

Volume 4: Potential Ground and Surface Water Impacts

Chapter 10: Response to Comments

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Table of Contents

Chapter 10: Response to Comments

10. Response to Comments	10-1
10.1. Peer Review Comments.....	10-1
10.1.1. Peer Review Comments from Dr. Patricia Holden, Donald Bren School of Environmental Science and Management, University of California, Santa Barbara.	10-1
10.1.2. Dr. Michael K. Stenstrom, Civil and Environmental Engineering Department, University of California, Los Angeles.....	10-10
10.1.3. Dr. Michael R. Hoffman, Executive Officer of Environmental Engineering Science, James Irvine Professor of Environmental Science, California Institute of Technology.	10-19
10.2. Public Review Comments.....	10-27
10.2.1. Michael C. Kavanaugh, Ph.D., P.E., and Andrew Stocking, P.E., Malcolm Pirnie, Inc.: Comments and LLNL Responses	10-28
10.2.2. Western States Petroleum Association (WSPA): Comments and LLNL Responses	10-31

10. Response to Comments

10.1. Peer Review Comments

The following responses address independent peer review comments on the draft State Water Resources Control Board (SWRCB) Volume 4, *Potential Ground and Surface Water Impacts*, which is part of the report to the California Environmental Policy Council titled, *Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate*.

10.1.1. Peer Review Comments from Dr. Patricia Holden, Donald Bren School of Environmental Science and Management, University of California, Santa Barbara.

Patricia Holden (Ph.D. University of California at Berkeley, 1995) is an Assistant Professor in environmental microbiology and microbial ecology. Dr. Holden researches the biotic mechanisms of hydrocarbon pollutant transformation in unsaturated systems. She is currently studying factors influencing the formation of biofilms in the vadose zone and the role of extracellular polymeric matrices in biodegradation kinetics. More recently, Dr. Holden has also been studying the phylogenetic composition and diversity of microbial communities in contaminated urban runoff. In this area of research, her laboratory group is trying to understand how urbanization affects water quality during dry and wet seasons in the south coast of California. She has eight years of professional experience in environmental engineering, design, and project management, and two years of similar experience during her postdoctoral research.

Volume 4, Chapter 1 Comments:

Comment: Figure 1: L in the UST is not shown. This is, in fact, a likely release scenario based on historical precedence. Show it; it is discussed in the text.

Response: The intent of the figure was to graphically show the steps in the production, distribution and use of ethanol in gasoline. Not all underground storage tanks (UST) leak. This is why the UST in the figure is not labeled as leaking "L."

Comment Table 1: no mention of safety issues in addition to toxicity issues. Ethanol is a flammable substance.

Response: This is a good comment. Safety issues have not been addressed as part of this evaluation because of time constraints to meet the required report delivery date of December 31, 1999. The evaluation of safety issues would be included in a complete life cycle analysis.

Comment Table 1: Where the word "degraded" is used to describe the fate of ethanol, it is hard to justify the use of this term because there is no supporting data provided in the chapter. Rather, distribution and loss should be used to describe the Risk Assessment issues.

Response: Comment noted. Table 1-1 edited to refer to “loss” where appropriate.

Comment Table 1: The Release assumptions for “Release during bulk ethanol transport by marine cargo tanker” should emphasize infinite solubility and not just the density difference.

Response: Comment noted. Table 1 edited to reflect this comment.

Comment Table 1-1: For Release Scenario “Release from watercraft emissions into surface waters,” the risk assessment issues section regarding expected rapid biodegradation and volatilization should be supported by citing literature in the text (see below) that demonstrates the importance of these fates in the presence of BTEX (even if it is bench scale data). Also, is there not a “Risk Management Option” here (for watercraft emissions) that is missing?---e.g. regulating / restricting watercraft usage on surface waters. If this is an inevitable release point, then there are only two ways to avoid it-either stop using the additive or stop using the watercraft to the current extent permitted.

Response: Comment noted. The risk management option of regulating / restricting watercraft usage on surface waters has been added to Table 1-1.

Comment: I strongly suggest listing physicochemical characteristics of ethanol up front in this section, describing its properties and delineating safety issues. This will also help readers follow the logic in later sections of this first chapter (e.g. 1.5.2).

Response: Volume 2, *Background Information on the Use of Ethanol as a Fuel Oxygenate*, provides this information. This information is provided as a separate volume because all the subsequent California Air Resources Board (CARB), SWRCB, and Office of Environmental Health Hazard Assessment (OEHHA) volumes draw upon this information, and repeating it in each volume would be redundant.

Comment Section 1.2.2.: The chemical composition of the corrosion inhibitors and detergents should be identified in the text and in Table 1-3. Additionally, the percent by weight should be provided in the text (it is a footnote in the table).

Response: Much of this information is proprietary and is not available at this time.

Comment Section 1.3.1.: Given the predicted reliance on marine bulk transport of EtOH, the risk to marine organisms from spilled tankers will need to be addressed.

Response: We agree with this comment and this issue should be addressed as part of a complete life-cycle analysis.

Comment Section 1.5.1: What is the basis for stating that biodegradation and /or volatilization were the important fates for ethanol in a bulk spill? Given its solubility in water, it seems more likely that ethanol would dissolve in groundwater and disperse. If there is a basis for emphasizing biodegradation here, it is better to provide a citation to the proper reference.

Response: Volatilization will likely be important if bulk ethanol is released to the ground surface, and significant amounts do not infiltrate into the subsurface.

Comment Section 1.5.2.: To the untrained reader, the reason for suspecting increased concentrations of hydrocarbons at existing subsurface petroleum spills is not obvious. If physicochemical characteristics are tabulated and described earlier, then the proper introduction to the “cosolvent effect” will have been done and the reasoning in this section would be more understandable to the reader.

Response: Comment noted.

Comment Section 1.5.5.: The preceding reviews of existing spills is very well done. If there is another or additional way to make a stronger recommendation to evaluate the Tacoma spill data, as was recommended in this section, then it is advised to do so. This seems critical-why not evaluate the data now, then make the decision regarding another fuel additive that may or may not be disastrous to water quality? Another point for this section-do local fire departments keep an inventory of gasohol versus gasoline in USTs? Page 1-9 of this section---a typographical error (perceive, not perceived).

Response: The focus of this report has been to perform a literature review, identify potential data sources, and perform as much screening analysis as possible in time permitted before the report was due to the Environmental Policy Council. A recommendation has been made to gather and evaluate available historical-case field data and this will likely occur once this report has been submitted.

Comment Appendix A: when did these releases occur? State either in the Appendix or in the text of section 1.5.4.

Response: The Nebraska contact that provided this information is unavailable to respond to this comment.

Volume 4, Chapter 2 Comments:

Comment: The emphasis on this Chapter is effects of ethanol on BETX in the environment. However, in Chapter 1, an additional important point is made: that BTEX and MTBE in existing spills are both potentially affected by the addition of ethanol to the spill site. Can this also be addressed in Chapter 2?

Response: The impact of an ethanol spill on benzene, toluene, ethylbenzene and the xylenes (BTEX) was described in Section 2.2.5.1. No mention of the impact of an ethanol spill on methyl tertiary butyl ether (MTBE) was included in this discussion because there is no data available to address this issue. A speculative comment regarding MTBE has been added to this section after the second paragraph.

Comment Section 2.2.2.1: The third paragraph in this section is confusing. It is not clear from Figure 2-5 where the 19.7 dyes/cm line is.

Comment Figure 2-5: Recommend a different symbol for isooctane because of the error bars. The index and the text in section 2.2.2.1 are difficult to co-interpret. In the legend, is the “surface tension-air” measured at the air/solvent interface (must be, since the solvent is expected to float)? It would help to clarify this in the text.

Response: We have improved Figure 2-5 and revised the third paragraph in Section 2.2.2.1. to improve the clarity.

Comment Section 2.2.2.2.: Unless I am mistaken, the word “cosolvent” first appears on pg 2-7, although the description of the effect occurs in the pages preceding. The word should be clearly defined early in the chapter with some additional background literature presented on cosolvency and what compounds generally show this behaviour. The phase diagrams are good, not easy to read by everyone and either a table of reported solubilities as a function of cosolvent effect or some language in the next would be useful.

Response: Section 2.1 had been edited to address to better define “cosolvent.”

Comment Section 2.2.2.3.: Typographical error: “Direct measurement(s) do...” It may not be appropriate to mention in this section, but an outcome of the reduced entrapment of gasoline in the vadose zone is that the remediation strategies that have been so well-developed for jet fuel and gasoline (venting and bioventing) will have a lesser utility for cleanup. Again, this is not relevant to the technical presentation here, but is an outcome of the possible effects of ethanol on hydrocarbon distribution.

Response: Comment noted. A recent report prepared by J. M. Davidson and D. N. Creek, Alpine Environmental, Inc., for the Western States Petroleum Association, evaluated several technologies commonly used at gasoline spill sites to determine how effective they would be for remediating ethanol-impacted sites and for treating ethanol-impacted water and soil.

Comment Section 2.2.3.2.1.: Here is where cosolvency is introduced and the background suggested in the above comments appears in 2.2.3.2.5. It would be easier to follow this if the background appeared early in the chapter. Perhaps the organization can be changed so that the physicochemical factors influencing distribution are first delineated, then each is defined then described in detail. Instead, we learn about the effects of cosolvency before the concept is introduced.

Response: Changes have been made earlier in this chapter to introduce the concept of cosolvency.

Comment Section 2.2.3.3.2.: Typographical error: “Inherent in these models (are) the assumptions...”

Response: Comment noted.

Comment Section 2.2.4.1.: It would be useful to define the word “sorption” so that the untrained reader can understand. This definition would include / differentiate adsorption and absorption, if possible.

Comment Section 2.2.4.2.: From the above recommendation it follows that isotherms are mathematical relationships that describe the proportions of sorbing compound in either phase. Some isotherm models are more theoretically (e.g., Langmuir) than empirically (Freundlich) based.

Response: Reference to “sorption” has been changed to “adsorption” for clarity.

Comment Section 2.2.6.2.: 2nd paragraph from bottom: Do the authors mean “overestimates” instead of “underestimates”? Wouldn't the processes of sorption and biodegradation diminish the extent of the plume?

Response: We agree with this comment. The section has been edited to improve clarity.

Comment: I would recommend a summary section at the end of this chapter. This chapter is very well done with considerable detail regarding the possible interphase behaviours of ethanol/gas/water mixtures. However, there are several occasions where we are informed that not enough is known. It seems really important to punctuate what is not known in a summary section because all of the uncertainties ultimately lead to an overall uncertainty in BTEX migration if EtOH is added to fuel. Particularly since this report is to the CA government where decisions can be made regarding funding of research to resolve the uncertainties.

Response: To facilitate the California Environmental Policy Council's review of important decision making information, the summary conclusions and recommendations for further research have been gathered into a separate chapter, Chapter 9, "Critical Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Further Research."

Comment Appendix A: HSA (pg A-2) was defined but how it is determined is not provided. Can one sentence be added here, or should the reader go to the reference?

Response: This is too detailed for the scope of this report. The reader is referred to the appropriate reference.

