Environmental Science & Technology LETTERS

Letter

pubs.acs.org/journal/estlcu

# Life Cycle of Methyl *tert*-Butyl Ether in California Public Water Supply Wells

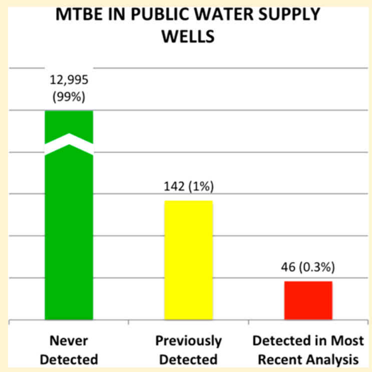
Thomas E. McHugh,*[,†] Sharon R. Rauch,[†] Shawn M. Paquette,[†] John A. Connor,[†] and Anthony D. Daus[‡]

[†]GSI Environmental Inc., Houston, Texas 77098, United States

[‡]GSI Environmental Inc., Newport Beach, California 92660, United States

*Supporting Information*

**ABSTRACT:** We have utilized the California Department of Public Health Water Quality Analyses database, with approximately 250000 results for methyl *tert*-butyl ether (MTBE), to evaluate the extent of MTBE in public water supply wells in California and how these impacts have changed over time. These data show that MTBE has never been detected in >98% of 13183 public water supply wells that have been tested for MTBE. The number of wells with first-time detections of MTBE peaked in 2000 and has decreased by 80% since that time. For the 188 wells in which MTBE has been detected at least once, MTBE was not detected in the most recent analysis of 142 of these wells. Tetrachloroethene, another common groundwater contaminant, has been detected more commonly, and new detections are declining more slowly. These results indicate that the impact of MTBE on public water supply wells has peaked and is declining.




## INTRODUCTION

Methyl *tert*-butyl ether (MTBE) was used as a gasoline additive between the 1970s and early 2000s to boost the octane rating and increase the oxygen content of gasoline.[1] MTBE is very soluble in water (51 g/L)[2] compared to other gasoline constituents. In the 1990s, the detection of MTBE resulted in the shutdown of a small number public water supply wells.[3] This combined with an increased frequency of detection of MTBE in shallow groundwater near leaking underground fuel tank (LUFT) sites raised concerns that MTBE-containing gasoline released from LUFT sites would have widespread impacts on groundwater used as drinking water. These concerns led to a phaseout of MTBE from gasoline beginning in the early 2000s.[3] The use of MTBE in gasoline ended in California and several other states by January 1, 2004, and its use in the remaining states largely ended by 2006.

In late 1990s and early 2000s, a number of studies attempted to quantify the impact of MTBE on public water supplies in California and throughout the United States.[1,4−6] These studies generally found that MTBE had been detected in 1−3% of public water supplies tested. However, because the testing of water wells for MTBE began only in the mid-1990s, these studies provided only a partial understanding of the magnitude of impacts because of the limited number of wells tested for MTBE and the limited number of sample events available. Some of these studies speculated that detection rates would increase over time as MTBE migrated from fuel release sites to water supply wells.[1,4] For example, Johnson et al. indicated that MTBE has the potential to threaten public water supply wells for tens to hundreds of years.[1]

MTBE is no longer used as a gasoline additive and is therefore no longer being released into the environment though new leaks or spills of gasoline. As a result, the impacts on groundwater and public water supply wells associated with past releases would be expected to eventually peak and decline as biodegradation and other attenuation mechanisms remove MTBE from groundwater. A previous study using the California GeoTracker database found that maximal MTBE concentrations in groundwater at LUFT sites decreased by a median of 96% from 2001 to 2011.[7] However, it is difficult to predict the time lag between decreases in contaminant concentrations observed at monitoring wells located close to the gasoline release location and the corresponding changes at public water supply wells located farther from the release locations. The frequency of MTBE detection in California public water supply wells was relatively stable between 2000 and 2010.[8] In other parts of the country, MTBE concentrations and detection frequencies in pubic water supply wells have begun to decrease in recent years.[9] The goal of this study was to evaluate the prevalence of MTBE in groundwater recovered by public water supply wells in California and to evaluate the changes in detection frequency and concentration over time. For comparison, we also looks at trends for tetrachloroethene (PCE) in public water supply wells.

