

February 21, 1999

TO: U.S. Geological Survey Reviewers of  
Health and Environmental Assessment of MTBE  
Groundwater Sections

FROM: Graham E. Fogg, Mary E. Meays, and James C. Trask  
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Davis, CA 95616

SUBJECT: General response to reviewer comments concerning MTBE impacts on  
California Groundwater

We sincerely thank the U.S. Geological Survey scientists who reviewed the groundwater portions of the UC report "Health and Environmental Assessment of MTBE." The insightful comments have helped us clarify several portions of the report. Our clarifications are delivered in two ways: minor modifications to the text and figures, to the extent allowed without reformating large portions of the report, and detailed responses to each substantive comment on the pages that follow this letter.

In general, the most significant comments were: (1) "...there is little evidence presented in the report that regional degradation of water resources would result from continued MTBE use" and (2) that our modeling analysis was conservative (toward overestimating impacts) because it assumed constant source concentrations and did not account for losses of MTBE due to biodegradation and volatilization. Regarding the first point, although we agree that MTBE will likely not permeate the entire groundwater supply in most basins, we think the impacts are already significant and will become more regionally significant in the future. Events in the Tahoe Basin provide a preview of this phenomenon. For detailed discussion, refer to pages 6 and 7 as well as pages 9, 12, 33-38, 58, and 59 below. Pages 33-38 specifically address why we concluded that even low-level detections of MTBE in California public supply wells are indicative of non-atmospheric sources, primarily from LUFT sites.

Regarding the second point, we have included additional discussion of the model and its assumptions on pages 16, 17, 50-56, and 64 below. The model roughly approximates a decaying source concentration indirectly through its stochastic time term. Regardless, as indicated in our numerical modeling experiments (e.g., Figure 12), we expect the average dissolved phase concentration in the immediate vicinity of the source will potentially remain high for many years or decades (p. 53-54) at typically complex California sites. Importantly, we assert that no tenable study yet exists to show, indicate or even strongly suggest that MTBE is biodegrading significantly under field conditions in groundwater (see p. 16, 17, 50, 51 below). In our reading of the literature, claims to the contrary are

based on subsurface transport models (both conceptual and theoretical) that inappropriately simplify the physical hydrogeologic processes.

Lastly, we thank the USGS for pointing out our neglect of recent NAWQA program data on ambient MTBE concentrations in non-urban areas of California. These data help reinforce our interpretations, and exemplify the type of long-term monitoring needed to ascertain the status of regional groundwater quality as related to resource management consequences.

In Reply Refer To: Mail Stop 409

Peter M. Rooney  
Secretary for Environmental Protection  
California Environmental Protection Agency  
555 Capitol Mail  
Suite 525  
Sacramento, California 95814

Dear Mr. Rooney:

United States Department of the Interior

US. GEOLOGICAL SURVEY  
Reston, Virginia 20192

Dec 23, 1998

The U.S. Geological Survey appreciates the opportunity to review and comment on the report: "Health and Environmental Assessment of MTBE" prepared by the University of California.

Our scientists have read the entire report. However, our review has focused on the following five topics that are consistent with our agency's mission and the technical expertise of our scientists:

1. Impact of MTBE on California's ground water,
2. MTBE in surface drinking water supplies,
3. Transport and fate modeling of MTBE in reservoirs and lakes,
4. Exposure of humans to MTBE in drinking water, and
5. Environmental behavior and fate of alternative oxygenates and gasolines

Major findings and recommendations from our review are summarized in Attachment I to this letter. Specific comments and suggestions on sections of the report will be mailed under a separate cover for your information and use. These detailed comments hopefully will be of value to the authors of each chapter in finalizing their manuscript(s).

The University of California's faculty and staff are to be congratulated for their timely completion of the report. It contains an impressive amount of information and research that will prove useful in addressing the complex issues associated with the use of methyl tert-butyl ether (MTBE) and other fuel oxygenates in gasoline. The environmental concerns associated with MTBE are relatively new and thus, there is limited water-quality information available to characterize

MTBE's occurrence in California's ground water, reservoirs, and drinking water. Accordingly, many of our comments and suggestions focus on the need for more comprehensive data sets to better address the questions posed by the Act.

We recognize that the very short time frame mandated by the Act precluded the collection of new data and information. Nevertheless, additional data would improve today's understanding of the significance of MTBE to California's water resources and drinking water and provide an improved basis for evaluating the policy options proposed to your legislature. The following data-collection strategies and analyses are suggested for providing this additional information.

(1) systematic sampling of a subset of reservoirs and public-supply and private wells to fully characterize the quality of California's surface-water and ground-water supplies; (2) random sampling of California's community and privately supplied drinking water to provide more accurate MTBE concentration data for use in exposure and risk assessments; (3) additional modeling and sampling to improve confidence in projections of future impacts to community water-supply wells from leaking underground storage tanks; and (4) field studies and research on the environmental behavior and fate of alternative oxygenates and gasolines to evaluate their impact, if any, to air and water resources. This latter point is especially important and we strongly concur with the report that additional research is needed prior to considering any shift from MTBE to alternative oxygenates and gasolines.

In closing, we again thank you for the opportunity to review and comment on this important report.

#### IMPACT OF MTBE ON CALIFORNIA'S GROUND WATER

An assessment of MTBE in groundwater is especially important because of the widespread use of ground water for drinking water in California, and because of this compound's slow rate of biodegradation in aquifers. This type of assessment should be unbiased relative to existing sources of contamination and should consider other contaminants (e.g. fumigants, solvents and hydrocarbons of concern in conventional gasoline) in addition to MTBE, to provide an overall perspective on the condition of the resource. The University of California's assessment was based on a compilation of existing data on MTBE concentrations in ground water: (1) at Leaking Underground Storage Tanks (LUST) sites, (2) in community water-supply wells, and (3) in the Lake Tahoe basin. The existing data document the common occurrence and often high concentrations of MTBE in ground water near LUST sites. In contrast, MTBE was reported to occur infrequently in community water-supply wells. MTBE concentrations of concern to drinking water were found primarily in wells of three communities: Santa Monica, South Tahoe, and Marysville.

The data from LUST sites are presumably more representative of locations with known or suspected contamination, than ground-water conditions throughout California. In aggregate, ground water contaminated by LUST sites represent a small fraction of California's ground-water resource. As part of our National Water-Quality Assessment Program, USGS has completed a regional-scale assessment of the occurrence and concentrations of a broad array of contaminants, including MTBE and other volatile organic compounds, for several of the most important aquifers in the San Joaquin-Tulare and Sacramento River Basins, and is beginning similar work in the Santa Ana River Basin. Adding the USGS data to the University of California assessment will help place MTBE and the LUST monitoring data in perspective. These data can be obtained by contacting our California District Office which is located at Placer Hall, 6000 J Street, Sacramento, California 95819-6129. The phone number of our District Office is (916) 278-3026. Similar monitoring of California's public-supply and private wells in other aquifers not studied by the USGS is needed to fully characterize California's ground-water supplies statewide. In addition to water sampling, further monitoring should involve the collection of ancillary information for each sampled well, so that the probable source(s) of MTBE and other contaminants, when detected, can be identified.

The University of California's report estimated the future risk posed to water-supply wells by MTBE released to ground water at LUST sites. A statistical-analytical ground-water model was used for this purpose. Models to predict future impacts of MTBE releases to water-supply wells should be used with caution because there are large uncertainties in the assumed processes and input conditions. The modeling approach used was conservative and may over predict the actual risk of LUST releases to water-supply wells because: (1) it assumes that the concentration of MTBE in the area of a gasoline release (i.e. the source strength) is maintained at a constant level over the period of prediction; (2) two processes that would reduce the concentrations of MTBE, degradation and volatilization (Borden and others, 1997; Schirmer and Barker, 1998; and Baehr and others, 1997), were not incorporated in model simulations; and (3) the analysis assumes that predicted plumes will travel across the contributing areas of water-supply wells and be drawn to the wells. The reliability of risk projections could be improved by long-term monitoring of MTBE in water-supply wells and ambient ground water.

**COMMENT 1****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume I: Summary &amp; recommendations

Section # and Title: 1. Executive Summary, Recommendations, Summary

Sub-section: Executive Summary

Page #: 12

Title:

Paragraph: 1

Sentence: Last 3 sentences

Statement: Since both groundwater wells and surface water reservoirs have been contaminated, alternative water supplies may not be an option for many water utilities. If MTBE continues to be used at current levels and more sources become contaminated, the potential for regional degradation of water resources, especially groundwater basins, will increase. Severity of water shortages during drought years will be exacerbated.

Comment: Monitoring of water-supply wells and surface water reservoirs for MTBE in California is incomplete and few community water-supply wells have been found to contain MTBE at levels above 5 µg/L. Additionally, there is little evidence presented in the report that regional degradation of water resources would result from continued MTBE use.

Response: Monitoring of water supply wells and surface water reservoirs for MTBE in California is indeed incomplete, but not so incomplete that a reasonable estimate of the MTBE threat to water resources cannot be made at this time. The data show that at least 3,000 to 5,000 LUFT sites (55 to 78% of the gasoline-groundwater LUFT sites) have contaminated groundwater with MTBE. All tenable field studies and theoretical analyses indicate that (1) dissolved concentrations of MTBE can be extremely high, (2) the dissolved MTBE moves approximately as fast as the groundwater, (3) MTBE does not degrade appreciably below the water table (see responses to related comments below), and (4) accordingly, despite the much shorter times available for transport of MTBE as compared to BTEX compounds, MTBE plumes are observed to have already migrated far beyond BTEX plumes at numerous locations. The volume of groundwater rendered non-potable by a single MTBE plume is on the order of 100,000 ac-ft. Hence, MTBE from LUFT sites has rendered on the order of 0.3 to 0.5 billion ac-ft of groundwater (developed and undeveloped) unusable without treatment. Furthermore, we showed the level of MTBE concentration and incidences to correlate directly with population. For example, Los Angeles County is the most populated, consumes the most MTBE, has the most LUFT sites in California, and has the highest number of public supply wells with MTBE detects (>0.5 µg/L).

