Steve and Meredith Wesolowski
34 Greenwood Street
Sherborn, MA 01770

January 21, 2024

To Sherborn Board of Health and Zoning Board of Appeals Members:

We're writing to express our reservations regarding the proposed development on Greenwood Street. We have serious concerns about the environmental and health implications of this and other nearby proposed developments, given Sherborn's reliance on private wells and septic systems. The parcel of land in question reflects how shallow the groundwater level of the area is, as standing water is regularly observed on the lot from the road – particularly in areas near directly abutting properties. Coupled with abundant wetlands nearby, including at least one vernal pool, the use of septic systems for the number of homes and apartments proposed nearby seems counter to logic and safety. Were the lot "buildable" by Sherborn standards, it would have been developed many years ago. Were an adequate public water/sewer system available for the lot, none of our concerns would exist.

We ask that consideration be given to the effect on existing properties and families, as well as for those located within a larger radius and who draw from the aquifer below us now and in the future. The glacial aquifer below Sherborn – and particularly the shallow groundwater it sits on – is vulnerable to contaminants (see Lindsey, et al., p. 583, attached, where New England wells tested the highest levels of MtBE; see also Solder, et al., p. 6, where our eastern portion of the larger glacial aquifer reflected faster groundwater turn-over, resulting in a "modern" age and moderate contaminant susceptibility relative to other northern glacial aquifer locations). Even if our aquifer is not significantly contaminated today, research suggests increased human activity – and in particular further development – will likely result in concerning contamination in the not-too-distant future, with a higher density of development quickening the pace. Were the proposed density of the Greenwood development on par, or even close to, that which Sherborn has historically allowed, we would not be concerned. But multiplying 3- or 4- fold the density of housing is a lot to ask of our local groundwater. Add to this the minor improvement in available affordable housing (the additional of just one 40B house for the entire project) – it just doesn't meet common sense standards.

Echoing what others have noted to the Board of Health and Zoning Board, recent precedent in exists to protect residential water in circumstances similar to those Sherborn is facing:

In an important victory for environmental protection and sustainability, the Appeals Court last week struck down a Chapter 40B "comprehensive permit" in the Town of Stow, MA for a 37-unit apartment building on a mere two acres of land in the town's Water Resource Protection District. See, Reynolds v. Stow Zoning Bd. of Appeals, Appeals Court No. 14-P-663 (Sept. 15, 2015). The Project's single septic system would have been in close proximity to drinking water wells used by an abutting affordable housing complex and other single-family residences. Like most suburban and rural communities, *Stow has a set of local bylaws that are more restrictive than state laws governing septic systems. These laws are intended to protect not only water quality but wetlands, streams and other natural resources from the effects of wastewater and stormwater pollution. The Zoning Board ignored the advice of its own engineering consultant and waived these bylaws for the Project, despite scientific evidence presented by neighbors (from hydrologist Scott Horsley) that the septic system would contaminate abutting wells.*

Under Chapter 40B, the state's affordable housing permitting statute, local bylaws and regulations are viewed as "barriers" to the construction of multi-family, affordable housing, and there is a strong legal presumption that any "local concerns" associated with the waiver of these bylaws are outweighed by the need for affordable housing. The precedent that has evolved over the last 40 years in our judicial system has made it nearly impossible for municipalities to deny Chapter 40B projects, or to deny requested waivers. Last week's Appeals Court ruling is the first appellate-level decision (precedent) that we are aware of revoking a comprehensive permit on substantive grounds, and sends a clear message that Chapter 40B does not override local protection of water resources. The decision will probably be cited to defend future municipal comprehensive permit decisions in which other public health, safety and environmental interests are at stake.

With these concerns in mind, and echoing others expressing similar concerns about this project, we request the following:

That no variances are granted for this project in issuing a comprehensive permit.

That the ground be tested again, now that the water levels are closer to historical norms.

That test holes are drilled around the site for monitoring purposes, should wells be drilled.

Thank you for your attention in this matter.

Sincerely,
Steve and Meredith Wesolowski

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Using groundwater age distributions to understand changes in methyl *tert*-butyl ether (MtBE) concentrations in ambient groundwater, northeastern United States

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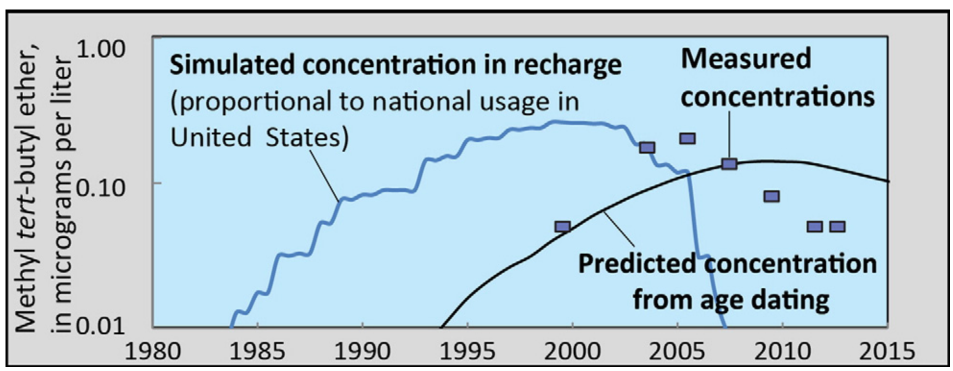
HIGHLIGHTS

- Discontinuation of use of methyl *tert*-butyl ether provides a tracer to track aquifer recovery.
- Age tracers and modeling allow prediction of how a well will respond to changes in contaminant sources.
- Models correctly predict changes in methyl *tert*-butyl ether concentration for many wells.
- Retrospective model analysis with independent data enhances understanding of contaminant behavior.
- Study scale shows the susceptibility of aquifers in the region to widespread low-level contamination.

GRAPHICAL ABSTRACT



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ABSTRACT

Temporal changes in methyl *tert*-butyl ether (MtBE) concentrations in groundwater were evaluated in the northeastern United States, an area of the nation with widespread low-level detections of MtBE based on a national survey of wells selected to represent ambient conditions. MtBE use in the U.S. peaked in 1999 and was largely discontinued by 2007. Six well networks, each representing specific areas and well types (monitoring or supply wells), were each sampled at 10 year intervals between 1996 and 2012. Concentrations were decreasing or unchanged in most wells as of 2012, with the exception of a small number of wells where concentrations continue to increase. Statistically significant increasing concentrations were found in one network sampled for the second time shortly after the peak of MtBE use, and decreasing concentrations were found in two networks sampled for the second time about 10 years after the peak of MtBE use. Simulated concentrations from convolutions of estimates for concentrations of MtBE in recharge water with age distributions from environmental tracer data correctly predicted the direction of MtBE concentration changes in about 65% of individual wells. The best matches between simulated and observed concentrations were found when simulating recharge concentrations that followed the pattern of national MtBE use. Some observations were matched better when recharge was modeled as a plume moving past the well from a spill at one point in time. Modeling and sample results showed that wells with young median ages and narrow age distributions responded more quickly to changes in the

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contaminant source than wells with older median ages and broad age distributions. Well depth and aquifer type affect these responses. Regardless of the timing of decontamination, all of these aquifers show high susceptibility for contamination by a highly soluble, persistent constituent.

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1. Introduction

Methyl *tert*-butyl ether (MtBE, formally 2-methoxy-2-methylpropane) is a volatile organic compound that was initially used at low percentages in gasoline as an octane booster starting in 1979 when tetraethyl lead was phased out (Squillace et al., 1997). A few years later, the Clean Air Act Amendments of 1990 (implemented in 1992), and the Reformulated Gasoline (RFG) Program (implemented in 1995) required increases in the oxygenate content of gasoline in order to reduce air pollutants. Oxygenates such as ethanol, ethyl tertiary butyl ether (ETBE), and tertiary amyl methyl ether (TAME) were options to attain the oxygenate requirements, but MtBE was by far the most highly used of these options. Gasoline had to contain 11 to 15% MtBE by volume to meet these standards and MtBE use increased rapidly through the 1990s accordingly (Fig. 1) (C&EN, 1993; U.S. Department of Energy, 2014). Due to its high solubility, weak sorption to soils, and resistance to biodegradation in groundwater, MtBE is highly mobile in the subsurface. Although not classified as a human carcinogen, neurological effects have been reported, as well as renal and hepatic tumors in laboratory animals (Agency for Toxic Substances and Disease Registry, 1996). The U.S. Environmental Protection Agency has set a drinking water advisory level of 20 to 40 μg/L for MtBE based on taste and odor issues (U.S. Environmental Protection Agency, 2012). An estimate of the cost of cleaning up MTBE spills from leaking underground storage tanks in the United States is about 2 billion dollars (Sweet et al., 2006).

MtBE quickly became a national issue in the United States in the 1990s because of its frequent detection in groundwater. Large spills caused concentrations in public-supply wells to reach levels high enough to cause the wells to be abandoned (Cooney, 1997), and widespread, low-level detections of MtBE quickly became common in groundwater (Squillace et al., 1996), particularly in the northeastern United States (Fig. 2) (Moran et al., 2004). Many states reacted by placing partial or complete bans on MtBE and in 2005, the Energy Policy Act (U.S. Congress, 2005) removed the oxygen requirement from gasoline causing MtBE use in gasoline to decline to negligible levels by 2007 (Fig. 1). Major plumes having concentrations in the thousands of micrograms per liter (μg/L) are a serious problem but cover a small fraction of groundwater systems. Recent studies of large plumes which are undergoing remediation show diminishing MtBE concentrations (McDade et al., 2015). A less serious but widespread problem is the large percentage of wells across broad areas, especially in the northeastern United States,

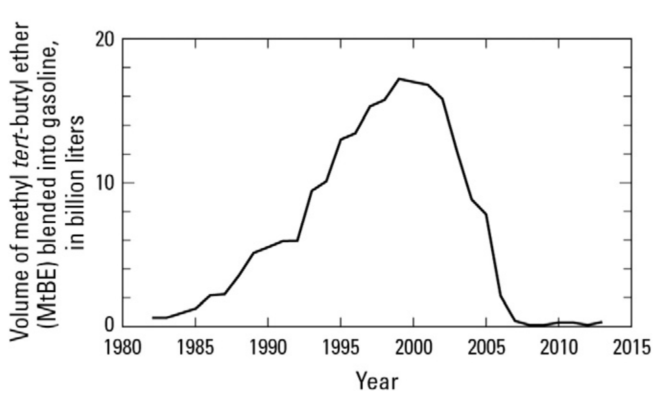

Fig. 1. The volume of MtBE blended into gasoline in the United States, 1982–2014, estimated from domestic production plus imports minus exports plus change in inventory (U.S. Department of Energy, 2014).

that have low-levels of contamination of MtBE. The question addressed in this study is, in the time since the discontinuation of MtBE usage, are widespread, low-levels of MtBE contamination in ambient groundwater changing, and can groundwater age explain these changes? Studies in areas with widespread, low-levels of MtBE completed shortly after the decline in MtBE use have been inconclusive (Ayotte et al., 2008; Peckenham, 2007).

MTBE also is a concern internationally, although the rise and decline in its use may have been more rapid in the U.S. than elsewhere. In Europe MtBE has been used mainly as an octane enhancer rather than as an oxygenate, and the average MtBE content in the gasoline pool in Europe in the late 1990s was 2% when the MtBE content in RFG areas of the United States averaged 11% by volume (Schmidt et al., 2002). However, MtBE contamination in groundwater has been reported many other parts of the world. In Japan, Tanabe et al. (2005) detected MtBE at low levels in about 30% of groundwater samples. Kolb and Puttmann (2006) found detection frequencies of MtBE in Germany to be similar to those found in the United States. Rosell et al. (2006) found concentrations of MtBE > 100 μg/L in groundwater near known spills in several European countries, but maximum concentrations in drinking water were typically very low (<0.5 μg/L). Possibly because of the lower incidence of spills contaminating major water supplies, MtBE is still in use in most of the rest of the world; however, its potential as a groundwater contaminant has been recognized. In Europe, for example ETBE market share has increased from 15% in 2002 to 60% in 2010, while MtBE has decreased correspondingly (Stupp et al., 2012).

The objective of this paper is to identify MtBE trends in groundwater in the northeastern United States, and to use groundwater age and plausible MtBE concentrations in recharge to explain observed temporal changes in MtBE. We identify where concentrations have increased, decreased, or remained unchanged during 1996–2012 based on repeated sampling by the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Project. Comparison of concentration-time trends with groundwater age distributions from age-tracers has not been done previously on a regional scale for a contaminant such as MtBE, which had large releases to the environment over a relatively short time period. The rapid increase of MtBE use in the United States since the 1980s, followed by an abrupt cessation in use, provides a unique opportunity to compare measured concentrations to model predictions. This groundwater age-based framework for understanding temporal changes in MtBE can also be used to understand aquifer vulnerability and potential aquifer response to other groundwater contaminants with changing source inputs.

