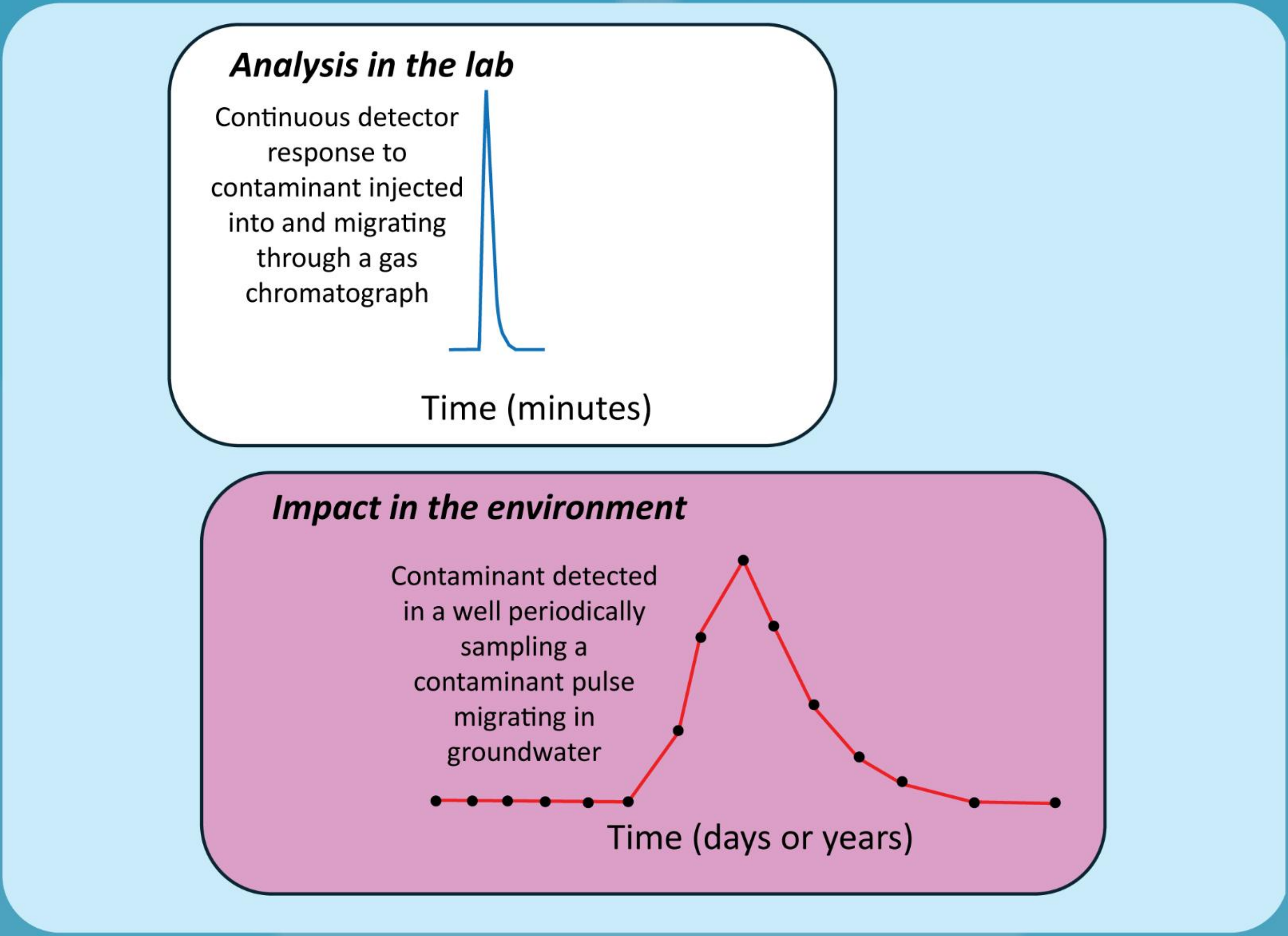

Estimating the Release Date of MTBE: A Case Study

Douglas M. Mackay

THE GROUNDWATER PROJECT

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Dedication

To Gary D. Hopkins, formerly of Stanford University, who taught me many things early in my career, including some quirks of gas chromatography. Gary seemed to know something about almost everything and was an absolutely crucial research collaborator on numerous field experiments addressing groundwater contamination and remediation. With no formal education beyond a B.S., he mentored and influenced a large number of students, post-doctoral researchers, staff, and faculty at Stanford University and the University of Waterloo. I found him a delight to work with and miss him greatly.