The number of California public supply wells with MTBE detects (~35; 1.2% of sampled wells) is indicative of a relatively rapidly advancing problem, given the relatively short

times intervals available for migration of MTBE as compared to other compounds that were released into the environment previously. Importantly, as indicated in responses to related comments below, these ~35 MTBE detects cannot generally be attributed to non-LUFT sources of contamination. Given the above findings, we believe our original statements are scientifically valid and prudent: “If MTBE continues to be used at current levels and more sources become contaminated, the potential for regional degradation of water resources, especially groundwater basins, will increase. Severity of water shortages during drought years will be exacerbated.” The geographically widespread MTBE impacts on Tahoe Basin groundwater due to many LUFT sites provide ample preview of exactly the types of impacts described in our forecast. South Lake Tahoe PUD does not have rights to surface water in Lake Tahoe and therefore faces a genuine water supply disaster caused directly by MTBE.

Some argue that MTBE has contaminated a small fraction of California groundwater resources and that the problem is therefore not serious. In fact, the same statement applies to all groundwater contaminants – most of our groundwater is still uncontaminated. Basing policy on such reasoning, however, can only lead to a condition of non-sustainability of groundwater quality. This would be especially unwise in California, where water shortages are common and are projected to become increasingly severe and where groundwater resources constitute an essential, massive portion of the water supply. Groundwater quality in the portions of California groundwater basins that are commonly tapped for public supply changes on time scales of years to centuries. Allowing perpetual buildup of mobile, recalcitrant contaminants in the shallow portions of these basins, even if much of the groundwater remains relatively clean, will lead to increasing impacts that will become ever more regional in scope. Moreover, the financial burden created by MTBE at LUFT sites is already formidable.

Based on a recent study of the leak histories of new and upgraded underground storage tank systems (SWRCB, January 1999), one cannot rely on better-engineered, upgraded tanks to adequately reduce the number of future LUFT cases.

SWRCB, 1999, Report of the State Water Resources Control Board’s Advisory Panel on the Leak History of New and Upgraded UST Systems, January, 8 p.

**COMMENT 2****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume I: Summary &amp; recommendations

Section # and Title: 5. Extent of Contamination of Drinking Water Supplies

Page #: 31

Sub-section title:

Paragraph: 4

Sentence: 3

Statement: In the cases where groundwater has been contaminated with BTEX (benzene, toluene, ethylbenzene and xylenes, common constituents of gasoline) compounds but not MTBE, the leak of BTEX either occurred before MTBE was added to gasoline, or insufficient time has elapsed for the MTBE to reach monitoring wells.

Comment: The authors need to describe the gasoline-release scenario that is being discussed. For example, is the leak a single release of gasoline containing MTBE or is it a release of conventional gasoline (i.e. no MTBE present in the gasoline) followed by a second release of gasoline that does contain MTBE? In the first case, MTBE might not be present in the monitoring well because it has already been transported past the monitoring well. In the second case, the release of conventional gasoline might have caused BTEX to reach the monitoring well and MTBE from the second release has either not been transported to the monitoring well yet or has already been transported past the monitoring well. The possibility that MTBE has already been transported past the monitoring well should be considered by the authors for ease of review.

Response: Added the sentence at the end of the statement: “Alternatively, it is possible that if the MTBE release only lasted for a finite period of time, the dissolved MTBE has already traveled past the monitoring well.”

**COMMENT 3****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume I: Summary & recommendations

Section # and Title: 5. Extent of Contamination of Drinking Water Supplies

Page #: 32

Sub-section title: 5.2 Groundwater

Paragraph: top of page 32

Sentence: last sentence in section of the paragraph

Statement: These groundwater concentrations will likely increase in the future, as MTBE continues to migrate from existing sources.

Comment: Many current MTBE source zones might well already be in a sort of steady state, at least as regards to source strength. Thus, the maximum groundwater concentrations found in a plume will not likely increase at most sites, though local concentrations might increase as previously contaminated water reaches uncontaminated zones. Simply put, many plumes might get bigger, but the maximum concentrations will likely not increase.

Response: The reviewer assumes that the maximum concentrations recorded are actually the maximum concentrations in the plumes. In fact, we anticipate that most of the typically sparse monitoring well networks associated with LUFT sites do not happen to intersect the maximum concentration in the plume. Thus, one can expect the recorded maximum concentrations to increase as the plumes continue to migrate. There is no evidence or hydrologic rationale to indicate that many of the MTBE plumes from LUFT sites might have already reached a steady state. The evidence and our knowledge of the transport processes indicates just the opposite.

**COMMENT 4****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume I: Summary &amp; recommendations

Section # and Title: 5. Extent of Contamination of Drinking Water Supplies

Sub-section: 5.2 Ground Water

Page #: 32

Title:

Paragraph: 2-4

Sentence: All

Statement: Data obtained through September 17, 1998 from CAL-DHS and submitted by Local Primacy Agencies were used to identify the public water systems that have been contaminated with detectable concentrations of MTBE. CAL-DHS identified 35 public drinking water wells that have reported MTBE contamination. This number of impacted wells constitutes 1.2% of all the public supply wells that were tested for MTBE and 0.3% of all public supply wells in counties where at least one well was tested. (That is, we exclude counties in which no public supply wells have been tested for MTBE.) The 35 wells constitutes 0.25% of all public water supply wells in California. As of September 17, 1998, 9.94% of the State's public water systems served by groundwater sources have been tested for MTBE and 21.47% of the public water system groundwater well have been tested for MTBE.

We consider the 1.2% an upper-bound estimate of statewide impacts on public water supply wells since some of these wells were presumably sampled preferentially because of their proximity to known fuel sources.

Accordingly, the 0.3% can be considered a lower bound for public supply wells. Applying these same percentages, we estimate that between 29 and 128 of the State's 10,931 unsampled active public supply wells have been impacted by MTBE. Thus, the total public wells that may be contaminated currently with MTBE is estimated to be on the order of 60 to 160.

Statement (cont.): Applying 0.3% and 1.2% to the 464,621 private wells reported in California during the 1990 United States Census leads to a crude estimate of the number of private wells that have been impacted – on the order of 1,000 to 5,000 wells. These numbers could be underestimates, as the shallower depths of private wells commonly make them more vulnerable to contamination than public wells.

Comment: The information on the frequency of detection of MTBE does not state the reporting level for MTBE water analysis and the assessment level used in the tallies. A common assessment level must be selected before analyses from varied sources with different lab reporting levels can be compiled. Assuming that this was not done, the reported frequency of detection may not be valid. The detection frequency of MTBE and other VOCs in water is known to increase as the analytical detection level (or the assessment level) is decreased. Additionally, the projections made for public wells and private wells affected by MTBE may be questionable, if a common assessment level was not used.

Response: The DHS MTBE reporting level was 5 µg/L until August 1998, when it was lowered to 3 µg/L. Nevertheless, the DHS data included many wells for which the maximum concentration did not exceed either of these levels. The reviewer is correct that one cannot compare these data on detects to MTBE from other geographic areas (e.g., other states) without first screening the data to a common assessment level; however, we are not specifically comparing these data to detects from other areas. We are merely stating the number of detects in large-capacity, public water supply wells. It is true that, if detection limits and reporting levels for MTBE decrease in the future, our estimated frequencies of detects will also increase. Hence, our estimates of future numbers of detects in public supply wells can be considered minimums.

**COMMENT 5****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume I: Summary &amp; recommendations

Section # and Title: 5. Extent of Contamination of Drinking Water Supplies

Sub-section: 5.3 Conclusion

Page #: 32

Title:

Paragraph: 4

Sentence: All

Statement: Contamination of wells, groundwater, and surface water has already been demonstrated. This will increase as more MTBE is introduced into the environment.

Comment: The continued use of MTBE may not necessarily result in additional surface waters containing MTBE at excessive levels. MTBE levels in reservoirs appear to decline markedly after watercraft use ceases or when recreation recedes to a wintertime level.

The extent to which MTBE contamination in wells and ground water (>14 µg/L) increases with time will largely be dependent on the number of releases from pipelines, gasoline storage tanks, refueling station spills, homeowner spills, auto accident gas spills, and so forth. Whether such releases will decrease, or stay the same should be discussed in more detail in the report, and, in part, be used to estimate trends.

Response to 2<sup>nd</sup> part of comment: Insert the word “potentially” after “will” in 2<sup>nd</sup> sentence.

The only type of release that we can anticipate decreasing appreciably in frequency is that from gasoline storage tanks, owing to the tank upgrade program. This is addressed in the report by Couch and Young in Vol. IV, albeit with limited data on performance of the upgraded systems. However, our current information (SWRCB, January 1999) suggests a disappointingly high incidence of leaks even in upgraded tank systems. Given this, the fact that one gallon of MTBE can contaminate a vast volume of groundwater, and the fact that plumes are still expanding, we think it is safe to conclude that as long as MTBE is used in vast quantities, impacts will increase in the near future. In general, it is unrealistic to expect that purely engineering solutions to subsurface contamination problems (e.g., UST tank upgrades) will adequately reduce or eliminate significant groundwater contamination. Experiences in landfill design and attempts to isolate nuclear waste provide excellent lessons in this regard.

SWRCB, 1999, Report of the State Water Resources Control Board’s Advisory Panel on the Leak History of New and Upgraded UST Systems, January, 8 p.

**COMMENT 6****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume I: Summary & recommendations

Section # and Title: 6.1.3 Groundwater

Page #: 37

Sub-section title: 6.1.3.1 Transport and Fate of MTBE in Groundwater

Paragraph: 1

Sentence:

Statement: "Although MTBE has been shown to degrade in biologically active soils, evidence to date suggests that MTBE is not biodegrading appreciably in groundwater"

Comment: This sentence should be referenced if it is to be retained. Alternately it may be better to indicate that this is the case at least for anoxic aquifers.

