EXPLORING THE ENVIRONMENTAL ISSUES OF MOBILE, RECALCITRANT COMPOUNDS IN GASOLINE

Organized by

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(Pages 225-228 in *Preprints of Extended Abstracts*, Vol. 40 No. 1)

Symposia Papers Presented Before the Division of Environmental Chemistry
American Chemical Society
San Francisco, CA March 26-30, 2000

EXTENSIVE DATABASE FROM OVER 500 SITES AND THREE YEARS ALLOWS EXAMINATION AND INTERPRETATION OF GROUNDWATER MTBE PLUMES IN SOUTHERN CALIFORNIA

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Summary
A unique regulator's tool in the form of a database has been developed which allows sorting, analysis and pinpointing of particular situations (i.e., high MtBE without benzene, rapid declines from high levels of MtBE). The Santa Ana Regional Water Quality Control Board has created an extensive database containing mainly groundwater concentration data. The database includes over 44,000 groundwater samples containing data from over 5300 wells from approximately 500 sites with two-thirds containing groundwater elevations and depths to water. Some groundwater treatment data, significant vapor extraction data containing amount removed and duration of vapor extraction, with some soil concentrations, are also part of the database. The vapor extraction data is useful to estimate the typical amounts of contamination removed and gives a feel for the elusive “volume of release” by comparison to the in situ concentrations. The database has the ability to create maps which show the proximity of UST sites and municipal wells within cities.

The data was analyzed in terms of frequency distribution of total petroleum hydrocarbons, benzene, toluene, ethylbenzene, total xylenes with emphasis on MtBE, on a quarterly basis. Some of the findings of quarterly breakdown concentrations of MtBE in groundwater shows the median concentrations increase over a three year period (1996 through 1998). The system increase in MtBE concentrations are consistent over all concentration ranges (10 to 100,000 ug/L). A site-specific analysis reveals a direct relationship between MtBE concentrations with water table elevation over a three year

period. A comprehensive comparative study of MtBE concentration determination by EPA Methods 8020/8021 and 8260/8260A reveals several problems with EPA Method 8020/8021.

Introduction

The persistence of MtBE in the subsurface continues to be a much talked about and very curious issue in groundwater science. This paper gives an update on several important matters related to MtBE in the environment by querying a recently developed database by The Santa Ana Regional Water Quality Control Board (SARWQCB) in Riverside, California. This comprehensive database has allowed many regulatory authorities in Southern California to assess several important aspects of MtBE release into the subsurface, with specific interest on its persistence in groundwater systems.

Median Values of Regional MTBE Groundwater Concentrations Increasing

In order to assess the long term impacts of MtBE in groundwater systems, the database developed by SARWQCB was utilized to assess certain behavior of MtBE over a three year period. Although the "length" of MtBE plumes has been the focus of many recent studies and papers (Keller, et al, 1998), our focus is on the persistence. Figure 1 is a plot of the median MtBE concentration in groundwater wells located primarily in Orange County, California for a three-year period (1996 through 1998). The plotted concentrations were obtained from a varying number sites which contained MtBE in groundwater wells and the median of concentration at each site in each quarter was calculated from the database. In order to be eligible for median analysis, at least one groundwater well on a site must have contained MtBE. Table 1 shows the number of sites in each quarter used in the calculations.

Table 1. Number of Sites in Each Quarter, Southern California (Region 8) 1996-1998

Quarter	1996	1997	1998
1	233	357	347
2	324	382	328
3	372	347	301
4	343	325	241

The trend in the data increases from approximately 250 ug/L in the first quarter of 1996 to 2000 ug/L in the fourth-quarter of 1998. This represents an increase in the median value of eight times in a three-year period. The next question is why. Odencrantz(1998) hypothesized a seasonal trend of 50th percentile MtBE in groundwater wells in Orange County due to an apparent lag from the high MtBE load period (summer) showing up in the wells in the winter months. The conclusion reached in that paper should be modified greatly to state that MtBE concentrations in groundwater wells are simply increasing at a steady rate. Of course, as more attention is drawn towards the problems associated with MtBE, our understanding and analysis is also better. For example, our analytical methodology is better. The number of sites with MtBE in wells is increasing. This may be true, however, MtBE is migrating further at numerous sites and is simply

showing up in more wells in larger concentrations.