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The Groundwater Project Foreword

The United Nations (UN)-Water Summit on Groundwater, held from 7 to 8 December 2022, at the UNESCO headquarters in Paris, France, concluded with a call for governments and other stakeholders to scale up their efforts to better manage groundwater. The intent of the call to action was to inform relevant discussions at the UN 2023 Water Conference held from 22 to 24 March 2023 at the UN headquarters in New York City. One of the required actions is *strengthening human and institutional capacity*, for which groundwater education is fundamental.

The UN-Water website↗ states that *more than three billion people worldwide depend on water that crosses national borders*. There are 592 transboundary aquifers, yet most do not have an intergovernmental cooperation agreement in place for sharing and managing the aquifer. Moreover, while groundwater plays a key role in global stability and prosperity, it also makes up 99 percent of all liquid freshwater—accordingly, groundwater is at the heart of the freshwater crisis. *Groundwater is an invaluable resource*.

The Groundwater Project (GW-Project), a registered Canadian charity founded in 2018, pioneers in advancing understanding of groundwater and, thus, enables *building the human capacity for the development and management of groundwater*. The GW-Project is not government funded and relies on donations from individuals, organizations, and companies. The GW-Project creates and publishes high-quality books about *all-things-groundwater* that are scientifically significant and/or relevant to societal and ecological needs. Our books synthesize knowledge, are rigorously peer reviewed and translated into many languages. Groundwater is 'hidden' and, therefore, our books have a strong emphasis on visualizations essential to support the spatial thinking and conceptualization in space and time of processes, problems, and solutions. Based on *our philosophy that high quality groundwater knowledge should be accessible to everyone*, The GW-Project provides all publications for free.

The GW-Project embodies a new type of global educational endeavor made possible by the contributions of a dedicated international group of over 1000 volunteer professionals from a broad range of disciplines, and from 70 countries on six continents. Academics, practitioners, and retirees contribute by writing and/or reviewing books aimed at diverse levels of readers including children, youth, undergraduate and graduate students, groundwater professionals, and the general public.

The GW-Project started publishing books in August 2020; by the end of 2024, we have published 55 original books and 77 translations (55 languages). Revised editions of the books are published from time to time. In 2024, interactive groundwater education tools and groundwater videos were added to our website, gw-project.org↗.

We thank our individual and corporate sponsors for their ongoing financial support. Please consider sponsoring the GW-Project so we can continue to publish books free of charge.

The Groundwater Project *Board of Directors*, January 2025

Foreword

Estimating the Release Date of MTBE: A Case Study, is a groundwater detective story with a plot that is frequently encountered by contaminant hydrogeologists in their day-to-day work. As the story goes, contamination is found in the groundwater beneath a property and the current property owner accuses the previous owner of causing the leak in or to avoid responsibility for remediation of the contamination.

In response, hydrogeologic consultants for both parties collect diverse forms of data from the site and, eventually, an independent expert is asked to examine all of the data and render an opinion on who is responsible, the existing or the previous owner. The backstory at all such sites has common features such as 1) a shallow aquifer separated to some degree from a deeper aquifer by a low permeability layer and 2) the contaminant is MTBE, an additive included in gasoline decades ago. The timing of the evidence and the hydrogeological circumstances are important to the conclusion.

As it turns out, like all good stories, guilt is recognized without doubt once the meaning of the data becomes clear, but like all good mysteries, the detective, who has much experience with such cases, has to recognize subtle clues and distill meaning from multiple forms of evidence. For those who know little about what contaminant hydrogeologists do in their work, solving mysteries by examining multiple limes of diverse evidence is a common activity. The author of this book, Dr. Douglas Mackay, is an adjunct professor emeritus at the University of California, Davis, who is the lead author on another GW-Project book, *Properties of Organic Contaminants*↗, that is recommended background reading for this case study.

