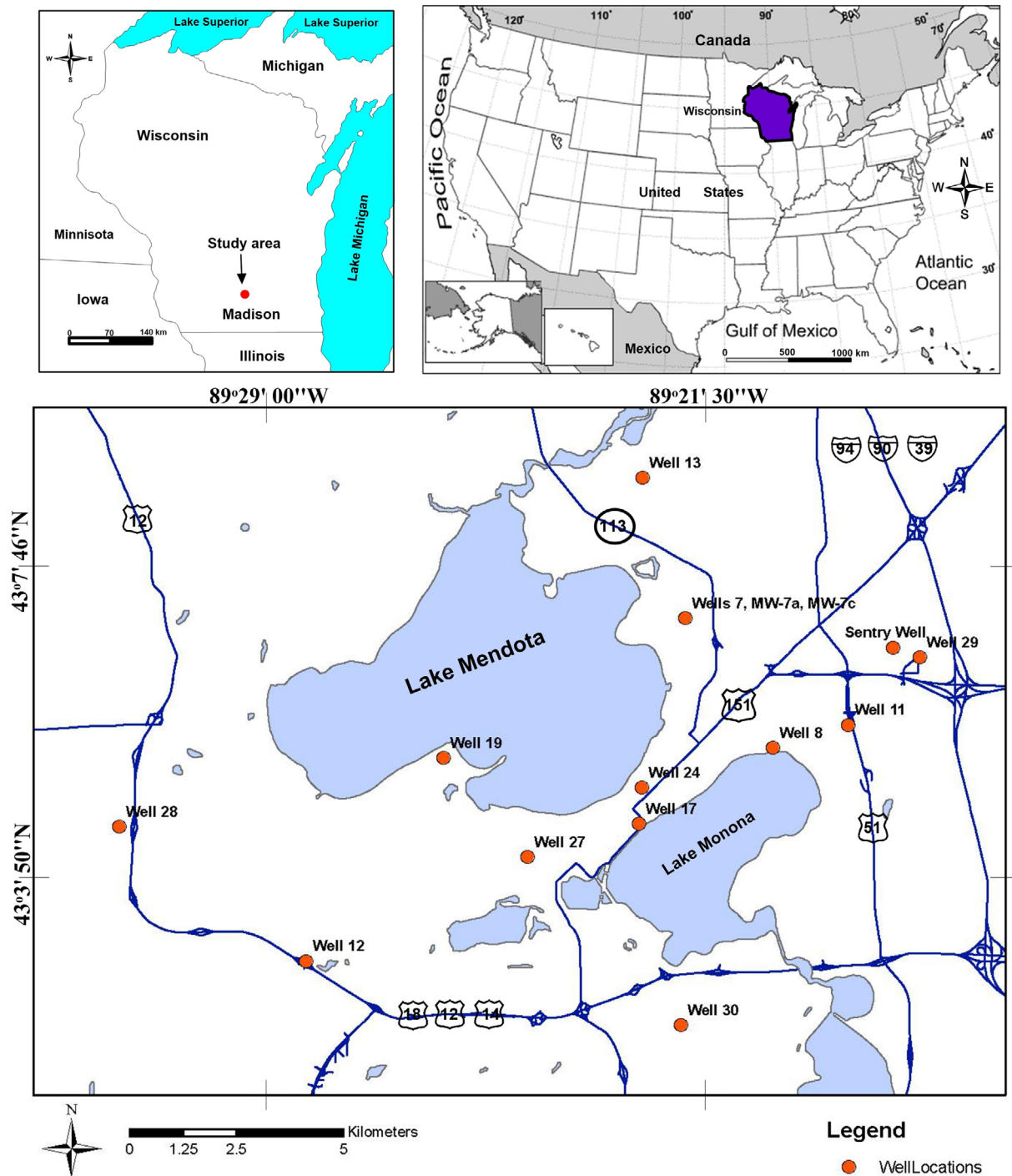
Fig. 1. Well location map.

precipitation (rain and snowmelt) at the land surface. Estimates of recharge vary spatially across the county from less than 5 inches to more than 15 inches in a typical year (Parsen et al., 2016). Shallow and deep groundwater systems are relatively well connected in Dane County. Where the water table is higher than the potentiometric surface, groundwater moves downward to recharge to Mount Simon aquifer. Where the potentiometric

surface is above the water table, groundwater moves upward from the Mount Simon aquifer into overlying units. The presence or absence of the Eau Claire aquitard and the hydraulic properties of the shallow Paleozoic rocks largely control the rate of vertical movement.

Groundwater withdrawals from high-capacity wells are focused near the Madison metropolitan area, with smaller withdrawals

Age		Stratigraphic Unit			Description
Cenozoic Era	Holocene Epoch	Unamed units			Unconsolidated till cosisting of gavelly, clayey, silty sand (Ostrom, 1978)
	Pleistocene Epoch	Keiler Fm.	Holly Hill Formation	Horicon member	
				Other members	
		Other formations?			
	?	Rountree Formation			Dolomite, sandstone and shale of Ordovician age (Kammerer, 1995; Ostrom, 1967)
Paleozoic Era	**Ordovician Period**	Makuoketa Formation			
		Sinnipee Group	Galena Formation		
			Decorah Formation		
			Platteville Formation		
		Ancell Group	Glenwood Formation		
			St. Peter Formation		
		Prairie du Chien Group			
	Cambrian Period	Jordan Fromation			Yellow to reddish, coarse- to fine-grained, dolomitic sandstone (Clayton and Attig, 1997)
		St. Lawrence Formation			Sandy dolomite
		Tunnel City Formation			The Tunnel City Formation, which contains glauconitic sandstone (Clayton and Attig, 1997)
		Elk Mound Group	Wonewoc Formation		Wonewoc contains medium to fine-grained sandstone Clayton and Attig, 1997
			Eau Claire Formation		Fine- to medium-grained dolomitic sandstone and shale upper part of the Eau Claire contains significant shale and siltstone (Braburry et al., 1999)
			Mount Simon Formation		Well-cemented, coarse to medium-grained sandstone (Braburry et al., 1999)
Precambrian Eras		Various unnamed units			

Fig. 2. Stratigraphic section for Dane County (from Clayton and Attig, 1997).

in outlying communities. Within Dane County, the average groundwater withdrawal rate during the period from 2006 to 2010 was estimated to be 52 million gallons per day (mgd) from a total of 385 high-capacity wells. The source for groundwater produced by municipal wells in Dane County is relatively local, and for almost every well the steady-state zone of contribution lies entirely within the county (Bradbury et al., 1999). Wells located near the Yahara Lakes may derive some water from downward leakage from the lakes themselves. Groundwater moves downward from surface water to groundwater along much of the shoreline of Lakes Mendota and Monona. Municipal wells located near the Yahara lakes could draw roughly 25 percent of their water from such downward leakage (Bradbury et al., 1999).