Comment: A final note about Chapter 2. This chapter is difficult for the untrained. Considering that this is a report to the Governor, it might be worth taking some of the analytical treatments of cosolvency and mass transfer back to the appendices and simplifying the language in the main chapter while being careful not to leave out any important concepts. It appears that there is redundancy between the text and the appendices anyway and thus improving the readability of the text should not require elimination of any important theory or analyses.

Response: We agree that this chapter is intended for a knowledgeable audience. The "condensed" version can be found in the Executive Summary, Volume 1, of the report.

Comment: Lastly, it seems worthwhile to examine the effects of EtOH on MTBE distribution-especially since MTBE already exists in the subsurface and is likely to be further distributed by the cosolvent effect. Is ethanol going to make MTBE cleanup more difficult?

Response: Ethanol is probably not going to make MTBE cleanup more difficult: 1) Although it has not been studied yet, the cosolvent effect for MTBE is likely to be very small because MTBE is hydrophilic. 2) Ethanol will most likely disappear before remediation of MTBE begins because the ethanol is readily biodegradable.

Volume 4, Chapter 3 Comments:

Comment Section 3.2.1 pg 3-3: check the spelling of the genera *Alcaligen(e)s* ?, *Noca(r)dia* ? What is the toxicity of ethanol to microbes? This could be clarified in the last paragraph of this section by stating that ethanol is toxic at high concentrations in water (70% ?) but is nontoxic at concentrations in water resulting from gasohol and water

in equilibrium (?). This is important because in Chapter 2, the main reference regarding mobility of gasohol was related to an 85% methanol blend.

Response: Those two genera are indeed misspelled in the text and need to be “Alcaligenes” and “Nocardia.” See comment below.

Comment Section 3.2.4.2: pg 3-5: Typographical error: Paul and Clark, 1989. (also in references)

Response: Comment noted.

Comment: The comments above (related to toxicity) are addressed in later sections of the chapter.

Response: Comment noted.

Comment Section 3.4.1.3: It would be helpful to the untrained to also provide the aqueous concentrations in units of % (w/w) as these are the units in earlier chapters (and in specification for reformulated gasoline) and thus provide a frame of reference for these toxicity discussions.

Response:

Comment: What about the effects of ethanol on MTBE biodegradation in the presence of BTEX? Preceding chapters acknowledged the existence of prior contamination and that there would be a potential interaction between MTBE and ethanol.

Response: We agree with this comment. The potential interaction between MTBE and ethanol should be evaluated as part of future laboratory and field studies. The postulation would be that ethanol could affect MTBE biodegradation in the same fashion as BTEX degradation.

Comment: There are a few misspellings in the References section-worth running a spell check and looking at authors’ names.

Response: Comment noted.

Comment: As with the other chapters, it would be useful to have a summary section that summarizes what is known (ethanol should biodegrade), what is not known and what should be known to provide better predictive capabilities.

Response: To facilitate the California Environmental Policy Council’s review of important decision-making information, the summary conclusions and recommendations for further research have been gathered into a separate chapter, Chapter 9, “Critical Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Further Research.”

Comment: The primary message carried into Chapter 4 from this section is that biotransformation of ethanol will remove electron acceptors and thus negatively affect BTEX biodegradation. How would this effect be potentially counterbalanced by the higher aqueous availability of BTEX due to the cosolvency effects (and the higher population sizes overall due to ethanol presence)?

Response: Possible beneficial effects are mentioned. How much the positive effects would balance the negative effects is unknown and one of the reasons for more research to be done.

Comment: The rate constants in Table 3-2 seem low (1/day), but are taken from other studies so must have been carefully confirmed. The reason this comes up is that in Chapter 5, the 1st order rate constant for biodegradation in surface water is 0.22 per hour in aerobic conditions. It would be useful in Chapter 3 to stress that aerobic rate constants in porous media are expected to be lower than rate constants in surface waters, because....

Response: The numbers in Table 3-2 are correct. This is addressed indirectly in Section 3.3.3.3.

Comment: Lastly, is ethanol involved in cometabolic processes at all?

Response: This question has been identified as an important knowledge gap in Chapter 9, "Critical Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Further Research," and will be a focus on ongoing research during the coming year. Some alcohol dehydrogenase enzymes that work primarily on ethanol do act on other alcohols. For example, the alcohol dehydrogenase of the human liver will convert methanol to formaldehyde (which is why methanol is toxic to people).

Volume 4, Chapter 4 Comments:

Comment Pg 4-3 (Section 4.2.1): Top of page is a lone right "parentheses". Next paragraph (1st full on this page) repeats the text in next to last paragraph of page 4-2. Next paragraph: define BOD in first use. Further in this paragraph, it seems unimportant to qualify the impossible model as "(analytical or numerical)"-suggest removing this clause as unessential. Next paragraph: It seems that the justification neglects retardation because of mechanical (not in previous model, validity of calculations) reasons. The next sentence seems to be the more important justification (low adsorption, so not important to include retardation term). Next page, next paragraph: "hydrophilic", not "hydrophillic".

Response: Comment noted.

Comment Section 4.2.1.: What is the basis for the first order rate constant of 0.01 per day, when the previous chapter (Table 3-2) provides a lowest rate of 0.1 per day? Some explanation for this 10-fold conservatism would be useful.

Response: The rate constant of 0.01 per day was used as part of a side calculation, separate from the main analysis, that was used to evaluate ethanol concentrations near the groundwater/LNAPL interface to assess the potential for cosolvency effects. The very conservative rate constant was used simply to illustrate the point that even if biotransformation of ethanol at the interface is minimal (which could be argued, based on toxicity effects at high concentrations), ethanol concentrations are still not high enough to produce an appreciable cosolvency effect on benzene.

Comment Section 4.2.2.: If only ethanol biodegradation is modeled (preceding paragraph), then why convert to BOD? It would help in a preceding paragraph to show stoichiometry assumed for BOD conversion so that the nearly non-technical reader can

see the relationship. Ah-this shows up in the Appendix. It might also help to have it here.

Response: Comment noted.

Comment: The results and model are quite interesting and dramatic. Would there be any benefit to increasing the 10% EtOH concentration and seeing how this changes the plume length? I realize that there is considerable effort in doing these simulations, but it seems that either here or at some point in the future it would be worthwhile to perform a sensitivity analysis with varying EtOH concentrations.

Response: We agree with this comment.

Comment: As with comments on the other chapters, a quick summary section at the end of this chapter would be useful-to encapsulate the figures and tables into a couple of capstone messages.

Response: To facilitate the California Environmental Policy Council's review of important decision making information, the summary conclusions and recommendations for further research have been gathered into a separate chapter, Chapter 9, "Critical Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Further Research."

Comment: As with comments on the preceding chapters, it seems an important question is the effect of ethanol on MTBE distribution. Granted it will not be added, but residual pollution will be mixed with new spills. This may be impossible to model, but might be worth discussing.

Response: At this point additional laboratory data would useful to support any future modeling efforts. Any discussion at this time would be very speculative at best.

Volume 4, Chapter 5 Comments:

Comment: Is rainout the preferred term or is wet deposition? Perhaps the latter is used to describe particulates only-but "rainout" is not a familiar term.

Response: We have indicated in the first paragraph of Section 5.3 that for purposes of discussing washout from the atmosphere of ethanol and MTBE, rainout and wet deposition are synonymous. Specifically, "... significant rainout (i.e. wet deposition) can potentially impact surface waters."

Comment: The biodegradation rates in the model are much higher than what was presented in Chapter 3. It would be useful to make the comparison between the two environmental compartments and their associated rate constants in this chapter as the biodegradation rate heavily influences the results in the analyses.

Response: We were able to find only one reference (Apoteker and Thévenot [1983]. Experimental simulation of biodegradation in rivers. *Water Res.* 17: 1267-1274; referenced in Chapter 5) that quantified the degradation of ethanol in surface water (i.e., Seine River), so it is difficult to draw strong conclusions from this one article regarding the differences in the biodegradation rates for ethanol in soil, groundwater, and surface water. Consequently, we have noted that additional biodegradation experiments are

needed for ethanol in surface waters. Typically, however, the biodegradation rate of ethanol will be faster in surface water because generally, surface water will possess an increased oxygen content compared to soils and ground waters. As noted by Alexander ([1999]. "Chapter 16. Bioremediation Technologies. In Situ and Solid Phase." In *Biodegradation and Bioremediation*, Second Edition [Academic Press, San Diego, CA], p. 341; §*In Situ* Groundwater Bioremediation), biodegradation typically is carried out most rapidly by aerobic bacteria, and little oxygen is present in groundwater, even under the best conditions. [Note: In comparison to ethanol and most other gasoline components, MTBE is considered resistant to aerobic microbial degradation (Sulfita and Mormile, [1993]. Anaerobic biodegradation of known and potential gasoline oxygenates in the terrestrial subsurface. *Env. Sci. Technol.* 27: 976-978). Because Section 5.4 only addresses surface water, no changes were made to the text, except to add the footnote in Section 5.4.1 (prior to Equation [5-4]) that as just mentioned, according to Sulfita and Mormile (1993), MTBE is considered resistant to microbial degradation.

Comment: In Table 5-1, provide reference temperature for solubility data.

Response: We address this point by citing the original measurement performed by Stephenson (1992). According to Stephenson (1992), the solubility of MTBE is 42 g/L at 19.8°C, and we report this value as 476 mol/m³ at 20°C in Table 5-1.

Volume 4, Chapter 6 Comments:

Comment Section 6.2.: A footnote defining the "Reid" vapor pressure would be useful.

Response: A footnote was added as suggested in page 6-1.

Comment Section 6.5.4.: Gasoline is indeed a complex mixture, despite it having been modeled as "one compound."

Response: Comment noted.

Comment: Early in this section it is important to state how much alkyate must be added to gasoline to boost the octane rating when ethanol is the fuel oxygenate. An evaluation of gasoline from 1996 (pg 6-4) is provided, but what really seems important here is how much would be added and how that additional fraction of alkylates will change the environmental consequences of gasoline release into the environment.

Response: There is not a simple answer to this question because there are other requirements that gasoline formulations must meet besides octane rating, and many of the specification parameters (including octane and vapor pressure) are not linearly additive properties. However, we did make a very rough estimation and incorporated this result to the introduction. Because the physicochemical properties of alkylate components resemble those of other hydrocarbons in gasoline, we would not expect that this increase could effect dramatically the way gasoline behaves in environmental releases.

Comment: Does the increase in alkylates increase the overall toxicity of gasoline? What are the consequences of elevated groundwater concentrations? Given their low solubility and high volatility, would we expect these compounds to be biodegraded in the vadose zone and thus fairly amenable to well-proven vadose zone cleanup strategies such

as vapor venting? Is the addition of these compounds important or inconsequential in the scheme of the entire hydrocarbon spectrum in gasoline? Overall, this chapter seemed a bit sparse in these areas. The reader is left a bit uncertain as to whether or not the concentrations actually added to gasoline would result in any substantial change in overall distribution of gasoline and/ or fate.