Effect of Water Table Fluctuations-Site Specific Case

Figure 2 is a plot of MtBE (and benzene, toluene, ethylene and total xylenes, BTEX) concentration in groundwater with the water table elevation for a period of approximately three years. There is a clear trend of increasing MtBE concentrations with a rising water table. The explanation is quite simple, as the water table rises close to a source in soil, there is more contact and the concentrations increase. In our particular example, we have chosen a site where the well with the highest concentration is relatively close to the source area. There is an apparent biologically active zone located close to the source area as evidenced by the low BTEX constituents. This behavior was seen at numerous sites with fairly shallow water tables (less than fifty feet below ground surface).

Analytical Methods for MtBE Determination

Figure 3 is a plot of over 500 MtBE concentration pair in groundwater by EPA Methods 8020 and 8260. EPA Method 8020 is a gas chromatographic technique utilizing a photoionization detector and EPA Method 8260 is a gas chromatographic technique with utilizes mass spectroscopy detection. This plot provides a comparison relationship by examining the distributuion of points of MtBE concentrations by EPA Methods 8020 and 8260 about the one to one line. Note the large concentration of points below the line depicted on the graph. It is obvious that there is a large discrepancy between concentrations determined by Method 8020 and 8260 especially in a key region of interest of 100 to 5000 ppb (ug/L), which entirely supports the possibility of false positive reporting by EPA Method 8020. One point in particular shows ~1000 ppb (ug/L) by Method 8020 and ~0.7 ppb (ug/L) by Method 8260 or an exaggeration of over 1400. The actual concentration of MtBE of 0.7 ppb by EPA Method 8260 falls far below the low risk level of 25 to 35 ppb. PID methods are subject to interference from the hydrocarbons present in gasoline. Second column confirmation can also produce false positives due to the many different constituents of gasoline.

Conclusions

This paper summarizes several important findings from data compiled by The Santa Ana Regional Water Quality Control Board in Riverside, California. The developed database can be used by regulators to establish regions of high risk of MtBE contamination close to drinking water wells and to establish trends in the data set. A snapshot of certain items of interest was undertaken to gain insight on MtBE fate and transport, persistence and analytical concerns. First, the median values of MtBE in groundwater wells over a three year period has increased eight times from 1996 through 1998. Second, a site-specific analysis of a site in Irvine, California reveals a direct relationship between the water table elevation and MtBE concentrations in groundwater near the source with fairly shallow water tables. Thirdly, there are obvious problems associated with the use of EPA Method 8020 for the estimation of MtBE concentration in groundwater. EPA Method 8260 is a far more reliable method of analysis.

References

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Keller, A, J. Froines, C. Koshland, J. Reuter, I. Suffet, and J. Last. 1998*. "Health & Environmental Assessment of MtBE"*. Volumes I though V, University of California, Davis and UC Toxic Substances Research & Teaching Program.