John Cherry, The Groundwater Project Leader

Guelph, Ontario, Canada, June 2025

Preface

This case study addresses a groundwater plume containing methyl *tert*-butyl ether (also called methyl *tertiary*-butyl ether, or MTBE). Starting in 1979, in some parts of the United States, MTBE was added to gasoline to increase its oxygen content, prevent engine-knocking, reduce emissions from combustion, and improve air quality. In other parts of the country, MTBE addition to gasoline did not occur until the mid-to-late 1980s. Unfortunately, studies showed that when MTBE-amended gasoline or its vapors contacted groundwater, MTBE dissolved readily into the water and its high mobility could lead to the creation of long plumes of contaminated water (e.g., Mackay et al., 2001; Smith et al., 2005). Initially, it was thought that MTBE was resistant to degradation during groundwater transport. So, there were dire predictions about the long-term impacts of MTBE plumes from the many gasoline service stations nationwide (e.g., Johnson et al., 2000). Hundreds of millions of dollars were spent to settle lawsuits claiming current and future damages and demanding remediation (e.g., Attorney General of NJ, n.d.; SL Environmental Law Group, n.d.). Also, at the height of the concern about MTBE, it was estimated that remediation costs for public water supplies could run from 4 billion to 85 billion USD (AWWA, 2005). However, ongoing research showed that MTBE could degrade *in situ*, in some cases yielding *tert*-butyl alcohol (TBA) as an intermediate, which itself proved to be degradable *in situ* (Landmeyer et al., 2010; Mackay et al., 2001; Wilson et al., 2002). These and other studies led to the conclusion that MTBE impacts on public water supplies had peaked by the early 2000s and were declining thereafter (McHugh et al., 2014). MTBE addition to gasoline was phased out in 2005 due to all the problems that had been encountered and to the change in USA regulations leading to the use of ethanol as a gasoline oxygenate (EPA, 2025).

The MTBE plume addressed in this case study had been migrating for years from beneath the site of a fuel service station that had been sold to a new owner in the mid-1980s. The new owner alleged that the MTBE originated from the station prior to its sale to them and thus the monitoring and cleanup was the responsibility of the former owner. In 2001, I was asked by the prior owners' lawyers to review a variety of reports by consultants and others and render an opinion about the timing of the release of MTBE-containing fuel to the subsurface. The available data and various calculations allowed me to conclude that the release had occurred after the sale of the service station. In this document, I summarize the steps taken to make that conclusion. Two of the key steps were studies of the time when peak concentration of contaminants occurred. These were: 1) peaks in early gas chromatography results for analysis of shallow water samples, and 2) peaks in MTBE concentrations over time at wells. The timing of these peaks tell a compelling story.

Acknowledgments

I deeply appreciate the thorough and useful reviews of and contributions to this book by the following individuals:

- Ray Carter, Environmental Engineering Lead at Syngenta, Manitoba, Canada;
- Mike Sklash, Senior Hydrogeologist, Dragun Corporation, Ontario, Canada; and,
- Murray Einarson, Service Leader Contaminated Site Management, Haley & Aldrich, Massachusetts, USA.

I am grateful to Amanda Sills for her oversight and many comments and Kathy Hamilton and others of the Formatting Team of the Groundwater Project for their insightful copyediting of this book. I thank Eileen Poeter (Colorado School of Mines, Golden, Colorado, USA) for reviewing, editing, and producing this book.

The sources of figures and/or tables are cited in their captions. Where a citation does not appear, the figures and/or tables are original to this book.

1 Overview

This case study pertains to MTBE in a groundwater plume that migrated from beneath a fuel service station. Figure 1 presents my simplification of details of the site infrastructure, the stratigraphy assumed by the site's consultants, and results of monitoring selected shallow and deeper wells. To maintain confidentiality, I do not cite the original documents herein nor provide details that would indicate the location of the site. In the area, there is significant rain and snowfall and the subsurface within the depth interval of interest to this study is composed of sand and gravel, glacial till, and fine-grained lacustrine deposits, which consultants assumed were layered within the depth interval of interest as shown in Figure 1. The water table in the upper sand is approximately 3.5 ft (1.1 m) below ground surface (bgs) most of the year. The site is approximately 1000 ft (304 m) from a large lake (to the right in Figure 1). The lake surface is approximately 50 ft (15 m) below the site's ground surface.