Response: No information is available on the chronic effects of isooctane—a major alkylate component—in humans. At acute doses, isooctane is a nervous system depressant, as are many other hydrocarbon solvents. *A priori*, there is no reason to believe that alkylates will affect—much less increase—the overall toxicity of gasoline. As a matter of fact, this is a complex problem because an increase of alkylate percentage implies a decrease in the percentage of other hydrocarbons (e.g., BTEX) and toxicity should be evaluated in an integral manner. The low solubilities of alkylate components in water and their high Henry’s law constants seem to suggest that vapor venting would be a viable cleanup strategy.

Volume 4, Chapter 7 Comments:

Comment: Physicochemical properties of ethanol are provided in this chapter; they were also provided in other preceding chapters. In Chapter 1, it was recommended that the properties be provided up front. It seems really important that all authors are consistent with the use of values for physicochemical properties.

Response: Detailed explanations of physicochemical properties of ethanol are not provided in this chapter. Sufficient discussion was included so that Chapter 7 could be used as a “standalone” document and provide a context for the following discussion. Volume 2, *Background Information on the Use of Ethanol as a Fuel Oxygenate*, provides information on the physicochemical properties of ethanol. This information is provided as a separate volume because all the subsequent CARB, SWRCB, and OEHHA volumes draw upon this information and to have it repeated in each volume would be redundant.

Comment Section 7.4.3.2.: Are there any data with AED detectors for ethanol?

Response: No data is available for AED detectors; that is why it might be of interest to explore the use of an AED in the future.

Comment Section 7.4.4.: Explain what cryofocusing is and how it is perceived to be beneficial.

Response: A brief footnote explaining cryofocussing and its benefits has been added to Chapter 7.

10.1.2. Dr. Michael K. Stenstrom, Civil and Environmental Engineering Department, University of California, Los Angeles

Professor Stenstrom is the Assistant Dean for Computing Resources for the School of Engineering and Applied Science (SEAS), and has developed the SEASnet Computing Facility. His research and teaching are in the environmental engineering area with emphasis on biological treatment methods and applications of computing technologies to environmental engineering research. Professor Stenstrom’s research interests center

around process development for water and wastewater treatment systems, including mathematical modeling and optimization. More recently he has applied these mathematical techniques to urban runoff and groundwater modeling. In the past two years, he has developed a land-use and drainage model for the Santa Monica Bay Water Shed. From this model it is possible to predict pollutant emissions to the Bay and how changes in land-use regulations will affect pollutant emissions. He is also conducting an experimental study to assess toxicity in urban runoff.

General Cover Letter Comments:

This letter and attachments are my review of Volume 4 Potential Ground and Surface Water Impacts. I wrote the attached comments as I read the report. In this letter I provide more general comments and an overview.

Professor Jenkins of UCB contacted me about this review. I am not sure if you have seen my resume. I am enclosing a short one. Also I worked two years for Amoco, which at that time was the refining and marketing subsidiary of Standard Oil (Indiana). At Amoco I worked as an environmental engineer designing end-of-pipe treatment plants as well as investigating various environmental aspects of refining. I recall we evaluated tertiary butyl alcohol (TBA) as a gasoline additive. This review reminded me of some of the things I did for Amoco.

I found the review informative and interesting. I have learned something from the review. Before I received it, I thought the exchange of ethanol (EtOH) for MTBE would be relatively simple, since health effects ingestion of EtOH are well known. After reading the review I understand it better and I think it is much more complicated.

Chapters 1 and 2 relate more to groundwater modeling. I have supervised two students to the completion of their Ph.D.'s in this area; however it is not my strongest area and you will find my comments directed more towards improving clarity than questioning the writers position or the results. I know Susan Powers is well respected in this area.

Response: Comment noted.

Comment: Chapter 3 relates to biodegradation. I found this chapter to focus on potential degradation of EtOH in the subsurface environment. It ignores a great deal of work on EtOH degradation in treatment plants. EtOH is very degradable and it is never considered a problem in treatment plants. In my own laboratory we have degraded EtOH in fixed film reactors in waste streams with 3 to 5% EtOH concentration (volume percent). The authors discussed EtOH degradation but soon turned to the potential changes in contaminant movement due to physical or chemical changes in the subsurface. I feel even more strongly than the authors that a large spill of EtOH containing gasoline can modify the movement of the more environmental significant constituents of gasoline, such as benzene. The EtOH can overwhelm the ability of the subsurface to degrade gasoline components. The metabolism can change from aerobic to anaerobic, which will reduce degradation rates and may even change the degradability of a constituent. In ground waters that are used as a potable supply, objectionable taste and odor may be

created due to residual concentrations of compounds produced during anaerobic condition.

I do not think the writers can accomplish very much on this aspect because it is a difficult and unknown topic. It seems to me that we are all speculating. I think we will need empirical results to better understand the potential impacts of a spill. I am surprised that we cannot find more information on EtOH-gasoline spills. I saw the list of Nebraska spills. I wonder if the writers have checked the international literature. I suspect that EtOH has been used in other countries. Lots of strange things were done in Europe due to war necessity. Perhaps there is some experience there that we do not know about. I have found direct contact with professors or researchers the most useful way to ferret out information about spills.

I urge you to continue your search for empirical results, or to recommend in the conclusions of the report that others continue to search for empirical results. Future projects should be created to study EtOH spills in order to verify the speculations in the report, and improve our understanding of potential mitigation techniques.

Response: We agree with the comment that field studies of ethanol spills is important to verify screening model predictions and improve our understanding of gasoline component migration in the presence of ethanol.

Comment: Chapter 5 describes scenarios for release to surface waters (I know Dr. Daniels well). It seems to me this chapter is typical of accidental release studies of a number of chemicals. I did not see all that I expected. They conclude that the extreme biodegradability of ethanol will prevent its widespread transport. I agree, however, I also wonder about the scenario of an EtOH spill, perhaps without a gasoline spill, into a potable water supply. I think it would be useful to answer this "acute" question. How much EtOH can be tolerated in a public water supply? What will be the rate controlling parameter?

After reading the documents, it occurs to me that the risks of replacing MTBE with EtOH are greater than I originally thought. I think this is in part because the review does its job and explores effects than we might not have considered. Also I think it results because in reading the chapters one continually learns about what we do not know about EtOH spills. One loses site of the problem we are trying to fix-- MTBE contamination of drinking water supplies. In order for the various chapters and volumes to have the appropriate impact, the risk of adding EtOH must be compared to the risks we reduce by eliminating MTBE. At someplace in this document, I believe it is important to indicate what we know about the risk of exposure to MTBE and other chemicals. I know this is difficult because of uncertain transport mechanisms and all the other phenomena that might reduce or facilitate EtOH transport to humans. I believe it important to balance this impression by including some other section or discussion (perhaps this is included in another volume I have not reviewed). One tends to lose track of the benefits of replacing MTBE with EtOH, and we need to correct this impression in some way.

Response: We agree with the perspective articulated by these points. However, a quantitative risk assessment is not the focus or intention of Chapter 5 and 6 in Volume 4, or the volume itself. Indeed, health-protective concentrations for benzene, ethanol,

MTBE, toluene, and xylenes are summarized and explained by the State of California Environmental Protection Agency, Office of Environmental Health Hazard Assessment (CalEPA/OEHHA) in *Volume 5, Potential Health Risks of Ethanol in Gasoline* of this report. For this reason, we have made a general statement in Section 5.6 (Summary) that generally relates our results to health-protective concentrations for MTBE and ethanol identified in *Volume 5: Potential Health Risks of Ethanol in Gasoline* of this report (see response to “*Stenstrom Comments #2*” below).

Comment: Chapter 8, which I read after the other chapters, helps put risks associated with the compounds into perspective. It is I made some specific suggestions about continuing this work in the attachment.

Response: Comment noted.

Comment: Chapter 9 functions as a summary or conclusions section. I suggest you consider a title change to indicate this function. Also there is little information from Chapter 8 in Chapter 9. Perhaps this is due completion dates of the chapters. In either case, I think Chapter 9 needs to include results from Chapter 8.

Response: The results from Chapter 8 have been incorporated into Chapter 9.

Specific Notes on LLNL Review of Ethanol–Gasoline

General Note: This document shows its varied authorship. Style changes from chapter to chapter (although there is good consistency for basic issues such as style of citing references). It occurs to me as I review Vol. 4, that there will be a need for an overall summary, which is acceptable to all authors. I have not seen Vol. 1, but it will be challenging to write such a summary.

Volume 4, Chapter 1 Comments:

Comment 1: What about exposures via small uses of gasohol, such as gardeners, gas lantern, stoves, hand warmers. Figure 1.

Comment 2: Copper content of gasohol is 0.1 mg/kg (1 ppm). Do a calculation to see what impact this will have on urban runoff. Table 1-2

Response: Both these issues are good ones to be addressed as part of a complete life cycle analysis.

Comment 3: Provide as much detail as possible on impurities in the EtOH so that one can calculate the impurities after a gasoline release or other spill. Can Table 1-3 be quantitative?

Response: Little quantitative information is available on the variation in ethanol impurities. Further many of the additives are proprietary and information is not available at this time.

Comment 4: Page 1-5. A good point is made about MTBE in Lake Tahoe from 2 stroke engines. Then the discussion just stops. What’s the implication for EtOH? Will their ban on 2-stroke engines continue? Does it need to be continued? What are the rest of the writers’ thoughts in this paragraph? Finish the idea.

Response: The risk management option to restrict watercraft use is a local and area specific decision. A discussion of the effectiveness of the current ban on gasoline containing MTBE in the Lake Tahoe area is presented in Appendix C of Chapter 5, Potential Impact of Ethanol-containing Gasoline on Surface Water Resources.

Comment 5: I live in Southern California, and it seems that every house uses a gardener who has at least two gasoline-powered tools - a weed whacker and a leaf blower. Gasoline powered leaf blowers have been outlawed by the LA City council, but there seems to be no impact on professional gardeners. Most of these tools use 2-stroke engines and blue smoke trails are abundant. It seems to me that this is probably a larger source than boaters in Lake Tahoe, and merits equal time in the review.

Response: We agree with this comment and this issue should be addressed as part of a complete life cycle analysis.

Comment 6: The search on Nebraska is a little surprising. It seems like a useful thing to do, and why is only Nebraska represented? Are there no other states that have kept such records?

Response: None that we could find in the time allowed for our literature search.

Volume 4, Chapter 2 Comments:

Comment 1: The reference is provided for the surface tensions (Figure 2-5), but I think you should still mention the method of measurement in the text.

Response: Comment noted.

Volume 4, Chapter 3 Comments:

Comment 1: It seems that one could put some bounds on concentrations that would create inhibitory conditions, as cited in 3.3.2.

Comment 2: In Section 3.3.3.2, 4th paragraph, it states that pH was observed from 4.5 to 7.8. Is this correct? 4.5 is very low, and if this is correct, it answers the speculation in the preceding paragraphs about low pH inhibition. Surely pH=4.5 would inhibit ethanol degradation and most other biodegradation. Also, groundwater at pH=4.5 would solublize many other contaminants, metals for example, that could inhibit biodegradation or facilitate their transport.

Comment 3: On page 3-12, just above section 3.3.3.3, the authors conclude that ethanol degradation is so rapid that that degradation is bound to occur, independent of electron acceptor, given favorable conditions of pH etc. One question that has not yet been addressed in the text, but seems obvious to me, is the impact of the gasoline components on ethanol degradation. Some of the compounds in gasoline, at higher concentrations, are inhibitory. The question of how rapid ethanol degradation will be in gasoline/ethanol spill, as compared to just ethanol, should be addressed.