Response: "Although MTBE has been shown to degrade in biologically active soils," replaced with "Although MTBE has been shown to potentially degrade in biologically active soils (Eweiss et al., 1998),".

**COMMENT 7****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume I: Summary &amp; recommendations

Section # and Title: 6.1.3 Groundwater

Page #: 37

Sub-section title: 6.1.3.1 Transport and Fate of MTBE in Groundwater

Paragraph: 3

Sentence: 2

Statement: Unlike petroleum hydrocarbons such as benzene, transport of MTBE does not appear to be limited appreciably due to sorption (i.e., temporary retention of the contaminant on soil and sediment particles) or biodegradation by native microorganisms

Comment: MTBE is not as dissimilar to the BTEX compounds at this sentence suggests. While the BTEX compounds will be retarded somewhat relative to MTBE in subsurface systems that have perhaps 0.5% by weight organic carbon in the aquifer material, benzene will still move at about 45% of the velocity of MTBE (NTSC, 1997). Furthermore, sand and gravel aquifer materials frequently have less than 0.5% organic carbon and benzene in these aquifers will move at velocities closer to that of MTBE. For example, in the Borden aquifer (which has a low organic carbon content ) benzene is predicted to move at approximately 84% of the velocity of MTBE (NTSC, 1997). Reference: NSTC (1997). Interagency Assessment of Oxygenated Fuels. National Science and Technology Council (NSTC), Committee on Environment and Natural Resources (CENR) and Interagency Oxygenated Fuels Assessment Steering Committee. White House Office of Science and Technology Policy (OSTP) through the CENR of the Executive Office of the President. Washington, D.C.: NSTC.

Response: Good point. We cannot overemphasize, however, how inappropriate an analog the Borden site is for most California aquifer systems, which commonly contain 20 to 70% fine-grained material (i.e., silt and clay) by volume. These fine-grained sedimentary textures, which occur as intergranular features, lenses, and laterally extensive confining beds, would tend to contain higher fractions of organic carbon. By comparison, the Borden aquifer is an unusually homogeneous, sandy deposit. Nevertheless, we would not be surprised if biodegradation rather than sorption accounts for most of the difference in transport behavior between BTEX and MTBE.

**COMMENT 8****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume I: Summary &amp; recommendations

Section # and Title: 6.1.3 Groundwater

Page #: 37

Sub-section title: 6.1.3.1 Transport and Fate of MTBE in Groundwater

Paragraph: 1

Sentence: last

Statement: Owing to MTBE's high solubility and rather large fraction in reformulated gasoline (~11% by volume), concentrations in groundwater can be very high, up to 6,000,000 (unintelligible units) (Zogorski et al., 1996; Happel et al., 1998).

Comment: The units on the 6,000,000 are unintelligible. Presumably, these are supposed to be ug/L.

It should be pointed out that while a concentration approaching 6,000,000 ug/L would be possible for a small volume of water in equilibrium with a large volume of gasoline containing 10+% MTBE, concentrations this large have never been observed at actual gasoline contamination sites, even in spill source zones.

The 6,000,000 value is not believed to be from Zogorski et al. Zogorski et al. (1996) does state the water solubility of MTBE from 10% MTBE RFG gasoline at room temperature to be 5,000,000 µg/L. This is a theoretical solubility limit and is not synonymous with measured ambient level.

Measured levels to date are considerably below this solubility limit.

Zogorski reference is not on the reference list on page 63.

Response: The statement refers to California reformulated gasoline and has been further clarified in Volume IV. Zogorski et al. (1996) reported that MTBE in a gasoline that is 10% (by weight) MTBE has a solubility in water of approximately 5,000 mg/L at room temperature. They also stated: "Gasoline that contains 15% MTBE (by volume) when equilibrated with water, results in no more than 7,500 mg/L (20.75% by volume) of MTBE in the water.

Happel et al. (1998) stated that "Thus MTBE and benzene concentrations in water fully saturated with California reformulated gasoline may be as high as ~6,000,000 µg/L and ~27,000 µg/L, respectively, based on methodology provided by the Office of Science and Technology Policy (OSTP).

See also response to Comment 15.

**COMMENT 9****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume I: Summary &amp; recommendations

Section # and Title: 6.1.3 Groundwater

Sub-section: 6.1.3.1 Transport and Fate of MTBE in Groundwater

Page #: 37

Title:

Paragraph: 3

Sentence: 2, 3, and 4

Statement: Unlike petroleum hydrocarbons such as benzene, transport of MTBE does not appear to be limited appreciably due to sorption (i.e., temporary retention of the contaminant on soil and sediment particles) or biodegradation by native microorganisms. Although MTBE has been shown to degrade in biologically active soils, evidence to date suggests that MTBE is not biodegrading appreciably in groundwater. Owing to MTBE's high solubility and rather large fraction in reformulated gasoline (~11% by volume), concentrations in groundwater can be very high, up to 6,000,000 (unintelligible units) (Zogorski, et al., 1996; Happel et al., 1998).

Comment: Two recent studies suggest that MTBE can biodegrade naturally in ground water. Field studies in Canada (Schirmer and Barker, 1998) and North Carolina (Borden et al., 1997) have shown large removals of MTBE, however, long half-lives were evident. To state that "MTBE is not biodegrading appreciably in groundwater" is not entirely descriptive of current scientific knowledge. In some settings, MTBE is partially or completely attenuated, however, the half life for such natural attenuation is much longer than BTEX compounds.

References: Borden R.C., and others, 1997, Intrinsic biodegradation of MTBE and BTEX in a gasoline contaminated aquifer: *Water Resources Research*, Vol. 33, no. 5, pp. 1105-1115.

Schirmer M., and Barker J.F., 1998, A study of long-term MTBE attenuation in the Borden Aquifer, Ontario, Canada: *Ground Water Monitoring and Remediation*, Spring 1998, pp. 113-122.

Response: We stand by our original statement. These studies, although useful and interesting, do not provide definitive or convincing evidence of biodegradation of MTBE under field conditions. Borden et al. (1997) used a simple mass-flux transport model including first-order decay to attempt to simulate field scale MTBE plume migration in a sandy aquifer containing substantial amounts of clay. The model neglects dispersion as well as potential diffusion into the low-permeability portions of the system. The authors

adjusted the decay constant (  $\lambda$  ) in the model to achieve a fit with the field data. It is not surprising then, with such a simplified model, that they had to use a nonzero  $\lambda$  to achieve a fit. The neglected dispersion, matrix diffusion, and three-dimensional, transient groundwater flow, among others, could potentially account for the migration of MTBE at rates and concentrations lower than would be predicted by their mass flux model with  $\lambda = 0$ . Further, they did not report existence of any MTBE degradation products in the groundwater. Borden et al. (1997) did find evidence of some MTBE degradation in laboratory microcosm experiments, but only under aerobic conditions – not the anaerobic conditions that would persist during long-term transport of MTBE in groundwater. This study in no way “shows” removal of any MTBE in the groundwater.

Schirmer and Barker (1988) revisited the Borden site, where in 1988 there had been a release of gasoline containing MTBE in a controlled experiment that lasted for 476 days. That previous study found no degradation of MTBE, but substantial degradation of the BTEX compounds. The authors resampled the site in 1995-96, 2700 to 3000 days following the original release, and nearly 7 years since the plume had been last monitored. With limited sampling on a grid much coarser than that of the original experiment, they could not find all the MTBE mass that was originally injected, and attributed this to biodegradation. During that 7 years, several things besides biodegradation could have caused diminishment of the plume, including diffusion into the underlying aquitard (which the plume had migrated close to), transient fluctuations of the hydraulic gradient causing plume migration into unanticipated locations and greater mixing, and relatively extreme precipitation events that could affect plume movement and concentrations. The study did not eliminate possibilities such as these and thus the case for biodegradation is very weak.

In summary, both studies are valuable contributions to the literature in different respects, but neither constitutes strong or compelling evidence of field-scale biodegradation of MTBE in groundwater. Clearly, more work is needed on this important question, but the prudent course in a study like ours is to assume no biodegradation of MTBE.

**COMMENT 10****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 1.1 Sources of MTBE in Groundwater

Page #: 6

Title:

Paragraph: 5

Sentence: 1

Statement: MTBE sources of groundwater contamination include leaking underground fuel tanks (LUFT's), above ground storage tanks, farm tanks, leaking petroleum fuel pipelines, underground storage tanks containing fuels other than gasoline, surface spills due to automobile or tanker truck accidents, surface spills due to abandoned or parked vehicles, MTBE contaminated surface water, and precipitation.

Comment: Atmospheric sources of MTBE include diffusion from the atmosphere to water in addition to precipitation.

Response: Text modified.

**COMMENT 11****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 1.1 Sources of MTBE in Groundwater

Page #: 7

Title:

Paragraph: 2

Sentence: 1 &amp; 2

Statement: Only a small portion of the MTBE consumed, 0.33 percent (OEHHA, 1989), is released to the atmosphere. Depending on local conditions, a fraction of the 0.33 percent is available to leach into groundwater.

Comment: Clarify...does 0.33 percent released to atmosphere mean the rest is combusted? Or are there other loss mechanisms?

Response: The reference in OEHHA (1998), not "1989." OEHHA reported an estimate that 30 tons per day was emitted from 9,000 tons of MTBE consumed in California per day. Additionally, OEHHA reported the California Air Resources Board data that the exhaust and evaporative emissions was about 43 tons per day in California in 1996.  $(30/9000 * 100 = 0.33\%)$

**COMMENT 12****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 1.1 Sources of MTBE in Groundwater

Page #: 7

Title:

Paragraph: 2

Sentence: 4

Statement: In the U.S. Geological Survey's National Water Quality Assessment (NAWQA), 97 percent of the samples from shallow urban wells detected MTBE at concentrations of less than 20 ugL<sup>-1</sup> (Pankow et al., 1997).