2. Study design and methods

2.1. Sampling and chemical analysis

The focus of the study is a set of 148 wells in 6 well networks in the northeastern United States that are part of the national NAWQA project (Fig. 2). The wells were selected using a stratified random selection method in order to represent ambient conditions in each respective study area. Nearly 70% of the samples were from wells used as a source of drinking-water supply. Shallow monitoring wells comprised two networks, and domestic and public-supply wells comprised the remaining four networks; well depths in these four networks were in the depth range typical of supply wells in their respective aquifers (Fig. S1). The northeastern region of the United States had 61% of the detections of MtBE in the nation (Zogorski et al., 2006), 70% of all measureable

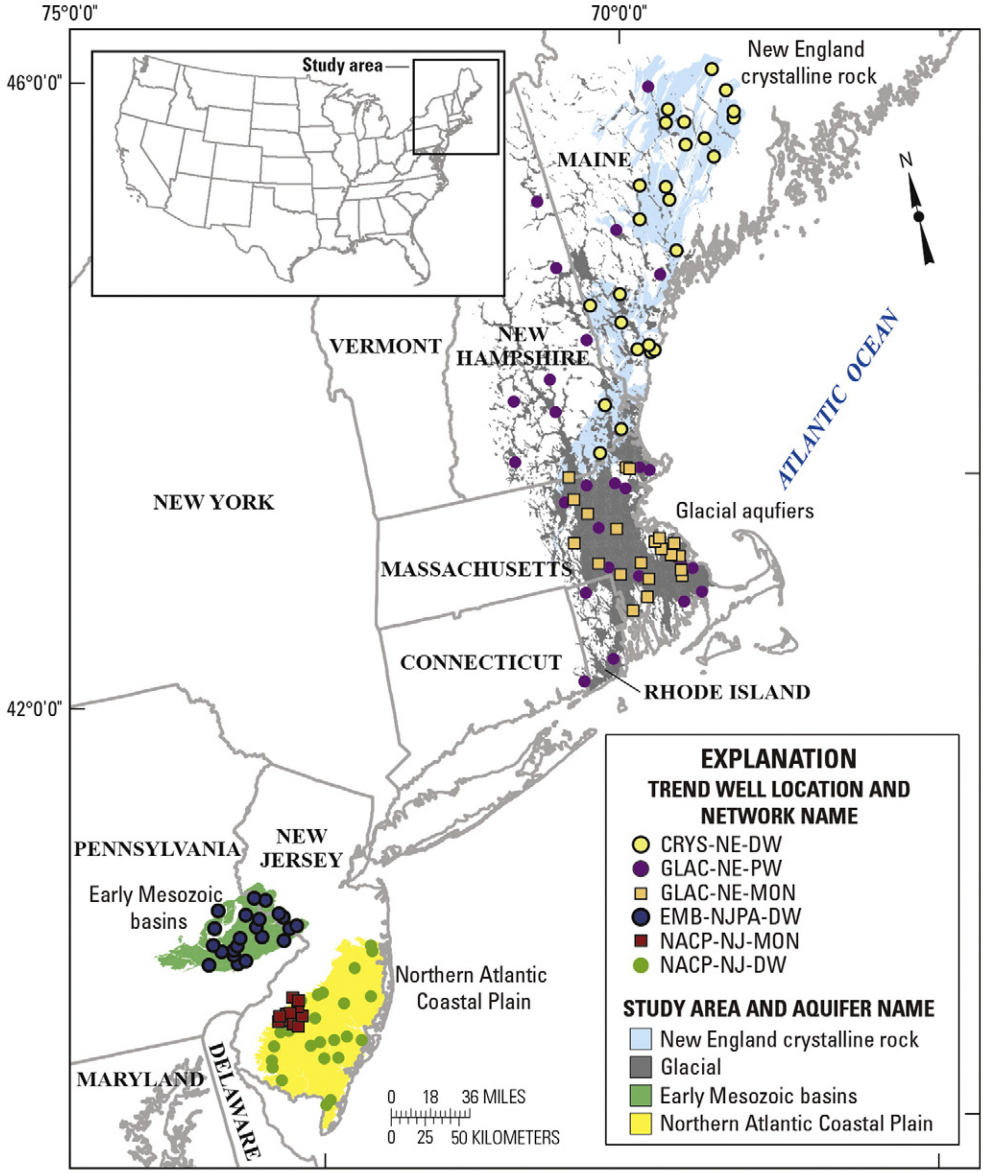

Fig. 2. Locations of wells in northeastern USA networks evaluated for change in MtBE concentration.

changes in MtBE concentrations in individual wells nationally, and 3 of the 4 networks in the nation with statistically significant changes in concentration of MtBE (Lindsey et al., 2016). Well networks contain 21–28 wells each that represent an aquifer and in some places, groundwater beneath a specific land use (Lapham et al., 1995). Each well in the network was sampled for MtBE between 1996 and 2001 and resampled a decade later between 2005 and 2012. Network design, sample collection, and trend analysis for MtBE and age tracers follow nationally consistent protocols (Lapham et al., 1995; Rosen and Lapham, 2008; U.S. Geological Survey, variously dated). About two-thirds (106) of the wells in the study area were analyzed for some type of age-dating tracer; wells were selected for age dating without respect to previous measurements of MtBE or other contaminants. Up to 6 wells from each network were sampled biennially starting in 2000 to evaluate temporal patterns. All MtBE data are available on the USGS National Water Information System (U.S. Geological Survey, 2014). Raw age-dating tracer data are available from published USGS reports (Hinkle et al., 2010; Shapiro et al., 2012). See supporting information for details on laboratory analysis, ancillary data, lumped parameter modeling, statistical analysis, uncertainty, and plots of predicted and simulated and measured MtBE concentrations.

2.2. Network descriptions

The six networks in the northeastern United States cover several aquifers, land uses and well types. Two networks consisted of monitoring wells drilled for this study at randomly selected sites in urban areas, one in the Northern Atlantic Coastal Plain in New Jersey (NACP-NJ-MON), and the other in the glacial aquifers in New England (Connecticut, Maine, Massachusetts, New Hampshire, and Rhode Island) (GLAC-NE-MON). Median well depths were 9 and 7.5 m (m), respectively, in the NACP-NJ-MON and GLAC-NE-MON networks (Fig. S1). Two networks consisted of domestic wells in fractured bedrock aquifers, one in the New England crystalline-rock aquifers (CRYS-NE-DW) and the other in New Jersey and Pennsylvania in the early Mesozoic basin (sandstone aquifers; EMB-NJPA-DW). Median well depths for these two networks in bedrock aquifers were 56 and 50 m, respectively. One network consisted of domestic and commercial supply wells in the Northern Atlantic Coastal Plain in New Jersey (NACP-NJ-DW). One network in New England consisted of public-supply wells in glacial aquifers (GLAC-NE-PW). Median well depths for these two networks were 30 and 18 m, respectively. Locations of all wells, including the monitoring wells, were selected to assess ambient conditions. Sites near known spills were intentionally avoided. All well networks used a stratified random selection program (Scott, 1990) that allows estimation of the proportion of the area affected by concentrations exceeding any selected threshold (Belitz et al., 2010).

2.3. MtBE in recharge

MtBE enters aquifers by spills of gasoline of various magnitudes. Major gasoline spills cause large plumes with concentrations of MtBE in the range of 10,000 to >1.000,000 μg/L (Ayotte et al., 2008, Einarson and Mackay, 2001; Connor et al., 2015). Concentrations measured in this study (<10 μg/L in all but two samples) are orders of magnitude smaller in concentration than would be expected in a plume near a major spill from an underground storage tank (Connor et al., 2015; New York State Department of Environmental Conservation, 2008). Some of the detections in this study could be on the margins of large plumes. Some contribution from atmospheric sources is likely, but based on MtBE concentrations in air (Pankow et al., 2003) (7 locations near the 6 networks) and calculated equivalent concentrations of MtBE in recharge (Baehr et al., 1999) (median equivalent concentration in recharge, 0.07 μg/L; 95th percentile = 0.8 μg/L), atmospheric deposition could not account for most detections of MtBE. Another likely source of MtBE is unreported small spills from gas stations (gasoline filling stations), which can amount to as much as 150 L per year per station (Hilpert and Breysse, 2014). Although much of this spill volume evaporates, even a small fraction of that amount infiltrating into the groundwater could account for the concentrations of MtBE measured in this study. A study in Maine identified very small spills of gasoline associated with refueling automobiles, lawn-care equipment, and recreational vehicles as the likely source of the majority of low-level MtBE detections (Nielsen and Peckenham, 2000). A study of MtBE in surface runoff showed concentrations of 1–2 μg/L from commercial, residential, and industrial land areas, which could be another source in recharge (Lopes and Bender, 1998). The annual volume of gasoline from the latter three sources – atmospheric deposition, small spills at gas stations, and small spills at private residences – would have been relatively consistent over time, and thus concentration of MtBE in recharge from these sources would vary temporally in proportion to the amount of MtBE blended into gasoline (Fig. 1). State bans on MtBE use in the study area closely matched the decrease in national use.

In the present study, MtBE was simulated using recharge concentrations of up to 1 μg/L distributed over various time periods, which produces concentrations in the range typically detected in this study. One scenario is that concentrations were proportional to the national use of MtBE with a peak of 1 μg/L in 1999. Another scenario is a short-term spill that was simulated using 1 μg/L in recharge over a span of 2 years. Recharge from plumes arriving and moving vertically or horizontally past the well was simulated with six curves of 10-year duration and 1 μg/L maximum concentration; with peak concentrations at 1996 and every second year through 2006. These recharge scenarios could also represent a spill, followed by remedial action that caused concentrations to decrease. A plume with a constant source was simulated by recharge concentrations increasing to 1 μg/L in 1992 and then remaining constant until 2007 (Fig. 3). Higher or lower assumptions for the concentration of MtBE in recharge affect the height of the predicted curve, but not the width or timing of the peak of the curve predicting MtBE concentrations in groundwater. Because the predictions in the present study focus on the timing and direction of change, not the magnitude of groundwater concentrations, concentrations of MtBE in recharge need not be precisely specified.

2.4. Groundwater age and modeled MtBE trends

Atmospheric contaminants such as chlorofluorocarbons (CFCs), sulfur hexafluoride (SF_6), and tritium (^3H) are uniformly distributed in recharge and vary in concentration temporally in a way that concentrations measured in groundwater can be used as age-dating tools for shallow groundwater (Busenberg and Plummer, 1992; Busenberg and Plummer, 2000; Schlosser et al., 1989; Aeschbach-Hertig et al., 1999; International Atomic Energy Agency, 2006). Contaminant concentrations in groundwater are compared to the concentrations that would be expected in recharge based on the partitioning of the atmospheric contaminant to water in a given year to estimate the apparent recharge year. Water in a well, however, commonly is a mixture of water of different ages, and it is important to understand the distribution of age when interpreting temporal changes of a contaminant in groundwater. Determining the distribution of ages requires multiple tracers and a modeling approach. Age distributions for each well were determined by fitting lumped parameter models (LPMs) to measured environmental tracer data using a modified version of the program TracerLPM (Jurgens et al., 2012) that performs nonlinear, weighted least-squares fits. Groundwater age-dating tracers such as CFCs, SF_6, ^3H, and tritiogenic helium-3 ($^3He_{trit}$) were available for some of the samples in each network, although not every network had all tracers analyzed. Model results including the selected LPM model, tracers used, mean groundwater age, model parameters, and model error are available in Table S1. To compare the central tendency of age across well networks, a single, characteristic age distribution was constructed from the wells where age dating tracers were collected in each network because age tracers were not collected at all wells. The *network characteristic age* was defined as the median of mean ages (time elapsed since recharge) for those wells in a given network that did have age dating (Fig. 4).

Age distributions determined from TracerLPM (Jurgens et al., 2012) were convolved with various estimates of MtBE in recharge (Fig. 3) to produce simulated concentrations of MtBE in the well. Simulations where MtBE in recharge varied in proportion to the national usage produced the best matches to measured concentrations; therefore, this scenario was used for all predictions. The simulation of a plume with peak concentrations in 1996 provided the second most accurate predictions of the direction of change, but predictions of peak concentrations were often too early. Simulations of short-term spills and a constant concentration plume matched biennial observations poorly and were not considered further. A *network characteristic curve* was created by calculating the annual median of all simulated MtBE concentrations for wells in that network. This curve is used for comparisons of generalized patterns of age distributions among networks; all actual predictions used simulated MtBE curves for individual wells.

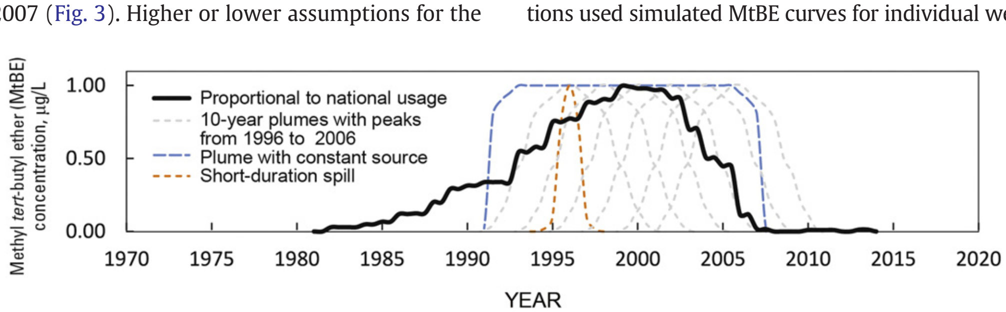

Fig. 3. Scenarios of concentrations of MtBE in recharge representing potential sources and used to simulate concentrations of MtBE in groundwater.