Response: We agree that this is an important issue that should be addressed by further research.

Comment 4: Later on this page, the authors suggest that ethanol degradation may be favored over degradation of compounds such as benzene. In wastewater treatment plants, where ethanol is considered so degradable that one doesn't worry about it very much, its presence will inhibit other degradation almost completely. In fact, the microbial populations can change so much in the presence of ethanol that physical properties change sufficiently to impede the process. The hydraulic conductivity of the soil and retention of gasoline components could be changed for the worse. A scenario comes to mind where degradation of the more toxic compounds in gasoline is reduced because organisms degrading ethanol out compete gasoline-degrading organisms, and deplete available nutrients and the most desirable electron acceptors.

Response: Comment noted. This information will be useful in designing future laboratory research experiments.

Comment 5: On page 3-14, the authors report toxicity of ethanol. My own experience, of microbial reactors degrading ethanol using nitrite and nitrate as electron acceptors, is that inhibition begins at about 4% EtOH concentration (e.g., 40,000 mg/L). This is for an acclimated culture. A non-acclimated culture can be inhibited at much lower concentrations.

Response: Comment noted. This information will be useful in designing future laboratory research experiments.

Comment 6: I see (Section 3.4.2.1) that the authors have also thought about a highly degradable substrate depleting nutrients and oxygen.

Response: Comment noted. This information will be useful in designing future laboratory research experiments.

Comment 7: Methanogens are not inhibited equally by all VFA's. Acetate is the least inhibitory. The pioneering work of McCarty describing anaerobic digesters is still generally accepted. However, his values of VFA's (measured in the days when Gas and Liquid Chromatography could not be routinely used), are predominately acetic acid. Several hundred mg/L of propionate can be more inhibitory than several thousand mg/L of acetate.

Response: Comment noted. This information will be useful in designing future laboratory research experiments.

Comment 8: On page 3-17 the authors speculate on methane production and the production of gas bubbles. We have some experience here that may be helpful. Anaerobic digesters, typically treat biosolids in the 3 to 8% range and produce gas, on a dry basis that is 65% methane and 35% carbon dioxide, with traces of other gases. The rates of production of carbon dioxide and methane are equal, but sufficient carbon dioxide dissolves to elevate the gas phase methane mole fraction. For low strength applications, the dissolved methane, even though it is a sparingly soluble gas, becomes important, and very little methane is observed in the gas phase. For systems treating 200 to 300 mg/L of COD, methane mole fraction is very low, under 20%. The nitrogen is not displaced, which accounts for the remainder of the gas.

Response: Comment noted. This information will be useful in designing future laboratory research experiments.

Comment 9: I question the value of Table 3-3. Various conditions mean different things. In reactors acclimated to ethanol, 100 mg/L can be degraded in a matter of hours, for both aerobic and anaerobic conditions. The table needs to be more restrictive. Also it seems to conflict with Table 3-2 (even though they are from the same reference). What is the difference between carbon dioxide as an electron acceptor in 3-2 and methanogenic conditions in 3-3? The rate coefficients do not correlate between the two tables. The products of λ and half-lives agree in Table 3-2; however, applying the values of l in Table 3-3 produces removal rates of 78, 80, 89, 92 and 77%. The rates for sulfur and carbon dioxide reducing conditions are reversed. It takes longer in Table 3-3 than in Table 3-2. Perhaps these are associated with the original reference, but even so, it needs to be clarified. I suspect most of these differences have simple explanations and are not out right errors, but they should be corrected or explained.

Response: Table 3-3 has been omitted and the text edited to improve clarity.

Comment 10: An effect not considered in the report is the content of biodegradable organic carbon in drinking water. Recent work in disinfection of potable waters has stressed the importance of removing biodegradable organic carbon (e.g. BDOC) from drinking supplies. The premise, which seems correct, is that indicator organisms and pathogens can persist or regrow in distribution systems in the presence of substrate. BDOCs in the range of 200 ug/L become important. EtOH would probably be an excellent substrate for regrowth. If potable water supplies are contaminated with EtOH, a consequence, which may not be apparent, is greater difficulty in disinfection.

Response: Comment noted.

Volume 4, Chapter 4 Comments:

Comment 1: This chapter needs a small conclusion.

Response: To facilitate the California Environmental Policy council's review of important decision making information, the summary conclusions and recommendations for further research have been gathered into a separate chapter, Chapter 9. *Critical Knowledge Gaps Regarding the Surface Water and Groundwater Impacts of Ethanol-containing Gasoline and Recommendations for Further Research.*

Comment 2: Graphs in color would be helpful.

Response: Figures are intentionally developed to be duplicated in black and white copiers. Color figures often do not copy in black and white well.

Volume 4, Chapter 5 Comments:

Comment 1: The introduction of this chapter might be shortened a little. This is not critical, but would improve the review. The current introduction was written as if the chapter were "stand alone."

Response: Comment noted, but no changes were made to text because authors felt it important that the chapter does stand alone, if necessary.

Comment 2: When I first started reading this review, I was expecting to see something of the relative risks of EtOH and the alternatives in this chapter. Perhaps it has been written before, but I think it would be useful to say something about the relative risk of MTBE and ethanol in drinking water. One could provide the risk of drinking water associated with the measured values of MTBE in water supplies. Perhaps Santa Monica groundwater would be a good choice. Then the authors could compare this risk with the risk of ethanol-contaminated water risk. The chapter now does a good job of trying to project EtOH concentrations for various conditions; however, there is no mention or way of understanding just how much risk is associated with MTBE, EtOH and the "do nothing" alternative (e.g. ordinary gasoline). The writers of this section are familiar to risk assessment; therefore they should be able to do this with relative ease.

Response: We agree with this comment in principle, but did not perform the suggested analysis because "quantifying health risk" was not the objective for Chapter 5 or Chapter 6, but such risk analyses certainly should be done comprehensively in the future. Nevertheless, we have added a statement to Section 5.6 (Summary), that generally links our results to health-protective concentrations for MTBE and ethanol in drinking water summarized by the State of California Environmental Protection Agency, Office of Environmental Health Hazard Assessment (CalEPA/OEHHA) in *Volume 5: Potential Health Risks of Ethanol in Gasoline* of this report.

Volume 4, Chapter 6 Comments:

Comment 1: The cover page is different.

Response: Comment noted.

Comment 2: What about the relative risk of alkylates? It makes sense to study their transport, but what are the risks associated with ingestion? The authors state they may not be so degradable. I think more information is needed to indicate whether these compounds are more or less risky than MTBE. If we do not know the risks, then we need to say it.

Response: No information is available on the chronic effects of isooctane—a major alkylate component—in humans. At acute doses, isooctane is a nervous system depressant, as are many other hydrocarbon solvents. *A priori*, there is no reason to believe that alkylates will affect—much less increase—the overall toxicity of gasoline. As a matter of fact, this is a complex problem because an increase of alkylate percentage implies a decrease in the percentage of other hydrocarbons (e.g. BTEX) and toxicity should be evaluated in an integral manner. The low solubilities of alkylate components in water and their high Henry's law constants seem to suggest that vapor venting would be a viable cleanup strategy. (Also see Dr. Holden's general comment on Chapter 6).

Volume 4, Chapter 7 Comments:

Comment 1: I suggest separating Table 7-1 into useful and non-useful methods by placing a bold line across the table and putting less useful methods below it. A column could be eliminated. Also change ppm to mg/L or appropriate unit. Are there no LC methods? I would have guessed a normal phase LC might be useful.

Response: Editorial comments noted. No information was found in the course of our literature search on the use of liquid chromatography (LC) techniques for analyzing ethanol. Further development of these methods may be useful.

Comment 2: The distinction of "useful" seems to be based upon detection limit. What about detection of EtOH in gasoline? Isn't it conceivable that a researcher might want to determine the EtOH in a field sample from a spill? This might be an analysis for percentage EtOH concentrations, as opposed to very low concentrations. There is no method listed for this application.

Response: Our review considered only the measurement of environmental concentrations of ethanol. While we acknowledge that methods for the detection of high (percent) concentrations of ethanol in gasoline are currently used by the gas industry, we chose to focus on methods which could be used to assess the impact of ethanol to the environment and which could be used to determine ethanol contamination of water supplies.

Volume 4, Chapter 8 Comments:

Comment: This chapter came last, after Chapter 9, but potentially is the most useful in understanding the overall risk. I have not had time to review the methodology, so I cannot critique its validity, but if I assume it is correct, the results provide a basis for more quantitative decision making. If one couples the probabilities of spills reaching wells with risk associated with specific concentrations in drinking water, one has a method to show that ethanol is or is not riskier than MTBE. If future work is to be done by this group on this problem, continuing the work from this chapter is a good starting point.

Response: We agree with this comment.

Volume 4, Chapter 9 Comments:

Comment 1: This chapter is almost a conclusions or executive summary of the earlier chapters. Consider using "conclusions" or similar word in a modified title.

Response: Comment noted. A title change in this chapter is not possible at this time. Such a change would have significant impact on meeting the December 31, 1999 deadline for submittal of this report to the California Environmental Policy Council.

Comment 2: Section 9.3.4.2 might be a good place to put risk information mentioned earlier. The average reader (I do not) will not know the risk of 10 ug/L of ethanol.

Response: Issues of risk to human health are covered in Volume 5: Potential Health Risks of Ethanol in Gasoline.

Comment 3: I generally agree with the conclusions and recommendations in this chapter. It is in the second mailing, but it would have been useful to read first, before the other chapters. I have a couple of other suggestions. The first is to continue to look for information on previous spills. Perhaps there is some foreign information that might be useful. I do not know how long you had to develop this review, but I suspect it was relatively short. Given such time, it is unlikely that you had time to conduct a thorough search. An approach might be to identify researchers who might have encountered ethanol spills from their publications. The references from each chapter are a starting point. Next go through each set of authors to identify senior authors who might have experience with spills. Next write or email them. The second is more specific. I think it might be easier to develop an extraction (SPE) and LC technique that might be a better than a GC approach (I do not recommend eliminating the GC approach).

Response: We agree with these suggestions.

10.1.3. Dr. Michael R. Hoffman, Executive Officer of Environmental Engineering Science, James Irvine Professor of Environmental Science, California Institute of Technology.

Professor Hoffmann received his B.S. from Northwestern University in 1968 and his Ph.D. from Brown University in 1974. Professor Hoffmann has been active in the subject areas of applied chemical kinetics, aquatic chemistry, atmospheric chemistry, catalytic oxidation, heterogeneous photochemistry, sonochemistry, pulsed plasma chemistry, and hazardous waste treatment. His recent research has been focused on the development of advanced technologies for water and wastewater treatment. These approaches involve the application of metal-catalyzed autoxidation, semiconductor electrocatalysis and photocatalysis, ultrasonic irradiation, pulsed-plasma discharges, and the use of highly potent oxidants, such as hydrogen peroxide, ozone, peroxymonosulfate, and periodate for the oxidative and reductive elimination of chemical contaminants from water. His atmospheric chemistry research has been focused on the chemical speciation of iron in clouds and aerosol, on the chemical characterization of aerosols over the remote Indian Ocean and Atlantic Oceans, and on the chemistry of carbonyl sulfide and other sulfur compounds in sulfuric acid aerosol.