## METHODS

The California Department of Public Health (CDPH) Water Quality Analyses Database is a publically available database

**Received:** October 1, 2014
**Revised:** November 27, 2014
**Accepted:** December 2, 2014
**Published:** December 2, 2014

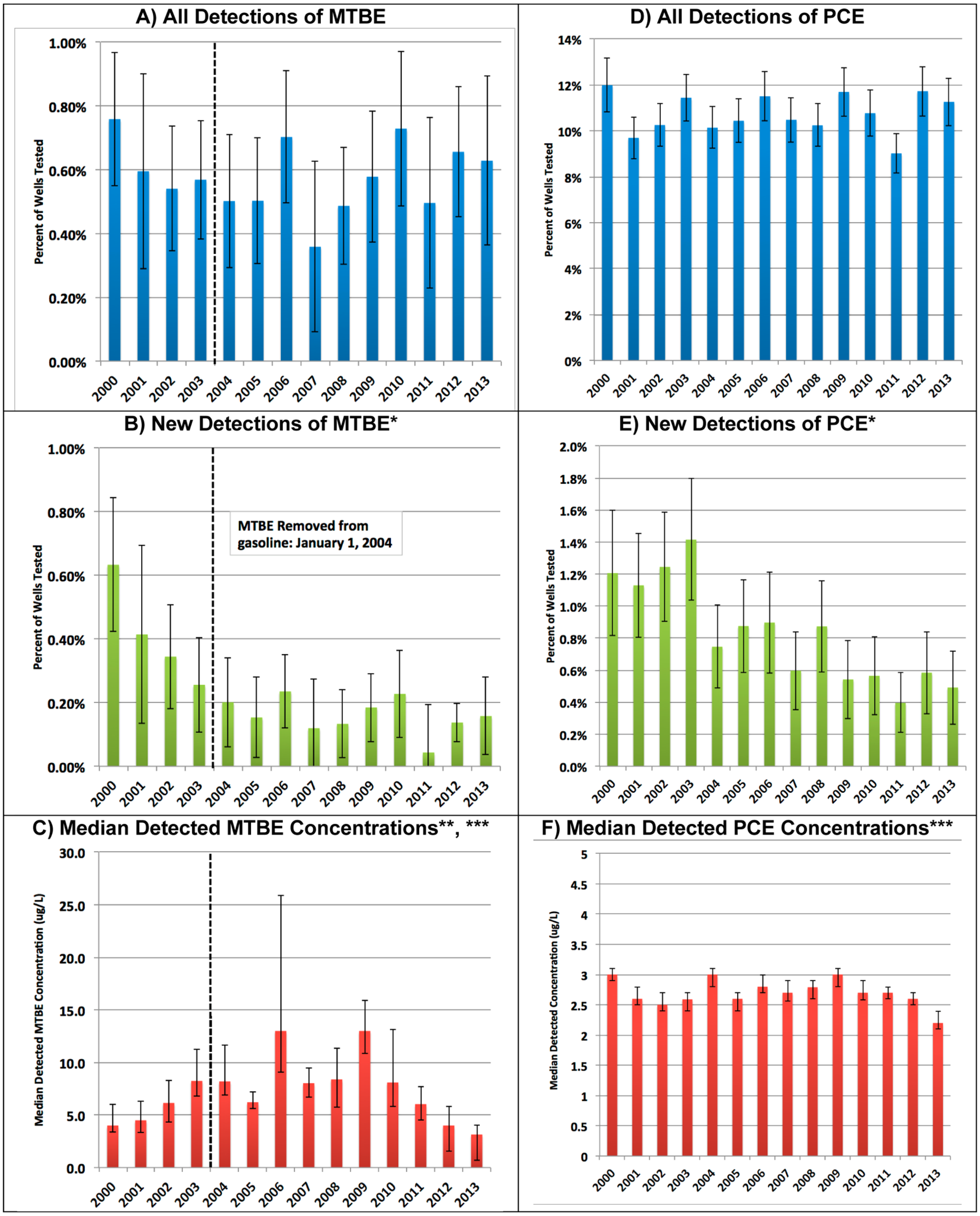



**Figure 1.** Trends over time in detection of MTBE and PCE in public water supply wells. The error bars represent the 95% confidence interval for the detection frequency (A, B, D, and E) and the 95% confidence interval for the median detected concentration (C and F). One asterisk indicates a statistically significant trend ($p < 0.05$) for the full evaluation period. Two asterisks indicate a statistically significant linear trend ($p < 0.05$) for the time period from 2006 to 2013. Three asterisks indicate a statistically significant linear trend ($p < 0.05$) for the time period from 2009 to 2013.