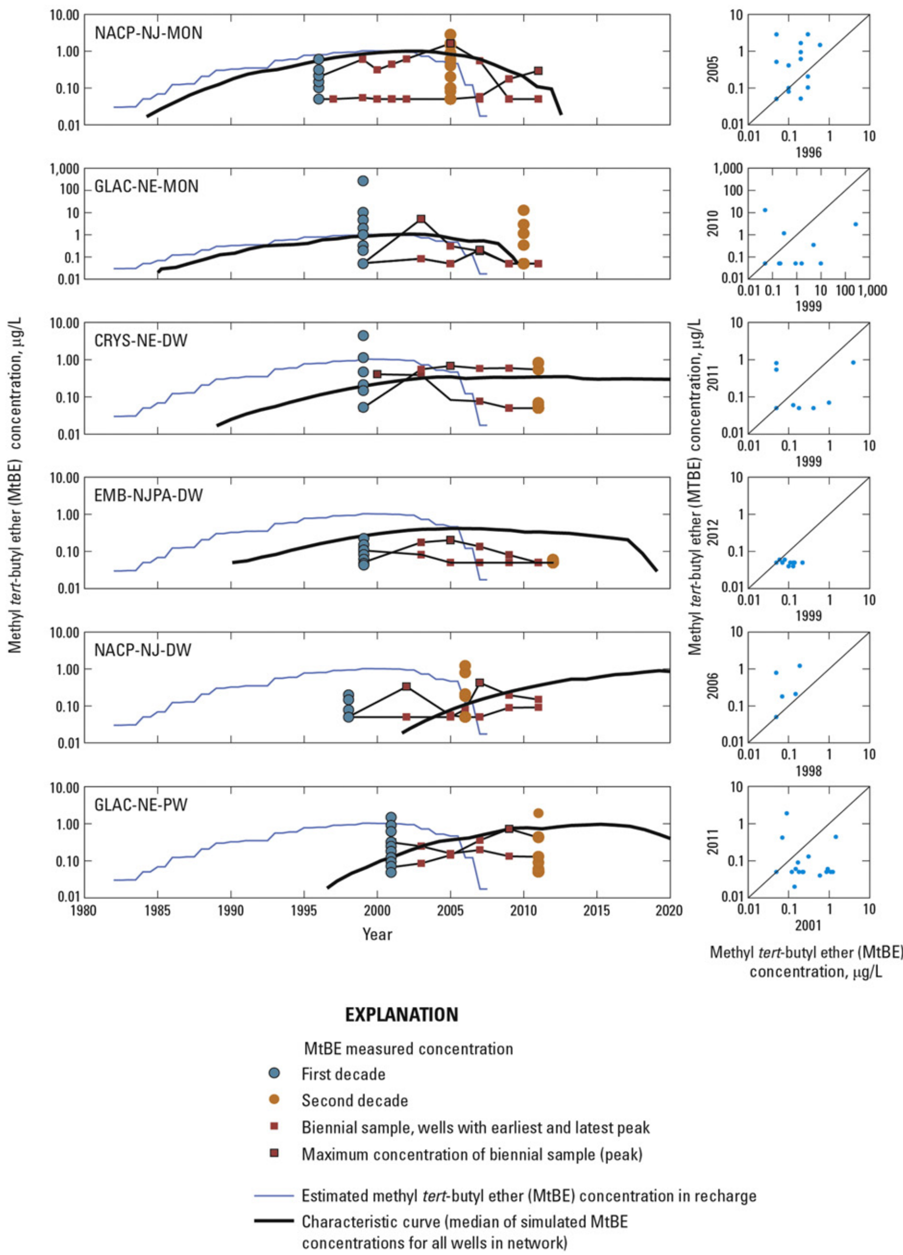

Fig. 4. Measured MtBE concentrations compared to simulated concentrations and measured concentrations in first sampling event compared to second sampling event.

During the analysis, the possibility of using MtBE as an age dating tracer was explored. Although trends in many wells in the Northeastern United States are similar to trends predicted by convolution of MTBE production history with the groundwater age distribution, in other cases, the source was more likely to have been a point-source spill. In addition, the concentration was not uniformly distributed in recharge, with many wells having no detections of MtBE at all. Consequently, MTBE fails to qualify as a tracer of groundwater age, but might qualitatively indicate the period at which MTBE entered the groundwater system.

2.5. Statistics

The Wilcoxon-Pratt signed-rank test, a matched pair test that includes zero-difference ties in the calculation (Pratt, 1959; Wilcoxon, 1945), was used to evaluate changes in observed concentrations at the network level. The test is a nonparametric statistical test used to compare matched pairs to determine whether or not the mean ranks differ between the two samples. The null hypothesis is that the median difference between pairs is zero, which in this case would indicate no statistically significant change in concentrations of MtBE between the two sampling periods. Details of data preparation and statistical analysis are provided in the supporting information.

3. Results

3.1. Age dating and residence time distribution

Age-dating tracers were used to determine residence time distributions for individual wells, and subsequently to model MtBE concentrations in those wells. Information about model selection and parameterization is provided in supporting materials. All comparisons of age-based model predictions to measured values were based on residence time-distribution curves for individual wells; however, some generalized measures of age – the network characteristic age and the network characteristic curve – are reported to allow general comparisons among networks. For example, the characteristic age for the two networks in shallow unconsolidated materials, NACP-NJ-MON and GLAC-NE-MON, had the youngest characteristic ages (3 and 8 years, respectively, Table 1.), as would be expected. The network characteristic curves also predict a relatively fast decrease in MtBE concentration for these two networks. For the other 4 networks, the range of ages and the span of ages (Fig. S2) provide more insight than the characteristic age. For example, the two deeper well networks in the unconsolidated aquifers, NACP-NJ-DW and GLAC-NE-PW, both have mean ages that are older than the monitoring wells, and also have a small range of mean ages, and a relatively small span of ages (time span from the youngest water arriving at the well to the oldest water arriving at the well). The two networks in bedrock aquifers, which have the deepest wells, have a large range of mean ages and some wells have a span of ages that measure in hundreds of years. Based on these measures alone, one would predict a contaminant would flush more rapidly in the networks with shallow monitoring wells. Also some of the wells in the bedrock aquifers would flush very rapidly, while others would continue to have low levels of contamination for many years. The characteristic curves (Fig. 4) illustrate these general patterns.

3.2. Observed and modeled MtBE trends in well networks

Trends were evaluated using observed changes in concentration with time (observations), modeled concentrations compared to observations (historical matching), and predicted future changes (projections). In this section, results are described by well network. For historical matching, the change in observed concentration was compared to the predicted change in concentration during the approximately 10-year time span on a well by well basis to determine how often the model correctly predicted increasing or decreasing concentrations. To account for the uncertainty in the age dating, a 95% confidence interval for modeled concentrations is compared to observed values as well. The network characteristic curve also was compared to both 10-year and 2-year (biennial) samples from wells in the network. Simulated concentrations of MtBE in recharge are plotted to illustrate lag times. For wells with biennial samples and age tracers, the timing of the observed peak in concentrations was compared to the model predicted peak in concentrations. Plots comparing modeled and observed concentrations for all wells that had detections of MtBE and age dating tracers are provided in the supporting information, Figs. S4 to S9.

3.2.1. NACP-NJ-MON well network

The NACP-NJ-MON network was sampled in 1996 and again in 2005. Concentrations increased at 8 wells, were unchanged in 14, and decreased at 5 wells (Wilcoxon-Pratt signed rank test indicates differences in mean ranks are not statistically significant; $p = 0.18$). Concentrations at biennially sampled wells peaked in 2005, or were increasing at the time of the last sample in 2011 (Fig. 4). Modeling yielded a network characteristic age of 3 years and the network characteristic curve predicted peak MtBE concentrations in 2003; these measures are for general comparisons of age distributions among networks only. Both the network characteristic curve and most biennial samples showed a prolonged period of MtBE detections, followed by an abrupt decrease (Fig. 4). For the well that had increasing concentrations when the last biennial sample was collected in 2011, the model predicted peak concentrations in 2012. Historical matching – comparing individual modeled MtBE concentrations to measured concentrations – correctly predicted the direction of change (during the 9-year time span) in 3 of 4 wells (Table 1). Both modeling and measured (observed) values indicate that concentrations in most of the wells in the network where MtBE had been detected were likely to be <0.05 μg/L by 2011.

3.2.2. GLAC-NE-MON well network

In the GLAC-NE-MON network, sampled in 1999 and 2010, MtBE concentrations decreased at 7 wells, were unchanged in 13 and increased at 2 wells (not statistically significant $p = 0.116$). Concentrations at biennially sampled wells peaked between 2003 and 2007 and were <0.05 μg/L by 2011 (Fig. 4). Age tracer modeling yielded a network characteristic age of 8 years. The network characteristic curve predicted that concentrations in 2011 would be less than in 1999, with peak concentrations in 2005 (Fig. 4). Two wells with biennial samples had multiple years of detectable MtBE, followed by an abrupt decrease in 2009, similar to their respective model prediction (Fig. 4). Historical matching predicted the direction of change correctly for 6 of 9 wells, increasing to 7 out of 9 when considering the 95% confidence interval for the mean ages (Table 1).

3.2.3. CRYS-NE-DW well network

The CRYS-NE-DW network was sampled in 1999 and resampled in 2011. MtBE concentrations decreased in 5 wells, were unchanged in 18, and increased in 2 wells (no statistically significant change; $p = 0.274$). Concentrations in biennially sampled wells peaked between 2000 and 2005 (Fig. 4). The network characteristic age is 20 years. The network characteristic curve shows a steady increase in concentrations until about 2009, when the concentrations plateau or decrease slowly (Fig. 4), which is consistent with concentrations at one of the wells with biennial samples. The direction of change was correctly predicted for 3 of the 7 wells. The predictions improved to 4 of 7 when considering the 95% confidence interval of the mean age (Table 1).

Table 1
Network description and summary of results for networks in the Northeastern USA.

	Well network					
	NACP-NJ-MON	GLAC-NE-MON	CRYS-NE-DW	EMB-NJPA-DW	NACP-NJ-DW	GLAC-NE-PW
Aquifer	Northern Atlantic Coastal Plan	Glacial aquifer system	New England Crystalline-rock aquifers	Early Mesozoic Basin (sandstone)	Northern Atlantic Coastal Plain	Glacial aquifer system
Geographic region	New Jersey	New England	New England	New Jersey and Pennsylvania	New Jersey	New England
Type of well	Monitoring	Monitoring	Domestic	Domestic	Domestic and commercial	Public supply wells
Time period of sampling	1996–2005	1999–2010	1999–2011	1999–2012	1998–2006	2001–2011
Number of wells (wells with at least one detection of MtBE)	27 (13)	21 (9)	25 (7)	22 (8)	25 (4)	28 (17)
Sample pairs with increasing/decreasing concentration	8/5	2/7	2/5	0/8	4/0	2/15
Probability value of Wilcoxon-Pratt signed rank test	0.180 (no change)	0.116 (no change)	0.274 (no change)	0.005 (decrease)	0.046 (increase)	0.004 (decrease)
Network characteristic age in years	3	8	20	12	21	14
Correctly predicted direction of change (95% confidence interval, if improved)	3/4	6/9 (7/9)	3/7 (4/7)	6/7	1/1	3/6 (5/6)

The CRYS-NE-DW network has a large range of mean ages, as previously discussed, likely because it includes some wells with short flow paths and others with much longer flow paths. Thus, the characteristic curve for the entire network is less meaningful than for the other networks, and a separate representation of separate curves is appropriate (Fig. 5). Both the length of the open interval and the proximity of the open interval to the land surface affect groundwater age, and as expected, separating the characteristic curves on the basis of these characteristics illustrates differences in age distributions. Shallow wells in the network (well depth < 61 m, and <7.5 m of well casing) have younger mean ages, and a characteristic curve that suggests that these wells would respond more rapidly than others to changes in contaminant sources (Fig. 5). Deep wells (>61 m deep and >7.5 m of casing) have a characteristic curve that suggests contaminants arrive at these wells later and at lower concentrations, but persist longer than in the shallow wells. Shallow wells had a high overall detection frequency (40%) and decreasing concentrations (Fig. 5), whereas deep wells had a lower detection frequency (11%) and increasing concentrations (Fig. 5). Previous studies in this aquifer have shown that deep wells with long casings have lower concentrations of anthropogenic contaminants (nitrate) when compared to shallow wells (Flanagan et al., 2012). This is likely because contaminants have not yet arrived at the deeper zones of the aquifer.

3.2.4. EMB-NJPA-DW well network

The EMB-NJPA-DW network was sampled in 1999 and again in 2012. MtBE concentrations decreased in 8 wells, were unchanged in 14, and did not increase in any wells (statistically significant decrease; $p = 0.005$). Concentrations in the wells sampled biennially peaked between 1998 and 2005 and all were <0.05 μg/L by 2012. The network characteristic age was 12 years. The characteristic curve predicted peak concentrations in 2005. The model correctly predicted concentration change for 6 of 7 wells, which did not improve when considering the 95% confidence interval.

Similar to the other fractured bedrock network (CRYS-NE-DW), this network has a large range in mean groundwater age and a large span of ages. Also, like that network, the characteristic curve for EMB-NJPA-DW varies depending on well depth and casing length. Shallow wells were twice as likely to have MtBE detected, had higher initial concentrations, and had larger decreases in concentrations as compared to deep wells (Fig. 5), as predicted by the model. For this aquifer the aggregate measures of characteristic age and the characteristic curve would not be effective to predict concentration changes for wells without age dating because of the large range of mean ages and the span of ages in the aquifer.

3.2.5. NACP-NJ-DW well network

The NACP-NJ-DW network was sampled in 1998 and again in 2006. MtBE concentrations increased in 4 wells, were unchanged in 21, and none had decreased concentrations (statistically significant increase; $p = 0.046$). Concentrations in the biennially sampled wells peaked in 2002 and in 2007. Age-tracer data for this network was limited (SF_6, 9 samples). The network characteristic age was 21 years. A single age tracer makes it difficult to constrain the groundwater age distribution. Only a single site had both measured concentrations of MtBE and the age tracer, and the model correctly predicted increasing concentrations. The characteristic curve predicts concentrations increasing from 1998 through 2006, and continuing to rise through about 2019. The biennial sampling, though limited, would indicate that this modeled late peak in concentrations overestimates the time to actual peak concentrations (Fig. 4). Without use of better age-dating tracers to constrain the model, few conclusions can be made about the future concentrations of MtBE in this aquifer.