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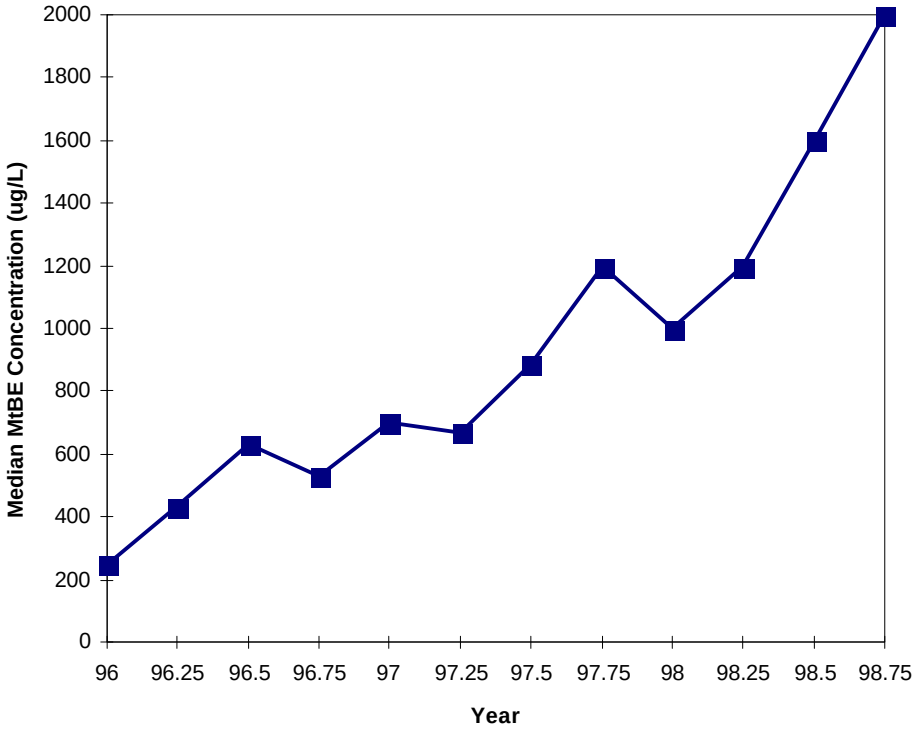

Figure 1. Rise in Median MtBE Groundwater Wells in Southern California (Orange County), 1996-1998