containing water quality analyses for public water systems in California.[10] In July 2014, responsibility for this database was transferred from the CDPH to the California State Water Resources Control Board. This database contains laboratory analytical results for most of the active and some inactive public drinking water wells in the state, dating from 1974 to the present. Drinking water analyses are reported directly from laboratories, and updates to the database are made on a daily basis. The analytical test results and Supporting Information about individual water systems, wells, and laboratories can be downloaded from the State Water Resources Control Board

Website.[10] Our database was downloaded in June 2014 and contains data for samples collected as recently as April 2014.

The CDPH database includes 17074 locations where water samples have been analyzed for MTBE and a total of 247544 water samples analyzed for MTBE. This includes 15287 groundwater locations, 1726 surface water locations, and 61 other (or unidentified) locations. The groundwater locations include active, standby, and inactive water wells, agricultural wells, monitoring wells, water treatment systems, distribution system sample points, and a small number of locations without location descriptions. Of the 247544 water samples analyzed for MTBE, MTBE was detected in 4559 of the samples (1.8%). For the samples in which MTBE was detected, the median detected concentration was 4.4 μg/L and the range (5−95‰) was from 0.66 to 42.2 μg/L. Analytical detection limits were reported for 41013 of the MTBE analyses. For these analyses, the most commonly reported detection limit was 3 μg/L (68%); 24% of the analyses had a detection limit of ≤1 μg/L, and fewer than 0.5% had a detection limit greater than the California MCL for MTBE of 13 μg/L. From 2000 to 2013, the detection limits reported for MTBE did not change significantly. The median detection limit was 3 μg/L for every year from 2000 to 2013. Over this time period, the annual percentage of analyses with a detection limit or ≤1 μg/L varied from 7 to 30% with no clear trend over time. In 2013, for example, 21% of analyses had a detection limit of ≤1 μg/L compared to 24% of analyses from the entire time period.

Our goal was to evaluate MTBE in groundwater recovered by public water supply wells. For this purpose, we focused our evaluation on sample locations associated with currently existing individual public water supply wells. This group consisted of groundwater wells identified as active raw, active untreated, standby raw, standby untreated, inactive raw, and inactive untreated. These criteria covered 13183 (86%) of the 15287 groundwater locations in the CDPH database analyzed for MTBE. Our evaluation did not include post-treatment sample locations, combined and distribution system sample locations, monitoring wells, or agricultural wells because these locations were not reflective of individual public water supply wells. We also did not include abandoned or destroyed wells because these wells cannot be used to evaluate current MTBE concentrations. The CDPH database showed detections of MTBE in only 21 of 975 public wells classified as abandoned or destroyed, so the exclusion of these wells had little effect on the overall evaluation of MTBE in public wells.

For comparison to MTBE, we also evaluated PCE, a volatile organic chemical widely used for dry cleaning and other industrial purposes. We selected PCE rather than benzene, a petroleum constituent associated with gasoline, because benzene has rarely been detected in public water supply wells in California and the infrequent detections have been attributed primarily to natural sources rather than gasoline releases.[11] Using the same selection criteria (i.e., raw and untreated active, standby, and inactive wells), we identified 15963 locations tested for PCE. Approximately 80% of the locations tested for either MTBE or PCE have been analyzed for both of these constituents; 92% of the detection limits reported for PCE analyses were 0.5 μg/L.

Three analyses were used to evaluate statistical significance. Changes in detection frequency were evaluated using binary logistic regression. Changes in median concentration over time were evaluated using ordinary least-squares regression (ORLS). Differences in detection frequency between MTBE and PCE were evaluated using the $Z$ test for proportions.

## ■ RESULTS AND DISCUSSION

For the 13183 active, standby, and inactive public water wells tested for MTBE, MTBE has been detected in 188 wells (1.4%). A list of these wells is included in Table S.1 of the Supporting Information. MTBE has been detected at a concentration greater than the California primary drinking water standard (13 μg/L) in 40 (21%) of these wells.