3.2.6. GLAC-NE-PW well network

The GLAC-NE-PW network was sampled in 2001 and again in 2011. MtBE concentrations decreased at 15 wells, were unchanged in 11, and increased at only 2 wells, a statistically significant decrease ($p = 0.004$). Concentrations at the wells sampled biennially peaked between 2001 and 2009 (Fig. 4). The network characteristic age for the wells in this network is 14 years and the characteristic curve for this network showed peak concentrations in about the year 2015, which is later than observed peaks in biennial samples. Historical matching predicted the direction of change correctly in only 3 of 6 wells, although, the predictions improve to 5 of 6 when considering the 95% confidence interval. Modeled ages for the GLAC-NE-PW were likely less accurate than the ages estimated for the other networks because CFCs were the only age-dating tracers for this network. CFCs alone are less reliable than

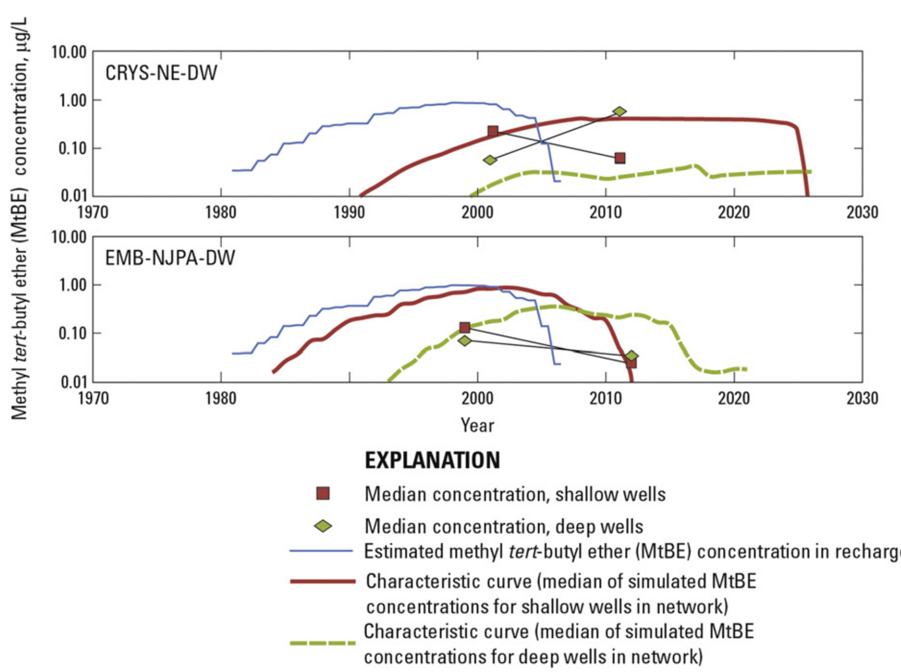

Fig. 5. Measured MtBE concentrations are compared to simulated concentrations in shallow and deep wells.

when sampled with other tracers concurrently. Another study including age dating in glacial public-supply wells using more tracers yielded apparent groundwater ages of <6 years (Brown et al., 2009). This age range would better explain the measured MtBE concentrations, with nearly all decreasing between 1999 and 2011.

For all six networks combined, predictions of increase or decrease in concentrations based on concentration in recharge varying in proportion to national MtBE usage were correct for 65% of wells; however, when considering the upper and lower confidence intervals, predictions improved to 76%. Alternate recharge scenarios account for the remaining cases; however, simulations of 10-year plumes with peaks later than 2000 were never correct for >32% of the wells. Remediation of existing plumes could also account for the increasing and decreasing concentration in recharge. A more simple observation is that, for wells with mean ages less than or equal to 10 years that were sampled >10 years after peak MtBE use, 88% had decreasing concentrations. Wells with longer residence times and wells sampled closer to the peak of MtBE usage had a lower percentage of wells with decreasing concentrations.

3.3. Uncertainty of predictions

For a given well, the source, concentration, and duration of MtBE in recharge are unknown. The fact that the recharge curve based on national usage results in the best matches to observations indicates that, whatever the source, most wells experienced a long exposure to MtBE that generally increased and decreased with the usage. Plumes moving vertically or horizontally past the well screen over a prolonged period are a likely source — but spills containing MtBE would have occurred between 1982 and 2007 and would have been most likely during the 1990s. Atmospheric deposition, small spills from gas stations, and spills from home use are also a likely source, and MtBE in these spills would follow the pattern of national usage. MtBE from a very small, but continuous leak from a gas station would also follow the national usage pattern. Although new spills of MtBE are unlikely since about 2007, the persistence of MtBE makes movement of existing plumes toward wells an ongoing possibility.

In addition to assumptions of recharge concentration, age dating and decay through biodegradation are also sources of uncertainty. Model parameters can be modified to fit observed biennial data, thus using the MtBE concentrations to improve understanding of groundwater age and recharge concentrations. Models that include decay were also simulated to fit the observed data, but required recharge concentrations an order of magnitude higher than the simulations without decay. Fig. S3 illustrates both of these scenarios. Continued refinement of groundwater age-dating and better understanding of contaminant decay in a given location can help approach a unique solution.

The frequency of sampling, even the biennial sampling, was not sufficient to evaluate all possible temporal fluctuations. Concentrations were not correlated with hydrologic conditions or water-level fluctuations; however, a rigorous evaluation of the potential effects of wet and dry spells on concentrations is not possible with the available data. Nevertheless, the decadal and biennial data revealed patterns that are helpful in understanding the longer-term temporal changes in MtBE concentrations.

4. Discussion and conclusions

The combination of observations and modeled concentrations can provide an informed indication of how aquifers are likely to respond to the introduction of a relatively persistent contaminant followed by a rapid reduction of the source. In the case of MtBE in the Northeast, two sampling events approximately a decade apart, biennial sampling in a subset of wells, and modeled concentrations provide sufficient understanding of changes in concentrations to conclude that concentrations in most wells where MtBE was detected were beyond peak concentrations by 2012 (Fig. 4). Historical matching and projections were of uncertain quality in networks with a single age-dating tracer. Differences in the expected patterns of contaminant flushing were observed, with shallow wells having the shortest flushing times, deeper wells having longer flushing times, and with the deepest bedrock wells having a mix of rapid and very long flushing times depending on the well depth and length of open interval. Wells with long open intervals are likely to have broad distributions of age and experience long periods (a decade or more) of increasing and decreasing concentrations. Concentrations will likely be lower than wells with narrow age distributions, where the contaminant arrives at the well over a short time span, as has been previously reported (Eberts et al., 2013). Despite the differences in the timing of contaminant decreases, the high level of detections in all of these aquifers reveals the susceptibility of the aquifers to a contaminant that is soluble and persistent, such as MtBE. Continued sampling in these networks will provide additional insight into these processes and the ultimate fate of MtBE in groundwater, as well as other contaminants that might be introduced into these aquifers.

This study illustrates, with specific examples and observable outcomes, the need for long-term and varied types of trend data collection. The USGS NAWQA Project groundwater sampling provided early and critical information on the presence of MtBE in samples from ambient groundwater in aquifers across the nation, and the ongoing sampling has provided information on the changes in concentrations. The study also illustrates the value of collecting age-dating tracers, and using software such as Tracer-LPM to interpret those data using age distributions rather than simple mean age. This approach helps predict contaminant movement through an aquifer with a small number of samples.

Comparing modeled MtBE concentrations from age-dating tracers and basic assumptions of recharge to independently collected MtBE measurements in a retrospective analysis has great value in understanding how the model works and understanding contaminant behavior. The scale of this study, covering a large part of the northeastern United States, helps illustrate the regional nature of the problem of MtBE in groundwater. Although the density of sampling – both temporally and geographically – is much less than for studies of individual plumes, the results show the temporal changes in MtBE over this large region. In addition, the study illustrates differences among the networks based on the type of aquifer and the well depth.

The findings from this study can help inform studies in other parts of the world where MTBE is still in use. The percent of MTBE mixed with gasoline is much lower in many areas, but its solubility and persistence still make it a potential threat to groundwater if spilled in sufficient quantities. As previously discussed, the usage of MtBE in other areas of the world did not increase to the levels that were seen in the United States, nor did usage cease rapidly. Although the input signal would likely not be as clear, this approach would be useful in predicting aquifer recovery in areas where usage decreases, or ceases completely. These findings also can be used in designing sampling frequency for any study of groundwater contamination, especially if the temporal variation of the source is known. Sampling for multiple age-dating tracers and interpreting the results using software such as TracerLPM could be very useful in cases where there is an interest in predicting the timing of a contaminant flushing from an aquifer. As illustrated by this study, age distributions vary in a general way by aquifer type, depth, and open interval. But age distributions also vary among wells with similar construction in the same aquifer. Early sampling for age dating and an understanding of age distribution could help in planning an efficient monitoring strategy based on the expected arrival of peak concentrations and eventual flushing of the contaminant from the aquifer.

Study methods, ancillary data, modeling details, statistical methods, model uncertainty, and illustrations comparing modeled to measured concentrations. 28 pages, 1 table, 9 figures.

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.scitotenv.2016.11.058.

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Research papers

Environmental tracer evidence for connection between shallow and bedrock aquifers and high intrinsic susceptibility to contamination of the conterminous U.S. glacial aquifer

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ABSTRACT

Covering a large portion of the northern conterminous United States (1.87 × 10^6 km^2), the glacial aquifer serves as the primary water supply for 30 million public and domestic water users. Mean groundwater age, groundwater age distribution, and susceptibility to land surface contamination, using a new metric (Susceptibility Index; SI) based on the full age distribution and less prone to bias than estimated mean age, is reported for 168 public and domestic wells across the aquifer. Comparison of groundwater age metrics between well networks of varying spatial scale suggest an extensive sample network of equally spaced, long screened interval wells can be used to characterize aquifer wide groundwater age. Estimated mean age ranges from 1 to 50,000 years and, according to the composite age distribution, approximately 63 percent of all sampled water recharged after 1950 (i.e., modern) and 18 percent of the sampled water was recharged greater than 10,000 years ago. The later finding strongly suggests a connection between the glacial aquifer and underlying bedrock aquifers. Statistical analysis of glacial aquifer hydrogeology and age metrics show groundwater ages are young (less than few 100 years) and more susceptible to land surface contamination (larger SI) in unconfined and shallow portions of the aquifer. Old groundwater (greater than 1,000 years) is more often associated with thicker sequences of fine grain sediments and/or shallow bedrock. Calculated SI is shown to be more strongly related to the number of land surface contaminants detected than mean age or fraction modern. Statistical analysis of SI and hydrogeology indicates SI is largely dictated by well depth and confinement. This study demonstrates how sample network design can be used to characterize groundwater age of large aquifers with a limited number of samples and how interpretation of environmental tracers can be used to improve conceptual models of groundwater aquifers and identify groundwater susceptible to contamination.

1. Introduction

The glacial aquifer system provides more water for public and domestic use (98 trillion liters per day in year 2000) than any other single aquifer in the nation (Maupin and Barber, 2005; Maupin and Arnold, 2010). The groundwater pumped from the glacial aquifer supplies approximately 30 million people and constitutes nearly 5 percent of all drinking water in the United States (Haj et al., 2018; Yager et al., 2019). The long-term susceptibility and sustainability of the glacial aquifer system for drinking-water supplies is of utmost importance.

Groundwater age is a fundamental metric of groundwater flow systems and can be understood as the elapsed time between recharge, once isolated from the atmosphere, to groundwater sample collection. The distribution of groundwater age represents the variability of ages from individual flow paths and integrates physical characteristics and processes (e.g., recharge rates, porosity, mixing, and aquifer geometry) effecting solute transport and groundwater availability. Age distributions can be used to assess susceptibility of groundwater to contamination (e.g., Mcmahon et al., 2008; Brown et al., 2009), estimates of the fraction of 'young' and 'old' groundwater being captured (e.g., Solomon et al., 2010; Jurgens et al., 2014), and the extent of flowpath mixing (e.g., Visser et al., 2013) which are critical for understanding groundwater flow systems. An increasingly popular approach to estimating groundwater age distributions is inverse modeling of

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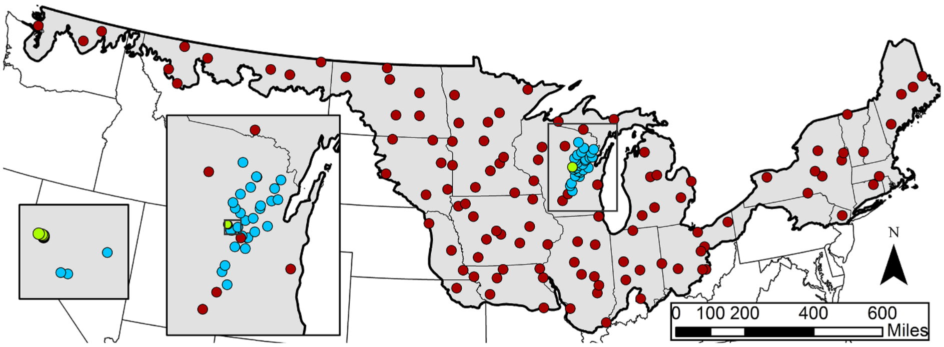

Fig. 1. Study area overview and well locations of the PAS (red), MSS (blue), and FPS (green) sample networks. Glacial aquifer system extent indicated by black line and grey fill. Insets shows detail of MSS and FPS sample network and respective select sites used in network comparison (see Section 3.7.2) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

environmental tracer concentrations by lumped parameter models (LPMs) (e.g., Zuber, 1986; Maloszewski and Zuber, 1982; Brown et al., 2009; McGuire and McDonnell, 2006; Visser et al., 2013; Jurgens et al., 2014). Previous studies indicate that the analysis of environmental tracer data with LPMs provide comparable results and are more cost effective for determining age distributions than building numerical flow models (Turnadge and Smerdon, 2014; Eberts et al., 2012; Yager et al., 2013). LPMs are fit to multiple tracers, assuming conservative tracer behavior except radioactive decay, to assess the validity of piston-flow (i.e., apparent age) and refine the parameterization of more complex age distributions caused by mixing and dispersion processes (Maloszewski and Zuber, 1996; Amin and Campana, 1996; Jurgens at al., 2012) with appropriate LPM selection requiring the evaluation of the hydrogeology and physical dimensions of the flow system.

Groundwater susceptibility is synonymous with groundwater vulnerability which the National Research Council (1993) defines as "the tendency or likelihood for contaminants to reach a specific position in the ground-water system". In addition to the age distribution of water captured by the well, groundwater susceptibility is a function of the presence of a contamination source and subsurface processes that effect transport and concentration of the contaminant (Focazio et al., 2002). While contamination source and subsurface geochemistry need be evaluated on a case-by-case basis, the age distribution describes the *intrinsic susceptibility* of groundwater. Conceptually, the shape (i.e, width) and scale (i.e., mean age) of the age distribution describes this susceptibility. For example, wells with wide age distributions and old mean age will be slow to respond to introduction (and removal) of contamination sources. Conversely, wells with narrow distributions and young mean age will capture contaminated water relatively quickly after introduction of the contaminant but return to background conditions over a shorter period of time. Given the wide spectrum of possible age distribution shapes and scales, a standardized measure is needed to facilitate comparisons and evaluate the susceptibility of groundwater wells or springs.