Comment: Reference to shallow ground water detections in NAWQA should be Squillace and others (1995), not Pankow (1997).

Response: Done.

**COMMENT 13****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 1.2 General Characteristics of MTBE Transport in Groundwater

Page #: 7

Title:

Paragraph: 3

Sentence:

Statement: Transport of MTBE in groundwater is controlled by the rate of groundwater movement, concentration and longevity of the source, and dispersion (i.e., the process whereby concentration of a dissolved chemical is reduced by dilution and the contaminant front spreads faster than the average rate of groundwater movement). Unlike petroleum hydrocarbons such as benzene, transport of MTE does not appear to be limited appreciably by sorption (i.e., temporary retention of the contaminant on soil and sediment particles) or biodegradation by native microorganisms. Consequently, MTBE will potentially move with the groundwater in a manner similar to subsurface transport of, for example, chlorinated organic compounds such as TCE (trichloroethene). Extensive TCE groundwater plumes are often observed – on the order of 1,000's of feet in length. Owing to MTBE's high solubility and rather large volumetric fraction in reformulated gasoline (~11 percent), concentrations in groundwater can be very high – on the order of 6,000,000 ug/L (Zogorski et al., 1996; Happel et al., 1998).

Comment: The authors should reconsider the analogy of MTBE to TCE plumes because of differences in partitioning and source type. For example, the aqueous solubility and the organic carbon/water partition coefficient,  $K_{oc}$ , of MTBE and TCE are quite different. These differences in properties (as well as other factors) will cause differences in the migration behavior of MTBE versus TCE.

The authors should consider describing these differences in their comparison of MTBE's behavior to TCE.

Alternatively, maybe a different compound, such as tritium or an inorganic salt, would provide a better comparison.

Response: Insert after "1,000's of feet in length." "MTBE plumes will potentially be even larger on the average, because it is more mobile and resistant to biodegradation than TCE."

We agree that tritium or an inorganic salt would be a more precise analogy for MTBE. Please be aware, however, that we are trying to form a perspective for a non-technical readership. There is abundant evidence in both newspapers and the scientific literature that, in stark contrast to BTEX plumes, many TCE plumes tend to be 1,000's of feet in length. Most of the readership has never heard of there being large tritium or chloride plumes. Thus, we are merely saying that (1) other contaminants have indeed been observed to migrate far beyond typical BTEX plumes, using as an example a compound that is familiar to much of the readership, and (2) one can expect similar behavior of MTBE as compared to TCE, on an order-of-magnitude basis. Such ideas are second nature to most groundwater hydrologists, but with the recent attention given to natural attenuation of petroleum hydrocarbons, we find that many have lost sight of the fact that some groundwater contaminant plumes become rather large in extent.

**COMMENT 14****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 1.2 General Characteristics of MTBE Transport in Groundwater

Page #: 7

Title:

Paragraph: 3

Sentence: 2

Statement: Unlike petroleum hydrocarbons such as benzene, transport of MTBE does not appear to be limited appreciably by sorption (i.e., temporary retention of the contaminant on soil and sediment particles) or biodegradation by native microorganisms.

Comment: As noted in another comment previously, in many cases, the BTEX compounds are not retarded by sorption much more than is MTBE.

References: Borden R.C., and others, 1997, Intrinsic biodegradation of MTBE and BTEX in a gasoline contaminated aquifer: Water Resources Research, Vol. 33, no. 5, pp. 1105-1115.

Schirmer, M., and Barker, J.F., 1998, A study of long-term MTBE attenuation in the Borden aquifer, Ontario, Canada: Ground Water Monitoring and Remediation, Spring 1998, pp. 113 – 122.

Response: See response to comment 7. The Borden aquifer is not an appropriate analog for California aquifer systems.

**COMMENT 15****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 1.2 General Characteristics of MTBE Transport in Groundwater

Page #: 7

Title:

Paragraph: 3

Sentence: Last

Statement: ... concentrations in groundwater can be very high – on the order of 6,000,000 µg/L (Zogorski et al., 1996; Happel et al., 1998).

Comment: Zogorski et al., (1996) report the solubility of MTBE in water at room temperature (from 10% MTBE RFG gasoline) as 5,000,000 µg/L (not 6,000,000 µg/L). Also, this is the maximum theoretical level and actual levels in ground water are expected to be less because of dilution, dispersion, and depletion of MTBE from the source.

Response: Insert after “groundwater” “saturated with California reformulated gasoline”.

Zogorski et al. (1996) reported that MTBE in a gasoline that is 10% (by weight) MTBE has a solubility in water of approximately 5,000 mg/L at room temperature. They also stated: “Gasoline that contains 15% MTBE (by volume) when equilibrated with water, results in no more than 7,500 mg/L (20.75% by volume) of MTBE in the water.

Happel et al. (1998) stated that “Thus MTBE and benzene concentrations in water fully saturated with California reformulated gasoline may be as high as ~6,000,000 µg/L and ~27,000 µg/L, respectively, based on methodology provided by the Office of Science and Technology Policy (OSTP).

**COMMENT 16****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 2.0 Regional Data Sources

Page #:

Title:

Paragraph:

Sentence:

Statement: ...

Comment: The report does not summarize ambient ground water data from USGS collected for NAWQA studies of the San Joaquin and Sacramento Basins. This is a major source of information with an emphasis on ambient water quality.

Response: This was an oversight. Dubrovsky et al. (1998) provides excellent evidence that atmospheric sources of MTBE are not significant in non-urban areas of the San Joaquin Valley and Tulare Basin.

Dubrovsky, N.M., C.R. Kratzer, L.R. Brown, J.M. Gronberg, and K.R. Burow, 1998, Water quality in the San Joaquin–Tulare Basins, California, 1992-95, U.S. Geologic Survey Circular 1159, 38 p.

**COMMENT 17**

HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE

Volume IV: Ground & Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 2.0 Regional Data Sources

Page #: 10

Title:

Paragraph:

Sentence:

Statement:

Comment: The authors should consider mentioning California Air Board and USGS monitoring programs in Section 2.

Response: Done.

**COMMENT 18**

HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE

Volume IV: Ground & Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 3.1 MTBE in Gasoline

Page #: 11

Title:

Paragraph: 4

Sentence: 3

Statement: By 1995 it was ranked twelfth, and by 1997 it was ranked second (OEHHA, 1998).

Comment: What compound was #1?

**COMMENT 19**

HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE

Volume IV: Ground & Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 3.2.4 Concentrations of MTBE in Groundwater at LUFT Sites

Page #: 28

Title:

Paragraph: Fig. 6

Sentence:

Statement:

Comment: The units for the "x" axis on figure 6 should be relabeled to be ug/L.

**COMMENT 20****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 3.2.4 Concentrations of MTBE in Groundwater at LUFT Sites

Page #: 28

Title:

Paragraph: 1

Sentence: Last

Statement: The high concentrations found at many sites are not surprising, given the high solubility of MTBE in water (50,000 ug/L Zogorski et al., 1996), the low sorption potential of MTBE, and its recalcitrance with respect to biodegradation.

Comment: Zogorski et al., (1996) report the solubility value of 50,000 mg/L for the dissolution of neat MTBE into water. Since this section concerns gasoline release sites, a solubility value of 5,000 mg/L is more applicable in that this latter value represents the theoretical solubility of MTBE in water with 10% MTBE gasoline as the source. Zogorski et al. (1996) provide equations to estimate the solubility of MTBE in water from gasoline.

Response: Deleted the parenthetical expression. Solubility already addressed on p. 7, paragraph 3 and in response to comment on that section.

**COMMENT 21****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 4.0 Other Sources of MTBE Groundwater Contamination

Page #: 32

Title:

Paragraph: 2

Sentence: all

Statement: Atmospheric deposition has been implicated as the source of low levels of MTBE identified, as part of the United States Geological Survey (USGS) studies, ...

Comment: The reference to atmospheric deposition studies of the USGS should include a summary of the following recent report:

Baehr, A.L., Stackelberg, P.E., and Baker, R.J., 1999, Evaluation of the Atmosphere as a Source of Volatile Organic Compounds in Shallow Ground Water, Water Resources Research, vol. 35, no. 1, pp. 127-136.

Response: We would have included reference to this Jan. 1999 paper if it had been published or available in preprint form at the time we were writing our contract report. In other responses to comments herein, we will refer to this important paper.

**COMMENT 22****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 4.0 Relevance of California Air Quality Data

Page #: 33

Title:

Paragraph:

Sentence:

Statement: ...

Comment: The air quality data summarized on page 33 is relevant with respect to possible detection of MTBE in ground water in urban areas. For example using the dimensionless Henry's Law value of .01 at 15 degrees implies that 1 ug/L in water corresponds to about 3 ppb in air. Therefore, the maximum and average MTBE air concentrations reported on Table 7 would be relevant and be a possible source for detection of low levels of MTBE in shallow ground water.

Response: Good point. The air concentrations of MTBE given in Table 7 correspond to equilibrium water MTBE concentrations that are less than 1 to 3  $\mu\text{g/L}$ , depending on what temperatures you assume.

**COMMENT 23****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 1.5.2 Detects in Public Water Supply Wells

Page #: 35

Title:

Paragraph: 3 &amp; 4

Sentence: All

Statement: The DHS Water Quality Information (WQI) Database (September 1998) listed 32 public water supply (PWS) wells which have reported detection in excess of 0.5 ug/L of MTBE in addition, information received from the 14 LPA's responding to our inquiries indicated that three public water system wells in San Luis Obispo have been impacted by MTBE. A total of 35 PWS wells have been impacted by MTBE to date, based on available information (Table 8; Fig. 7). If it is assumed that cost of the impacts that have been identified resulted from contamination entering the subsurface environment prior to 1996, then it can be expected that the impacts will continued to increase, regardless of whether MTBE's use is discontinued, because the use of MTBE has increased since 1996.