**Changes in Detection Frequency and Concentration.** Over time, the percentage of wells with detectable MTBE has varied within a relatively narrow range with no statistically significant trend over time [$p$ = 0.99 (Figure 1A)]. However, new detections of MTBE (i.e., a well in which MTBE was detected for the first time) have decreased over time from 0.63% of wells tested in 2000 to 0.16% of wells tested in 2013 (Figure 1B). The decrease in the frequency of new detections over time is statistically significant when evaluated using binary logistic regression ($p < 0.001$). The decline in new detections of MTBE began in 2001, three years before MTBE was removed from gasoline in California in January 2004.

For comparison, PCE was more commonly detected in public water supply wells than MTBE. Total detections of PCE varied between 9.0 and 12.0% of wells tested with no significant trend over time [$p$ = 0.78 (Figure 1D)]. A list of the public water supply wells with any detection of PCE is provided as Table S.2 of the Supporting Information. New detections of PCE declined from 1.2% of wells tested in 2000 to 0.49% in 2013, a significant decrease [$p$ < 0001 (Figure 1E)] but a decrease smaller in magnitude than the decrease in new detections of MTBE. Although the median detection limit for PCE (0.5 μg/L) is lower than the median detection limit for MTBE (3 μg/L), this difference only partly explains the difference in detection frequency for the two constituents. Since January 1, 2000, 375 public water supply wells have had detections of PCE greater than 3 μg/L while only 90 wells have had detections of MTBE greater than 3 μg/L.

For wells with detectable MTBE, the median detected MTBE concentration increased in the early 2000s, reaching a peak in 2006, and has decreased since that time (Figure 1C). For the full evaluation period (2000−2013), there was no significant linear trend in MTBE concentration ($p$ = 0.88). However, the decrease in MTBE concentration was significant over the time period from 2006 to 2013 ($p$ = 0.005) or from 2009 to 2013 ($p$ = 0.007). For comparison, the median detected PCE concentration was relatively stable between 2000 and 2013 with a small decline in concentration beginning in 2009. There was no statistically significant trend over the full evaluation period [$p$ = 0.27 (Figure 1F)]; however, the decrease in median detected PCE concentration over the period from 2006 to 2013 approaches significance ($p$ = 0.065), and the decrease from 2009 to 2013 is significant ($p$ = 0.02). In summary, new detections of both MTBE and PCE in public wells have declined significantly since 2000, but the decline in new detection of MTBE has been greater. The median detected concentration of MTBE peaked in 2006 and has declined significantly since that time. The median detected concentration of PCE has also decreased since 2009.

**Persistence of MTBE in Public Wells.** For many of the 188 public wells with detected MTBE, the presence of MTBE has been sporadic. For wells tested 20 or fewer times, 63% of the wells with MTBE detections show only a single detection

**Table 1. MTBE and PCE Detection Frequencies in California Public Water Supply Wells**

| no. of times a well was analyzed | no. of wells with no detection | no. of wells with one detection | no. of wells with multiple detections | no. of wells with one detection of >3 μg/L | no. of wells with multiple detections of >3 μg/L |
|---|---|---|---|---|---|
| | | | (A) MTBE | | |
| 1 | 1895 (99.7%) | 6 (0.3%) | NA | 2 (0.1%) | NA |
| 2 | 1494 (99.3%) | 8 (0.5%) | 3 (0.2%) | 6 (0.2%) | 2 (0.2%) |
| 3 | 1264 (99.4%) | 7 (0.6%) | 1 (0.1%) | 2 (0.2%) | 1 (0.1%) |
| 4 | 1051 (98.9%) | 9 (0.8%) | 3 (0.3%) | 4 (0.4%) | 1 (0.1%) |
| 5–10 | 4009 (99.3%) | 19 (0.5%) | 8 (0.2%) | 9 (0.2%) | 3 (0.1%) |
| 11–20 | 1879 (98.3%) | 14 (0.7%) | 19 (1.0%) | 7 (0.4%) | 15 (0.8%) |
| ≥21 | 1403 (93.9%) | 22 (1.5%) | 69 (4.6%) | 13 (0.9%) | 49 (3.3%) |
| | | | (B) PCE | | |
| 1 | 3825 (99.5%) | 19 (0.5%) | NA | 5 (0.1%) | NA |
| 2 | 2000 (98.9%) | 13 (0.6%) | 9 (0.5%) | 1 (0.1%)[a] | 4 (0.2%) |
| 3 | 1454 (97.7%)[a] | 8 (0.5%) | 27 (1.8%)[b] | 10 (0.7%)[b] | 9 (0.6%)[b] |
| 4 | 1058 (97.5%)[a] | 12 (1.1%) | 15 (1.4%)[b] | 2 (0.2%) | 5 (0.5%) |
| 5–10 | 3258 (96.7%)[a] | 54 (1.6%)[b] | 57 (1.7%)[b] | 12 (0.4%) | 17 (0.5%)[b] |
| 11–20 | 2062 (92.8%)[a] | 63 (3.1%)[b] | 86 (4.1%)[b] | 11 (0.5%) | 29 (1.4%) |
| ≥21 | 1188 (56.8%)[a] | 128 (6.1%)[b] | 776 (37.1%)[b] | 58 (2.8%)[b] | 384 (18.4%)[b] |