2. STUDY METHODS

2.1. Data Collection, Water Sampling and Analysis

Data presented here reflect samples collected from municipal wells completed in the confined Mount Simon aquifer, municipal wells that are open to multiple aquifers (multi-aquifer wells), and several short-screened monitoring wells. The chemical and isotopic compositions are based on samples collected and
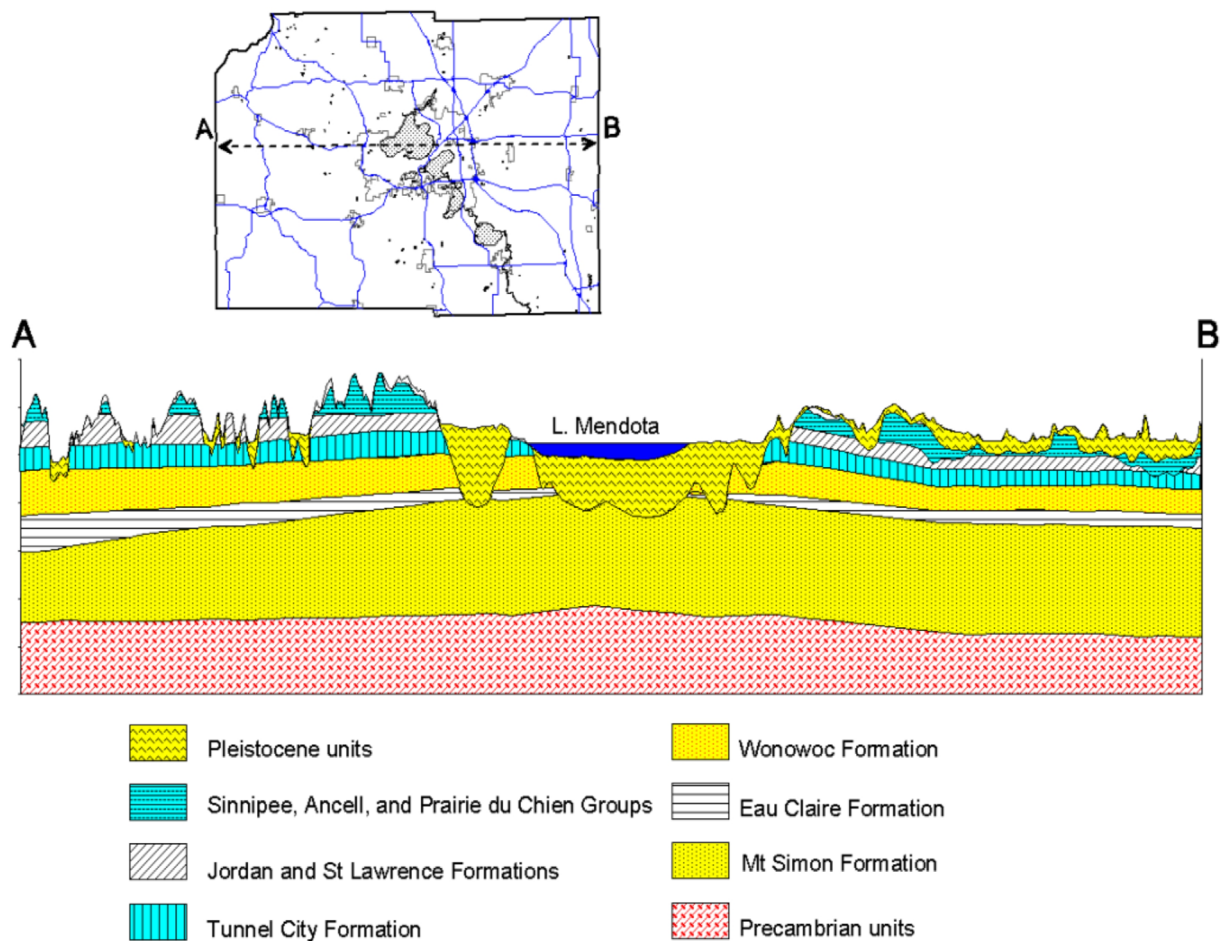
Fig. 3. An east–west geologic cross section across Dane County (Massie-Ferch et al., 1997).

Table 1. Construction data for the studied groundwater wells

Well ID	Screen (feet)	Depth (feet)	Aquifer
Well 7	237.60–736.80	736.80	Mt. Simon
MW-7A	32.80–47.88	47.88	Tunnel City Group
MW-7C	203.36–214.84	214.84	Wonewoc Fm.
Well 8	280.00–774.00	774.00	Mt. Simon
Well 11	110.67–752.00	752.00	Multi-aquifer
Well 12	260.00–973.00	973.00	Multi-aquifer
Well 13	128.00–780.00	780.00	Multi-aquifer
Well 17	144.80–801.11	801.11	Multi-aquifer
Well 19	260.00–718.00	718.00	Mt. Simon
Well 24	235.00–729.00	729.00	Mt. Simon
Well 27	246.00–744.00	744.00	Mt. Simon
Well 28	400.00–882.00	882.00	Mt. Simon
Well 29	342.00–815.00	815.00	Mt. Simon
Sentry well-Port 1	90.00–95.00	815.00	Tunnel City Group
Sentry well-Port 2	207.00–212.00	815.00	Wonewoc Fm.
Well 30	312.00–800.00	800.00	Mt. Simon

analyzed by the Madison water utility in the summer of year 2012. Later, in May 2014 a few samples representing lakes Mendota and Monona, groundwater from the monitoring wells completed in the upper bedrock and from deeper and multi-aquifer municipal wells in Madison were collected and analyzed by the author for silica determination. Well construction

information, including the open intervals of the municipal wells, is included in Table 1.

2.2. Data Interpretation Methods

2.2.1. Hydrochemistry and stable isotopes

Hydrochemistry along with environmental stable isotopes (δ^{18}O, δD) studies were applied to ascertain or deny the interrelationship between the different adjacent aquifers and other water bodies. Chemical equilibrium speciation and water type calculations were made using Aquachem 5.1.151 (Waterloo Hydrogeologic, Inc.). Oxygen-18 was correlated with deuterium and both the global meteoric water line (GMWL) and the local meteoric water line (LMWL) from Dane County (Swanson et al., 2006b) were included for samples categorization. The silicon versus total dissolved solids (TDS) relationship were also used to classify water samples and identify recharging sources. The saturation index (SI) computed by WATEQ program is used to describe the equilibrium state of water with respect to mineral phases and to determine the dissolution or precipitation of minerals in rock-water interactions. The SI of a particular mineral is defined as:

$$SI = Log\left(\frac{IAP}{K_T}\right), \tag{1}$$

where IAP is the ion activity product of the mineral-water reaction and K_T is the thermodynamic equilibrium constant adjusted to the temperature of the given sample. Partial pressures of CO_2 (P_{CO2}) in water were calculated from measured pH and alkalinity data using the program WATEQ, which is included within NETPATH program to characterize the state of carbonate minerals.

2.2.2. Geochemical and mathematical inverse modeling

The approach in the current study has two main components: a conceptual mathematical model and a NETPATH geochemical mass-balance model. These models are applied to calculate the proportions of four reference waters known as initial waters or end members (lake water, Tunnel City Group groundwater,

Wonewoc Formation groundwater and the deepest Mount Simon Formation groundwater) in samples from the Mount Simon Formation aquifer thought to be affected by such reference waters. Waters designated as Ports 1 and 2 were collected from a multilevel monitoring well located very close to well 29, and used as end members (initials 1 and 2) corresponding to the Tunnel City and Wonewoc, respectively, to interpret the mixing ratios in wells 8, 19 and 27. On the other hand, monitoring wells MW-7A and MW-7C located very close to well 7 were used as the Tunnel City and Wonewoc end members in the well 7 for interpretation. The water sample from well 30 was used as initial 3, as it has the most depleted values for δ^{18}O and δD (-10.74‰, -72.41‰), to compute the percent of deep Mount Simon water in each final water. Lake Monona was used as initial 4 in case of well 8, while Lake Mendota was used as initial 4 in the case of the other wells (Table 2).