PWS wells with detections of contaminants undergo an assessment to determine the source of the contamination. In many cases this is complex because it involves issues of property damage with litigious implications. Agencies require a high level of certainty before identifying a responsible party. Additionally, some DHS districts are severely understaffed and not able to respond at the speed that new PWS wells are impacted by MTE. Full site histories and characterizations of possible sources of the MTBE contaminants detected in these wells were not obtained for all wells. Assessments in other states (Hitzig et al, 1998) indicate that .....

Comment: The terms detected and impacted are not interchangeable terms and should be used cautiously. Impacted has a regulatory context, that is, a well contaminated above a maximum contaminant level (i.e. drinking water standard) or guideline.

Which agency or entity conducts the assessment to determine the source of PWS contamination?

Response: Clarifications made.

**COMMENT 24****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 1.5.2 Detects in Public Water Supply Wells

Page #: 35

Title:

Paragraph: 1

Sentence: 1

Statement: Public Water Supply (PWS) wells with detections of contaminants undergo an assessment to determine the source of contamination.

Comment: A review of the California Department of Health Services (DHS) web page that lists MTBE monitoring data for public drinking water sources and systems indicates that most of the high level detection of MTBE (> 5 ug/L) are for wells in 3 cities (Santa Monica, South Tahoe, and Marysville). The source of MTBE for these wells are known UST releases. Nearly all of the remaining detections of MTBE in drinking water supply wells (n=21) were low level detections with many concentrations in the 1-2 ug/L range, or less. The source of these low level detections is not specified in the DHS data base or in the CA assessment. The possible sources of low level detections of MTBE in ground water include both point and non-point sources (Squillace and others, 1996). The source of the low detections should be investigated so that targeted regulatory approaches can be implemented in an effective manner. The State of Maine's study of MTBE in water supply sources found that the proximity of gasoline storage tanks to sampled wells did not explain MTBE detections. Sources of MTBE other than storage tank releases may explain some of the low level detections in CA's drinking water supply wells.

Response: We agree that the sources of these detections needs to be investigated further and that for the low-level detections, non-storage tank releases cannot be completely ruled out as alternative sources. That point should have been made clear in the report. Nevertheless, it is important to remember that in this work we were called upon to make scientific judgements using the available data to advise the Legislature on whether MTBE was a significant threat to California groundwater. Below we provide discussion aimed at clarifying why we concluded that even the low concentrations in the public supply wells are most likely from leaking gasoline tanks.

One must carefully consider the hydrogeologic conditions and well types in the USGS and Maine studies in comparison to California conditions. For example, the USGS's urban groundwater sampling campaigns have tended to use wells that are best for

characterizing and tracking movement of contaminant fronts near surface sources, i.e., relatively shallow wells that have fairly short screened intervals (e.g. Baehr et al., 1999). In contrast, public supply wells in California are primarily deep wells (100's to 1,000's of ft) that have long screened intervals, drawing water from substantial thicknesses of the aquifer or aquifers and capable of pumping at rates of 100's to 1000's of gallons per minute. Because of the physics of groundwater flow and contaminant transport and surface locations of the MTBE sources, most of the aquifer volumes tapped by these supply wells are not yet contaminated with MTBE, except perhaps in locations where the aquifers are shallow and the wells are very close to leaking gasoline tanks. Thus, when a typical California water-supply well is pumped in the vicinity of shallow MTBE contamination, it is drawing most of the water from portions of the aquifer that are uncontaminated by MTBE. Consequently, the MTBE concentration registered in the pumped water results from mixing of small (often minute) fractions of contaminated groundwater with the rest of the groundwater tapped by the well. In this scenario, for MTBE concentration in the mixed discharge water to exceed 0.1 to 0.5 µg/L, concentration of MTBE in the contaminated zone must be much higher than occurs in precipitation, say, by a factor of 10 to 1,000,000. Importantly, concentrations of MTBE in the atmosphere are low, and resulting MTBE concentrations in shallow groundwater due to atmospheric sources are also low (<1 µg/L; e.g., Baehr et al., 1999). The air MTBE concentration data from various locations in California (Table 7) indicate that concentrations in precipitation cannot be expected to exceed 1 to 3 µg/L.

In the State of Maine's study they did indeed sample public supply wells and found many MTBE detects that they could not readily attribute to leaking tanks. However, the hydrogeologic conditions in Maine, with relatively thin aquifers, shallow water tables, and high precipitation amounts, are quite different than in California. Under Maine conditions, low-level atmospheric contamination of substantial percentages of the groundwater that are tapped by the public supply wells is much more likely on the time scale that MTBE has been in use. Our working assumption, therefore, was that most of the MTBE detects in public supply wells in California were not likely due to atmospheric sources. USGS NAWQA data from non-urban areas of the San Joaquin Valley in California (Dubrovsky et al. 1998) indicate little to no MTBE in shallow as well as deeper groundwater – suggesting that atmospheric sources outside of urban areas are minimal.

Baehr, A.L., Stackelberg, P.E., and Baker, R.J., 1999, Evaluation of the Atmosphere as a Source of Volatile Organic Compounds in Shallow Ground Water, *Water Resources Research*, vol. 35, no. 1, pp. 127-136.

Dubrovsky, N.M., C.R. Kratzer, L.R. Brown, J.M. Gronberg, and K.R. Burow, 1998, Water quality in the San Joaquin–Tulare Basins, California, 1992-95, U.S. Geologic Survey Circular 1159, 38 p.

**COMMENT 25****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 1.5.2 Detects in Public Water Supply Wells

Page #: 35

Title:

Paragraph: 4

Sentence: 3

Statement: A total of 35 PWS wells have been impacted by MTBE to date, based on available information (Table 8; Fig. 7).

Comment: The number of wells affected is clearly stated, however, no characterization is given in terms of the concentrations of MTBE found versus California's 5 ug/L and 14 ug/L benchmarks. Experience elsewhere suggests that most of the wells that contain MTBE, have low levels of MTBE. More importantly, what levels were detected in the drinking water itself of the systems reflected by the 35 wells? Another area of potential concern about California's PWS monitoring data set and associated analysis is that varied reporting levels are used by the laboratories that did the testing and the assessment by the authors presumably did not consider this. The frequency of detection of MTBE and other VOCs increases as the reporting level is decreased. Characterizing the frequency of occurrence of MTBE in PWS wells must use a common assessment level (0.1 µg/L, 1 µg/L, 5 µg/L, etc.). Because of the above, the estimated PWS wells impacted may not be correct. The authors should consider incorporating more discussion about laboratory reporting limits, and how this variability was addressed in their evaluation.

Response: Clarifications were made regarding designations "detect" vs "impact" pursuant to comment 23. As stated above, each of the contaminated sites should be studied in greater detail than afforded in this statewide assessment. However, we believe that a discussion in our report of the actual MTBE concentrations in the public wells relative to the 5 and 14 µg/L benchmarks would contribute little to the fundamental question of groundwater impacts, because (1) even the low levels of MTBE contamination in California public supply wells (not shallow monitoring wells) are most likely from leaking tanks rather than atmospheric sources (see response to comment 24) and (2) when low to moderate concentrations of MTBE are found in CA public supply wells, purveyors typically shut these wells down to prevent further contaminant migration. Clearly, if most of the sources causing the MTBE detects in public supply wells are from leaking tanks, even low concentrations in these wells today will likely grow to much higher concentrations as the plumes continue to grow or as the wells continue to pump. As stated

in the comment, experience suggests that most of the wells (monitoring wells and supply wells) in which MTBE has been detected in the U.S. have low levels of MTBE. That “experience,” however, comes mainly from shallow monitoring wells potentially influenced by low-level atmospheric sources (e.g., Baehr et al., 1999), rather than relatively deep public supply wells that are typical in California.

Baehr, A.L., Stackelberg, P.E., and Baker, R.J., 1999, Evaluation of the Atmosphere as a Source of Volatile Organic Compounds in Shallow Ground Water, *Water Resources Research*, vol. 35, no. 1, pp. 127-136.

**COMMENT 26****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 5.0 Contamination of Drinking Water Wells by MTBE

Page #: 40

Title:

Paragraph:

Sentence:

Statement: ...

Comment: In providing statistical summaries of the public supply wells (eg. 5% of wells had MTBE detected at .5 ug/l and above) it would be meaningful to provide the analogous statistic for select VOCs to provide context for the MTBE data. Without such a comparison one can not evaluate the uniqueness of the MTBE problem. The list of VOCs should include BTEX compounds in addition to select chlorinated compounds which have been frequently detected in ground water (eg. DBCP, chloroform, PCE, TCA, TCE).

Response: We believe this would be a good idea, but one would have difficulty determining whether differences between, say, MTBE, BTEX, and VOC impacts are due to the relatively short time frame during which MTBE has been released into the environment as compared to BTEX and VOC's.

**COMMENT 27****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 5.3 Estimated Statewide Impacts on Public Water Supply Wells

Page #: 40

Title:

Paragraph:

Sentence:

Statement: General comment on contamination at detectable levels of PWS due to other sources.

Comment: In general, all sources of MTBE originate at or very near land surface. Given that a PWS well in a surficial aquifer can draw in very young water from within its contributing area, the relevance of non LUFT sources for low level detection should be considered. LUFT sources or other sources involving spilled gasoline is required to explain higher concentrations.

Response: See response to comment 24. Again, we assert that low levels of shallow contamination by MTBE (e.g., ~1 µg/L) from non-LUFT sources cannot account for most of the public supply well detects in California because that would require that the low-level MTBE contamination has permeated more or less the entire aquifer tapped by the well. It is well-known by hydrogeologists that, even though surface recharge sustains aquifers, most of the water produced by a well at any instant in time comes primarily out of storage from the portions of the aquifer in the vicinity of the well. Insufficient time has elapsed since use of MTBE began for low levels of MTBE contamination to have permeated the 100's to 1,000's of ft of stratified sedimentary deposits that compose the aquifers that are tapped by typical public supply wells in California.