[a]The observed frequency for PCE is significantly lower ($p < 0.05$) than the frequency for MTBE as determined by the $Z$ test for proportions. [b]The observed frequency for PCE is significantly higher ($p < 0.05$) than the frequency for MTBE as determined by the $Z$ test for proportions.

(Table 1A). For comparison, 45% of these less frequently monitored wells with PCE detections show only a single detection of PCE (Table 1B). For the wells analyzed for MTBE more than 20 times, MTBE has been detected only once in 24% of the wells with any detection MTBE and more than 10 times in 38% of these wells. For wells analyzed for PCE more than 20 times, PCE has been detected only once in 17% of the wells with any detection of PCE and more than 10 times in 67% of these wells

For the entire set of 188 wells in which MTBE has been detected at least once, MTBE was not detected in the most recent analysis for 142 (76%) of these wells. For the entire set of 1267 wells in which PCE has been detected at least once, PCE was not detected in the most recent analysis for 634 (50%) of these wells.

These analyses indicate that the detections of both MTBE and PCE in public wells can be sporadic with only a single detection of the constituent observed in many of the wells where it has been detected at least once. However, PCE is more likely to be detected multiple times (77% of wells compared to 55% for MTBE) and is more likely to be detected in the most recent analysis (50% of wells compared to 24% for MTBE). The different in persistence between MTBE and PCE does not appear to be due to the difference in detection limits. Looking only at wells with at least one detection at a concentration of >3 μg/L (i.e., above the median detection limit for MTBE), MTBE was detected two or more times at a concentration of >3 μg/L in 71 of 114 wells (62%) while PCE was detected two or more times at a concentration of >3 μg/L in 447 of 547 wells (82%). This difference in the proportion of wells with multiple detections above 3 μg/L is statistically significant ($p < 0.001$) as determined by the $Z$ test for proportions. Similarly, for this set of wells, the most recent analysis for MTBE was a detection of >3 μg/L in 34 of 144 wells (30%) while the most recent analysis for PCE was a detection of >3 μg/L in 244 of 547 wells (44%). This difference is also significant ($p = 0.003$).

Despite the disappearance of MTBE from many wells, the overall percentage of wells with detectable MTBE has not decreased over time (Figure 1A) likely because of a bias toward resampling of wells with previous MTBE detections. In recent years, wells with prior detections of MTBE were more likely to have been retested for MTBE than wells without prior detections. For example, in 2013, 29% of all wells previously tested for MTBE were tested again in that year. However, 41% of wells with any prior detection of MTBE were retested in 2013, and 59% of wells with a prior detection of >5 μg/L were retested.

MTBE was used as a gasoline oxygenate in California from the 1970s until the end of 2003. Overall, our analyses indicate that the impact of MTBE on groundwater used as a source of public water supply has been limited in extent and duration. MTBE has never been detected in more than 98% of 13183 public water supply wells analyzed for MTBE. MTBE has been detected at a concentration above the California MCL in only 40 of these public water supply wells. New detections of MTBE in public water supply wells peaked in 2000, three years before MTBE was removed from gasoline in California. New detections of MTBE decreased significantly (by 80%) from 2000 to 2013.