In this study, a combination of tracers for modern water recharged after 1950 (tritium, ^{3}H; sulfur hexafluoride, SF_6; chlorofluorocarbons, CFCs; tritiogenic helium, $^{3}He_{trit}$) and pre-modern water recharged 1000 years before modern (carbon-14, ^{14}C) were used to parametrize LPMs. Estimates of mean groundwater age, the groundwater age distribution, and susceptibility index (SI) are presented for 168 public and domestic groundwater wells sampled from three networks in 2013 and 2014 as a part of the USGS National Water Quality Assessment (NAWQA) Project (Arnold et al., 2016; Arnold et al., 2017). The differing purpose and design of three well networks (see section 3.1 and Supporting Information A.1.3) was, in part, to represent distinct spatial areas as well as physical and chemical processes of glacial aquifer. Our investigation was used to address the following questions: What extent do the results from each network 'overlap'? How 'representative' of the larger groundwater flow system is a well network given the limited number samples that can be practically collected? How do glacial aquifer and well characteristics indicate groundwater age? Which groundwater age metrics best predict intrinsic susceptibility? We aimed to characterize groundwater age across the glacial aquifer by: assessing the effects of network design on regional synthesis of the data, comparison of hydrogeology and groundwater age metrics to improve understanding and provide context for age results, and provide a framework for evaluation of environmental tracers for determination of groundwater age, age distributions, and the susceptibility of groundwater to land surface contamination.

2. Study area

The glacial aquifer system, as defined by Yager et al. (2019), is a series of confined and unconfined aquifers composed of Quaternary sediments north of the maximum glacial extent in the conterminous United States. The aquifer system extends from the Atlantic northeast to the Pacific northwest spanning an area of 1.87 $\times$ 10^{6} km^{2}. The glacial aquifer system includes all unconsolidated aquifers above bedrock north of the line of continental glaciation (Fig. 1) and is not a single hydraulically connected system. Not all unconsolidated sediments north of the maximum extent of glaciation are glacial in origin and glacial sediments are not present everywhere in this region. Sediment provenance varies widely across the aquifer (Yager et al., 2019) with components of felsic crystalline bedrock in the east, metamorphic rock in the north central portion, and mafic volcanic and plutonic rock in the far west. The majority of bedrock underlying the glacial aquifer system, however, consists of sedimentary clastic and carbonate rock. Variability in land use, recharge rates, total aquifer thickness, lateral continuity of confining and water bearing units, and aquifer source material (Yager et al., 2019) make the glacial aquifer physically and chemically complex (Warner and Ayotte, 2014).

3. Methods

3.1. Sample networks

Three networks of wells in the glacial aquifer system (Fig. 1) were sampled in 2013 and 2014 and collected samples were analyzed for environmental age tracers and other water-quality parameters (Arnold et al., 2016; Arnold et al., 2017). The three networks differ in scale and purpose. Results from each network were compared to assess the effect of network scale and design on regional analysis of estimated groundwater age and susceptibility.

The largest network was the principal aquifer study (PAS), designed to assess water quality conditions for public drinking-water supplies across the glacial aquifer system (Stackelberg, 2017; Burow and Belitz, 2014). The 115 wells of the PAS are equally spaced (Belitz et al., 2010), generally have relatively long screened intervals (<1 to 31 m) across multiple glacial sediment units, and are pumped at relatively high rates of 100's liters per minute, as dictated by demand. The second well network was a model support study (MSS) designed to provide physical and water-quality data to support a regional groundwater flow modeling (Juckem et al., 2017). The 29 wells of the MSS are mixed use and have relatively short screened intervals (<1 to 12 m) in shallow and deep portions of the aquifer targeting specific geologic units. One of the public supply wells in the MSS is also in the PAS (well number GLACPAS1-45) and will be reported in section 4.2. The third well network was the flow-path survey (FPS) designed to assess the geochemical evolution of water-quality in central Wisconsin (Tesoriero et al., 2007; Saad, 2008). The 25 wells of the FPS are multi-level monitoring wells along an approximate flow path (Saad, 2008) with short screened intervals (<1 m). LPM age interpretations for FPS samples which were collected in 2004 (including 2 sites not sampled in 2014) and 2014 are presented here. Three stream bed well transects (PIEZO 700 s, PIEZO 800 s, mp2s) installed across the stream and perpendicular to flow were sampled in 2014. The transects consist of shallow piezometers installed on the right, left, and center of the stream channel. Additional sample network details are provided in the Supplemental Information (A.1.3).

3.2. Chemical analysis

Water samples from the three well networks describe above were analyzed for a broad suite of inorganic and organic constituents as well as environmental tracers (Arnold et al., 2016; Arnold et al., 2017). For this study, we used environmental tracer concentrations of tritium (^3H), sulfur hexafluoride (SF_6), tritiogenic helium-3 ($^3He_{trit}$), radiogenic helium-4 ($^4He_{rad}$), and corrected carbon-14 (^{14}C) for estimating groundwater age. Not all tracers were collected from every well. $^3He_{trit}$ and $^4He_{rad}$ were calculated following methods described by Solomon and Cook (2000) and Solomon (2000). Dissolved gases (argon, nitrogen, neon, krypton, and xenon) were used to estimate recharge temperature, excess air, and gas fractionation using methods described by Aeschbach-Hertig et al. (2000). Calculated tracer concentrations and dissolved gas model results, including recharge temperatures, excess air, and noble gas fractionation, are reported in Solder et al. (2018). A study of the major ion chemistry in relation to inorganic carbonate chemistry was used for correction of measured ^{14}C concentrations (Solder and Jurgens, 2018). Corrected ^{14}C concentrations were determined with a novel implementation of inverse geochemical and analytical models of ^{14}C dilution in conjunction with lumped parameter age modeling (Solder and Jurgens, 2018). Details of sample collection, analytical, and interpretation procedures are provided in the Supplemental Information (A.1.1) and the above references.

3.3. Groundwater age

Mean ages and groundwater age distributions were modeled by calibrating lumped parameter models (LPMs) to measured environmental tracer data using a modified version of the program TracerLPM (Jurgens et al., 2012). TracerLPM simulates the tracer concentration at the time of sampling for each tracer based on the mean age, distribution type and parameters, and the respective atmospheric tracer history. Tracers used for age determination were presumed to be conservative or have a predictable decay/accumulation rate. Tracers showing non-conservative behavior were identified by comparing measured tracer data to each other and known atmospheric concentration histories. Tracers with inconsistent concentrations were excluded from subsequent analyses. LPM parameters were varied to minimize the misfit (i.e., sum of chi-squared statistic (χ^2)) between measured and simulated concentrations of the selected modeled tracers. Age interpretation was not possible at all sites due to sample loss or contaminated tracers.

The approach for assigning an age category (premodern, modern, mixture) and calibrating LPMs varied for each sample on the basis of measured tracer concentrations. Samples with ^3H concentrations greater than ~4 tritium units (TU) were indicative of recharge after about 1950. Above ground nuclear testing, starting in early-1950s, drastically increased ^3H in the atmosphere and presence of ^3H greater than 4 TU is clear indication of recent recharge (i.e., modern groundwater). Such samples were usually accompanied with measurable amounts of $^3He_{trit}$ and SF_6 (typically post-1970 recharge for SF_6). Samples with ^3H less than 0.3 TU were indicative of recharge before about 1950 and usually accompanied with measured ^{14}C activity less than 75 pMC and no measurable SF_6. These two sample groups ($^3H > 4$ TU, $^3H < 0.3$ TU) indicated by region specific estimates of ^3H in precipitation (Michel, 1989) suggested a single mixing model in LPM was appropriate. Samples that had ^3H greater than 0.3 TU, but less than 4 TU, were suggestive of mixing between water parcels of differing ages and recharge sources. Such samples often contained measurable SF_6 while ^{14}C activity remained less than 75 pMC. These 'mixed' samples of pre-1950 and post-1950 recharge were modeled with a binary mixing model (BMM). The dispersion model was assumed for the old binary component with a dispersion parameter of 0.1 which simulated longitudinal dispersion approximately equal to a several kilometer scale aquifer (Gelhar et al., 1992). Appropriate age distributions for the young single mixtures and young component of the binary mixtures were determined from regional hydrogeology, well-logs, and LPM model fit. The full suite of available tracers and ancillary knowledge of the site, surrounding wells, and adjacent aquifers (well construction, land-use, location relative to surface water, etc.) was considered during LPM selection and iterative model refinement. Final LPM interpretations were selected based on model fits and conceptual understanding of model type and parameters. Groundwater age estimates calculated by LPM were categorized as '*modern*' with estimated mean age less than 63 years, '*pre-modern*' with estimated mean age greater than 63 years, or as a '*mixture*' when best fit by a BMM. Dissolved tracer concentrations from a number of wells within the glacial aquifer yielded conflicting results (e.g., significant SF_6 and low ^3H) and additional analysis was required. The LPM interpretation procedure and tracer systematics are more fully described in the Supplemental Information (A.1.2).

3.4. Assessment of environmental tracer sources

The groundwater age interpretations were dependent on accurate accounting of environmental tracer sources whether in-situ or atmospheric. Environmental tracers $^3He_{trit}$ and SF_6 in the glacial aquifer are primarily derived from ^3H decay and equilibration of groundwater with the atmosphere, respectively. Identification of a potential secondary tracer source or sink is required to evaluate the utility of the tracer in a given sample. Secondary sources and sinks, if unaccounted for, result in erroneous estimates of mean age. The large number and spatial distribution of sites allowed for explicit identification of potential secondary sources and sinks in the glacial aquifer system.

Tracer anomalies were calculated as the difference between LPM predicted and measured tracer concentrations. Expected concentrations of $^3He_{trit}$ were based on a helium isotope mass balance (Solomon and Cook, 2000; Solomon, 2000), the ^3H input, and estimated age. Expected SF_6 was based on equilibrium between groundwater and atmospheric sources after accounting for excess air. In addition to the $^3He_{trit}$ and SF_6 anomalies, we calculated the fraction of helium-4 derived from terrigenic sources ($^4He_{terr}$) in relation to total measured helium-4 ($^4He_{terr}/^4He_{tot}$) (Solder et al., 2018). Values greater than 70 percent $^4He_{terr}$ were indication of possibly inaccurate $^3He_{trit}$ calculated values and presence of a component of older water greater than a few 1000 years old.

3.5. Susceptibility index

From the estimated groundwater age distribution, we calculated a susceptibility index to provide a quantitative estimate of susceptibility of a well to land surface contamination. The susceptibility index (*SI*) is a relative measure of how quickly a conservative contaminant spilled within the recharge area of a well travels from the water table to the well via the groundwater system. The SI is different from the mean age in that the SI takes into account the entire age distribution whereas the mean age is the first moment about zero of the age distribution. As the

SI was determined using conservative tracers, measuring travel time from the water table to sample collection well, it does not account for transport properties and reactivity of contaminants or unsaturated zone travel time.

The SI is calculated as the normalized Hellinger distance between the cumulative distribution function (CDF) of age for the well of interest and a reference CDF. The Hellinger distance (D_H) is defined by Nikulin (2001) as:

$$D_H = \frac{\sqrt{\sum_{i=1}^{k} (\sqrt{P_{(i)}} - \sqrt{Q_{(i)}})^2}}{\sqrt{2}} \tag{1}$$

where P(i) and Q(i) are the cumulative probability of the age distribution of interest and a reference age distribution, respectively, for a given age. Values for the Hellinger distance range between 0 (perfectly similar) and ∞ (perfectly dissimilar). The susceptibility index is then calculated as:

$$SI = \frac{1}{1 + D_H} \tag{2}$$

where the *SI* ranges between 1, indicating young ages and a narrow age distribution, and 0, indicating older ages and a broad age distribution. For this metric, the more rapidly a land surface contaminant arrives at the well, the more susceptible the given well. Thus, the reference CDF is defined as piston flow model with a mean age of 1 year.

The important difference between SI and mean age can be illustrated by comparing the age distributions and SI of hypothetical samples all with the same mean age of 200 years (Fig. 2). The susceptibility of a well to land surface contamination is a function of the fraction and mean age of the 'young' component of flow which will move the contaminant to the well rather than the overall mean age of the sample. The concept of the SI is particularly important for mixtures of water from differing recharge sources, flow paths, and groundwater ages. For example, BMM-2 has the highest SI (0.41) of the hypothetical samples (Fig. 2) and is binary mixture of water with mean ages of 5 and 5000 years; only a small amount of 'old' water needs to be mixed into a sample to bias the mean age older and potentially confuse interpretation of the mean age. The susceptibility index takes into account the full age distribution and is less prone to bias than the mean age.

As an additional proof of concept, calculated SI for PAS wells was compared to measured nitrate, the herbicides atrazine, metolachlor, prometon, and common herbicide degradates deethylatrazine, deisopropylatrazine, deethylhydroxyatrazine, hydroxyatrazine, metolachlor sulfonic acid, alachlor sulfonic acid, and acetochlor sulfonic acid. These analytes were chosen because application of fertilizer and herbicide is

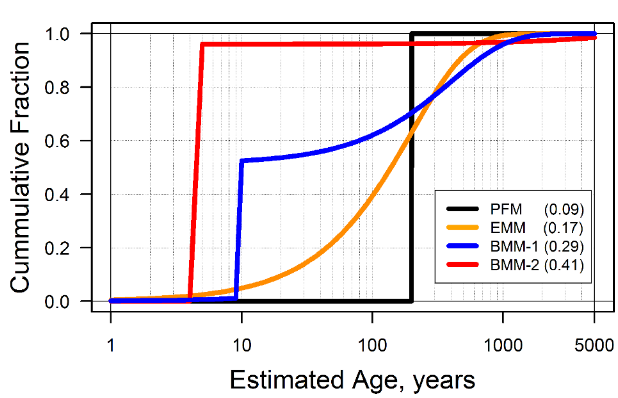

Fig. 2. Cumulative age distributions of hypothetical samples with a mean age of 200 years. Respective susceptibility indices are indicated in parentheses. The binary mixtures (BMM) are composed of a piston-flow (PFM) and exponential mixing models (EMM) with respective mean ages of 10 and 400 years (BMM-1) or 5 and 5000 years (BMM-2). CDF curves developed and SI calculated in modified TracerLPM (Jurgens et al., 2012; B. Jurgens, USGS, written communication, 2016).

relatively ubiquitous across the glacial aquifer and typical application procedures widely disperse the product at land surface (i.e., non-point source). Measured contaminant concentrations were converted to a presence/absence metric (i.e., detection) based on the reported analytical detection limits and compared to the estimated mean age, fraction modern, and SI to assess the utility of each age metric in determining the intrinsic groundwater susceptibility.