**COMMENT 28****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 5.4 Estimated Statewide Impacts on Private Wells

Page #: 42

Title:

Paragraph:

Sentence:

Statement:

Comment: The data on MTBE concentrations in ground water collected by the USGS NAWQA program studies in the San Joaquin-Tulare Basins and the Sacramento Basin should be cited by the author. The San Joaquin-Tulare Basins study sampled 88 private domestic water supply wells in alluvial fan deposits in agricultural areas of the eastern San Joaquin Valley from 1993 through 1995. MTBE was not detected in any of the wells (MRL = 0.2 ug/L). Similarly, 30 domestic water supply wells were sampled in the alluvial fan deposits in rural areas of the eastern Sacramento Valley in 1996, and only one well had a low-level detection. An additional 19 monitoring wells were installed and sampled in 1998 in the Sacramento urban area. These wells were not located near any known point sources (LUST etc.) and only one well had a detectable MTBE concentration (1.47 ug/L). The studies in the Sacramento Basin had a slightly lower analytical detection level for MTBE (MRL 0.05 ug/L).

Response: We thank the reviewer for pointing out the existence of these data. Although it is too late to incorporate this information in our report, the data strongly indicate that atmospheric sources of MTBE in non-urban areas of California are having negligible impact. We refer to these data and the publication in responses to comments 16 and 24.

**COMMENT 29****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 5.4 Estimated Statewide Impacts on Private Wells

Page #: 42-43

Title:

Paragraph: Entire section

Sentence:

Statement:

Comment: The State of California has not collected statewide information of MTBE levels in drinking water provided by homeowner wells. As of 1998, only the State of Maine has completed such statewide monitoring and it is important to note that the occurrence of MTBE in domestic wells in Maine was not related to the nearness of gasoline storage tanks (State of Maine, 1998). Estimating the impact of MTBE RFG use in California on private wells from public supply well data is questionable. For example, the contributing area of public supply wells would be much larger than private wells due to the difference in pumping rates and other factors. At a minimum the authors should acknowledge the limitations of their approach and offer suggestions on how to assemble a definitive MTBE data set for private wells.

Reference: State of Maine, 1998, The presence of MTBE and other gasoline compounds in Maine's drinking water: A preliminary report October 13, 1998; prepared by Maine Department of Human Services; Bureau of Health, Maine Department of Environmental Protection, Bureau of Waste Management and Remediation; Department of Conservation, Maine Geological Survey, 15 p.+ attachments.

Response: We fully endorse the idea of conducting statewide monitoring programs for MTBE as well as other contaminants. We refer to the Maine study on p. 43 and in Appendix D, p. 79. We also fully agree that our estimates of impacts to private wells are questionable because little private well data are available in California. The limitations of our approach to the private well problem were not adequately emphasized in the report. We do not believe, however, that California need wait for a better statewide database on MTBE in groundwater before deciding whether its impacts on California groundwater is significant. Such data will nevertheless be needed in the future for prevention of further impacts and site clean up.

**COMMENT 30****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 5.4 Estimated Statewide Impacts on Private Wells

Page #: 43

Title:

Paragraph: 3

Sentence: "Direct comparisons between our results and those of Maine are difficult due to differences in detection limits."

Statement: Comparison of CA and Maine frequencies of MTBE detection.

Comment: The authors should consider mentioning that there are huge climate and hydrogeologic differences between Maine - the most obvious that Maine has high precipitation and shallow depths to ground water, while California has little precipitation and great depth to ground water. In general, these factors make ground water in Maine much more susceptible than ground water in California. Reference to the State of Maine's MTBE study is appropriate to provide general context for another state's assessment of the occurrence of MTBE in drinking-water wells. Because of the differences in laboratory reporting levels (as noted by the authors) between the California community well data set and the State of Maine's study, and the differences in climatic and hydrogeologic conditions noted above, the findings in the State of Maine for domestic and community water supply wells are not directly applicable to California. The authors might consider stating this more explicitly in their discussion of results from the State of Maine's study.

Response: Excellent points. The reviewer is correct that State of Maine hydrogeology is not very analogous to that of California, and private well impacts in Maine may not be indicative of what can be expected in California. The paragraph has been modified accordingly.

**COMMENT 31****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 6.1.1 Precipitation Sampling

Page #: 45

Title:

Paragraph: General Comment

Sentence:

Statement:

Comment: Additional evidence that little or no MTBE in precipitation contributes to Lake Tahoe MTBE concentrations can be cited. USGS sampling of lakes in the Tahoe Basin (3 lakes) that have little or no motorized boat traffic showed no MTBE (Boughton and Lico, 1998). If atmospheric input was significant, these lakes would have measurable concentrations of MTBE.

Reference: Boughton, C.J., and M.S. Lico, 1998, Volatile organic compounds in Lake Tahoe, July-September, 1997: USGS Fact Sheet FS-055-98, 4 p.

**COMMENT 32****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 6.1.2 Shallow Groundwater Sampling

Page #: 46

Title:

Paragraph: 2

Sentence: last

Statement: These Nevada sites are part of the USGS groundwater monitoring network for the Lake Tahoe Basin (Boughton et al., 1997) and were sampled in cooperation with Tim Rowe and Kip Allander of the Carson City office of the USGS.

Comment: The appropriate citation for cooperation is with the USGS's Carson City office. Recognition of individual USGS staff in the narrative text is not necessary.

Response: Done.

**COMMENT 33**

HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE

Volume IV: Ground & Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 6.1.2 Shallow Groundwater Sampling

Page #: 46

Title:

Paragraph: 3

Sentence: 3

Statement: Groundwater samples were dispensed into 45 ml amber VOA vials, which were filled to the rim such that no headspace was present in the capped vial.

Comment: VOA vials are usually 40 mL, not 45 mL. The authors should check to make sure the volume of the VOA vials as stated is correct.

Response: Done.

**COMMENT 34****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 6.1.3 Summary of Non-LUFT Site Data

Page #: 48

Title:

Paragraph: 1

Sentence:

Statement: Snow samples collected June 5, 1998 at 8,600 ft elevation downwind from an urbanized area of Lake Tahoe contained no detectable MTBE ( $<0.1 \text{ g-L}^{-1}$ ). Two shallow wells located in Pope Marsh at approximately 50 and 110 ft from the Lake Tahoe shoreline tested positive for MTBE in replicate samples, at levels between 0.1 and  $0.2 \text{ g-L}^{-1}$ . The source of MTBE in the two Pope marsh wells was most likely water from Lake Tahoe because: (1) nearby water samples from Lake Tahoe contained MTBE at  $1\text{-}2 \text{ g-L}^{-1}$ , (2) groundwater flow is from Lake Tahoe into the marsh during summer months (Green, 1998), and (3) eight other shallow wells in this marsh, all located further away from Lake Tahoe, tested negative for MTBE ( $<0.1 \text{ g-L}^{-1}$ ).

Comment: USGS water chemistry and stable isotopes of water do not support the authors' conclusions that lake water is the source of MTBE in the shallow ground water in the marsh.

Delta D Delta O-18

Well #20 (8-13-95)  $-92.4 \text{ } -12.2$ Lake Tahoe  $-58 \text{ } -5.5$  (approx)Precipitation in Tahoe Basin  $-99 \text{ } -14.3$  (USGS unpublished data)Shallow gw in Tahoe Basin  $-106 \text{ } -14.5$  (Thodal, 1997)

Comment (cont.): Gradients appear to be toward the lake at all times of the year according to the data USGS has collected. Another piece of evidence to support no lake water in the shallow aquifer in Pope Marsh is the specific conductance of the well water. This sample had a specific conductance of  $150 \text{ uS/cm}$  and lake water is usually  $<90 \text{ uS/cm}$ . It seems likely that the source of the water in the well is from upgradient in the marsh and has been slightly evaporated to produce the higher specific conductance and slightly heavier isotope values.

Reference: Thodal, C.E., 1997, Hydrogeology of Lake Tahoe Basin, California and Nevada, Results of a

ground-water quality monitoring network, water years  
1990-92: U.S. Geological Survey Water-Resources  
Investigations Report 97-4072, 53 p.

Response: The reviewer seems to be confusing the “Well #20” that we sampled in Pope Marsh with a different “Well #20” referenced by Thodal (1997). On p. 46 we state that the wells sampled in the Marsh were installed by Green (1998). Well #20 referenced in the comment and used in Thodal (1997) is located more than 2 miles from the wells in Pope Marsh that we sampled. Green (1998) shows conclusively that the part of Pope Marsh where we detected MTBE in the groundwater is an area where groundwater flow is from the Lake to the Marsh in summer months.

**COMMENT 35****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 6.2.3 Focus on Southern Portion of the Lake Tahoe Basin

Page #: 51

Title:

Paragraph: 4

Sentence: 3

Statement: Another LUFT site has an MTBE plume of length >640 ft extending to within 500 ft of STPUD wells Backrock #1 and #2, and to within....

Comment: Add "l" to "Backrock" to read Blackrock.

Response: Done.

**COMMENT 36****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 6.2.3 Focus on Southern Portion of the Lake Tahoe Basin

Page #: 52

Title:

Paragraph: 1

Sentence: 2<sup>nd</sup> to last sentence

Statement: The second LUFT site is located 1,500 ft from Tata well #4 (pumping capacity 70 gpm), at a 45 degree angle upgradient to the regional surface water gradient (Pinnacle Environmental Solutions, 1998).

Comment: Do you mean "ground-water gradient", or "surface-water gradient" as written?

Response: Text clarified.

**COMMENT 37****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 6.2.4 Summary of LUFT Site Data in Tahoe Basin

Page #: 53

Title:

Paragraph: 2

Sentence: last

Statement: These analyses pertain mainly to alluvial aquifers consisting of unconsolidated to semi-consolidated materials (sand, gravel, silt and clay).