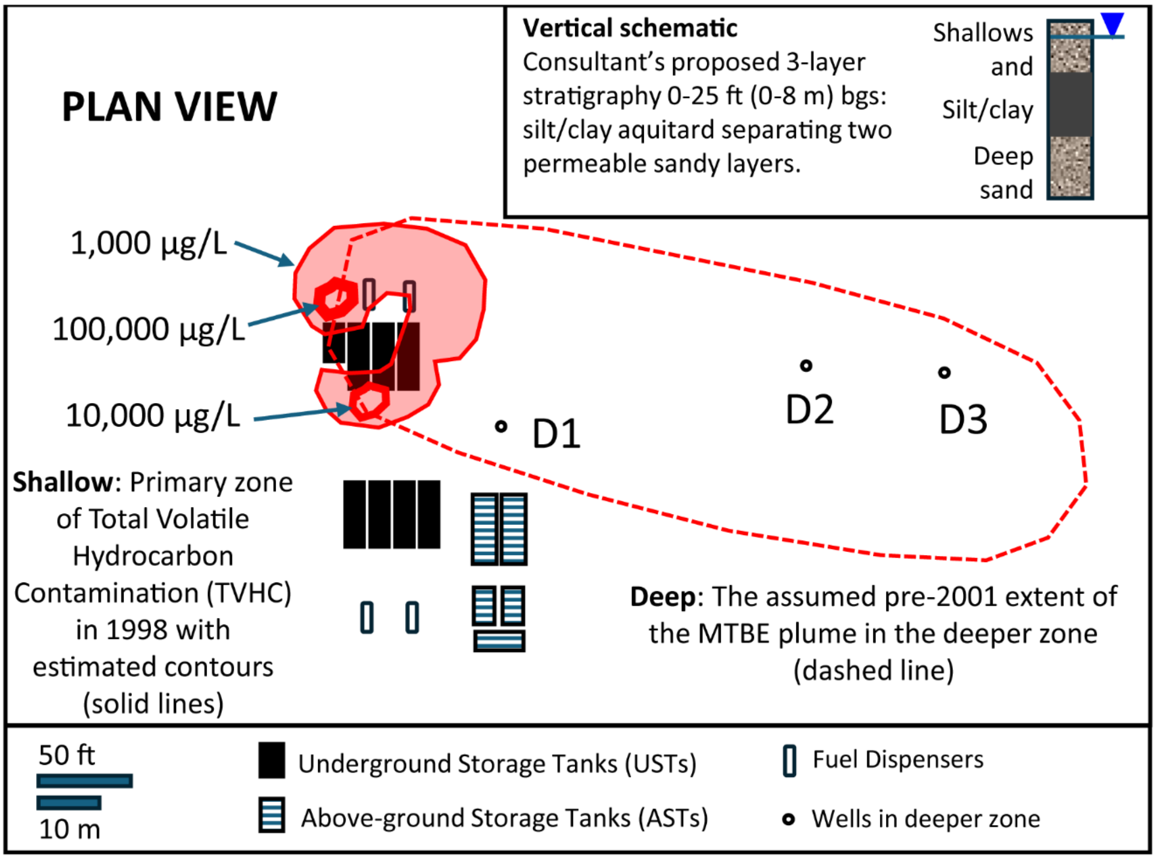


Figure 1 - Layout of the site facilities, results of shallow total volatile hydrocarbon (TVHC) groundwater monitoring in 1998, locations of 3 wells (D1, D2, D3) in what was called the deeper zone, and my hypothesis for the extent of the deeper zone impacted by MTBE in 2001, when I conducted analyses in this case study. I do not have information on the construction dates of the three indicated wells, nor any deep zone monitoring data that may have been available in 1998 when the shallow spill was evaluated. The inset shows the layering assumed by the consultants to the new owners (a shallow permeable layer and a deeper permeable layer separated by a layer of less permeable media) and the approximate water table during most of the year.