Overall Comments

The nine chapters of Volume 4 of the *“Report to the Governor of the State of California in response to Executive Order D-5-99”* collectively represent a very commendable effort to provide a state-of-the-art analysis of the potential environmental impacts of ethanol and ethanol-containing gasoline on surface and ground waters. This volume examines in detail current knowledge pertaining to our understanding of the behavior and eventual fate of ethanol in the aquatic environment. Primary and secondary effects of the intrinsic physicochemical properties of ethanol and the subsurface transport characteristics of gasoline-ethanol mixtures are explored in detail. It is too bad that this type of thorough analysis was not undertaken before the widespread introduction of MTBE into reformulated gasoline. Perhaps some of the current problems related to the

apparent persistence of MTBE in the aquatic environment could have been predicted if this type of pre-use analysis had been performed.

Specific Comments by Chapter

Volume 4, Chapter 1 Comments:

Chapter 1 provides a general background perspective on ethanol production, usage, distribution and potential environmental release pathways.

Comment: However, this chapter contains too many ‘gray’ literature references that are not academically satisfying. Some primary refereed literature articles should be included.

Response: The extensive use of ‘gray’ literature reflects the absence of peer-reviewed literature regarding life-cycle issues associated with the use of ethanol as a fuel oxygenate.

Volume 4, Chapter 2 Comments:

Chapter 2 provides a critical review of the effects of ethanol in gasoline on the fate and transport of the BTEX family of compounds in the subsurface aquatic environment. This chapter gives an excellent systematic overview of the physical organic chemistry of ethanol and ethanol-BTEX mixtures with appreciable attention focused on the physicochemical phenomenon of co-solvency. Mass transfer and mass transport considerations are also addressed in a thorough manner.

Comment: However, I question the use of the Greek symbol lamda, λ , to represent the apparent first-order rate constant for biodegradation. Traditionally, microbiologists have used the Monod kinetic terminology of μ (i.e., specific growth rate constant, t^{-1}), μ_{\max} , and K_s . Schwarzenbach et al. (Environmental Organic Chemistry, Wiley, New York, 1993), use k_{bio} to denote the apparent first-order biodegradation rate constant. Why the switch away from more conventional terminology?

Response: We used “lambda” for biodegradation because it was used by the Malcolm Pirnie, Inc., report that we were referencing. The monod kinetics would be inappropriate to use here, but k_{bio} could be used in place of λ . This change in notation would require editing a number of chapters to be consistent and do the late receipt of Dr. Hoffmann’s comments, this change has not been made.

Volume 4, Chapter 2, Appendix A Comments:

Comment: On pg. A-1, eq. A-1b: g’s in eq. A-1b should be gamma’s, γ ’s. (i.e., change g into γ).

Response: Comment noted.

Comment: Techniques for the determination of γ for methanol, ethanol, isopropanol, THF, and methanol-hexane mixtures are presented by Pividal et al. in the *J. Chem. Eng. Data*, **37**, 484-487, 1992.

Response: Comment noted. There are many means of estimating gamma.

Comment: It should also be noted that much of Appendix A is repeated verbatim in the main body of chapter 2.

Response: We agree that there is redundancy between Appendix A and the main text, but there is much more detail (approximately three times the length) in the appendix in comparison with the main text. This approach was adopted in order to allow readers who did not wish the detail supplied in the Appendix to nonetheless receive a useful level of detail.

Volume 4, Chapter 2, Appendix B Comments:

Comment: On pg. B-2, pg. 4, ln. 4: Cussler (~~1997~~) should read Cussler (1984).

Response: Comment noted.

Comment: In transforming eq. B6 into B7 explain or justify the formal logic behind the substitution of $x = L/4$. In addition, some logic is needed in going from eq. B7 to B9. Some assumptions about τ_z and α_z need to be stated to make the aforementioned transformation obvious to the reader.

Response: Comment noted. The “Tau” and “Alpha” transformation are very standard in contaminant transport. We felt that it was too elementary to elaborate further, especially in an appendix.

Comment: Why is the term, $\partial^2 C_i'' / \partial y^2$, ignored in the plume dispersion equation of eq. B11? It is subsequently included in the Appendix of chapter 8. This needs to be explained as a 2-D model. Assumptions in model development should be stated clearly, because later on a 3-D model is presented as the frame of reference for the Monte Carlo analysis.

Response: This is a good comment. The two sections should have been made consistent, but unfortunately, due to the late receipt of Dr. Hoffmann’s comments, these editorial changes cannot be made in time to deliver the report on December 31, 1999. However, to clarify that when a two-dimensional model is used (p. B-4, second paragraph), we have edited the following sentence: “Holman and Javandel (1996) extended the complexity of the mass transfer problem in a two-dimensional vertical cross section to include. . . . “

Volume 4, Chapter 3 Comments:

Comment: The initial background material on microbial ecology and metabolism is quite elementary, too lengthy, and perhaps unnecessary given the level of treatment by the authors of the other chapters.

Response: Comment noted. Unfortunately, the author is unavailable to respond due to the late receipt of Dr. Hoffmann’s comments.

Comment: There definitely needs to be a discussion of co-metabolism. The authors define enzymes as “polymers of amino acids.” This definition is overly simplistic and limited. A more realistic definition of enzymes is desirable.

Response: Unfortunately, the author is unavailable to respond due to the late receipt of Dr. Hoffmann's comments.

Comment: The authors state that the average pH of groundwater is 7? If this is in reality true, then the authors need to provide an authoritative reference. The pH of groundwater should cover a much broader range depending on the specific mineral content of the aquifer solids. For example, would the authors expect that groundwater flowing through limestone or calcite to have a pH of 7? The pH of groundwater could vary from pH 5 to 9 depending on local influences and the level of alkalinity.

Response: Author unavailable to respond due to the late receipt of Dr. Hoffmann's comments.

Comment: On pg. 3-7, pr. 3, ln. 4: insert a '**the**' between operate and Krebs (operate **the** Krebs cycle).

Response: Comment noted. Editorial corrections have been made.

Comment: On pg. 3-10, pr. 0, ln. 1: please subscript the naught on concentration (i.e., C₀). This should also be done in eq. 3-3 and in ln. 4.

Response: Comment noted. Editorial corrections have been made.

Comment: pg. 3-10, pr. 4, last line: delete 'removal of' before "alcohol was removed by washing."

Response: Comment noted. Editorial corrections have been made.

Comment: pg. 3-16, pr. 3, sec. 3.4.2.3 on Bioavailability: the authors need to refer back to chapter 2 on co-solvent effects and then re-evaluate their last statement of this section which reads "the extent to which ethanol might hinder these processes, however, is unknown.

Response: Comment noted. Editorial corrections have been made.

Comment: There appear to be some relevant recent references that are missing. For example,

C. Goudar, K. Strevett, and J. Grego (1999) "Competitive substrate (BTEX) biodegradation during surfactant-enhanced remediation," *J. Environ. Eng. ASCE*, **125**, 1142-1148.

F. Domenech, P. Christen, J. Paca, and S. Rehad (1999) "Ethanol utilization for metabolite production by *Candida utilis* strains in liquid medium," *Acta Biotechnol.*, **19**, 27-36.

J. E. Landmeyer, F. H. Chapelle, P. M. Bradley, J. F. Pankow, C. D. Church, and P. G. Tratnyek, (1998) "Fate of MTBE relative to benzene in a gasoline-contaminated aquifer (1993-98)," *Ground Water Monitoring and Remediation*, **18**, 93-102.

Another useful reference source for ethanol metabolism is available at <http://www.labmed.umn.edu>

Response: Unfortunately, the author is unavailable to respond due to the late receipt of Dr. Hoffmann's comments.

Volume 4, Chapter 4 Comments:

Chapter 4 focuses on the determination of the effects of ethanol on benzene plume lengths in the subsurface.

Comment: Why were the calculations done in terms of the somewhat archaic BOD instead of more relevant compound-specific transformation rates?

Response: BOD, reflecting electron acceptor depletion as a result of ethanol transformation, is a convenient means for quantifying the total electron acceptor demand at some location in the model. We can assume that the rate of benzene transformation will be inversely proportional to the BOD to some extent (based on the abundant literature from field and laboratory studies suggesting this, as well as simple thermodynamic arguments), hence the inverse correlation between the benzene biotransformation rate and the BOD in the model. We do not understand what is meant by relying on compound-specific transformation rates; these data for different redox regimes in the presence of ethanol is not available.

Comment: There are two consecutive pages numbered as the same 4-7. The second in that series should be 4-8.

Response: Comment noted.

Comment: Why were the calculations done in English units. Metric units would have been more appropriate. In addition, IUPAC approved chemical units should have been used throughout.

Response: This was to maintain consistency with other studies that also used English units.

Volume 4, Chapter 5 Comments:

Chapter 5 addresses potential problems associated with ethanol-containing gasoline usage and its possible effects on surface water resources.

Comment: I would prefer to see in eq. 5-1, units of concentration in rain in terms of moles / L or μM , air units in moles / m^3 and pressure in units of atm (atmospheres).

Response: Preferred units have been added to text. However, it is agreed that Equation (5-1) could be simplified, but in its present form yields units that the authors feel are more representative and perhaps useful. Therefore, Equation (5-1) was not changed.

Comment: On pg. 5-5, eq. 5-5: Something appears to wrong with eq. 5-5 as written. The use of the factor of 10^6 in the denominator needs to be explained better. In Jobsen's paper (*vide infra*), C_u is defined as the unit concentration with units of reciprocal time, which is 10^6 times the observed river concentration at a particular cross section times the river discharge divided by the total mass to pass the cross section. The units used in the glossary below eqs. 5-5 and 5-6 differ from the units used in the subsequent paragraphs. For example, in the written paragraphs Q is in m^3/s while in the glossary it is given in L/s. The original paper by Jobsen (H. E. Jobsen, "Predicting Travel, Time, and Dispersion in Rivers and Streams, *J. Hydraul. Eng.*, **123**, 971-978, 1997) uses units of m^3/s .

Furthermore, in the subsequent paragraph's river velocity, v , is given in km/h while in the glossary v is in units of m/s. What further transformations did the authors of chp. 5 make to arrive at eq. 5-5? Please check for self-consistency. Also, the authors should reference the formal Jobsen paper (*vide supra*).

Response: Comment noted. We followed the methodology described in the technical report by Jobsen (1996). The factor of 10^6 shown in Equation (5-5) arises from the fact that Jobsen (1996) arbitrarily defines the "unit concentration" (identified now as k_{pc} in Equation (5-5) as 10^6 times the concentration produced in a unit discharge due to the injection of a unit mass of substance. Jobsen (1996) further relates the "unit concentration" to a mass flux of solute (mass/time) per unit of mass injected. This statement now appears as a footnote to the new term in Equation (5-5), "nf" that replaces 1×10^6 . The journal article cited by Dr. Hoffmann in his comment was not available at the time this chapter was prepared.