3.6. Composite age and SI distributions

Age distributions represent the probability of a water parcel with a given estimated age occurring in a single sample. Full age distributions are presented in this study as cumulative probabilities and provide the fraction of sample younger than a given age (i.e., proportion of sample recharged after a given year). Plots of cumulative age distributions are a useful visual representation of the extent of mixing and/or dispersion in a sample; wider distributions indicate a larger range of water parcel ages in a sample. Cumulative distributions of the SI values were constructed for sets of samples by ordering the values and normalizing the number of samples within the sample set.

Composite age distributions were constructed by averaging the cumulative age distributions of the wells of interest. The composite distributions provide means of summary and characterization of age at selected wells. The composite SI distributions were plotted in reverse order (1 to 0) to better correlate with the respective composite age distributions (i.e., young, highly susceptible wells on the left to old, low susceptibility wells on the right). Boxplots of mean age and SI were included to illustrate the distribution of values that are represented by composite distributions.

A comparison of estimated mean age and SI from each network was conducted and idealized statistical distributions were fit to the composite age distributions (as described in Supplemental Information (A.1.5)) for comparison amongst sample groups and to other groundwater age studies. Composite age and best-fit idealized distribution parameters are presented in the Supplemental Information A.2.3.

3.7. Statistical comparison of age metrics

3.7.1. Comparison of groundwater age, hydrogeology and well characteristics

A comparison of age class, estimated mean age, and SI calculated in this study to the hydrogeology from Yager et al. (2019) and well construction characteristics was conducted to investigate the primary controls on groundwater age and provide context for discussion. The comparisons of hydrogeology and age presented in this study are representative of the given network. The analysis has limited utility as a predictor of groundwater age using hydrogeology and well construction and should not be used to that end. The statistical analysis was performed using the *stats()* base package and *vcd()* package (Meyer et al., 2016) in R statistical software (R core team, 2016). Methods for determination of hydrogeologic metrics are provided in the Supplemental Information A.1.4 and general well characteristics are provided in Supplemental Information Table B.1.

Composite distributions and boxplots of estimated mean age and SI were constructed for each category (separated on 20th, 40th, 60th, and 80th percentiles) of the selected hydrogeologic and well metrics to illustrate the differences between the respective groups. The relationships between the respective categorized hydrogeology metrics and age were formally evaluated using the Cramer's V statistic (0 to + 1) which is the analog to Pearson's correlation coefficient for nominal variables. Only the hydrogeology metrics that are correlated with the age metrics at the 95% significance level are reported here. It is important to point out that Cramer's V does not indicate the direction (inverse or proportional) of the correlation. The mean age and mean SI for each category of a given hydrogeology metric were compared using a multiple comparisons test (Tukey's honest significant difference test) at the 95%

significance level.

3.7.2. Comparison of groundwater age between well networks

Mean age, SI, and respective distributions from each sample network were used to assess the effect of sample network design (e.g., spatial distribution, well characteristics) on mean age and SI. As the spatial scale of each network is vastly different (Fig. 1), the immediately adjacent PAS wells (n = 6) were compared to the full MSS network and the adjacent MSS wells (n = 3) were compared to the full FPS network. The relatively simple comparison of wells based on proximity is meant to provide some indication of the commonality between networks and whether a given network is representative of groundwater age in the entire flow system. The mean age and mean SI for each subset or full network of wells was compared using a multiple comparisons test (Tukey's honest significant difference test) at the 95% significance level.

4. Results

4.1. Groundwater age and susceptibility index

LPM age distributions were assigned and susceptibility indices calculated at 168 individual groundwater wells in the glacial aquifer. A summary of the LPM results (Table 1) show that mean estimated age was 2,400 years in the glacial aquifer and the majority of wells (56 percent) classified as modern. Based on individual composite age distributions, the fraction of modern recharge (after 1950) and within the last 10,000 years (e.g., Holocene) is also calculated for each sample (Supplemental Information Table C.1). Based on the composite distribution of all wells, on average 68 percent of water is modern recharge and 90 percent was recharged within the last 10,000 years (Table 1). On average, mixtures consist of 45 percent modern water and the pre-modern samples have approximately 10 percent modern water. Composite and best-fit age distribution parameters are reported in the Supplemental Information A.2.3.

4.2. PAS well network

Groundwater age estimates for the PAS network wells range from recent recharge with a mean age of 1 year to approximately 52,000 years (Table C.1) with a median estimated age of 40 years (Table 1). The 115 sites are approximately evenly distributed between modern and some component of pre-modern water either in a mixture or entirely pre-modern. Spatially, groundwater east of Ohio and west of central Montana have a larger portion of modern water, while pre-modern water is more dominant in the west central portion of the aquifer (Fig. 3a). Interestingly, the central region greatly varies between predominately modern and pre-modern water with a significant number of wells indicated as mixtures modern and pre-modern water. The median SI for the entire PAS is 0.208 and spatially the SI follows a similar pattern to the age class with higher susceptibility groundwater coincident with modern water in the glacial aquifer (Fig. 3b). Chi-squared fit of LPMs to measured tracer data are generally very good with an average chi-squared of 0.32 with 106 of the 114 samples having a chi-squared value less than 1. Only three sites (GLACPAS1-82, -U01, -U13) have chi-square values greater than 2. The single mixture dispersion model was most frequently (n = 50) the best fit to the tracer data with an average dispersion parameter of 0.2. LPMs with an exponential component (EMM or PEM) were fit to 21 sites (Table C.1). One site, GLACPAS1-14, was clearly pre-modern based on ^{3}H below detection limit and high percent $^{4}He_{terr}$ (0.89). Unfortunately, it was not possible to assign an estimated age with reasonable confidence because a ^{14}C measurement was either not collected or the bottle broke prior to analysis. Based on the PAS composite distribution for all samples 64 percent of water was recharged prior to 1953 (Table 1) and 82 percent recharged in the last 10,000 years.

Estimated mean age, fraction modern, and SI of PAS wells were compared to detections (i.e., above analytical detection limit) of the land surface contaminants nitrate, herbicides, and their degradates (Fig. 3c,d,e). Results indicate SI has a stronger correlation to contaminant detection than the other age metrics.

4.2.1. Influence of hydrogeology and well characteristics on age

Exploratory analysis of the relationship between groundwater age and the hydrogeology or well characteristics (Fig. 4a) indicates that relative contribution of a given age class systematically varies between the categories of select metrics: depth to the top and bottom of the screened interval, total well depth, confinement, depth to bedrock, percent chance confined, aquifer depth, and the number of aquifers. The depth of the screened interval (top and bottom) and total well depth display similar patterns and correlation (Fig. 4b) with the age metrics, so only the total well depth metric is displayed in Fig. 4a for brevity. The Cramer's V statistic indicates that age class is correlated with 95% confidence to a larger number hydrogeology and well metrics while the categorical SI has the stronger correlations (Fig. 4b).

Composite age and SI distributions for each group of select

Table 1
Summary of LPM estimated age, fraction modern, and susceptibility index (SI) for all samples in the PAS, MSS, and FPS sample networks in the glacial aquifer, USA.

Network Age Classification	Count	Mean Estimated Age	Median Estimated Age	Fraction Modern	Mean Age Modern Fraction	Mean Age pre-Modern Fraction	Mean SI	Median SI
All*	**168**	**2430**	**35**	**0.68**	**22**	**7461**	**0.229**	**0.224**
Modern	93	20	18	0.97	20	89	0.326	0.294
Mixture	48	4089	1813	0.45	28	6948	0.125	0.088
pre-Modern	27	7589	3059	0.1	43	8713	0.085	0.045
PAS	**115**	**3398**	**40**	**0.64**	**19**	**9050**	**0.228**	**0.208**
Modern	58	17	15	0.98	17	84	0.35	0.329
Mixture	32	5442	2152	0.46	26	9258	0.129	0.075
pre-Modern	25	8491	5000	0.1	41	9363	0.074	0.026
MSS	**29**	**777**	**310**	**0.62**	**27**	**2072**	**0.192**	**0.159**
Modern	11	26	18	0.99	23	76	0.306	0.291
Mixture	16	1382	932	0.44	31	2461	0.117	0.12
pre-Modern	2	66	—	0.13	58	68	0.154	—
FPS-2014	**25**	**27**	**29**	**0.96**	**25**	**97**	**0.278**	**0.248**
Flow path	16	25	29	0.97	25	87	0.281	0.243
Stream Reach	9	30	29	0.96	26	104	0.271	0.262
FPS-2004	**19**	**30**	**31**	**0.93**	**25**	**53**	**0.277**	**0.245**

*Not including FPS-2004

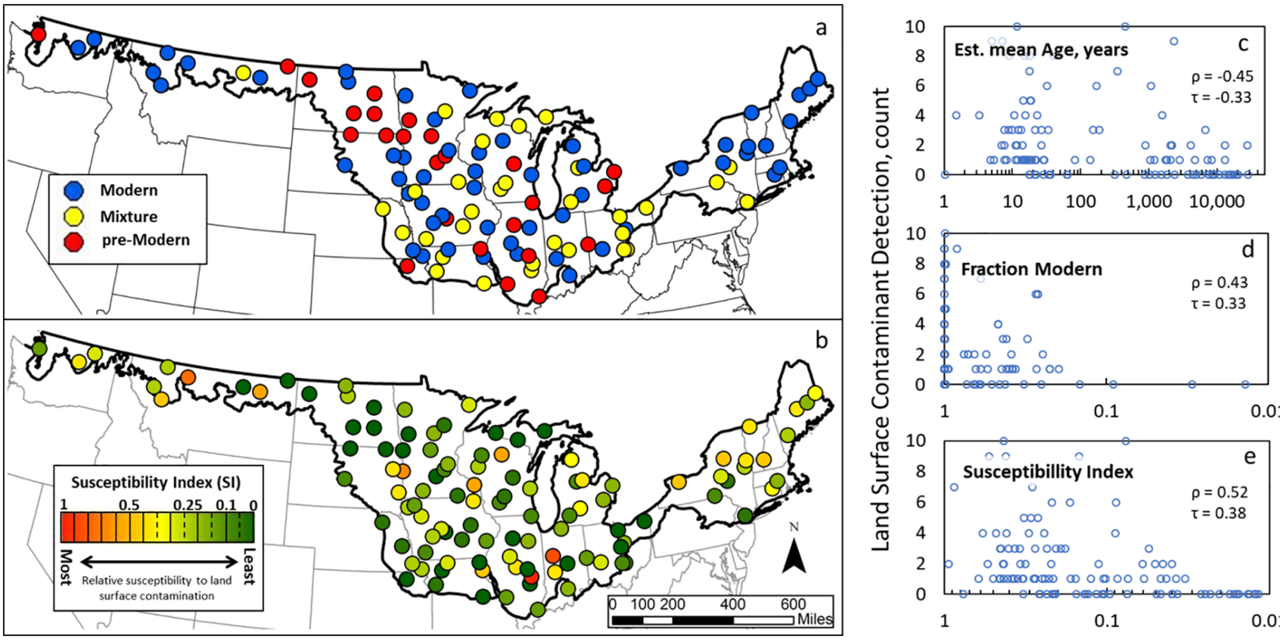

Fig. 3. Map of PAS sample network (a) age class with modern (blue), mixture (yellow), and pre-modern (red) indicated by color, (b) susceptibility Index (SI) with more susceptible (SI = 1) to less susceptible (SI = 0) indicated by color gradient (red to green, respectively), and number of contaminant detections versus (c) mean age, (d) fraction modern, and (e) SI. Glacial aquifer system extent indicated on maps with black line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

hydrogeology and well metrics (Fig. 5) allow a detailed examination of the relationship between age and hydrogeology. The multiple comparison test indicates that the mean age and mean SI have a statistically significant difference amongst the categories of well bottom depth (Fig. 5a) and confinement (Fig. 5b) while no significance difference in mean age and mean SI was found between the categories of the other select metrics.

4.2.2. Environmental tracer uncertainties

Maps of the tracer anomalies in the PAS (Fig. 6) show variability in the $^{3}He_{trit}$ anomaly while more spatially coherent localized regions of elevated SF_6 and percent $^{4}He_{terr}$ are apparent. The lack of spatial pattern in $^{3}He_{trit}$ anomalies suggests additional factors, such as error in He sampling and balance calculations, are influencing the calculated tracer concentration. Conversely, the SF_6 and $^{4}He_{terr}$ positive anomalies are likely related to terrigenic sources.

4.3. MSS and FPS well networks

Groundwater age estimates in the MSS network range from 10 to 4,600 years (Table C.1) with a median estimated age of 310 years (Table 1). Of the 28 sites in the MSS network, 11 sites are characterized as modern, 15 sites are best fit by a mixture, and 2 sites are predominately pre-modern water (Table 1). Based on the composite age distribution, approximately 62 percent of water sampled from the MSS network was recharged before 1953 and 99 percent was recharged in the last 10,000 years. The median susceptibility index for all MSS sites is 0.16 (Table 1). LPMs are generally good fits to MSS tracer data with an average χ^2 of 0.05. The MSS wells were most commonly fit by LPM's with some component of PEM or EPM (Table C.1).

Groundwater age estimates for the FPS network wells sampled in 2004 and 2014 range from 2 to 52 years (Table C.1) with respective median ages of 31 and 29 years (Table 1). The median susceptibility index for all 2014 FPS sites is 0.25 (Table 1). Based on the composite age distribution approximately 96 percent of water sampled in 2014 from the FPS network was recharged after 1950, and all water was recharged in the last 10,000 years. LPM fits to tracer data is good with a mean χ^2 of 0.4, with the exception of samples collected from fss1a and fss4b with respective χ^2 fits of 2.2 and 7. FPS network site were most commonly fit by the EPM (Table C.1). Samples collected along the flow path are overall similar but slightly younger that stream bed samples (stream reach, Table 1). Re-interpreted ages of the FPS-2004 network using LPMs (Tables 1 and C.1) are not significantly different from apparent ages described in Tesoriero et al. (2007).