The service station had been operated for years by one owner but was sold to a new owner in the mid-1980s. By 2001, when I conducted this study, the plume in the deeper permeable zone—with its assumed extent denoted by the dashed red line in Figure 1—contained methyl *tert*-butyl ether (MTBE) and hydrocarbons (e.g., benzene (B), toluene (T), ethylbenzene (E), and xylene (X), also called BTEX). The new owner alleged that they had not spilled MTBE-containing fuel and that the MTBE plume originated from the station prior to its sale to them; thus, the plume was the responsibility of the former owner. Figure 1 shows the results of shallow monitoring in 1998 which allowed the contractor to draw contours of total volatile hydrocarbon (TVHC) contamination.

I was hired in 2001 by the former owner to review the case and provide an opinion regarding the timing of the MTBE release(s) that created the contested groundwater plume. For reasons described in this case study, I concluded that the release of MTBE-containing fuel that created the contested groundwater plume occurred after the sale of the service station. In this write-up, I have presented some of the arguments in ways different from my original 2001 report.

If MTBE contamination detected in the subsurface arose solely from the operations of the new owner after their mid-1980s purchase, then the following must be true.

1. MTBE was not released to the subsurface at the site by the prior owners during the time the site was owned by them.
2. One or more releases of MTBE to the environment occurred after the beginning of the operations by the new owner.
3. The MTBE released after initiation of the new owner's operations could migrate fast enough to reach the wells where it was eventually detected.

Each of these items is considered in the subsequent three sections of this book.

2 MTBE Was Not Released to the Subsurface by the Former Owner

The evidence that MTBE was not released to the subsurface by the former owner had been collected by others and summarized verbally for me. Sales/delivery records and testimony showed conclusively that MTBE or MTBE-containing products were never transported to, stored at, or sold at the property during the time period it was operated by the former owner. Although MTBE addition to gasoline had begun in 1979 throughout various locations around the United States, it was reportedly not included in gasoline delivered to the study area, which was a relatively rural location far from the locations of early use of MTBE.

3 MTBE Was Released by the New Owner

As summarized in Box 1↴, there are many general arguments that suggest it is highly likely that the new owner received, stored, sold, and had leaks of products containing MTBE. Of more interest to us are the specific pieces of evidence that prove they did. All of this was derived from careful interpretation of peaks in shallow groundwater monitoring data.

The evidence that the new owner released MTBE-amended gasoline to the subsurface was, in effect, hidden in a report issued in the spring of 1998 by a leak detection contractor addressing their shallow groundwater investigation. The contractor did not report MTBE detections. However, an examination of their analytical results suggests that they had detected MTBE but did not realize it, or they perhaps chose not to report it. The fact that they conducted the shallow groundwater investigation suggests there were concerns about fuel leaks. In 1998, twenty-five groundwater samples were collected from 4 ft (1.2 m) below ground surface (just below the water table) in and around the service station. Samples were analyzed by the new owner's contractor using a gas chromatograph (GC) equipped with a flame ionization detector (FID). Figure 1 presents the contours of TVHC (results estimated by the contractor in what was referred to as the shallow zone. Because contours can be misleading, I note the following:

- within the 1000 μg/L contour, there were many detections of compounds with Total Volatile Hydrocarbon (TVHC) values reported to be in the range 25,000 to 75,000 μg/L;
- the one sample taken within the 100,000 μg/L contour was reported as 690,000 μg/L; and
- the one sample within the 10,000 μg/L contour was reported as 51,000 μg/L.