We used NETPATH to develop mixing models that account for geochemical reactions along groundwater flow paths. The following constraints were considered: C, S, Ca, Al, Mg, Na, Cl, Si, Sr, Fe, Al, Mn, δ^{18}O and δD. A set of plausible phases were chosen according to: (1) the constraints used, (2) aquifer matrix in which water circulates, (3) type and state of phases induced by WATEQ program. Chloride was considered to be conservative so no chloride phases (minerals) were included and the mixing ratio was automatically based on Cl. Mixing ratios calculated by Chloride were checked on the basis of δ^{18}O and δD. The MATLAB program was used, where Cl, δ^{18}O and δD were used as inputs, to refine the outputs (models) generated by NETPATH program. The models computed by NETPATH that contain phases that correspond in their state, (whether they dissolved or precipitated), to those selected in the WATEQ program, and at the same time being compatible with the mixing ratios calculated by the MATLAB program were chosen. MATLAB is an acronym that stands for MATrix LABoratory, which refers to a matrix as its main data element (array or matrix). It is widely used in universities and colleges in introductory and advanced courses in mathematics, science, and engineering. With MATLAB, one may perform mathematical computations, model and simulations, data analysis and processing, visualization and graphics, as well as method creation (Gilat, 2014). The mathematical tool employed in this

Table 2. Description of initials and finals used in both MPPI and Netpath calculations

Initials	Description	Aquifer	Finals
Initial 1	MW-7A, Port 1 (90–95 feet)	Tunnel city group	
Initial 2	MW-7C, Port 2 (207–212 feet)	Wonewoc Formation	Wells 7, 8, 19 and 27
Initial 3	Well 30	Mount Simon Formation	
Initial 4	Mendota and Monona	Lake	

Note: MW-7A and MW-7C were only used as initials 1 and 2 to calculate mixing ratios in well 7 as they are located very close to it, while Port 1 and Port 2 were used as initials 1 and 2 in the rest of the samples. Similarly, lake Mendota was used as an initial 4 in case of wells 7, 19 and 27 as it is located close to these wells, whereas lake Monona was considered as initial 4 in case of well 8 for the same reason.

modeling effort calculates a Moore-Penrose pseudo inverse of matrix and is implemented using MATLAB (http://www.mathworks.com). The Moore-Penrose pseudo-inverse is a general method to solve the following system of linear equations:

$$Ax = b. \tag{2}$$

If A is a square matrix of full rank, then the inverse of A exists (A is referred to as an invertible matrix) and has the solution:

$$X = A^{-1}b \text{ or } \{X = \text{inv. } (A)*b\}. \tag{3}$$

The Moore-Penrose pseudo inverse is a generalization of the matrix inverse when the matrix may not be invertible. In this case it will have the solution:

$$X = \text{pinv. } (A)*b. \tag{4}$$

The mixing ratio (x) was computed based on the chemical composition of the initial waters (A) and final waters (b). However, some of the calculated values were negative. In that case linear least square with non-negativity constraints was applied. Then X can be recalculated according to the equation:

$$X = \text{lsqnonneg } (A,b), \tag{5}$$

which returns the vector X that minimizes NORM (b − A*X) subject to $X \geq 0$. A and b must be real.

The multiplication operation is executed by MATLAB according to the rules of linear algebra. This means that if A and X are two matrices, the operation A*X can be carried out only if the number of columns in matrix A is equal to the number of rows in matrix X. The result is a matrix that has the same number of rows as A and the same number of columns as X. For example, as in the case here, if A is a 3×4 matrix and X is a 4×1 matrix (in case three variables, such as Cl, $\delta^{18}O$ and δD, were used). The product of the multiplication is a matrix B with a size of a 4×1. If one variable only, such as Cl, was used, then the sizes of the three matrices will be 1×4, 4×1 and 1×1 for A, X and B, respectively. This means that, in both cases, the mixing ratios expressed by X matrix would be four-element column vector, which in turn represent the contribution percent of the four reference waters.

Such calculations will be compared with those computed by other tools that, in part, use mixing models as a supplement to geochemical reactions that account for the observed groundwater compositions. For example, the NETPATH code (Plummer et al., 1991) examines all possible phases that satisfy the chosen constraints as well as the contribution of the initial waters. The model is of the form:

Initial water + "Reactant phases" → Final water + "Product phases".
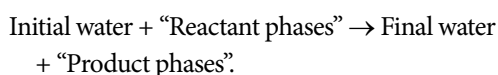
The composition of the observed or final groundwater equals that due to the sum of mixing and reactions. The model allows mixing of as many as five initial waters. It assumes that the selected initial waters mix in some proportion, with or without further mineral-water reactions. It should be noted, when considering mixing, that one less phase can be included in a model for each additional initial water in the mixture. This simply means that if η initial waters are mixed, η-1 constraints may be included that are not contained in any of the selected phases.

3. RESULTS AND DISCUSSION

3.1. Hydrochemistry

The hydrochemical variables (consisting of major ions, and isotopic data) in the compiled database, were used in this study (Table 3).

Water from lakes Mendota and Monona is classified according to major ions as $Mg\text{-}Ca\text{-}HCO_3\text{-}Cl$ and $Mg\text{-}Ca\text{-}Na\text{-}HCO_3\text{-}Cl$ respectively. Water from the confined deep aquifer of Mount Simon is characterized by $Ca\text{-}Mg\text{-}HCO_3$ while waters from the overlying Wonewoc Formation and Tunnel City Group belong to $Ca\text{-}Mg\text{-}Na\text{-}HCO_3$ or $Mg\text{-}Ca\text{-}HCO_3$ and $Ca\text{-}Mg\text{-}HCO_3\text{-}Cl$ or $Ca\text{-}Mg\text{-}Na\text{-}HCO_3$ water types respectively. For samples collected from multi-aquifer wells, the groundwater is a mixture of $Ca\text{-}Mg\text{-}HCO_3$ and $Mg\text{-}Ca\text{-}HCO_3$ types. Generally, the major ion chemistry of both deep and multi-aquifer samples is of calcium-magnesium-bicarbonate type, even though the wells are open to different parts of the sandstone aquifer. This reflects dissolution of carbonate bedrock and/or cement in the sandstone. Although the chemical water types of the deep aquifer did not show evidence of any large-scale mixing with lake waters and/or shallow groundwater, concentrations of some ions such as chloride and sodium show slight increases in some samples that suggest mixing with other sources. Trilinear plots of cations and anions for the studied water samples are presented in Figure 4.

These show that some of the deep groundwater samples (such as wells 7, 8 and 27) plot between the deep groundwater samples (with low chloride as a percentage of anions) and the lake and shallower groundwater (with higher chloride percentages).

