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

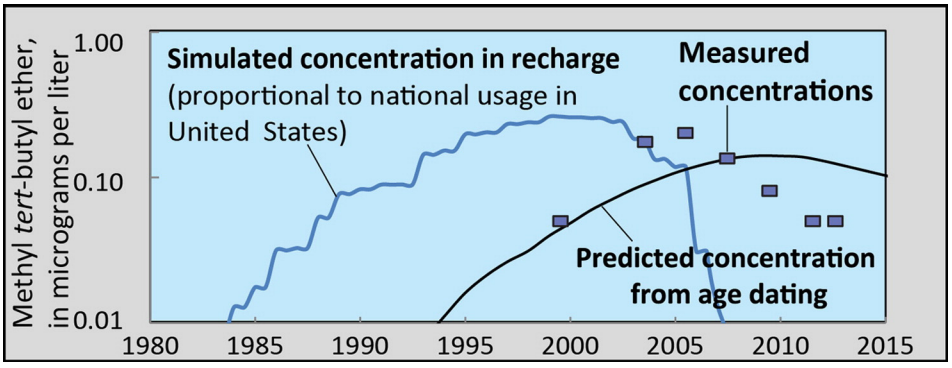
Bruce D. Lindsey [a,*], Joseph D. Ayotte [b], Bryant C. Jurgens [c], Leslie A. Desimone [d]

[a] U.S. Geological Survey, 215 Limekiln Road, New Cumberland, PA 17070, United States
[b] U.S. Geological Survey, 331 Commerce Way, Pembroke, NH 03275, United States
[c] U.S. Geological Survey, Placer Hall, 6000 J Street, Sacramento, CA 95819, United States
[d] U.S. Geological Survey, 10 Bearfoot Road, Northboro, MA 01532, United States

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

* Corresponding author.
E-mail address: blindsey@usgs.gov (B.D. Lindsey).

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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, 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).

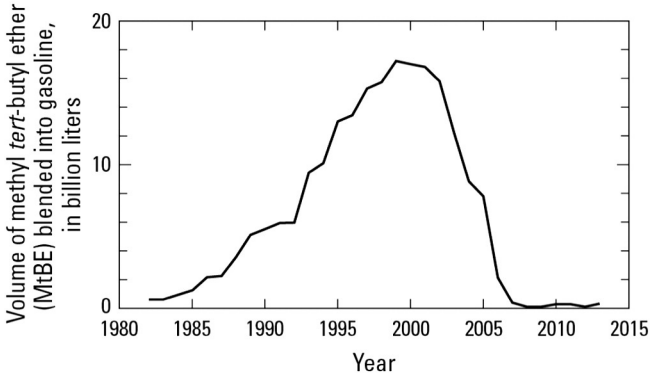

Fig. 1. The volume of MtBE blended into gasoline in the United States, 1982–2014, estimated from domestic production plus imports minus exports plus change in inventory (U.S. Department of Energy, 2014).

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

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