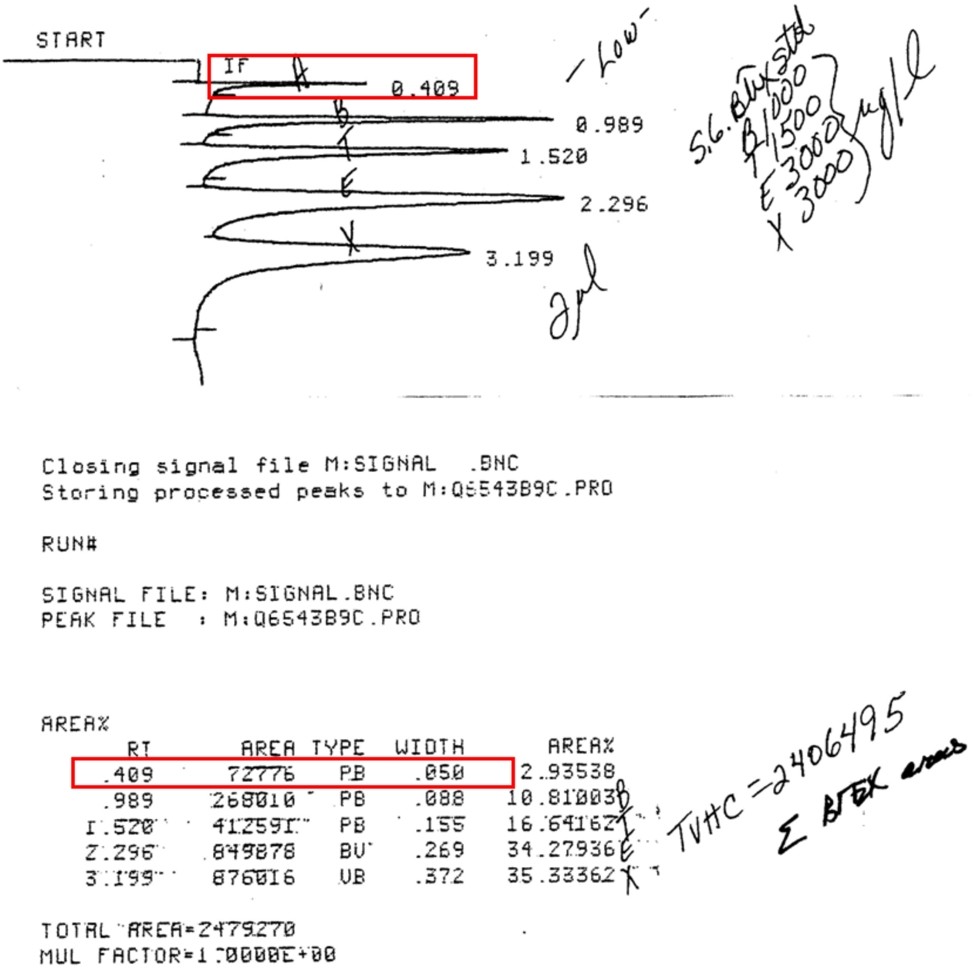
To understand what these reported concentrations mean, it is necessary to consider how their analytical method worked. Box 2↴ describes the basic components of a GC like the one they used and the features of the printed output it created for each analytical run, to which I had access.

The contractor collected groundwater samples in 40 mL glass vials, decanted half, and shook the capped vial to allow time for equilibrium to be approached for volatilization of the chemicals into the air-filled headspace. Then, a small sample of the headspace from the container was collected by syringe and injected into their GC. As indicated in Figure Box 2-1, the gas from the syringe became mixed into the flow of carrier gas, which flowed through the GC's column and then through the FID. The FID responses were recorded by an integrator that printed a chromatogram depicting the arrival time, shape, magnitude, and area of each peak for chemicals collected from the headspace and detectable by the FID. Since chemicals pass through the column at different rates (as shown by Figure Box 2-2), they were identified by the time it took for them to pass through the column, which is called their "retention time," or RT.

To calibrate their GC, the analyst injected 2 μL of headspace in equilibrium with a standard solution containing known amounts of known analytes. Figure 2 is a chromatogram created in 1998 for analysis of a standard. The elution of the peaks is shown at the top (in this old chromatogram, elution time increases from top to bottom, and peaks rise from left to right). Data from the integrator is shown in a table at the bottom (RT, peak area, peak type, peak width, and % of total area of all peaks). Here we ignore peak type and width. Figure 2 also shows the contractor's notations and one that I added.

- At the top right, the contractor noted the known composition of the standard, containing benzene (B), toluene (T), ethylbenzene (E), and xylene (X), referred to as BTEX, in μg/L.
- At the bottom right, the contractor wrote "TVHC=2406495" which means the Total Volatile Hydrocarbon—or for this analysis—the sum of the peak areas for B, T, E, and X printed by the analytical system in the second column of the table below the graph.
- I added one handwritten notation ("Σ BTEX areas" in bolder ink), meaning I'd checked that their notation of TVHC was the sum of the peak areas of the reported peak areas of benzene, toluene, ethylbenzene, and xylene.
- The integrator calculated the percent of the total area under each peak and listed that in the fifth column of the table at the bottom. The peak area is proportional to the mass of analyte, the ratio referred to as a response factor. Typically, the response factors for the BTEX compounds are nearly equal, so the peak area for benzene (1000 μg/L in the standard) is about two thirds of the peak area for toluene (since it was 1500 μg/L in the standard) and one third of the peak areas of ethylbenzene and xylene (since they were 3000 μg/L in the standard).