4.4. Groundwater age and SI between well networks

Comparison of groundwater age metrics from the PAS, MSS, and FPS-2014 networks show that the three networks have generally disparate composite distributions and mean estimated age and SI (Table 1 and Fig. 7). Selection of PAS wells adjacent to the MSS network show improvement in general match of the composite age and SI distributions (Fig. 7), and agreement between the fraction modern, mean age of the modern fraction, and the mean SI (Table 2). The mean age of the pre-modern fraction, although in better agreement, remains significantly different between the select PAS and MSS networks (Table 2). Comparison of age distributions, quantified as the Hellinger Distance (D_H, Eq. (1)), for PAS and PAS select to MSS (D_H = 5.17 and 4.48, respectively) show improved agreement although minor. The persistent disagreement between the pre-modern components in the select PAS and MSS networks is possibly a result of the PAS being deeper public supply wells with larger screened intervals and higher pumping rates, which potentially captured older flow paths relative to the MSS with a mixture of public supply and domestic wells. Comparison of the select MSS to the FPS-2014 network shows significant improvement in agreement in all metrics between the two networks (Fig. 7). Comparison of age distributions for MSS and MSS select to FPS-2014 (D_H = 3.97 and 0.7, respectively) show significantly improved agreement. The differences in mean estimated age and SI between the select PAS and MSS and between the select MSS and FPS-2014 are not statistically significant with 95% confidence (equal variance and unequal sample size Tukey-Kramer test).

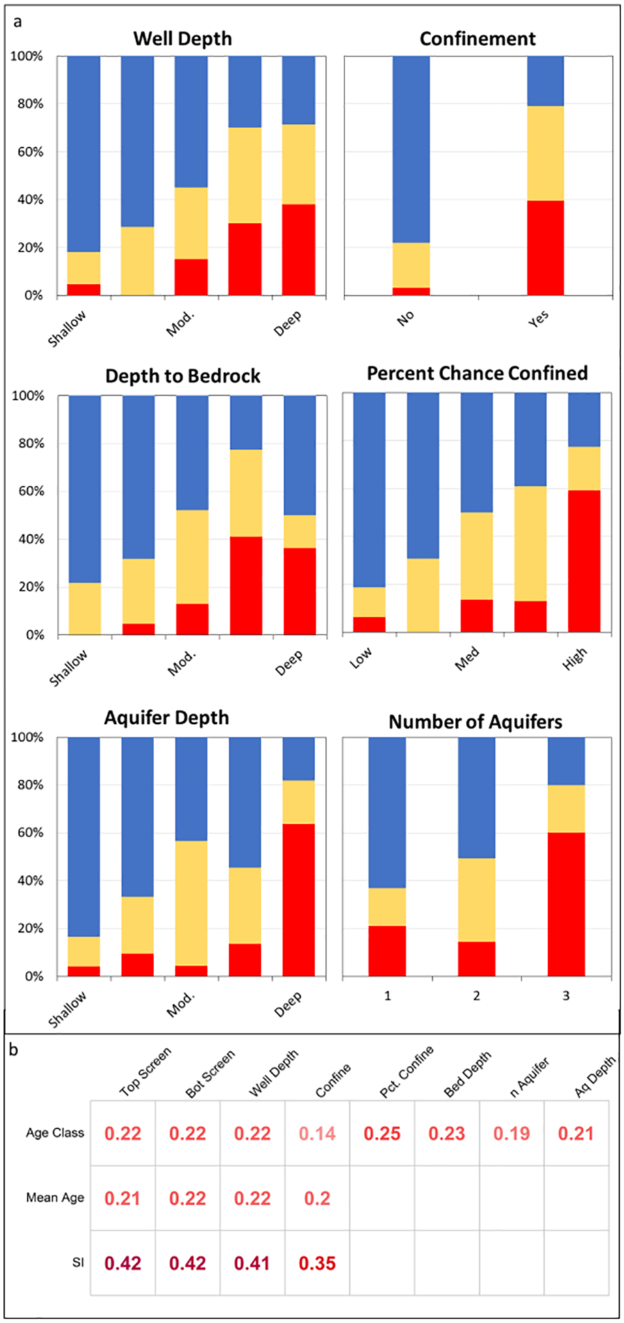

Fig. 4. Relationship between categorical hydrogeology and well characteristic to categorical age metrics for PAS sample network. (a) Percentage of total sites by age class, and (b) associated Cramer's V correlation matrix at the 95% confidence interval. Blank locations in the correlation matrix did not have statistically significant correlations. Respective sample count in each category is provided on Fig. 5. The depth of the screened interval (top and bottom) and total well depth display similar patterns and correlation (b) with the age metrics, so only the total well depth metric is displayed in (a) for brevity.

5. Discussion

5.1. Sample network design

Analysis of scale results indicate better agreement between smaller networks and select wells of the larger networks (Table 2 and Fig. 7). On a broader scale, this finding suggests the deep municipal wells of the PAS network provide a reasonable representation of the glacial aquifer as a whole. Reasons that the PAS appears to be representative likely include intentional equal spacing of wells across the aquifer following recommendations of Belitz et al. (2010), long well screen intervals, and high well pumping rates (dictated by municipal demands). It is acknowledged that the comparison across scale is limited to a small region of the overall aquifer (Fig. 1) and may not capture scalability of groundwater age in other regions of the aquifer. However, the PAS provides a particularly good representation of the *modern* component of groundwater when compared to the other networks (Table 2 and Fig. 7) indicating that the modern fraction and overall susceptibility is reasonably represented by the PAS wells. We suggest that discussing groundwater age metrics across the glacial aquifer in terms of the results from the PAS network is reasonable and such a scaling comparison is an improvement over blind characterization of an aquifer based on limited samples.

5.2. Groundwater age metrics

Groundwater age in the glacial aquifer is generally modern (64 percent modern based on PAS composite distribution; Figs. 5 and 7a) although there is a clear presence of 1000s of year old water (Fig. 3a, Table 1, Figs. 5 and 7a,c). Spatially, the northeast and northwest are dominated by modern water (mean age of the one pre-modern sample in Washington being 63.2 years) with the central portion of the region having a greater mixture of age classes (Fig. 3a). The presence of 1000s of year old water across the aquifer in an important finding and might be considered unusual given moderate median recharge rates and relatively shallow aquifer total depth (Yager et al., 2019). But some portion of pre-modern groundwater is not all together unexpected as the complex hydrogeology, generally consisting of low permeability tills with lenses of sands and gravels, conceptually supports the possibility of connate water. Within the glacial aquifer itself, old groundwater may be a result of long flow-paths in the deep confined permeable aquifer units or slow diffusion dominated transport in fine grain sediments. The central portion of the glacial aquifer, specifically the east and north central regions, containing older groundwater (Fig. 3a) in fact coincides with deeper and more continuous sequences of layered till and permeable lenses (Yager et al., 2019).

Pre-modern water captured from the glacial aquifer in the south central, southwest central, and the west central regions (Fig. 3a) is more likely to have been sourced from another flow system. The mentioned regions with large components of pre-modern water have relatively high precipitation rates and limited depth of the Quaternary glacial sediments (Yager et al., 2019) making significant amounts of pre-glacial retreat water (>10,000 years old) unlikely in the glacial sediments. We propose that a hydrologic connection between the glacial and underlying bedrock aquifers is a more reasonable explanation for such large contributions of pre-modern water than relatively hydraulically "stagnant" zones within the Quaternary glacial sediments containing connate waters. In the south central region, the Cambrian-Ordovician bedrock aquifer (Lloyd and Lyke, 1995) containing dominantly pre-modern water (Stackelberg et al., 2018) is thinly overlain by glacial sediments (Yager et al., 2019). Deep wells, long screen intervals, and high pumping rates at the public supply PAS wells conceptually support capture of shallow bedrock aquifer water. In the southwest and west central regions, the presence of pre-modern water (Fig. 3a) might similarly be explained by hydraulic connection to the Cretaceous and Paleozoic sedimentary bedrock aquifers (Whitehead, 1996; Olcott, 1992) and fractured igneous and metamorphic bedrock aquifers (Olcott, 1992). Previous investigations have measured bedrock derived groundwater ^{3}H below detection limit (0.8 TU for that study; Bartos et al., 2002) and there is suggestion of localized hydraulic connection between shallow and deep aquifers (Strobel et al., 2000) in the southwest and west central glacial aquifer. Although previous investigations have been limited in scope, a hydraulic connection between shallow glacial sediments and the deeper bedrock systems seems a reasonable hypothesis supported by results from this study. This finding has

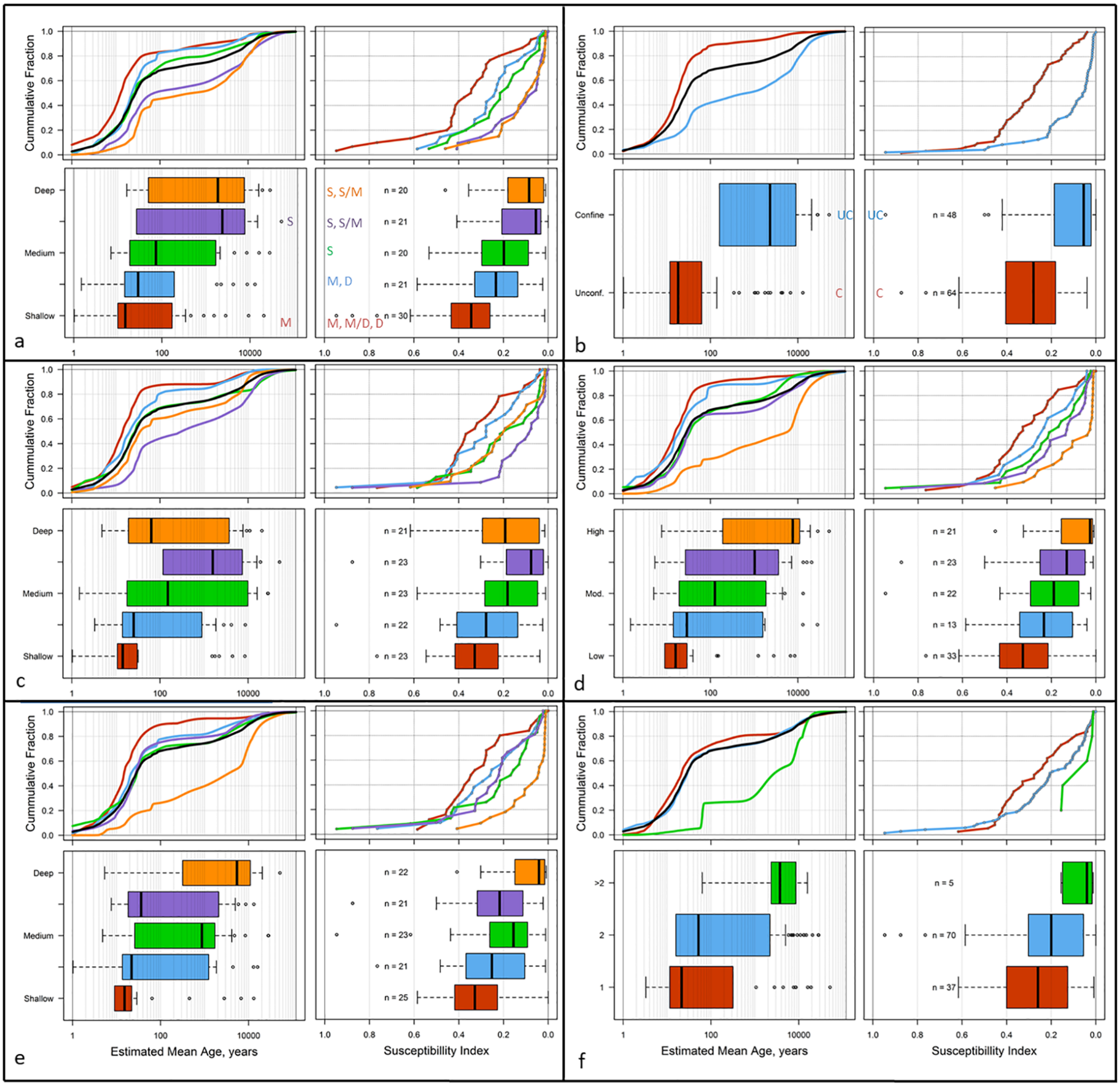

Fig. 5. Composite distributions and boxplots of mean age and susceptibility index (SI) for the PAS sample network grouped by (a) well bottom depth, (b) confinement, (c) depth to bedrock, (d) percent chance confined, (e) depth to aquifer, (f) and number of aquifer units. Composite distributions and corresponding boxplots are color coded. The black composite age distribution represents all PAS samples. The individual values of SI indicated by open circles with number of samples indicated left of the SI boxplot. Statistically significant difference in mean age and mean SI indicated by colored letters; alpha value refers to the group with statistically different mean from group indicated by the color (red, R; blue, B; green, G; purple, P; orange, O). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

important implications in understanding and managing groundwater resources across the region.

5.3. Hydrogeology and well characteristics

Statistical analysis of hydrogeology and well characteristics to age in PAS network, indicates that the relative contribution of modern and pre-modern water is affected by well depth, confinement, depth to the top of the aquifer, depth to bedrock, and aquifer complexity (i.e., number of aquifers) (Fig. 4a). The contributions of mixed waters are relatively constant in respect to well depth and depth to bedrock but follow a general pattern of increasing and then decreasing in relation to percent chance confined, aquifer depth and number of aquifers. That a component of modern and pre-modern water (either as mixture or solely pre-modern) is present in all categories of each metric illustrates the complexity of groundwater age in the glacial aquifer. The formal evaluation of the correlation (Fig. 4b) supports that there is a statistically significant (with 95% confidence) effect of select hydrogeology on the respective age metrics, although the correlations are generally modest (Cramer's V < 0.5) to weak (<0.2). Age class is correlated to more hydrogeology metrics than either the categorical mean age or SI, while the categorical SI is more strongly correlated (Fig. 4b) to select metrics.