3.2. Stable Isotopes

The stable isotopes deuterium (δD) and oxygen-18 ($\delta^{18}O$) can be used to identify which wells, if any, produce some groundwater that may have recharged from surface-water bodies, such as the Madison lakes, that have been affected by evaporation. They could also provide information on mixing of waters from aquifers

Table 3. Groundwater chemical and stable isotope data

| Well name	Aquifer	Water type	Temp. (ºC)	EC (μs/cm)	pH	TDS (mg/l)	Ca (mg/l)	Mg (mg/l)	Na + K (mg/l)	CO₃ + HCO₃ (mg/l)	SO₄ (mg/l)	Cl (mg/l)	Si (mg/l)	Al (μg/l)	Fe (mg/l)	δD (‰)	δ¹⁸O (‰)
Well 7	Mount Simon	Ca-Mg-HCO₃	13.2	679	7.40	370	76.0	44.0	7.80	388.53	35.00	13.0	8.58	2.20	0.39	−64.72	−8.46
MW-7A	Tunnel city gp.	Ca-Mg-HCO₃-Cl	–	1133	7.13	579	108.8	52.0	48.90	439.95	33.97	115.0	13.53	–	–	–	–
MW-7C	Wonewoc Fm.	Ca-Mg-Na-HCO₃-Cl	–	1174	7.17	602	107.9	55.9	56.55	436.26	39.97	123.0	10.10	–	–	–	–
Well 8	Mount Simon	Ca-Mg-HCO₃	10.0	658	7.70	344	69.0	41.0	11.20	367.36	17.00	22.0	0.00	0.80	0.22	−53.62	−8.20
Well 11	Multi aquifer	Mg-Ca-HCO₃	13.2	846	7.30	427	77.0	47.0	19.30	406.91	26.00	54.0	7.11	0.90	–	−57.32	−8.86
Well 12	Multi aquifer	Ca-Mg-HCO₃	14.2	530	7.50	280	61.0	33.0	3.10	340.92	9.50	2.9	5.42	0.50	–	−59.56	−8.93
Well 13	Multi aquifer	Ca-Mg-HCO₃	9.2	746	7.50	385	79.0	45.0	15.30	379.88	19.00	37.0	7.11	0.60	0.02	−59.26	−8.96
Well 17	Multi aquifer	Mg-Ca-HCO₃	10.8	759	7.60	407	72.0	46.0	19.60	343.21	51.00	47.0	5.70	1.40	0.10	−54.92	−7.88
Well 19	Mount Simon	Ca-Mg-HCO₃	13.2	553	7.50	287	65.0	34.0	5.40	336.05	7.70	7.1	5.37	0.60	0.19	−55.01	−8.10
Well 24	Mount Simon	Ca-Mg-HCO₃	10.4	533	7.50	284	58.0	35.0	6.00	328.74	14.00	6.3	4.53	0.50	0.23	−60.2	−8.80
Well 27	Mount Simon	Ca-Mg-HCO₃	10.2	753	7.40	409	81.0	43.0	18.60	373.92	40.00	39.0	5.16	0.60	0.12	−57.3	−9.01
Well 28	Mount Simon	Ca-Mg-HCO₃	9.8	544	7.50	294	64.0	34.0	3.10	336.05	22.00	2.9	6.30	0.40	0.17	−59.28	−9.19
Well 29	Mount Simon	Ca-Mg-HCO₃	–	594	7.40	315	71.0	36.0	4.10	381.22	8.40	4.5	4.56	0.50	–	−59.35	−9.09
Port #1	Tunnel city gp.	Ca-Mg-Na-HCO₃-Cl	–	1290	7.41	651	101.0	53.2	80.35	384.87	32.40	191.0	7.46	–	–	−57.00	−8.45
Port #2	Wonewoc Fm.	Mg-Ca-HCO₃	–	571	7.42	305	63.8	37.9	5.373	375.11	5.50	4.9	11.48	–	–	−53.27	−8.62
Well 30	Mount Simon	Ca-Mg-HCO₃	11.6	526	7.40	282	59.0	35.0	4.90	317.89	19.00	5.3	4.50	0.60	0.20	−72.41	−10.74
Mendota	Lake	Mg-Ca-HCO₃-Cl	12.6	502	8.55	231	26.1	30.4	22.20	185.73	20.10	38.0	0.11	–	–	−42.38	−5.86
Monona	Lake	Mg-Ca-Na-HCO₃-Cl	14.7	563	8.88	247	26.6	27.7	26.70	178.71	24.50	48.5	0.48	–	–	−43.35	−4.88

Note: (–) data is not available.
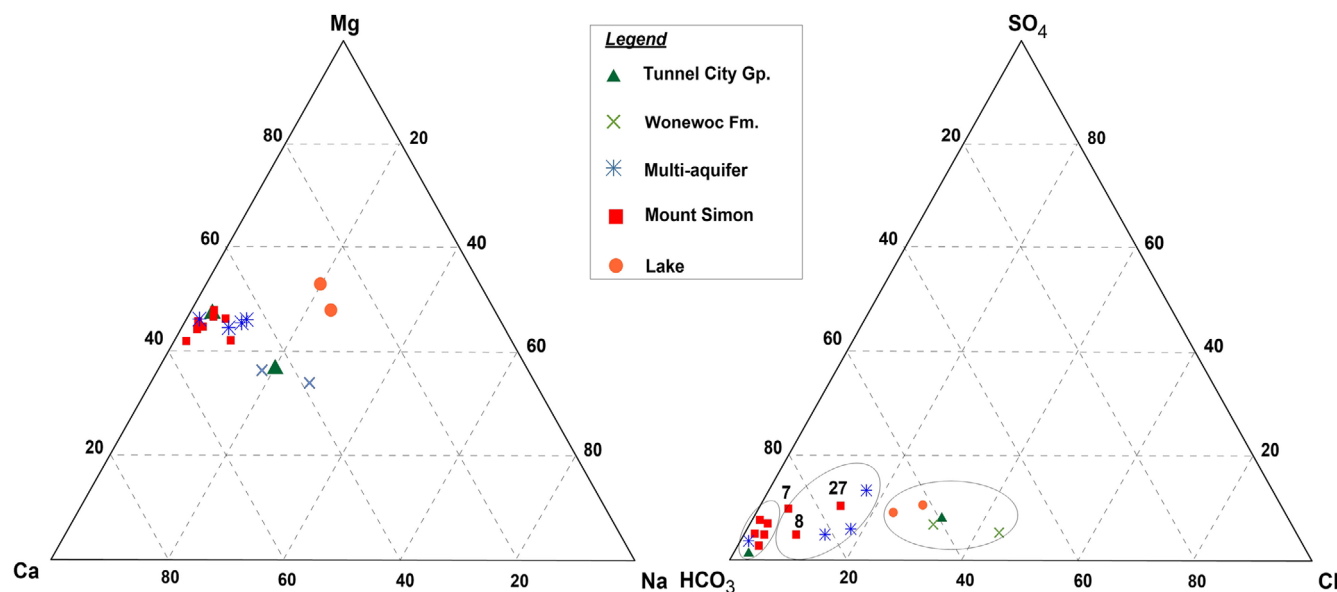
Fig. 4. Trilinear plot.

with distinct groundwater isotope signatures. Groundwater samples originating from terrestrial recharge should plot on or close to the local meteoric water line (LMWL). Surface water samples often plot to the right of the LMWL because water that has been exposed to open-water evaporation (lakes, wetlands) becomes depleted in lighter isotopes and enriched in heavier ones. Accordingly, surface water samples from both Mendota and Monona lakes plot to the right of the LMWL (Fig. 5).