The impacts of MTBE appear to be dissipating in a number of public water supply wells in California. The median detected MTBE concentration peaked at 13 μg/L in 2006 (two years after MTBE had been removed from gasoline) and declined to 3.2 μg/L in 2013. For the 188 wells in which MTBE has been detected at least once, MTBE was not detected in the most recent analysis for 142 (76%) of these wells. These observations are in contrast to predictions in the early 2000s that MTBE would threaten public water supply wells for tens to hundreds of years and the impacts would last for decades.[1]

Our analysis of the CDPH database is consistent with another recent study of MTBE concentrations in groundwater at LUFT sites in California. This prior study found that maximal MTBE concentrations in groundwater at these sites decreased by a median of 96% from 2001 to 2011.[7] These studies together suggest that the impact of MTBE on public water supply wells in California has peaked and will likely continue to decrease over time.

## ASSOCIATED CONTENT

### Supporting Information

Public water supply wells in California with one or more detections of MTBE (Table S.1) and public water supply wells in California with one or more detections of PCE (Table S.2). This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION


### Corresponding Author

*E-mail: temchugh@gsi-net.com. Phone: (713) 522-6300.


### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This project was funded by the GSI Environmental Research Fund (Project 9400-020).

## REFERENCES


(1) Johnson, R.; Pankow, J.; Bender, D.; Price, C.; Zogorski, J. MTBE: To What Extent Will Past Releases Contaminate Community Water Supply Wells? *Environ. Sci. Technol.* **2000**, *34*, 210A−217A.

(2) Technical Information Review. Methyl tertiary Butyl Ether (CAS Registry No. 1634-04-4); Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency: Washington, DC, 1993.

(3) McCarthy, J. E.; Tiemann, M. MTBE in Gasoline: Clean Air and Drinking Water Issues. Congressional Research Service Report, Paper 26; 2006 (http://digitalcommons.unl.edu/crsdocs/26) (accessed August 20, 2014).

(4) Fogg, G. E.; Meays, M. E.; Trask, J. C.; Green, C. T.; LaBolle, E. M.; Shenk, T. W.; Rolston D. E. Impacts of MTBE on California Groundwater. Health and Environmental Assessment of MTBE: Report to the Governor and Legislature of the State of California as Sponsored by SB 521. Volume 4: Ground and Surface Water; 1998 (http://www.clu-in.org/contaminantfocus/default.focus/sec/methyl_tertiary_butyl_ether_%28mtbe%29/cat/Environmental_Occurrence/) (accessed August 20, 2014).

(5) Williams, P. R. D. MTBE in California Drinking Water: An Analysis of Patterns and Trends. *Environ. Forensics* **2001**, *2* (1), 75−85.

(6) A Review of Cost Estimates of MTBE Contamination of Public Wells. Technical Report for the American Water Works Association: Denver, CO; 2005 (http://www.clu-in.org/contaminantfocus/default.focus/sec/methyl_tertiary_butyl_ether_%28mtbe%29/cat/Treatment_Technologies/) (accessed August 20, 2014).

(7) McHugh, T. E.; Kulkarni, P. R.; Newell, C. J.; Connor, J. A.; Garg, S. Progress in Remediation of Groundwater at Petroleum Sites in California. *Groundwater* **2014**, *52*, 898−907.

(8) Williams, P. R. D. MTBE in California Public Drinking Water Wells: Have Past Predictions Come True? *Environ. Forensics* **2011**, *12* (3), 270−289.

(9) Trend Report on MTBE in Public Water Supplies. Technical Report for Dutchess County Department of Health: Dutchess County, NY; 2014 (http://www.co.dutchess.ny.us/CountyGov/Departments/Health/MTBE_Trend_Report_Final_v4.pdf) (accessed August 20, 2014).

(10) EDT Library and Water Quality Analyses Data and Download Page. California State Water Resources Control Board (http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/EDTlibrary.shtml) (accessed August 20, 2014).

(11) Landon, M. K.; Burton, C. A.; Davis, T. A.; Belitz, K.; Johnson, T. D. Statistical Evaluation of Variables Affecting Occurance of Hydrocarbons in Aquifers Used for Public Supply, California. *J. Am. Water Resour. Assoc.* **2014**, *50* (1), 179−195.