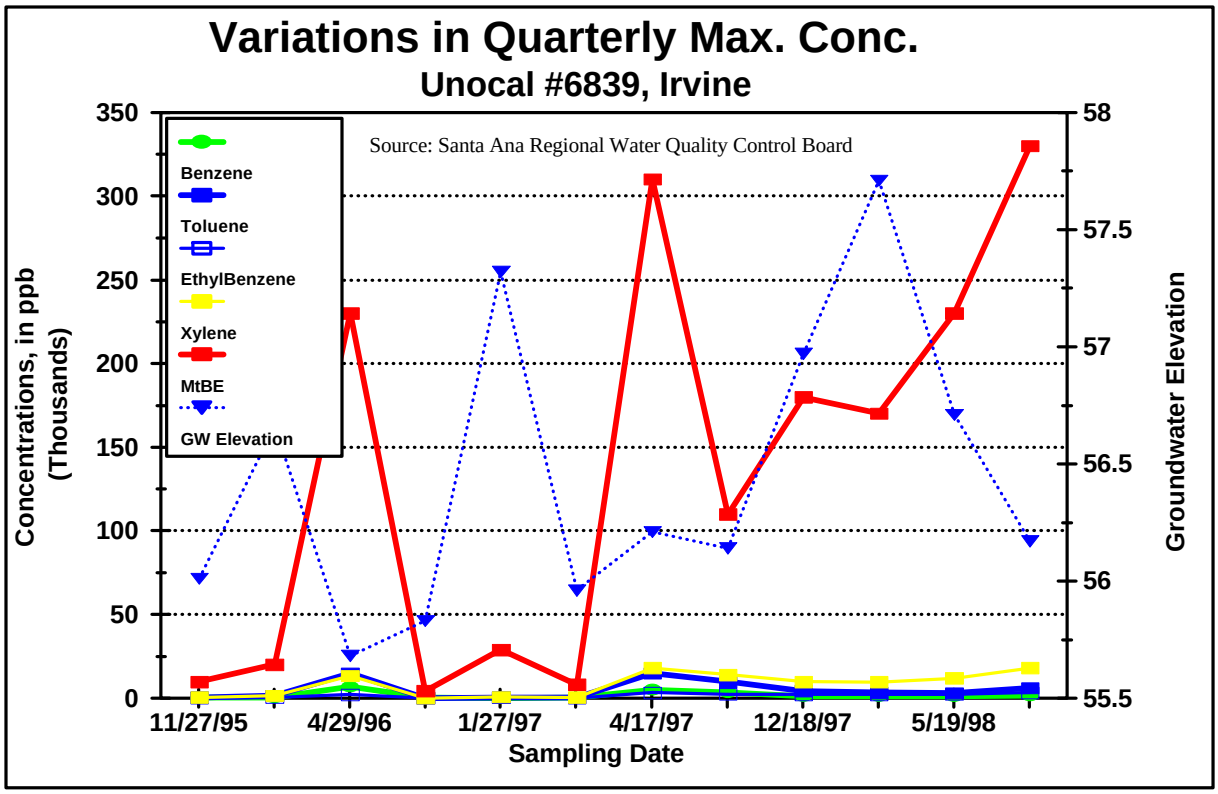

Figure 2. Influence of Water Table Fluctuations and MtBE Concentrations in Groundwater, Irvine, California.

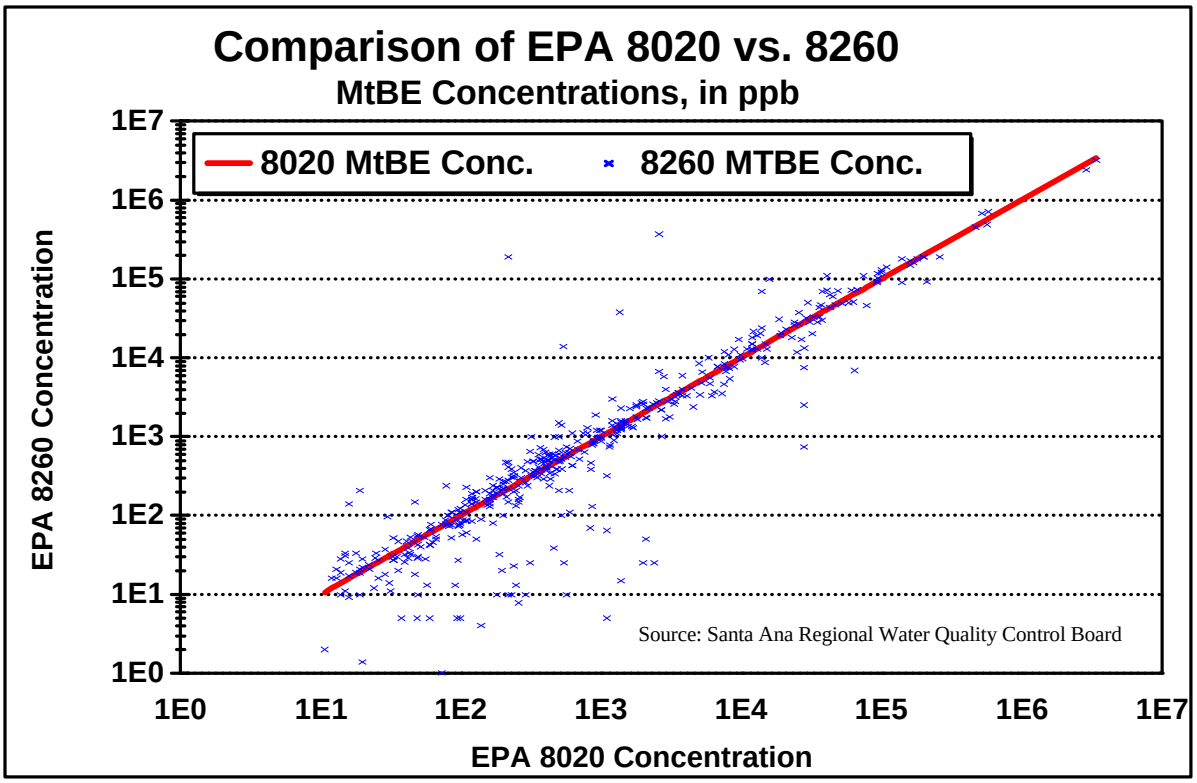

Figure 3. Laboratory Data Illustrating the Relationship Between Reported MtBE Concentration in Groundwater By Methods 8020 and 8260 (pair analysis).