The oxygen-18 values were −5.86‰ and −4.88‰, while the deuterium values were −42.38‰ and −43.35‰ for Mendota and Monona lakes, respectively. The oxygen isotope data (see Table 3) indicate that none of the sampled wells are dominated by recharge from surface water sources. Shown in Figure 5, samples from wells 8, 19 and 17, with oxygen-18 and deuterium values of (−8.20‰, −8.10‰, −7.88‰) and (−53.62‰, −55.01‰, −54.92‰), respectively, lying to the right of a local meteoric
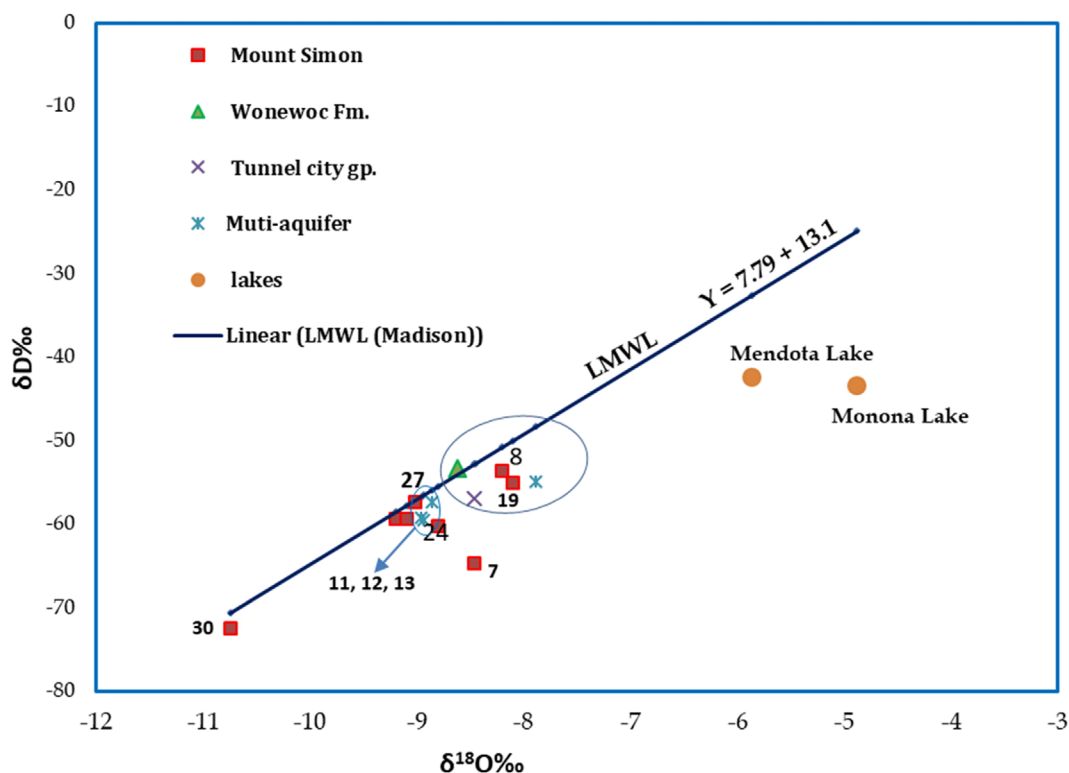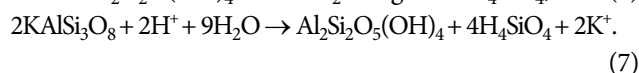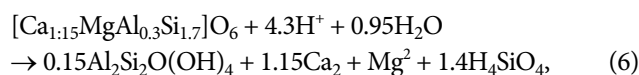
Fig. 5. Oxygen-18 and deuterium relationship in groundwater and surface water samples.

water line (LMWL) but are not as enriched as the lake samples. These wells are similar in isotopic composition to samples from both Tunnel City Group and Wonewoc Formation. These could be interpreted as falling along a mixing line between the lake samples and the shallow bedrock groundwater. Well 7 also plots to the right of the LMWL and has a lower $\delta^{18}O$ ($-8.46‰$) than the previous group of wells. If Well 7 represents a mixture of evaporated surface water and groundwater, the groundwater end member must be similar to well 30, which has a $\delta^{18}O$ composition lower than that reported for modern groundwater by Bradbury et al. (1999). These low values of $\delta^{18}O$ and deuterium for well 30 ($-10.74‰$, $-72.41‰$) may indicate recharge under cooler temperatures, suggesting that well 30 produces some fraction of groundwater recharged during glacial periods during the Pleistocene. The oxygen isotope ratios from the multi-aquifer wells 11, 12, 13 and 24 lie along the LMWL midway between the lakes and well 30, suggesting little to no contributions of surface water or Pleistocene recharge at these wells.

3.3. Silica

Silica dissolved in natural waters has been considered as a good indicator of weathering and water circulation conditions (Dobrzyński, 2005). In near-surface environments, silica concentrations can provide useful information on water exchange, and have

been used to estimate groundwater contributions to stream flow (Wels et al., 1991; Asano et al., 2004). The amount of silica released into the water is controlled by different factors, including water saturation state of the unsaturated zone, seasonal fluctuations of precipitation and temperature, and bedrock chemistry. Weathering of silicate minerals increases the concentrations of cations and silica in the aqueous phase, for instance by hydrolysis of pyroxene or orthoclase to form kaolinite:

$$[Ca_{1:15}MgAl_{0.3}Si_{1.7}]O_6 + 4.3H^+ + 0.95H_2O$$
$$\rightarrow 0.15Al_2Si_2O(OH)_4 + 1.15Ca_2 + Mg^2 + 1.4H_4SiO_4, \quad (6)$$
$$2KAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + 2K^+. \quad (7)$$

Silica concentrations are low in rain water, normally less than 1 mg/l (Freeze and Cherry, 1979). Hydrolysis of primary silicate minerals is considered to be the main source of silica dissolved in groundwater. High silica content in groundwater indicates active dissolution of silicate minerals or increased flow distance and groundwater age (Freeze and Cherry, 1979). Since groundwater has significantly higher silica concentrations than precipitation, silica can be used to estimate groundwater contributions to a surface water body (Hinton et al., 1994).

Silicon values were correlated with TDS and Cl$^-$ values, using the conventional graphical methods, to understand the impact of the recharge from different sources and/or naturally-occuring
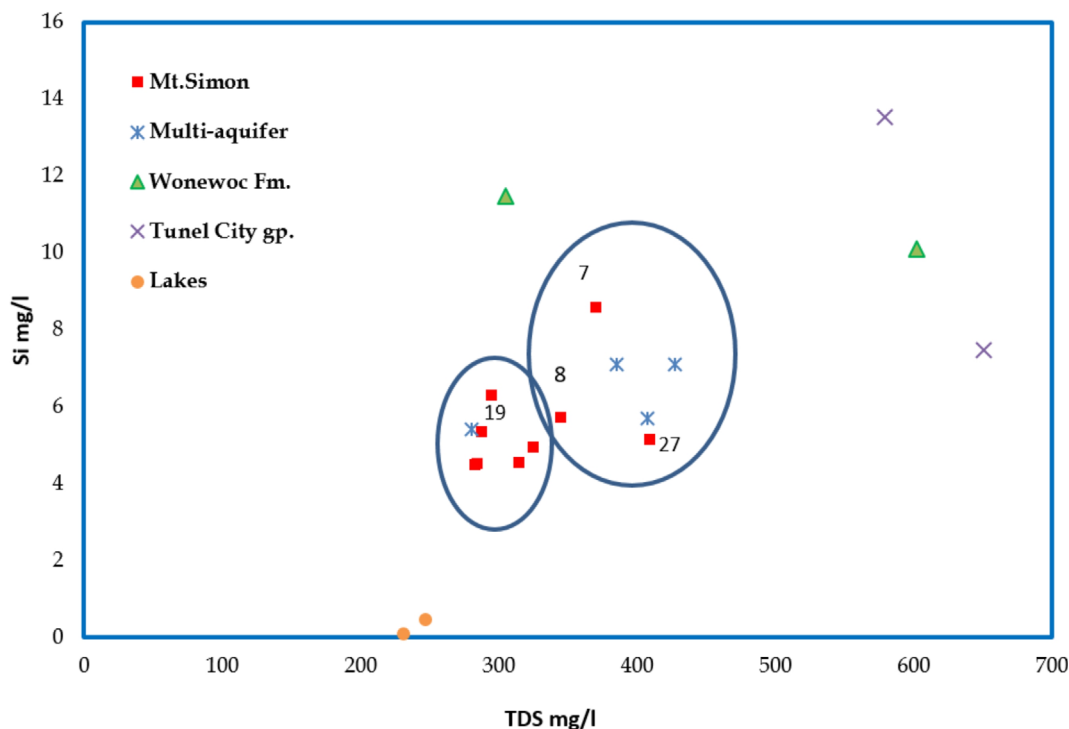
Fig. 6. TDS vs. Silicon relationship in groundwater and surface water samples.