Comment: On pg. 5-8, eq. 5-7: I believe that there is a factor of 10^9 missing from the numerator of eq. 5-7. For example, the LHS of this equation has units of $\mu\text{g}'\text{s}$ while the input, E_r , on the RHS of the equation is in kilograms per day, kg/d. Thus, there are 10^3 g per kg and 10^6 $\mu\text{g}'\text{s}$ per g yielding the factor of 10^9 .

Response: The calculations were performed correctly using Equations (5-7) and (5-8); however, a units conversion factor was omitted from Equation (5-7) (typographically). That conversion factor has been restored and is noted as "cf", which is equal to 10^9 $\mu\text{g}/\text{kg}$.

Volume 4, Chapter 5, Appendix C-1 Comments:

Comment: On pg.C-4, pr. 1., ln. 4: the i.e. needs a **comma** after it (e.g., i.e.,).

Response: Comment noted, and the paragraph has been changed. There is no longer an (i.e.) starting parenthetical statement and instead (that is, ...) now appears.

Comment: On pg. C-5, pr. O, last line: It would be nice to actually know the analytical methods employed (not just a personal communication from an unknown person) and the QA/QC procedures used to have any faith in the numbers presented.

Response: Comment has been addressed by adding additional analytic method and QA/QC information following the statement "personal communication citation (Koester, 1999)".

Volume 4, Chapter 6 Comments:

Chapter 6 deals with the possible environmental consequences of an increased usage of branched alkanes as additives.

Comment: On pg. 6-3, pr. 2, ln. 2: 'registry number' should read registry numbers.

Response: Comment noted.

Comment: On pg. 6-4, pr. 1, eq. 6-2: The units of equation 6-2 are not given. The terms are defined but the units are missing. They should be given.

Response: The units of Equation (6-2) have been added.

Comment: pg. 6-5, pr. 2, ln. 7: In urban, near urban, and continental regions, the hydroxyl radical concentrations on average may be 10^7 molec cm^3 or higher. Thus, the projected lifetimes of isooctane and related molecules would be shorter by a factor of ten. The mean global OH concentration may not be the most appropriate in this case.

Response: Good comment. The text of this Chapter 7 section has been modified to reflect this comment.

Comment: The authors of this Appendix should reference the book by Schwarzenbach et al. (1993).

Response: This comment is unclear. There is no appendix in Chapter 6.

Chapter 7:

This chapter addresses the need for appropriate analytical methods for the precise, accurate, and reliable determination of ethanol in natural water samples.

Comment: This chapter is the least thorough and least satisfying of Volume 4.

Response: Comment noted. This points to the lack of good analytical methods for trace-level ethanol analysis.

Comment: One obvious analytical technique that was not mentioned is APS-ES-MS (i.e., atmospheric pressure ionization electrospray mass spectrometry). It may also be possible to couple APS-ES-MS with HPLC to determine ethanol at extremely low concentrations (See: Nishikawa et al., *J. Chromatogr. B*, **726**, 105-110, 1999).

Response: Ethanol is not usually considered to be a candidate for LC/MS analyses--primarily because it is volatile and detected easily by GC/MS. It appears from examining the complete title of the article that LC/MS is used primarily for the analysis of ethyl glucuronide (ethanol's metabolite). However, LC/MS might merit additional investigation as an analysis technique because it might eliminate the necessity of extraction prior to GC/MS analysis.

Comment: It may also be possible to employ Laser Raman spectroscopy (see: Giles, et al., *J. Raman Spectroscopy*, **30**, 767-771, 1999), FT-NIR, or FT Raman Spectroscopy for the determination of oxygenates (see: Choquette et al., *Anal. Chem.*, **68**, 3525-3533, 1996).

Response: The primary objective of Chapter 7 is to review methods applicable to the routine analysis of ethanol in environmental waters. The above reference discusses the use of Raman spectroscopy to "determine whether near-IR and/or Raman methods could quantitate oxygen species in SRM (standard reference material, i.e., gasolines) ampules." While this method might be amenable to quantitate percent concentrations of ethanol in gasoline, it probably would not be suitable to the determination of trace quantities of ethanol in water (Raman spectroscopy is not a very sensitive technique). For this reason, the reference was not included in this chapter. In addition, we realize that there exist some papers describing the use of nuclear magnetic resonance (NMR) spectroscopy for the determination of oxygenates in fuel--however, these references were also omitted because they did not pertain to the analysis of ethanol in environmental waters.

Comment: Another recently reported technique for the determination of ethanol in water uses a gold-coated unclad optical fiber system (see: Misushio and Kamata, "Alcohol analysis using a gold-coated unclad fiber sensor system," *Bunseki Kagaku*, 48, 757-762, 1999).

Response: This article is written in Japanese and would require translation. To meet the required report delivery date of December 31, 1999, our literature search was biased towards the selection of articles that were written in English.

Volume 4, Chapter 8 Comments:

Chapter 8 focuses on the use of a detailed Monte Carlo analysis of the dispersion equation employed in Chapter 3 to analyze the parametric effects of a variety input variables on the BTEX plume lengths.

Comment: On pg. 8-11: Were any variations in the solids/mineral characteristics factored into account in this analysis? Was the sensitivity of the plume length (vis-à-vis retardation) on the organic carbon content (OC) of the aquifer solids examined?

Response: Stoichiometric calculations were not assessed in this section (although this method is discussed in McNab and Dooher, 1998) due to, what we believe are, a reasonable approximation of the degradation population associated with benzene throughout California. Details of these rates are available in references provided in Chapter 8. Retardation is one of the sensitivity parameters examined. Please see the response to Dr. Hoffmann's comment on Table 8-2, below.

Comment: On pg. 8-14, Section 8.5 Conclusions: A summary of the effects of variations in parameter space on plume lengths and durations should be presented.

Response: This is discussed in detail in Dooher, 1998.

Comment: On Table 8-1 – no page number given: Units must be given for each term in the glossary of parameters given in Table 8-1.

Response: The program described used metric units, which were then translated into English for uniformity of the presentation of results.

Comment: On Table 8-2 – no page number given: The fractions of organic carbon, f_{OC} , seem to be too low. Are they truly realistic for a typical California subsurface environment?

Response: These data were developed from several sources. The distribution itself was developed in Dooher (1998) from data collected around the Lawrence Livermore National Laboratory (LLNL) Superfund site. This data was compared to data compiled in Domenico and Schwartz (1990) for a 'reality check.' The maximum organic carbon described therein is a 0.0226 measurement from a river sediment environment, described as fine silts, at Oconee River (exact location unknown). The author attempted to contact the one of the originator's of these measurements to get more information, but the source was generally unresponsive. Others in the Ontario area ranged from 0.00017 to 0.00102—all in glacial-fluvial environments, ranging from sands and gravels to fine sands. A measurement of 0.01 was referenced from Palo Alto Baylands, California,

described as a silty sand. LLNL's environment is alluvial, encompassing many soil types, and is typical of coastal valleys in California. Although the 99th percentile for that environment is approximately 0.01, we believe it is representative of a great number of sites in California. We could expand the distribution as part of future work, but this should have little effect on the potential for well impacts, especially for MTBE. Of greater importance is knowledge of the LUFT site's maximum concentration.

Volume 4, Chapter 9 Comments:

Chapter 9 summarizes the apparent knowledge, science, and engineering gaps that need to be bridge to provide a more reliable assessment of the potential aquatic impacts of gasoline containing ethanol.

Comment: On pg. 9-3, pr. 1, ln. 4: Although California has 'implemented' improved

Response: Comment noted.

Comment: On pg. 9-3, pr. 2, ln. 1: This is a bad sentence. Perhaps it can be salvaged as follows:

“An important consideration, which is related to the decision to use ethanol, is the potential effect that it may have on the fate and transport of toxic gasoline components.”

Response: Comment noted.

Comment: On pg. 9-6, pr. 1, ln. 4: 'adaptedto' should read, “**adapted to**”

Response: Comment noted.

Comment: On pg. 9-6, pr. 2, ln. 7: 'transitionsin' should read, “**transitions in**”

Response: Comment noted.

Comment: On pg. 9-6: The possibility of co-metabolism should be noted.

Response: We have discussed lack of information regarding the effect of ethanol on microbial population shifts (that is, microbial ecology) and the resulting catabolic diversity. We indicate that among the possible effects are enrichment of ethanol-degrading bacteria in relation to BTEX-degrading bacteria, fortuitous enrichment of bacteria that can degrade (co-metabolize) both ethanol and BTEX compounds, and decreases in populations of certain bacteria as a result of toxicity.

Comment: On pg. 9-11: I would favor APS-ES-MS techniques for ethanol determination.

Response: Comment noted.

10.2. Public Review Comments

The following responses address external review comments on the draft State Water Resources Control Board (SWRCB) Volume 4, “Potential Ground and Surface Water Impacts”, which is part of the report to the California Environmental Policy Council titled, “Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate.” The following Organizations and individuals have submitted comments:

Michael C. Kavanaugh, Ph.D., P.E., and Andrew Stocking, P.E., Malcom Pirnie, Inc.;
Western States Petroleum Association;

10.2.1. Michael C. Kavanaugh, Ph.D., P.E., and Andrew Stocking, P.E., Malcolm Pirnie, Inc.: Comments and LLNL Responses

I recently attended the public workshop in Sacramento regarding the fate and transport of ethanol in the environment. As part of the public comment process, we are providing written comments to you on issues that we recommend should be further addressed in the study being conducted by the Lawrence Livermore National Laboratory (LLNL).

Malcolm Pirnie, Inc has been retained by the American Methanol Institute to prepare these comments on the LLNL analysis of potential impacts of the use of ethanol in gasoline on the fate and transport in groundwater of other constituents in gasoline, namely the aromatic compounds, benzene, toluene, ethylbenzene and the xylenes (BTEX). We believe that these comments will help to clarify and expand the LLNL conclusions presented at the Sacramento public workshop regarding impacts on the BTEX plumes due to the use of ethanol-blended gasoline.

Using a screening-level model, LLNL concluded that the use of ethanol-blended gasoline could extend BTEX plumes by approximately 25%. These results presented by LLNL are consistent with two other recently completed modeling efforts to assess this issue. As referenced in the LLNL presentation, Malcolm Pirnie completed a detailed analysis of ethanol fate and transport in the environment last year entitled, "Evaluation of the Fate and Transport of Ethanol in the Environment." Included in that analysis was a preliminary modeling evaluation of the effect of 10% ethanol in gasoline (gasohol) on the fate of BTEX plumes.

The Malcolm Pirnie report concluded that a primary disadvantage of adding ethanol to gasoline is the potential impact of ethanol biodegradation on the natural biodegradation of other gasoline constituents present in the groundwater. Ethanol is known to readily biodegrade under a variety of aerobic and anaerobic conditions. Under these conditions, ethanol is a preferred substrate and will be preferentially utilized in the presence of BTEX. However, as ethanol is aerobically biodegraded, oxygen and other electron acceptors, as well as nutrients will become depleted in the groundwater. As a result, BTEX plumes may be lengthened due to the delay in biodegradation in the presence of ethanol. Based on modeling results, the presence of ethanol is expected to increase BTEX plume lengths by approximately 27% under typical California groundwater conditions (ranging from 16% to 34% increase in BTEX plume lengths). The potential impact of increasing BTEX plume lengths is either a greater probability that drinking water well fields could be impacted by BTEX or higher BTEX concentrations at wells that are already contaminated. Additional migration of the BTEX plumes could also cause greater property damage due to plumes extending beyond the boundaries of the source property. These impacts would result in higher cleanup costs for BTEX plumes, if cleanup is warranted.