Comment: There appears to be inconsistent use of terminology regarding the makeup of the shallow aquifer lithology. Is "unconsolidated glaciofluvial" the same as "alluvial aquifers of unconsolidated to semiconsolidated materials"?

Response: The statement here is in fact not in sub-section 6.2.4 on the Tahoe Basin. It is in Section 7.0 on Future Impacts of LUFT Plumes. Thus, the statement does not refer to Tahoe Basin, and there is no inconsistency in terminology.

**COMMENT 38****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 7.0 Future Impacts of LUFT Plumes

Page #: 53

Title:

Paragraph: 3

Sentence: 4

Statement: Further, we have found no definitive, field studies demonstrating degradation of MTBE in groundwater.

Comment: Two field studies have documented the natural attenuation of MTBE in ground water via biodegradation.

Reference: Borden, R.C., and others, 1997, Intrinsic biodegradation of MTBE and BTEX in a gasoline contaminated aquifer: *Water Resource Research*, vol. 33, no. 5, pp. 1105 – 1115.

Schirmer, M., and Barker, J.F., 1998, A study of long-term MTBE attenuation in the Borden aquifer, Ontario, Canada: *Ground Water Monitoring and Remediation*, Spring 1998, pp. 113 – 122.

Response: We stand by our original statement. These studies, although useful and interesting, do not provide definitive or convincing evidence of biodegradation of MTBE under field conditions. Borden et al. (1997) used a simple mass-flux transport model including first-order decay to attempt to simulate field scale MTBE plume migration in a sandy aquifer containing substantial amounts of clay. The model neglects dispersion as well as potential diffusion into the low-permeability portions of the system. The authors manipulated the decay constant (  $\lambda$  ) in the model to achieve a fit with the field data. It is not surprising then, with such a simplified model, that they had to use a nonzero  $\lambda$  to achieve a fit. The neglected dispersion, matrix diffusion, and three-dimensional, transient groundwater flow, among others, could potentially account for the migration of MTBE at rates and concentrations lower than would be predicted by their mass flux model with  $\lambda = 0$ . Further, they did not report the existence of any MTBE degradation products in the groundwater. Borden et al. (1997) did find evidence of some MTBE degradation in laboratory microcosm experiments, but only under aerobic conditions – not the anaerobic conditions that would persist during long-term transport of MTBE in groundwater.

Schirmer and Barker (1998) revisited the Borden site, where in 1988 there had been a release of gasoline containing MTBE in a controlled experiment that lasted for 476 days. That previous study found no degradation of MTBE, but substantial degradation of the BTEX compounds. The authors resampled the site in 1995-96, 2700 to 3000 days

following the original release, and nearly 7 years since the plume had been last monitored. With limited sampling on a grid much coarser than that of the original experiment, they could not find all the MTBE mass that was originally injected, and attributed this to biodegradation. During that 7 years, several things besides biodegradation could have caused diminishment of the plume, including diffusion into the underlying aquitard (which the plume had migrated close to), transient fluctuations of the hydraulic gradient causing plume migration into unanticipated locations and greater mixing, and relatively extreme precipitation events that could affect plume movement and concentrations. The study did not eliminate possibilities such as these and thus the case for biodegradation is weak.

In summary, both studies are valuable contributions to the literature in different respects, but neither constitutes strong or compelling evidence of field-scale biodegradation of MTBE in groundwater. Clearly, more work is needed on this important question, but the prudent course in a study like ours is to assume no biodegradation of MTBE.

**COMMENT 39****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 7.1 Generalized Analysis of MTBE Plume Growth

Page #: 54

Title:

Paragraph:

Sentence:

Statement: Authors statement on relation of MTBE plume growth to predicted increase in detection frequency in public supply wells.

Comment: Models to predict future impacts of MTBE releases to water-supply wells should be used with caution because there are large uncertainties in the assumed processes and input conditions. The modeling approach used was conservative and may over predict the actual risk of LUST releases to water-supply wells because: (1) it assumes that the concentration of MTBE in the area of a gasoline release (i.e. the source strength) is maintained at a constant level over the period of prediction; (2) two processes that would reduce the concentrations of MTBE, biodegradation and volatilization (Borden and others, 1997; Schirmer and Barker, 1998; and Baehr and others, 1997), were not incorporated in model simulations; and (3) the analysis assumes that predicted plumes will travel across the contributing areas of water-supply wells and be drawn to the wells. Additional modeling would suggest the potential importance of the above noted conditions/processes. The reliability of risk projections could be improved by long-term monitoring of MTBE in water-supply wells and ambient ground water.

Reference: Borden, R.C., and others, 1997, Intrinsic biodegradation of MTBE and BTEX in a gasoline contaminated aquifer: Water Resource Research, vol. 33, no. 5, pp. 1105 – 1115.

Schirmer, M., and Barker, J.F., 1998, A study of long-term MTBE attenuation in the Borden aquifer, Ontario, Canada: Ground Water Monitoring and Remediation, Spring 1998, pp. 113 – 122.

Baehr, A.L., and others, 1997, Transport of MTBE across the water table to the unsaturated zone at a gasoline-spill site in Beaufort, SC: preprint of papers,

213<sup>th</sup> ACS National Meeting, vol., 37, no. 1, pp. 417 – 418.

Response: We appreciate the reviewers concern about models and their application, but believe we have indeed used the model with caution and not overstated its implications. Of course any attempt to model using process-based equations the generalized plume behavior in an entire state will have significant limitations (and lead to some discussion). You correctly point out that the model assumes the source concentration is constant but that in reality the source concentration will vary in time – commonly decreasing with time. Although the model does not simulate directly a transient source concentration, it does account for this effect approximately through use of a distribution of times (Appendix H) as stochastic input. That is, each of the 5,000 to 8,000 plumes generated by the model for each scenario represents a different point in time since the plume began migrating. Had we chosen a distribution of times that were too great, our benzene and MTBE historical simulations runs would have produced plume lengths and concentrations greater than had been measured (Figures 9 and 10) – similar to what would happen if one deterministically modeled a plume produced by a decaying source concentration but incorrectly used a constant source concentration. In other words, our chosen distributions of transport times (and source concentration as well) compensate for the fact that in each individual model run the source concentration is constant. Otherwise, the fits to distributions of measured plume lengths in Figures 9 and 10 would not be nearly as good. Clearly, although our model is process-based in terms of simple groundwater flow, dispersion, sorption and biodegradation, it is necessarily empirical in many respects. Without the fit to measured plume lengths of benzene and MTBE using carefully chosen parameters (Figs. 9 and 10), such a model would be relatively useless.

It is also important to realize that the analytical model “source concentrations” represent volume-averaged, dissolved-phase concentrations in the general vicinity of the source, not the source itself. Most of the numerical modeling of plume behavior that we have done in typically complex California hydrogeologic settings (e.g., Fig. 12) shows that such concentrations near the source can remain elevated for decades, even when the contaminant is only released for a short period of time or as a pulse. This is due to retention of the contaminant in relatively immobile regions of the heterogeneous system owing to molecular diffusion and other processes. Such behavior is also being observed in carefully controlled field experiments in settings that are moderately more heterogeneous than, say, the Borden aquifer (e.g., Boggs et al., 1992; Berkowitz and Scher, 1995), but less heterogeneous than typical California alluvial aquifer systems (Fogg et al., 1998; Carle et al., 1998).

Regarding the potential for reduction of the source concentrations via biodegradation, we are convinced that the references cited by the reviewer do not provide a scientific basis for assuming any biodegradation of MTBE under field conditions. (See response to comment 38.) Regarding the potential for reduction of source concentrations via volatilization, we would expect that to happen, but, as described above, have partially accounted for such an effect. The fact that plume lengths are already approaching our

model's 2010 predicted maximum lengths in the Tahoe Basin and elsewhere suggests that the model may in fact underestimate future plume lengths and, in turn, impacts.

Again, we enthusiastically support the need to long-term monitoring of MTBE, as stated in our Recommendations.

Boggs, J.M., S.C. Young, L.M. Beard, L.W. Gelhar, K.R. Rehfeldt, and E.E. Adams, Field study of dispersion in a heterogeneous aquifer 1. Overview and site description, *Water Resources Research*, 28(12), p. 3281-3291.

Berkowitz, B. and H. Scher, On characterization of anomalous dispersion in porous and fractured media, *Water Resources Research*, 31(6), p. 1461-1466.

Carle, S.F., E.M. LaBolle, G.S. Weissmann, D. Van Brocklin and G.E. Fogg, 1998, Geostatistical simulation of hydrostratigraphic architecture: a transition probability/Markov approach, *in* Concepts in Hydrogeology and Environmental Geology No. 1, SEPM (Society for Sedimentary Geology) Special Publication, p. 147-170.

Fogg, G.E., C.D. Noyes and S.F. Carle, 1998, Geologically-based model of heterogeneous hydraulic conductivity in an alluvial setting, *Hydrogeology Journal*, 6, p. 131-143.

**COMMENT 40****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 7.1 Generalized Analysis of MTBE Plume Growth

Page #: 54

Title:

Paragraph: 2

Sentence:

Statement: ...

Comment: If I understand the authors analysis correctly, they have assumed that the increase in MTBE plume length of 3-4 by the year 2010 will result in a corresponding increase in the probability of impact on public water supplies. Since the implications of increased detection are significant, I think the authors should discuss the basis for that assumption (and possible problems with the assumption) in greater detail. This might include how do uncertainties in the values of 0.3 and 1.2% affect the extrapolated values?

How does the increase in concentration of MTBE in gasoline since 1996 likely to affect the probability of detection independent of longer plume lengths?

The relationship between plume length and probability of detection depends upon a number of factors including width of capture zone, vertical spreading, and horizontal spreading. These factors in turn depend upon the aquifer and pumping conditions, recharge, regional flow direction.