(geogenic) processes on groundwater chemistry (Khan et al., 2015). On a plot of silicon (Si) versus total dissolved solids (TDS) (Fig. 6), the silicon concentrations of the two surface waters samples collected from Mendota and Monona are 0.11 and 0.48 mg/l, respectively. Si is slightly higher in Monona Lake. This could be due to the fact that Lake Monona has a smaller volume than Lake Mendota and hence, more affected by evaporation. If the groundwater samples contain a significant component of recent recharge from lake water, a decrease of silicon concentration would be expected due to dilution.

In the study area, the silicon concentrations of groundwater in both Tunnel City Group and Wonewoc Formation aquifers are much higher than those of lake waters and also somewhat higher than most of the samples from the Mt. Simon aquifer. This could be attributed to the enhanced circulation of groundwater in the shallow local groundwater system. Generally, the plot showed that almost all samples exhibited a positive correlation between Si and TDS, which indicates that both water-rock interaction and other recharging sources influenced the chemistry of the groundwater. This relationship could be explained more specifically based on Si concentrations, where the deep and multi-aquifer groundwater samples can be divided into two groups. One group has been slightly affected by the shallower Tunnel City groundwater with higher silicon, while the other group was dominated by Mount Simon water type with lower silicon concentration. This illustrates that silicon concentration

can be used as a tracer to indicate mixing between different types of waters. It should be also noted that well 7 has higher silicon concentrations than the other deep groundwater samples. A reasonable explanation for this is that it is affected by the groundwater from shallower aquifers rich in silicate minerals in their host parent rocks. This is clearly reflected by the saturation index values (discussed below), which suggest that the solution is oversaturated with respect to Ca-montmorillonite and illite minerals that contain aluminum and iron (see Tables 3 and 4).

3.4. Mineral Saturation Indices

In the absence of anthropogenic contaminant sources, water-rock interactions are likely to be the main processes responsible for the observed chemical characteristics of groundwater in an aquifer. Assessment of such processes requires knowledge of the main mineral assemblage constituting the rocks in which water is found and the identification of the chemical reactions that account for the geochemical evolution of groundwater. From the available studies in the literature cited previously in this paper, the host-rocks are mainly composed of sandstone sequences interbedded with shale and dolomite. Reactions of interest include chemical weathering of rock-forming minerals and dissolution-precipitation of secondary carbonates. Table 4 summarizes the most plausible phases as well as the equilibrium partial pressure of CO_2 (P_{CO_2}) based on the chemical analysis

Table 4. Saturation indices and log PCO$_2$ for the studied water samples

Well ID	Log Pco$_2$	Saturation Indices											
		Calcite	Aragonite	Dolomite	Gypsum	Anhydrite	SiO$_2$	Chalcedony	Quartz	Kaolinite	Albite	Ca-Mont.	Illite
Well 7	−1.90	0.19	0.04	0.32	−2.06	−2.32	−0.70	0.18	0.65	3.27	−2.52	1.95	0.88
MW-7A	−1.59	0.09	−0.06	0.04	−1.99	−2.22	−0.50	0.38	0.85	–	–	–	–
MW-7C	−1.63	0.12	−0.03	0.13	−1.93	−2.19	−0.63	0.26	0.72	–	–	–	–
Well 8	−2.23	0.42	0.26	0.77	−2.40	−2.65	−0.79	0.10	0.57	1.77	−2.97	0.17	−0.64
Well 11	−1.79	0.11	−0.04	0.19	−2.20	−2.45	−0.78	0.10	0.57	2.51	−2.70	0.93	−0.23
Well 12	−2.05	0.19	0.04	0.30	−2.67	−2.92	−0.91	−0.03	0.43	1.27	−4.31	−0.63	−1.65
Well 13	−2.03	0.24	0.08	0.34	−2.30	−2.56	−0.75	0.15	0.63	2.32	−2.70	0.77	−0.26
Well 17	−2.17	0.27	0.12	0.48	−1.92	−2.18	−0.86	0.03	0.51	2.45	−2.62	0.83	−0.05
Well 19	−2.06	0.19	0.04	0.28	−2.74	−2.99	−0.91	−0.02	0.44	1.55	−3.91	−0.30	−1.22
Well 24	−2.08	0.09	−0.07	0.09	−2.51	−2.77	−0.95	−0.06	0.42	1.62	−3.90	−0.33	−1.34
Well 27	−1.94	0.15	0.00	0.15	−1.98	−2.23	−0.90	0.00	0.48	2.09	−3.11	0.29	−0.74
Well 28	−2.08	0.13	−0.03	0.10	−2.28	−2.54	−0.81	0.09	0.57	1.79	−3.89	0.07	−1.02
Well 29	−1.91	0.17	0.02	0.22	−2.68	−2.93	−0.97	−0.09	0.38	1.46	−4.32	−0.52	−1.58
Port #1	−1.93	0.28	0.12	0.45	−2.05	−2.30	−0.96	0.12	0.59	–	–	–	–
Port #2	−1.94	0.14	−0.01	0.23	−2.90	−3.15	−0.57	0.31	0.78	–	–	–	–
Well 30	−1.99	0.00	−0.15	-0.08	−2.38	−2.63	−0.97	−0.08	0.39	1.80	−4.07	−0.15	−1.17
Mendota	−3.38	0.58	0.43	1.40	−2.66	−2.91	−2.60	−1.72	−1.25	–	–	–	–
Monona	−3.74	0.90	0.75	2.03	−2.58	−2.83	−2.01	−1.13	−0.67	–	–	–	–

Note: Plus (+) sign means precipitation; Minus (−) sign means dissolution; En dash (–) means mineral is not present.

data, calculated values of SI and the mineralogy.

The chemistry of groundwater may be evolved by a number of physiochemical parameters such as temperature, pressure and the partial pressure of CO$_2$ in the soil atmosphere (P$_{CO2}$). Almost all groundwater originates from rain or snowmelt which contains a small amount of CO$_2$ derived from the atmosphere. As this water percolates into the partially saturated soil, its chemistry is changed prior to reaching the water table. One of the major causes of alteration is the uptake by the water of soil-zone CO$_2$ to form H$_2$CO$_3$, HCO$_3^-$ and CO$_3^-$ (Palmer and Cherry, 1984). The CO$_2$ is brought into solution because the partial pressure of CO$_2$ (P$_{CO2}$) in the soil atmosphere is generally greater than the atmospheric P$_{CO2}$ of 10$^{−3.5}$ bar (Mirtov, 1961). The Log P$_{CO2}$ values of all groundwater samples are shown to be higher than that of the earth's atmosphere (−3.5 atm).