Finally, the University of Waterloo, Ontario, Canada has recently completed a modeling effort to evaluate the use of ethanol-blended gasoline on gasoline in

groundwater. Preliminary results from this research have been presented at the National Ground Water Association meeting in Houston, Texas, 1999 at the Petroleum Hydrocarbon Conference. This study concludes that the use of ethanol in gasoline could extend BTEX plumes 24 to 33%. Thus, three independent assessments using different groundwater modeling approaches have reached similar conclusions regarding the impact of ethanol on BTEX plumes, namely, that BTEX plumes may be extended 24 to 33%.

A second scenario not evaluated in the Malcolm Pirnie report or the LLNL analysis, but of importance for fully understanding the impact on groundwater of the use of ethanol, is the expected BTEX plume elongation resulting from a release of pure ethanol onto an existing BTEX plume with some residual gasoline containing BTEX in the soil or groundwater. The University of Waterloo has also presented preliminary results from this research at the National Ground Water Association meeting in Houston, Texas, 1999 at the Petroleum Hydrocarbon Conference. The Waterloo model evaluated the effects of increased benzene dissolution, rapid depletion of electron acceptors due to the biodegradation of ethanol, and more rapid ethanol biodegradation rates. The scenario involved a release of pure ethanol onto a 10-year old BTEX release. The results indicate that BTEX plumes could be elongated from 55% to 142%, relative to non-ethanol conditions. The highest BTEX elongation occurred in soil with low organic carbon content, which results in limited retardation of the benzene in the groundwater. Results from Waterloo suggest that BTEX plume elongation will increase as the contact time between the ethanol and BTEX increases, i.e., the longer ethanol remains in contact with the BTEX plume, the more the BTEX plume will elongate.

The results from these evaluations of ethanol's impact on BTEX plumes pose two questions. First, are these predicted BTEX plume extensions significant? Second, are there limitations with these modeling efforts that may underestimate the actual impacts under field conditions? The following presents a list of three factors that have not been addressed in any of the modeling analyses, which could result in BTEX plumes extending beyond what has been predicted in these three modeling studies.

1. Due to the complexity of modeling real systems, all of the models have ignored subsurface heterogeneities, which may prove to be their most significant limitation. Subsurface heterogeneities can result in preferential groundwater pathways, where the impact of ethanol on BTEX compounds is unknown. Similarly, the fate of BTEX compounds in fractured bedrock is likely to change when exposed to ethanol. Under both of these conditions, i.e., preferential pathways and fractured media, groundwater velocities are high and the fraction of organic carbon is low. Under these conditions, the Waterloo results suggest that BTEX plumes could be extended up to 142% of the plume length without ethanol compared to the 30-50% predicted by models that ignore preferential pathways.
2. A second factor that could result in further elongation of BTEX plumes occurs when multiple discrete releases of gasohol occur over several years. Under these conditions, ethanol will be released in pulses to the subsurface over a period of several years and thus, will remain in contact with the BTEX over several years. As the Waterloo results suggest, a long contact time between ethanol and BTEX could lead to increased BTEX plume elongation.

3. Due to the lack of field data to verify modeling, dissolution kinetics of gasoline in groundwater have been estimated from controlled lab, modeling, and limited field experiments. Based on an evaluation of the properties of ethanol, ethanol dissolution should occur very quickly under ideal mixing conditions; however, if dissolution occurs slowly, ethanol will remain in contact with BTEX longer and BTEX plumes may experience greater elongation. A similar issue has been addressed with respect to MTBE. One would expect MTBE to dissolve from the source area rapidly, resulting in detached MTBE plumes. However, in the field, MTBE plumes remain attached to the source for extended periods. Recently, Dr. Bill Rixey at the University of Houston estimated that over 100 pore volumes could be required for complete MTBE dissolution in a heterogeneous source area with minimal groundwater/NAPL interfacial contact. Ethanol is expected to behave similarly to MTBE in heterogeneous environments, and thus, ethanol dissolution may occur over a much longer period than theoretically predicted.

Each of these factors could result in BTEX plumes that are extended beyond their non-ethanol maximum length. The relevant question is whether these elongated BTEX plumes are more likely to impact drinking water wells. We suggest that this issue should be addressed quantitatively by the LLNL study.

In conclusion, there are significant unknowns regarding the real impact of ethanol on BTEX plumes; however, it is generally acknowledged that the use of ethanol in gasoline will extend BTEX plumes. Three independent modeling assessments have consistently concluded that the use of ethanol-blended gasoline will extend BTEX plumes 24 to 33% on average, relative to gasoline without ethanol under presumed homogeneous aquifer conditions. In addition, modeling results at the University of Waterloo suggest that a pure release of ethanol on an existing BTEX plume could extend the BTEX plume up to 142%, relative to non-ethanol conditions. As noted, however, it is likely that release and subsurface factors exist where BTEX plumes could be extended even further. Thus, the use of ethanol in gasoline and the increased transport of pure ethanol are expected to increase the probability of detecting benzene in drinking water wells as well as exacerbating property impact issues. We therefore recommend that LLNL carefully consider the potential impacts of these findings on costs of soil and groundwater cleanup in California, and on the potential for impacts of drinking water wells. The effects of heterogeneous aquifer conditions on BTEX plume lengths in the presence of ethanol should be further evaluated. Finally, the potential impacts on groundwater quality of denaturants that must be added to ethanol should be considered to provide a more comprehensive assessment of the relative merits of ethanol in gasoline compared to other options.

Response: The observation that the various modeling efforts referenced in the comment all indicate approximately the same general results for predicted benzene plume behavior in the presence of ethanol is important. These similar results in spite of the different modeling approaches taken, suggests that there is an important common assumption in the modeling that dominates the results. This common assumption is likely associated with the interaction of biodegradation rates between ethanol and benzene. All the models referenced assume that there is no biodegradation of benzene within the ethanol groundwater plume and that once benzene migrates beyond this

ethanol biodegradation zone, that a constant benzene biodegradation rate can be applied. These assumptions are made because very little is known about the spatial distribution of degradation rates with either ethanol or benzene groundwater plumes.

Because the biodegradation factors may be a dominant factor, it is important to note that, if biodegradation of benzene is later found to be occurring within the ethanol biodegradation zone, or if benzene biodegradation rates are higher at the margins of the benzene groundwater plume, then benzene plumes lengths measured in the field could be much shorter than the referenced modeled predictions.

Fracture flow is very unpredictable and is difficult to compare to a benzene plume in sedimentary porous media. It is important to recognize that the issue of fractured flow raised by the comment is also true for MTBE. The significant difference between benzene and MTBE is that benzene will likely biodegrade in a much shorter period of time compared to MTBE and, thus, will not travel as far through fractured flow as MTBE.

Regarding the dissolution rates of ethanol, if dissolution is slower, then the concentrations of ethanol in the aqueous phase will be very small and will have relatively little effect. There should be almost no cosolvency effect. The impact on biodegradation will depend on how fast the electron acceptors are replenished. It is premature to attempt to quantify the significance of these effects, but a comprehensive modeling study will address some of these concerns.

Regarding the comparative dissolution of MTBE, there are some very different properties between ethanol and MTBE that could result in vastly different dissolution rates. First of all, ethanol is completely miscible with water. This results in a much higher driving force for mass transfer than for MTBE and, therefore, a higher flux. Secondly, preliminary results suggest that free convection is an important mechanism that increases the flux of ethanol from the gasoline to the water. This phenomenon results from the higher density of ethanol than standard gasoline. MTBE, on the other hand, has a density very similar to gasoline and would, therefore, not be subject to this transport mechanism. The net effects of these phenomena are unknown. It might be true that ethanol dissolves slower in a natural setting than in a laboratory column although the differences described above illustrate that we cannot extrapolate the behavior of MTBE to ethanol.

10.2.2. Western States Petroleum Association (WSPA): Comments and LLNL Responses

The Western States Petroleum Association (WSPA), is a nonprofit trade association, representing approximately 30 companies that explore, produce, transport, refine and market petroleum and petroleum products in the six western states.

WSPA has reviewed the eight chapters¹ of Volume 4 prepared by Lawrence Livermore National Laboratory (LLNL) that were posted on the World Wide Web on

¹ Chapters 1-7 were read, as was Chapter 9. At the time of this review, Chapter 8 was not yet available. Once Chapter 8 becomes available, WSPA and other reviewers will need adequate time to provide review and comment.

12/10/99. WSPA has several general concerns regarding these water chapters, and they are as follows:

Cover Letter Comment 1: The Volume is a useful and accurate compilation of the data available to date. However, there are numerous knowledge gaps, uncertainties and data gaps identified in the eight Chapters which we believe need to be addressed. Indeed, in Chapter 9, LLNL lists over 20 significant knowledge gaps identified throughout the Volume. WSPA agrees that these gaps exist, and that additional research is needed to fill them. Collectively, these gaps reflect the uncertainty in many of the water analyses presented in this Volume. WSPA is concerned that ethanol data, in general, is quite limited at this time. WSPA also believes there are additional gaps which were not mentioned in Volume 4, including:

- a. UST compatibility
- b. Distribution system changes required for ethanol
- c. Ethanol remediation & treatment, and
- d. Impacts of benzene plume elongation.

We encourage the State to continue to seek answers to these and other issues. In that regard, WSPA and its members are committed to assist the SWRCB in answering some of these outstanding concerns.

Response: We agree that additional knowledge gaps exist and UST compatibility, distribution system changes required for ethanol, and ethanol remediation and treatment need to be addressed. These are among the issues have not been addressed as part of this evaluation because of time constraints to meet the required report delivery date of December 31, 1999. The evaluation of these would be included in a complete life-cycle analysis.

A preliminary analysis of the impact of possible benzene plume elongation in the presence of ethanol is presented in Chapter 8, which WSPA had not reviewed at the time these comments were prepared.

Cover Letter Comment 2: Not all of the Chapters have a definitive “Conclusion” or “Summary” section. Likewise, there is no executive summary or interpretation of Volume 4 as a whole; we believe this to be a significant oversight. As such, the report does not provide a comprehensive overview of the potential water impacts of extensive ethanol use. As with many reports, the executive summary is the most read section of the report. Not having an executive summary can easily mislead the reader who does not have the time or technical background to review the remainder of the report. Lastly, WSPA requests that the executive summary be available for prior review before its presentation to the Environmental Policy Council.

Response: To facilitate the California Environmental Policy Council’s review of important decision-making information, the summary conclusions and recommendations for further research that normally would be part of individual chapters have been gathered into a separate chapter, Chapter 9, “Critical Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Further Research.”

The Volume 1, *Executive Summary*, has been created using text from the report's technical volumes. This information has been peer reviewed and open for public comment, and no new information has been introduced in the Executive Summary.