The peak they hand-labeled "A," which is enclosed in a red box in the figure, was not included in their handwritten calculation of TVHC. That peak, which accounted for only 3% of the total of all peak areas, could have been a response to the carrier gas, or an unknown chemical—or to a group of unknown chemicals that moved at the same rate through the GC system.



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RUN#

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     .989     268010   PB    .088    10.81003
    1.520     412591   PB    .155    16.64162
    2.296     849878   BV    .269    34.27936
    3.199     876016   VB    .372    35.33362

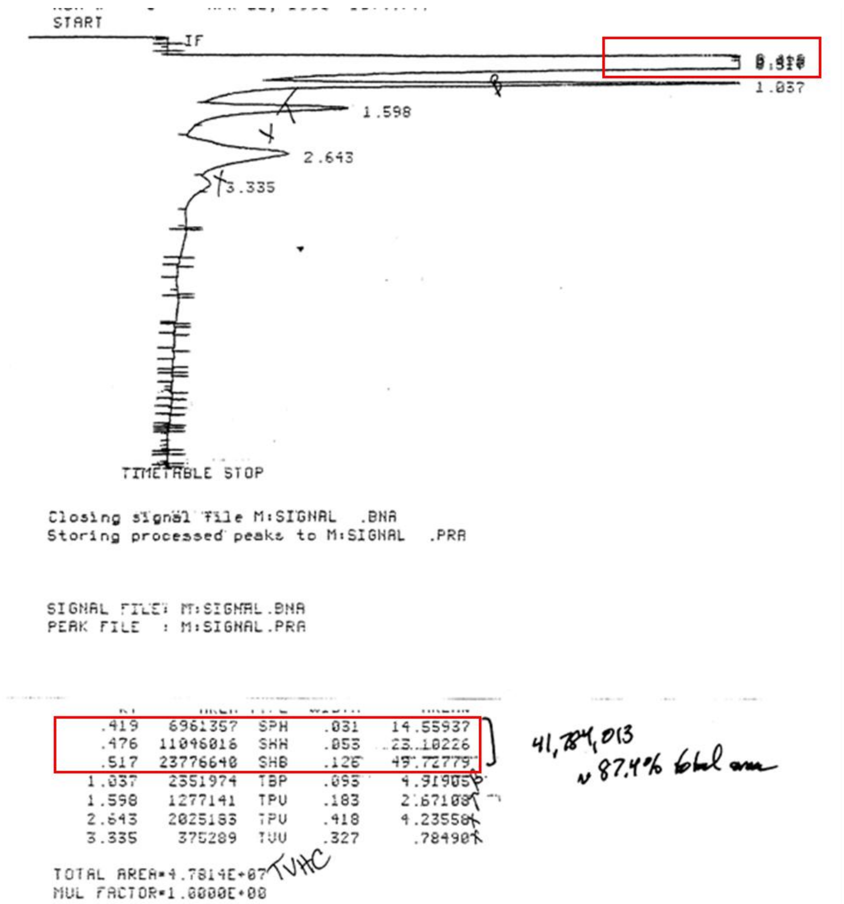
TOTAL AREA=2479270
MUL FACTOR=1.0000E+00
```

Figure 2 - Example of a chromatogram for a calibration standard analyzed in 1998. An unidentified peak occurred at RT 0.409 minutes in the red rectangle. As handwritten on the printout, 2 μL of the headspace was injected.

The early peak labeled "A" in Figure 2 has an RT of 0.409 minutes. There was no discussion in the contractor's report as to the identity of the compound or compounds that were detected and subsequently labeled as "A."

The chromatogram in Figure 2 shows that xylene was the last analyte to elute at about three minutes. This very short run time is desirable if many samples must be run in succession. However, the unidentified peak "A" may have roughly the same RT as other potentially important compounds present in the environmental samples but not present in the standards. Standards should contain all compounds of potential interest, so that their RTs can be determined and chromatography conditions changed if one or more are found to have the same or very similar RT as the presumably unimportant background peak or other compounds of concern. An example of the need to alter GC conditions to allow separation of peaks is discussed in Box 3↴. The site contractor had not included MTBE in their calibration standard. Therefore, they could not have optimized the GC settings to make sure MTBE's peak arrived later than, and could be distinguished from, the mystery peak at about 0.4 minutes. This could have been accomplished by adjusting the column temperature if MTBE had been included in the standard.

The contractor did not ignore the peak at an RT of about 0.4 minutes in the analyses of the shallow groundwater samples from the site since it was often very large compared to BTEX peaks. Instead, as shown in Figure 3, they considered the early peak (actually three peaks very close together) to be included in the group they called TVHC, including hydrocarbons with 1 to 9 carbon atoms, sometimes denoted as TVHC (C1C9).



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Storing processed peaks to M:SIGNAL  .PRA


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PEAK FILE  : M:SIGNAL.PRA


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   .476  11046016  SHH    .053    23.10226
   .517  23776640  SHB    .126    49.72779
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  1.598   1277141  TPU    .183     2.67108
  2.643   2025183  TPU    .418     4.23558
  3.335    375289  TUU    .327      .78490

TOTAL AREA=4.7814E+07
MUL FACTOR=1.0000E+00
```