According to Deutsch 1997, this could be attributed to two scenarios. The first scenario is one in which below the water table the aquifer is a closed system with respect to exchange with gases in a separate vapor phase. Assuming that there are no external sources or sinks for dissolved inorganic carbon in groundwater below the water table (that is, no carbonate minerals are present), the total dissolved inorganic carbon concentration will remain constant with pH change. However, ion speciation reactions still occur and the dominant inorganic carbon species remain a function of the solution pH. In the second scenario, the system is closed to addition or loss of CO$_2$ gas. As the pH of

the groundwater increases due to weathering reaction, the concentration of CO$_3^-$ increases in the water and carbonate minerals become oversaturated and precipitate removing carbonate from solution. This reaction lowers the total inorganic carbon concentration in the groundwater while transferring it to the solid phase. The second assumption is probably the case here where the carbonate minerals either in the dolomite or as cement in the sandstone are abundant in this system. Moreover, the data shown in Table 4 suggest that the solution is oversaturated with respect to calcite and dolomite, which makes this assumption plausible. This results in facilitating the process of selecting models that are compatible with this hypothesis, or restricting those models to the state of minerals in terms of dissolution or deposition.

The calculated saturation indices (SI) (see Table 4 and Fig. 7), show that almost all groundwater samples are oversaturated with respect to quartz, kaolinite and dolomite and saturated with respect to chalcedony, calcite and aragonite.

This indicates the influence of siliceous and carbonate minerals that exist within the sandstone aquifers and interbedded units (see Fig. 2). On the other hand, all samples are undersaturated with respect to albite, illite, amorphous silica, gypsum and anhydrite and have no pattern with respect to Ca-montmorillonite. This is consistent with the relatively low concentration of sodium, magnesium, silica and other trace elements such as aluminum and iron.
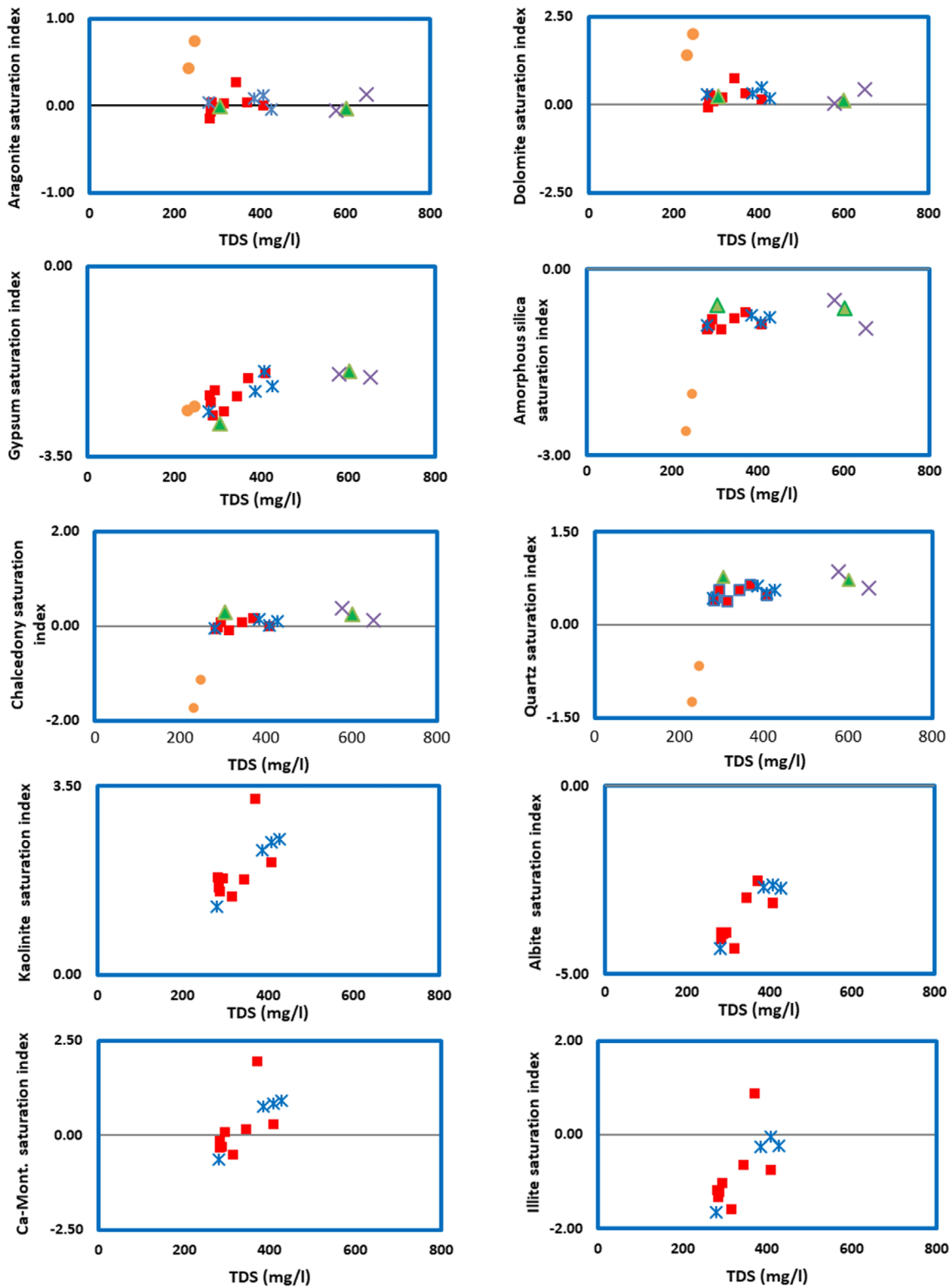
Fig. 7. Relationship between total dissolved solids (TDS) and SI (Note: Symbols are the same as them used in Figures 4, 5 and 6).

3.5. Mixing Ratio Calculation

It should be noted that the calculations of the mixing ratios in the final wells using both NETPATH and MPPI depended on the availability of the necessary data. For example, the mixing ratio calculations in well 7 were determined on the basis of chloride only, as the results of δ¹⁸O and δD were not available in the initial samples. In addition, there are some wells in which

the mixing ratios were computed based on two components, while the others were based on three components (as in the case of using MPPI to calculate the ratios in wells 8, 19, 27). This depends on whether or not these components generated models.

3.5.1. Inverse mathematical model (MPPI), (implemented in MATLAB)

It is used to quantify the mixing proportions in the groundwater pumped from wells (the final water) by comparing the chemical composition of a sample with a set of reference or end member (initial) waters. In this method, it is assumed that the composition of the final water is primarily a result of simple mixing of a number of distinct water types or reference waters, without any induced reactions. The results from mixing calculations using this method are then compared and/or integrated with those calculated from the NETPATH geochemical mass balance model. The differences between the two calculations are attributed to rock-water interactions. In this method mixing proportions were generated randomly from a uniform distribution containing four end members (initials), each characterized by 3 variables (Cl, δ^{18}O and δ^2D), which are considered to be conservative, that are mixed to obtain 4 mixed samples (Wells 7, 8, 19 and 27). Table 5 shows the mixing proportions in wells 7, 8 19 and 27 that were calculated using Equations (4) and (5).