Cover Letter Comment 3: Several studies on possible benzene plume length increases due to ethanol usage are discussed, but there is no consideration of the possible impacts of longer benzene plumes. The possible impacts (eg: remediation methodology changes, impacted receptors, altered plume management, legal & policy issues, etc.) must be considered if benzene plumes might indeed become 20-100% longer as the modeling indicates. In addition, it needs to be emphasized in the report that the modeling results should be considered preliminary as they are based on limited laboratory data and not field data.

WSPA believes these concerns are significant and need to be addressed if ethanol is to be used extensively in California for gasoline blending. Specific comments that demonstrate and support the above-listed general concerns are presented in Attachment A. Attachment B is a report recently prepared for WSPA entitled "A Preliminary Evaluation of Ethanol Remediation and Treatment" by Davidson and Creek of Alpine Geophysics. WSPA requests that this report be entered in the record and utilized in the SWRCB studies.

Response: A preliminary analysis of the impact of possible benzene plume elongation in the presence of ethanol is presented in Chapter 8, which WSPA had not reviewed at the time these comments were prepared.

The comment that the modeling results are preliminary and based on laboratory data and not field data is an important one that we agree with. The evaluation of field data will be important to improving the predictive value of future modeling efforts.

Specific WSPA Comments on "Volume 4: Potential Ground and Surface Water Impacts," December 17, 1999

Introduction: WSPA has provided comments on the SWRCB ethanol studies since the initial presentation of the agency's work plans. In extensive written comment (dated 08/24/99), WSPA requested the development of key information, some of which still remains unanswered. A few of those unaddressed issues are briefly reiterated below, but most of our specific comments are new and relate directly to the Volume 4 technical analyses conducted by LLNL and SWRCB. WSPA has focused our comments on major issues and significant data gaps, rather than provide lengthy comments on minor points.

Volume 4, Chapter 2 Comments:

Comment: There is insufficient data (i.e., limited experimental data and extremely limited field data) to fully determine how ethanol will impact several important abiotic subsurface processes.

Comment Explanation: In Chapter 2, the technical review of how ethanol might affect numerous subsurface processes was well done, considering the limited amount of information available. However, there are only a few laboratory studies that directly relate to these ethanol issues, and almost no field studies with which to correlate the

limited experimental data. As such, there is still much uncertainty about how ethanol might impact the subsurface fate and transport of gasoline components (e.g., cosolvency, changes in attenuation capacities of soil, alterations of protective clay layers, etc.). These important subsurface processes need to be understood much better if ethanol is to be used much more extensively for gasoline blending.

Response: This comment is also one of the uncertainties identified in Chapter 9, “Critical Knowledge Gaps Regarding the Ground and Surface Water Impacts of Ethanol-containing Gasoline and Recommendations for Further Research.” We agree that additional field studies clearly are needed.

Volume 4, Chapter 3 Comments:

Comment: Chapter 3 lacks a conclusion section regarding probable ethanol impacts on BTEX biodegradation.

Comment Explanation: The Chapter 3 biodegradation literature review presents several different reasons why BTEX biodegradation will be delayed, slowed, or inhibited in most subsurface locales when ethanol is present. As a result, it seems likely that BTEX plumes will be lengthened to some degree. When the possible BTEX plume-lengthening effects of co-solvency and reduced retardation are also added in, an increase in BTEX plume length and in plume longevity both seem highly likely. Because no summary, or integration, of all these factors is presented, the discussion is not complete.

Response: A screening analysis of the impacts of ethanol biodegradation on plume length are provided in Chapter 4, Screening Model Evaluation of the Effects of Ethanol on Benzene Plume Lengths and the potential impact of increased benzene plume lengths in the presence of ethanol are evaluated in Chapter 8, Screening Analysis of Potential Groundwater Resource Impacts From Gasoline Containing Ethanol.

Volume 4, Chapter 4 Comments:

Comment: The results of LLNL’s modeling effort are not applicable to most ethanol-gasoline spills and most neat ethanol releases.

Comment Explanation: In Chapter 4, the authors present their screening model of how ethanol may impact benzene plume length. Their approach is valid, but only for the narrow set of conditions they model. They did not vary biodegradation rates and they greatly simplified the spatial oxygen deficiency created by the ethanol (i.e., they assumed a high Biological Oxygen Demand due to ethanol degradation only by the source area). Also, only a single spill condition was modeled (an ethanol-gasoline blend release at “less than 3 gallons/day”). As a result, the LLNL modeling results are not applicable to many of the possible release scenarios defined in Chapter 1.

Response: We agree that the screening modeling performed for Chapter 4 is not applicable to many of the possible release scenarios defined in Chapter 1. This release scenario was selected because it is one of the most likely to occur. The other release scenarios have not been addressed as part of this evaluation because of time constraints to meet the required report delivery date of December 31, 1999. The evaluation of these scenarios would be included in a complete life-cycle analysis.

Comment: The LLNL modeling results are not put into context.

Comment Explanation: The LLNL modeling predicted that benzene plumes would get 20% longer (50 feet longer) at the 10-ppb benzene level, and 100% (200–250 feet) longer, when defined at the 1-ppb benzene level. The possible 100% increase in benzene plume lengths (at 1-ppb level) may be the most applicable in California as the benzene MCL is 1-ppb in California. The Chapter should clarify which results of the LLNL modeling effort, and which results of modeling done by others, is most pertinent in California, i.e., the results need to be put into context.

Response: The LLNL model is intended as a screening tool and makes a variety of simplifying assumptions, as does the modeling recently performed by a variety of others. In particular analytical solution treats the dispersion phenomena in a simplistic manner. Caution should be exercised in applying the results of these models too broadly. The screening analysis is for comparative purposes and should not be used for absolute predictions. Predictive analysis pertinent to other release scenarios would likely be part of a more comprehensive life-cycle analysis that we recommend be performed.

Comment: Possible increased benzene plume lengths are not put into context.

Comment Explanation: Several modeling studies on possible benzene plume length increases due to ethanol usage are presented and discussed², and the models predict a 20%–100% increase (i.e., 50–250 feet longer than non-ethanol gasoline). The general agreement among the models is promising, but these modeling efforts must be considered preliminary as none could be verified against field data. The significance of the possible (probable) increased benzene plume lengths is not put into context or summarized.

Response: Chapter 8, “Screening Analysis of Potential Groundwater Resource Impacts from Gasoline Containing Ethanol or MTBE,” which WSPA had not reviewed at the time these comments were prepared, places possible increased benzene plume lengths in to context from a resource impact perspective.

Volume 4, Chapter 5 Comments:

Comment: The ethanol concentrations predicted to occur in urban precipitation (37–64 (g/L) imply a strong need for more in-depth research on this topic.

Comment Explanation: Modeling of air in the Los Angeles basin indicates that ethanol concentrations in precipitation could reach 37–64 (g/L. Although it appears that the methods and assumptions used for this analysis are reasonable, it is a preliminary analysis. This important issue requires more in-depth study under a wider variety of conditions, and with temperature-specific Henry’s Constants.

Response: We strongly agree with this point and recommendation.

² Another pertinent study has recently been released: Molson, John W., James F. Barker, Mario Schirmer, and Emil O. Frind, 1999. Modeling the Impact of Ethanol on the Persistence of BTEX Compounds in Gasoline-Contaminated Groundwater, DRAFT, National Water, Resource Institute, Fountain, Valley, CA, 64 pages. That modeling study found generally similar results, but by considering more variables and more different spill scenarios, Molson et al. (1999) predicted that in a few cases, benzene plume lengths could increase significantly more.

Comment: The results of the surface water spill modeling are not well described in the text.

Comment Explanation: After modeling a surface water release of ethanol, Chapter 5 described the impacts as being limited to “immediately downstream.” However, this conflicts with the accompanying graphs that appear to indicate that toxic levels will reach 27 to 33 km downstream. A revised or more detailed discussion is needed of ethanol fate in rivers and streams. In addition, it’s not clear how the fate of ethanol (as predicted by the model) compares to that of other compounds, like MTBE. As such, it’s difficult to judge the significance of the results for ethanol.

Response: To address this comment we have modified the text in Section 5.4.2 to describe the potential extent of downstream toxicity from a catastrophic spill of ethanol.

Volume 4, Chapter 8 Comments:

Comment: Not Reviewed - At the time of this review, Chapter 8 was not yet available.

Response: Chapter 8 was available December 17, 1998.

Volume 4, Chapter 9 Comments:

Comments & Explanations: WSPA agrees with the gaps identified, but WSPA believes there are additional knowledge/data gaps that were not mentioned. Specifically:

- UST Compatibility - This issue was only mentioned briefly in Table 1-1 of Volume 4, and yet it is a critical topic if ethanol-gasoline releases are to be avoided/minimized.
- Distribution System Changes Required for Ethanol - There are numerous procedures that are needed to adapt the gasoline transport, storage and distribution systems (i.e., pipelines and USTs) for ethanol-blended gasoline. These issues, and their costs, should be recognized.
- Ethanol Remediation and Treatment - Volume 4 did not discuss the remediation or treatment of ethanol, whether from a neat ethanol spill, or from a release of ethanol-blended gasoline. To start discussion of this important topic, WSPA has had a preliminary ethanol remediation report prepared³ (see Davidson and Creek, 1999 in Attachment B).

³ In Davidson and Creek (1999), several technologies commonly used at gasoline spill sites were evaluated to determine how effective they would be for remediating ethanol-impacted sites and for treating ethanol-impacted water and soil. The report concluded:

- At the present time, there is very little monitoring, remediation, or treatment data available for ethanol.
- Based on ethanol’s physiochemical properties, and upon the reviewed technologies’ performance on gasoline compounds, the following technologies are expected to be effective for remediating subsurface ethanol contamination: ground-water extraction (for plume control); soil vapor extraction; enhanced bioremediation; and, monitored natural attenuation.
- Biotreatment and advanced oxidation process are both expected to be effective for above-ground treatment of ethanol-impacted water. Conversely, the more common water treatment methods of air stripping and granulated activated carbon are not expected to be effective for ethanol.

- Impacts of Benzene Plume Elongation - Ethanol's presence might make addressing ethanol-enriched gasoline spills more complex or costly if the longer benzene/BTEX plumes mandate a technology change (eg: make natural attenuation less applicable), complicate plume management (as the plume expands), raise costs (due to the plume's greater size and volume), or increase the chances of benzene/BTEX impacting a receptor.

Response: We agree that additional knowledge gaps exist and underground storage tank compatibility, distribution system changes required for ethanol, and ethanol remediation and treatment need to be addressed. These are among the issues have not been addressed as part of this evaluation because of time constraints to meet the required report delivery date of December 31, 1999. The evaluation of these would be included in a complete life-cycle analysis.

A preliminary analysis of the impact of possible benzene plume elongation in the presence of ethanol is presented in Chapter 8, which WSPA had not reviewed at the time these comments were prepared.

-
- The most effective above-ground technologies for treating ethanol-impacted soils are expected to be biotreatment and thermal desorption.
 - Until greater fate and transport knowledge of ethanol-gasoline mixtures is obtained, the remediation and treatment of ethanol-gasoline mixtures are difficult to evaluate in detail.

Davidson, James M. and Daniel N. Creek, 1999. A Preliminary Evaluation of Ethanol Remediation and Treatment, prepared for Western States Petroleum Association, Sacramento, CA, 36 pages.