Composite distributions (Fig. 5) provide a detailed illustration of the

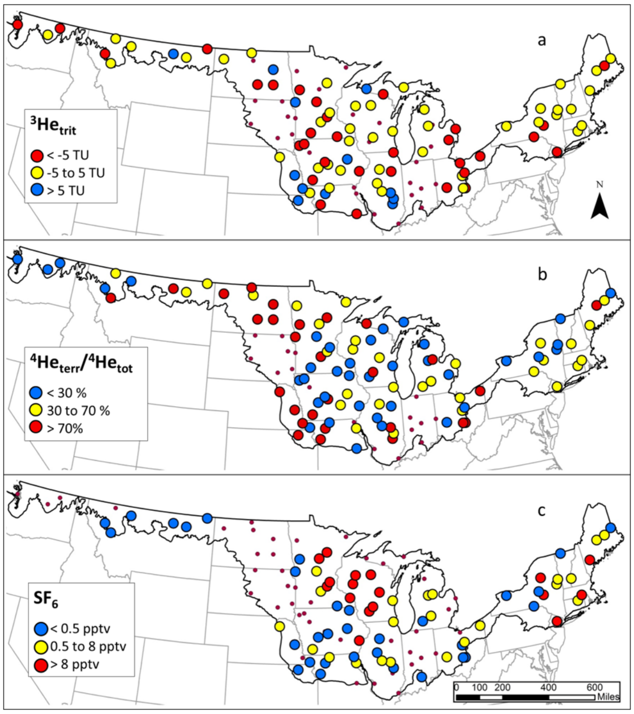

Fig. 6. Tracer anomalies for (a) $^3He_{trit}$, (b) $^4He_{terr}$, and (c) SF_6 for PAS sample network wells (see Section 3.4).

differences in age and SI for the given hydrogeology metrics. Some overall findings of note include the median age and the width of the age distributions generally increase across the categories, and each category has some component of 1,000's of years old water across all the metrics. The opposite is true for the SI with the spread of values generally decreasing and more heavily skewed to lower SI values across categories. Also, of interest is that the shape of the age distributions are generally very similar with increasing width across the categories, with the exception of highest percent chance confined (Fig. 5d), deepest depth to aquifer (Fig. 5e), and greater than 2 aquifers (Fig. 5f). The similarity in general shape is further manifestation of the broad range of ages in each category while the widening of age distributions indicates the increasing influence of flow path mixing across categories. This increasing extent of mixing is in part related to the ever-presence of modern water with an increased proportion of pre-modern water, but also likely influenced by additional longitudinal mixing along pre-modern flow paths. While there is an observable difference in age class proportion (Fig. 4a), mean age, and SI among the categories (Fig. 5), and a statistically significant correlation between the age and hydrogeology metrics (Fig. 4b), multiple comparisons test indicates that only separation by well bottom depth (Fig. 4a and 5a) and confinement (Fig. 4b and 5b) resulted in statistically significant differences in mean age and SI. The lack of strong correlation between age and hydrogeology metrics and lack of clear differences in the mean age and SI among the hydrogeology categories demonstrates the complexity of groundwater age as a metric integrating many well and aquifer properties. More robust statistical analysis of the limited sample set considering the interdependency between hydrogeology metrics in relation to age could possibly be insightful but is outside the scope of this study.

5.4. Susceptibility index

Calculated values of SI for the different networks and age classes show higher susceptibility (larger SI) in shallow FPS network wells and modern groundwater samples and lower susceptibility (smaller SI) in pre-modern samples (Table 1). Similarly, comparisons of SI to hydrogeology in the PAS network show decreasing values of SI with increasing well bottom depth (Fig. 5a), confinement (Fig. 5b), percent chance confinement (Fig. 5d), and decreasing aquifer complexity (Fig. 5f). Conceptually, these findings are in agreement with what is expected; shallow wells in unconfined portions of the aquifer have a greater likelihood of capturing land surface contaminants. In fact, statistically significant differences in mean SI was found between differing well bottom depth (Fig. 5a) and confinement (Fig. 5b). The distribution of SI values, regardless of sample network, is non-normal and skewed to

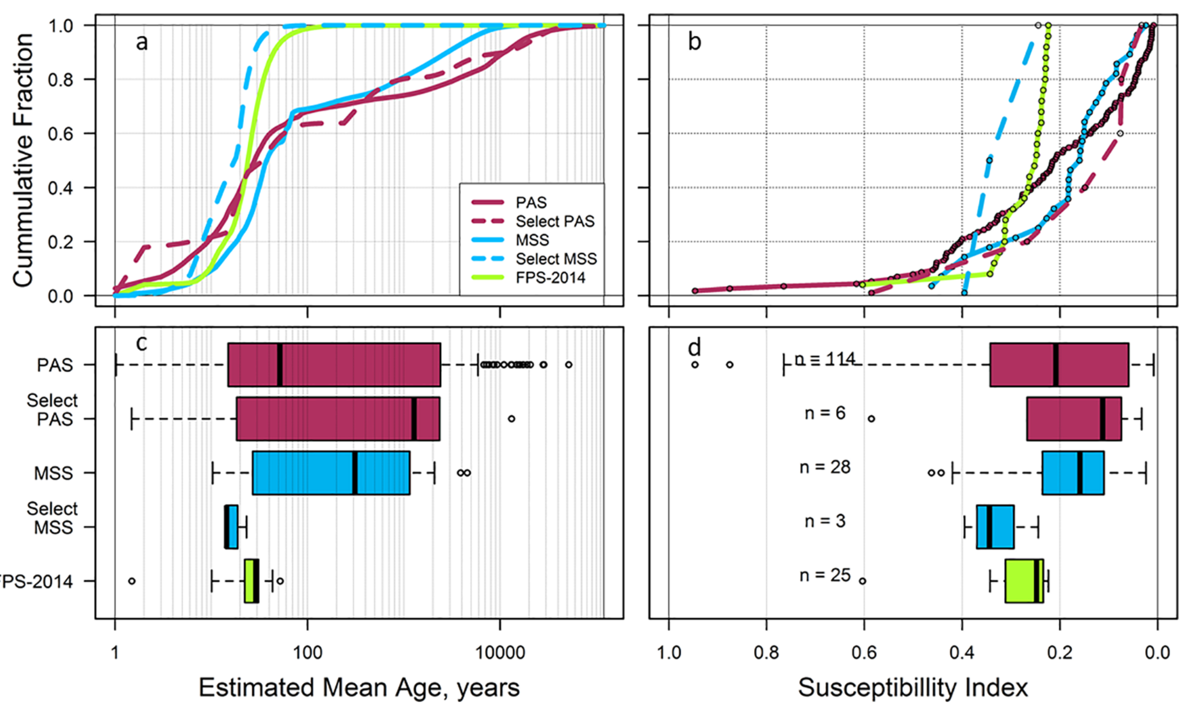

Fig. 7. Cumulative distributions and boxplots of (a,c) estimated age and (b,d) SI for respective sample networks. The individual values of SI indicated by open circles (b) with number of samples indicated left of the SI boxplot (d).

Table 2
Summary of LPM estimated age, fraction modern, and susceptibility index (SI) for select samples in the PAS, MSS, and FPS-2014 networks in the glacial aquifer, USA.

Network	Well Count	Mean Estimated Age	Fraction Modern	Mean Age Modern Fraction	Mean Age pre-Modern Fraction	Mean SI
PAS	115	3,398	0.64	19	9,050	0.228
PAS Select	6	2,804	0.61	18	7,220	0.198
MSS	29	607	0.63	28	2,810	0.197
MSS Select	3	18	0.99	16	103	0.328
FPS-2014	25	27	0.96	25	97	0.278

lower values (Figs. 5 and 7b, d) as a result of how SI is defined. Further investigation of SI in other groundwater systems would be instructive. SI has a less distinct spatial pattern than age class (Fig. 3a, b) but overall indicates a high level of susceptibility (SI > 0.2) across the aquifer. Overall, the findings of SI presented here are consistent with the conceptual model of the glacial aquifer, moderate recharge and shallow aquifer depth (Yager et al., 2019), indicating a relatively high susceptibility of groundwater to land surface contamination.

Comparison of the multiple age metrics (mean age, fraction modern, and SI) to the number of land surface contaminants detected (Fig. 3c, d, e) shows the SI provides the best correlation (Spearman's $\rho = 0.52$, Kendall's $\tau = 0.38$ with 95% confidence) indicating a subtle but measurable improvement over mean age or fraction modern for predicting groundwater susceptibility with environmental tracers. The comparison presented (Fig. 3c, d, e) somewhat controls for variability in source concentration, application rates, and uptake and transport by converting to a presence/absence but is only meant to illustrate the differences between age metrics when compared to measured contaminant data. It is worth emphasizing that the susceptibility index used here is a measure of relative susceptibility to land surface contaminants behaving conservatively and originating near the water table. Furthermore, naturally occurring contaminants such as arsenic and manganese are also of concern in the glacial aquifer. Under appropriate geochemical conditions (e.g., kinetically limited reduction) the concentration of such contaminants is inversely related to the age of a given parcel of water. It is tempting then to use the SI inversely; 1 indicating lower and 0 indicating higher relative susceptibility to natural contamination. While in theory the SI is potentially useful in this manner, the metric does not account for factors other than the age distribution. Any significant differences in geochemical conditions between sites may render the comparison of SI meaningless. Cautious use of the SI as a measure of susceptibility to natural or contamination behaving non-conservatively is required.

5.5. Environmental tracer sources

Maps of tracer anomalies (Fig. 6) are instructive in identify regions impacted by terrigenic tracer sources, informing the age interpretations of this study. Calculated $^{3}He_{trit}$ is sensitive to the assumed isotopic ratios of mantle and terrigenic helium sources and previous study has shown glacial sediments can be a significant source of terrigenic helium (Solomon, 2000). Appropriately so, positive $^{3}He_{trit}$ anomalies (Fig, 6a) occur more frequently at sites with high terrigenic helium (Fig. 6b). Negative $^{3}He_{trit}$ anomalies can be partly explained by the low solubility of helium making gas loss from sampling error or excess air degassing prior to sampling a primary issue. The lack of clear spatial pattern (Fig. 6a) reflects the complexity of measuring and calculating reliable $^{3}He_{trit}$ values in glacial terrains. In contrast, spatially coherent regions of high percent terrigenic helium ($^{4}He_{terr}/^{4}He_{tot}$; Fig. 6b) and terrigenic source of SF_6 (Fig. 6c) indicate strong hydrogeologic and geologic controls. High $^{4}He_{terr}$ is generally related to sites with some component of pre-modern water (Figs. 3 and 6b) providing additional support of a hydrologic connection to bedrock aquifers where He has accumulated over a longer period. Elevated SF_6 is coincident with intrusive volcanic bedrock, namely in eastern Minnesota and Wisconsin, and relatively shallow intrusive bodies in the Northeastern states (Fig. 6c).

6. Conclusion

The unconfined and confined water bearing sediments of the glacial aquifer cover a large spatial extent (1.87×10^{6} km^{2}) and serve as a public water supply for 30 million people. Estimates of mean groundwater age, groundwater age distribution, and susceptibility to land surface contamination is of critical importance. Groundwater age metrics for 168 public and domestic wells from three sample networks are presented in this study to evaluate the aquifer. Groundwater age distributions from the largest network (PAS) indicated groundwater is dominantly modern and recharged after 1950 (63 percent). This coincides with relatively high values of SI (Susceptibility Index) which is better correlated with measured detections of contaminants than mean age or fraction modern groundwater. Both groundwater age and susceptibility index were statistically most influenced by well depth and confinement, providing a conceptual check on the analysis, and further illustrating the susceptibility of the generally shallow and unconfined glacial aquifer. Presence of 1000s year old water across the glacial aquifer suggests a hydrologic connection between the shallow sediments and deeper fractured bedrock groundwater sources. Pre-modern groundwater originating in underlying bedrock aquifers is a more likely explanation than pre-glacial retreat recharge for the observed fraction of 1000s year old water. Such exchanges between the aquifers provides a mechanism of transport for land-surface and anthropogenic contaminants to the deep bedrock aquifer and geogenic contaminants accumulated over long periods to the shallow aquifer. Comparison of age metrics and hydrogeology in the PAS indicates the fraction of pre-modern water in a sample is systematically affected by the total well depth, depth to bedrock, depth to aquifer unit, aquifer complexity, and confinement. The findings indicate groundwater resources of the glacial aquifer are vulnerable to contamination sourced both from land surface and deep geologic materials.

This study provides a framework and new methods for interpretation of environmental tracers in determination of groundwater age and susceptibility. We show through comparison of groundwater age metrics across the spatial scales of three sample networks in the glacial aquifer (PAS, MSS, and FPS; large to small) a limited sample set can accurately characterize a complex continuous system. Specifically, equally spaced, deep, long screened-interval public supply wells provide a reasonable representation of modern groundwater age and susceptibility to contamination in the glacial aquifer. Inclusion of statistical analysis of the age metrics and hydrogeology was shown to provide vital context for understanding groundwater age results and help improve the conceptual model of the glacial aquifer. Maps of tracer anomalies presented here provide useful guidance both for interpretation and selection of appropriate tracers. In terrains with deep sequences of fine grain sediments derived from old rock, with high accumulated helium, use of $^{3}He_{trit}$ can be challenging. Igneous terrains, even when deeply buried, contribute significant amounts of terrigenic SF_6. Given the relative dearth of available environmental age tracers, rather than selecting or discarding tracers based on geology alone, an exploratory sampling and evaluation of a tracer's utility for a particular study is a practical approach. Further work to characterize groundwater using the presented methods will be of value to the scientific community and resource managers.

CRediT authorship contribution statement

John E. Solder: Conceptualization, Methodology, Formal analysis, Writing - original draft, Visualization. **Bryant Jurgens:** Conceptualization, Methodology, Writing - original draft. **Paul E. Stackelberg:** Formal analysis, Writing - review & editing. **Christopher L. Shope:** Formal analysis, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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