What are the assumptions necessary in order to extrapolate the probability? As an example, the longer the plume, the more likely it will be able to move downward and reach the well screen. This could cause the probability of impact to increase more than simply in proportion to plume length.

Response: We agree that the model may underestimate impacts because by assuming the increase in risk is directly proportional to plume length, we are possibly neglecting factors like vertical spreading in response to pumping wells etc. On the other hand, this may counteract other aspects of the model that potentially bias the results in the other direction (e.g., source concentration not decaying fast enough). Overall, we believe any projections of future statewide risk from a groundwater contaminant are necessarily somewhat speculative. Accordingly, the important point is not whether the risk increases by a factor of 3 or a factor of 6, but whether the risk is likely to increase enough to make the problems measurably worse. The model indicates that the plumes are likely to continue growing well into the future, and one can expect greater and greater impacts. Indeed, since MTBE came into widespread use in California, the observed impacts have increased with remarkable regularity. The Tahoe Basin is a case in point, where the

incidences of MTBE contamination (not at one or two sites but at multiple sites over a considerable area) have increased steadily during 1997-98.

**COMMENT 41****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 7.2 Vertical Migration

Page #: 59

Title:

Paragraph:

Sentence:

Statement: Figure 12. Re: vertical migration.

Comment: The most relevant vertical migration would be that induced by a flowing well. It appears that in the simulation presented that the plume is within the contributing area of the well. What would be the relevance of vertical migration if this was not the case? This other important case should be discussed by the authors.

Response: We assume the reviewer means “pumping well,” not “flowing well.” We have added the following clarification to the end of section 7.2: “Had the pumping well not been located near the plume, results of this simulation would have been different – not as much vertical transport would have occurred. Importantly, though, most developed groundwater basins in California exhibit vertical hydraulic gradients similar to those in this simulation because of regional effects of pumping on hydraulic heads at the deeper horizons. Thus, one can expect the kind of behavior exhibited in Figure 12 in many groundwater systems, even when pumping wells are not close to the plume.”

**COMMENT 42****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 8.1 General Impacts

Page #: 62

Title:

Paragraph: 4

Sentence: Last

Statement: Given the transport behavior of MTBE, these concentrations will likely increase in the future.

Comment: The reason why MTBE concentrations will increase in the future should be stated. While a yet to be sampled release site may be found in the future to have a higher maximum value, the distribution of MTBE levels (considering all sites) may not change much from the sampled sites to date. We are not aware of any completed studies that show a mechanism to “concentrate” MTBE with time or distance from the source.

Response: The statement is based partly on the recognition that monitoring for point-source plumes with limited monitoring well networks cannot be expected to capture all the relevant details of plume geometry and concentrations. In fact, with many monitoring schemes, depending on the release histories of MTBE, transport processes, and monitoring strategy, intersecting the maximum plume concentrations is a “hit-or-miss” proposition unless exorbitant numbers of wells are installed for each plume. As time progresses, however, the probability of the maximum concentration migrating downstream and intersecting a monitoring well will increase. Furthermore, the statement is also based on the fact that aggressive actions to remove gasoline product from groundwater have not been pursued in most areas of California, and the source concentrations have therefore remained high at many sites.

**COMMENT 43****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 8.1 General Impacts

Page #: 62

Title:

Paragraph: 1-5

Sentence: (all of 8.1)

Statement:

Comment: The assessment described in this chapter focused almost exclusively on ground water at LUFT sites and ground water supply wells. While these are two important aspects of California's ground water, the authors have not addressed MTBE impacts to the State's entire ground water resource. In aggregate, ground water contaminated by LUST sites represents a small fraction of California's ground-water resource. Also, the extent to which MTBE levels in PWS wells are diminished during blending (with water from other wells with no MTBE) or during treatment should be examined by the authors.

Response: We agree that the volume of groundwater contaminated by MTBE is a tiny fraction of the total groundwater resource in storage in California. One can make the same argument, however, for all other groundwater contaminants – most of the groundwater is still clean. The question is: "If we continue contaminating shallow groundwater unabated, 50 to 100 years from now will we still be saying that the groundwater is mostly clean?" Definitive answers to this question may not exist presently, but ample evidence and analysis suggest that the answer may very well be "no." This and the facts that much of California is arid or semi-arid and the State depends heavily on groundwater have led to the adoption of non-degradation policies by the State that are intended to aggressively protect groundwater quality. Further, when a volume of groundwater becomes contaminated, the volume of *impacted* groundwater can be many times larger, because wells need only tap a small fraction of the contaminated groundwater to render well head concentrations that are unacceptably high.

We agree that other contaminants such as nitrates, pesticides and irrigation salinity may seriously degrade far greater volumes of groundwater than will MTBE.

The question of effects of blending on MTBE concentrations at the tap is very site-specific, depending on local public opinion and water utility infrastructure. It was beyond the scope of our study.

**COMMENT 44****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 9.0 Recommendations

Page #: 63

Title:

Paragraph:

Sentence:

Statement: A statewide survey of California's groundwater quality should be performed. Groundwater samples from public and private wells should be collected and analyzed. A thorough scientific survey will provide information to document fully the extent of MTBE's impact on California's groundwater resources.

Comment: The last paragraph of pg 64 describes a very important part of this assessment. How would the indicated research proceed? Do predictions made in this chapter need to be revisited based on further study?

Response: The question of how to proceed in surveying California's groundwater quality is indeed very important but beyond the scope of our study. As to the second question in the comment, we do not believe that California need wait for a statewide groundwater quality survey to decide whether MTBE is a serious threat to groundwater. Purposes of the State survey would be to provide essential information on the condition of groundwater quality in the State, to identify and prevent problems before they become disasters, and to help evaluate and optimize the State's groundwater protection strategies.

**COMMENT 45****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 9.0

Page #: 64

Title:

Paragraph: 3

Sentence:

Statement: A statewide survey of California's groundwater quality should be performed. Groundwater samples from public and private wells should be collected and analyzed. A thorough scientific survey will provide information to document fully the extent of MTBE's impact on California's groundwater resources.

Comment: The proposed study should consider characterizing the quality of California's major aquifers regardless of their current use for drinking water. Also, the sampling of PWS wells should be expanded to also include analyses of drinking water itself—to understand the effect(s) of blending and treatment, and to better characterize the exposure level from drinking water.

Response: Agreed.

**COMMENT 46**

HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE

Volume IV: Ground & Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 1.10 References

Page #: 65

Title:

Paragraph: Title

Sentence: I

Statement: 1.10 References

Comment: Should this section be numbered 10.1, not 1.10? Same goes for the contents page.

Response: Yes. Fixed.

**COMMENT 47****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: 1.10 References

Page #: 65

Title:

Paragraph: 2

Sentence:

Statement: Boughton, C.J., and M.S. Lico, 1998, Volatile organic compounds in Lake Tahoe, Nevada and California, USGS Fact Sheet FS-055-98, July-September 1997.

Comment: The "July-September, 1997" should be part of the title, not at the end of the reference as written. Date published is June, 1998. The correct title for the citation is:  
Boughton, C.J., and M.S. Lico, 1998, Volatile organic compounds in Lake Tahoe, July-September 1997:  
USGS Fact Sheet FS-055-98, 4 p.

Response: Done.

**COMMENT 48****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: Appendix H

Page #: 94

Title:

Paragraph:

Sentence:

Statement: ...

Comment: There is probably considerable uncertainty in the lengths of the BTEX plumes from the Happel study because of the difficulty in separating the source (i.e., the zone containing smeared NAPL) from the dissolved-only phase plume.

Consequently, there is a good chance that the actual dissolved portions of the BTEX plumes are even shorter than reported. It is unclear exactly what the implications of this might be for fitting the BTEX data and for the subsequent extrapolation of MTBE plume length.

Modeling BTEX disappearance as a first-order process approximates field-scale behavior, but probably is not that good a model of the substrate-limited degradation process. It is unclear what impact, if any, the 1st order model might have on the fitting of parameters and upon MTBE plume length extrapolation.

The report should discuss the implications of uncertainties associated with BTEX plume length and their relation to MTBE plume length.

The report should also discuss the implications of assuming a first order degradation rate and add a discussion regarding persistence of MTBE in anoxic aquifers.

Response: We agree that the benzene plume lengths of the Rice et al. (1995) and Happel et al. (1998) studies are highly approximate. Perhaps a more severe problem than “separating the source from the dissolved-only phase plume” is the relatively small number of monitoring wells used to delineate each of those plumes. Our fitting of the stochastic transport model to the estimated historical benzene plume lengths merely provides a baseline for comparison with MTBE. We do not claim that the transport model used in this analysis represents all the relevant processes with a high degree of accuracy. It merely captures the general behavior of the plumes in a comparative context.

**COMMENT 49****HEALTH & ENVIRONMENTAL ASSESSMENT OF MTBE**

Volume IV: Ground &amp; Surface Water

Section 1: Impacts of MTBE on groundwater

Sub-section: Appendix H

Page #: 97

Title:

Paragraph:

Sentence:

Statement: ...

Comment: The simulations used an apparently low and constant value for the MTBE source concentration. These assumptions may not be representative of real conditions. The source concentration used may be low (e.g., the “most likely value” for the simulations was 1.8 mg/L), although the values used are generally consistent with field measured values for plumes. However, source strength can vary markedly and some point source measurements within or just down-gradient from sources can give concentrations 2-20 times higher than the values used for the source concentration in the model. On the other hand, because the concentration is set as a constant throughout the simulations, it will not drop off as a function of time and thus the model may over-estimate concentrations coming from a “weathered” source. Unfortunately there are few MTBE data to allow a more accurate description of the MTBE source concentration and how it changes with time. This lack of knowledge of MTBE source information may cause significant uncertainty in the model’s projections. The report should discuss the implications of the source function used for these simulations and how higher concentrations and/or decreasing source functions would impact MTBE plume length.

Response: See response to comment 39.