Using Groundwater Age Distributions to Understand Changes in Methyl *tert*-butyl ether (MtBE) Concentrations in Ambient Groundwater, northeastern United States

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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 percent 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 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.

KEYWORDS: Methyl *tert*-butyl ether, groundwater contamination, groundwater age, contaminant modeling

GRAPHICAL ABSTRACT:

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 percent MtBE by volume to meet these standards and MtBE use increased rapidly through the 1990s accordingly (Fig. 1) (Chemical Engineering News, 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. Public Law, 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 ($\mu\text{g/L}$) 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, 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 percent when the MtBE content in RFG areas of the United States averaged 11 percent 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 percent of groundwater samples. Kolb et al. (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 greater than 100 $\mu\text{g/L}$ in groundwater near known spills in several European countries, but maximum concentrations in drinking water

were typically very low (less than 0.5 $\mu\text{g/L}$). 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 percent in 2002 to 60 percent in 2010, while MtBE has decreased correspondingly (Stupp et al., 2012).

Figure 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).

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

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 percent 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 percent of the detections of MtBE in the nation (Zogorski et al., 2006), 70 percent of all measureable 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 meters (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 more than 1,000,000 $\mu\text{g/L}$ (Ayotte et al., 2008, Einarson and Mackay, 2001; Connor et al., 2015). Concentrations measured in this study (less than 10 $\mu\text{g/L}$ 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 $\mu\text{g/L}$; 95th percentile = 0.8 $\mu\text{g/L}$), 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 liters 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ in 1999. Another scenario is a short-term spill that was simulated using 1 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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 $\mu\text{g/L}$ 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.

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

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 ($^3\text{He}_{\text{trit}}$) 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.

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-percent 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, figures S4 to S9.

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 Plain	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 percent confidence interval, if improved)	3/4	6/9 (7/9)	3/7 (4/7)	6/7	1/1	3/6 (5/6)

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 less than 0.05 $\mu\text{g/L}$ by 2011.

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

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 less than $0.05 \mu\text{g/L}$ 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-percent confidence interval for the mean ages (table 1).

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-percent confidence interval of the mean age (table 1).

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

The CRY-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 less than 61 m, and less than 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 (greater than 61 m deep and more than 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 percent) and decreasing concentrations (Fig. 5), whereas deep wells had a lower detection frequency (11 percent) 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.

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 $< 0.05 \mu\text{g/L}$ 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-percent 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.

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.

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-percent 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 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 percent of wells; however, when considering the upper and lower confidence intervals, predictions improved to 76 percent. Alternate recharge scenarios account for the remaining cases; however, simulations of 10-year plumes with peaks later than 2000 were never correct for more than 32 percent 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 more than 10 years after peak MtBE use, 88 percent 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. Figure 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.

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

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