3.5.2. Geochemical mass balance calculations (NET-PATH)

Modeling with NETPATH requires hydrologic, geologic and chemical data, as well as soft knowledge of the system to select end-members, phases and constraints. The constraints and phases used in this NETPATH model are listed in Table 6.

The selection of phases is based on the potential reactions of the groundwater with the minerals in the host bedrock and interbedded geologic units (see Table 4). A number of potential mixing and mass-balance models were developed. The expectation of some minerals to be products or reactants helps narrow the choice of models among the selected phases. For example, kaolinite is expected to be a product rather than a reactant in a weathered siliceous environment. Considering some forms of silica, waters are saturated and oversaturated with respect to quartz and chalcedony (see Table 4). This indicates that common forms of silica could be precipitated and explains why silica concentrations in the groundwater are relatively low.

The results obtained by MPPI (Table 5) and NETPATH (Table 6) calculations showed that well 7 is mainly affected by recharge from lake water and the deeper Mount Simon aquifer water (about 20% and 70%, respectively). The proportion of the shallower Tunnel City and Wonewoc Formation waters increased

Table 5. Results of the estimated mixing proportions using MPPI in "final" wells

Well ID	Elements used	Mixing ratio
Well 7	Cl	Initial 1: 0.02 Initial 2: 0.07 Initial 3: 0.71 Initial 4: 0.20
Well 8	Cl and O-18	Initial 1: 0.09 Initial 2: 0.40 Initial 3: 0.34 Initial 4: 0.17
Well 19	Cl and O-18	Initial 1: 0.07 Initial 2: 0.35 Initial 3: 0.41 Initial 4: 0.17
Well 27	Cl, D and O-18	Initial 1: 0.15 Initial 2: 0.30 Initial 3: 0.38 Initial 4: 0.17

Note: The mixing ratio calculations in well 7 were determined on the basis of chloride only, as the results of δ^{18}O and δD were not available in the initial samples. Regarding the other finals, some models were generated with three variables, while other models were generated with only two.

slightly in wells 8 and 19, reaching (5% and 2%, respectively, based on NETPATH; 9% and 7%, respectively, based on MPPI). This proportion increased significantly in well 27, reaching 15% and 30% (at the expense of Mount Simon Formation water). It should be noted that the contribution of lake water in each final water is nearly the same with the MPPI calculations, while it changes slightly, when applying NETPATH. It can be inferred from such observations that the long-term pumping from these wells, or others nearby, creates a cone of depression that facilitates recharge from surface water bodies. Another explanation, similar to that suggested by Gellasch et al. (2013), is that it might be due to a hydraulic short-circuiting effect. It is also clear that all final waters (except well 7) appear to be affected by Wonewoc Formation groundwater with lower total dissolved solids (TDS) when compared with the shallower and higher TDS, Tunnel City Group groundwater. The other deep groundwater wells (24, 28 and 29) did not generate either models or even consistent results when both MPPI and NETPATH are applied. This could be attributed to little or no mixing with these initials due to a physical hindrance such as depth or geological structure that might prevent mixing from occurring or the need for other initials such as snow melt and precipitation.

The mixing proportions computed by MPPI and/or NETPATH reflect the compositions of groundwater withdrawn from specific wells and may not necessarily represent the mixing proportions of recharge that contributes to groundwater at other wells. It is possible that at least part of the mixing indicated by MPPI and NETPATH results was caused by the convergence of many flow lines into wells screens during pumping.

Table 6. Results of the estimated mixing proportions using NETPATH geochemical model in "final" wells

Well ID	Minerals involved (m.mol/kg H_2O)		Constraints used	Mixing ratio
Well 7	KAOLINITE	0.85580	Ca, Mg, Na, K, Al, C, S, Si, Cl	Initial 1: 0.00 Initial 2: 0.11 Initial 3: 0.66 Initial 4: 0.23
	CALCITE	−1.01433		
	DOLOMITE	−0.39650		
	GYPSUM	0.15782		
	SiO_2	0.00000		
	ILLITE	−0.01977		
	ANORTH	−1.00775		
Well 8	KAOLINIT	0.31420	Ca, Mg, Na, K, Al, C, S, Si, Cl, O-18	Initial 1: 0.05 Initial 2: 0.30 Initial 3: 0.37 Initial 4: 0.28
	CALCITE	−0.58426		
	DOLOMITE	−0.29954		
	SiO_2	0.00000		
	ILLITE	−0.01275		
	ALBITE	−0.07555		
	ANORTH	−0.45416		
	Ca-MONT	−0.16515		
Well 19	Ca-MONT	0.35992	Ca, Mg, Na, K, Al, C, S, Si, Cl, O-18	Initial 1: 0.02 Initial 2: 0.24 Initial 3: 0.55 Initial 4: 0.19
	KAOLINIT	0.00246		
	DOLOMITE	−0.39394		
	GYPSUM	0.01960		
	ANORTH	0.45335		
	SEPIOLIT	0.11296		
Well 27	Ca-MONT	−0.01465	Ca, Mg, Na, K, Al, C, S, Si, Cl, O-18	Initial 1: 0.15 Initial 2: 0.30 Initial 3: 0.39 Initial 4: 0.15
	SEPIOLIT	−0.25170		
	ALBITE	−0.03413		
	CALCITE	−0.47680		
	DOLOMITE	−0.70774		
	GYPSUM	0.23823		
	SiO_2	0.75808		

Note: Plus (+) sign means dissolution; Minus (−) sign means precipitation.

4. CONCLUSION

The geochemical NETPATH model was combined with an inverse mixing model (MPPI) to help understand the effects of different end members on mixed waters. NETPATH is applied to interpret the hydrochemical evolution of groundwater along its flow path, giving information on plausible reactions (such as dissolution, precipitation, ion exchange, etc.) and the extent of multiple intial waters that mix in the final hydrochemical system. The mixing model applied by MPPI was used as a complementary tool to help identify the best fit model that accounts for a certain mixing process.

While the NETPATH model might have allowed unique estimates given sufficient hydrologic, geologic and chemical data to fully constrain the problem, the use of MPPI in this case of more limited data served as a useful tool to exclude or confirm some of the models computed by NETPATH. The saturation index calculations aided in the selection or exclusion of certain

minerals according to their dissolution/precipitation state, but this still left more than one feasible model indicating different mixing proportions. In this case, the use of MPPI was a successful way to constrain the results. Moreover, MPPI is a readily available mathematical tool that can be used along with mass-balance calculations at a site scale.

It should be noted that in this setting, in the deeper bedrock, mixing with other waters dominates over rock-water interactions because of the relatively young age of most of the groundwater and the slow kinetics of many inorganic reactions hinder water-rock interactions. This explains the relatively low salinity of the deep groundwater in the area under consideration. On the other hand, the relatively high salinity in the shallower aquifers is probably due to near surface sources of solutes such as discharge from a leaky sewer system or road salt used as a deicing material. The results in this paper suggest that all of the examined groundwater wells are much more affected by the groundwater from the Wonewoc Formation, followed by lakes. On the other

hand, they were much less affected by the Tunnel City Group aquifer, which is relatively more susceptible to contamination.

The application of such models can be considered as a valuable way to understand the significance of single interpreted process for a hydrological system. For example, the integration of chemical mixing results with flow simulation may improve our understanding of the hydrogeology of fracture zones within the bedrock such as those identified by Gellasch et al. (2013). In addition, it would be a good tool with which to evaluate the extent to which individual wells have been affected by possible sources of pollution, if any, due to anthropogenic activities.

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