41,784,013
~87.4% total area

TVHC

Figure 3 - Example of a chromatogram from analysis of an environmental sample taken near a fuel dispenser at the site in 1998. In this sample BTEX compounds were detected, but three much larger peaks were noted at RTs under 0.5 minutes. As discussed in the text, one of those early peaks was almost certainly MTBE. The others may have been low molecular weight hydrocarbons present in gasoline (e.g., butane, pentane). Although not handwritten on the excerpt of the GC's printout shown here, the original noted 50 µL of the headspace had been injected. I believe the analyst mislabeled the ethylbenzene peak at RT 2.6 minutes as a first xylene peak.

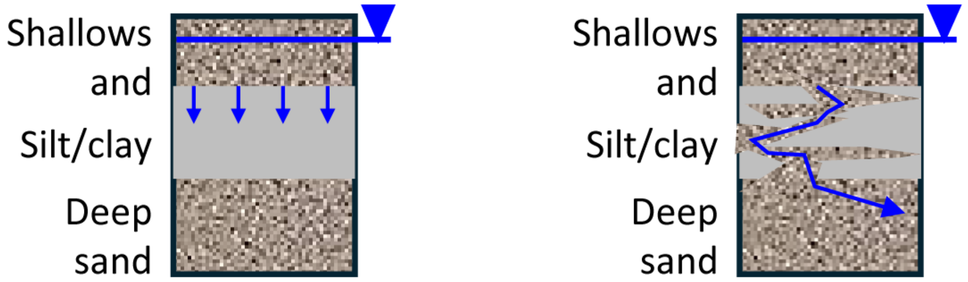
In Figure 3, the analyst assumed the TVHC was the sum of the areas of all detected peaks (see analyst's handwritten notation next to "TOTAL AREA=4.7814E+07). That total area was dominated by three peaks with apparent RTs in the range of 0.4—0.5 minutes. Those three unidentified peaks comprised over 87% of the total area (as handwritten by me on the chromatogram in Figure 3). Since the calibration standard had not included any of the three early peaks, the response factors for them were unknown; thus, the concentrations of the peaks could not be confidently determined.

The 1998 contractor's report found that most analyses of shallow groundwater samples had unidentified peaks at RTs of approximately 0.4 minutes, which accounted for more than 80% of the total peak area of the detected compounds. In nine of the samples, the early eluting unidentified peak was the only peak detected. In those cases, the single early peaks were labeled as TVHC. Though I strongly suspected those early peaks included MTBE, I wanted to provide more support for that assertion. So, as described in Box 4↴, I convinced a collaborator to assemble a GC system as identical as possible to that used by the site contractor in 1998. Once done, and after analyzing a standard containing MTBE, my collaborator confirmed that the RT of MTBE in such a system would have been on the order of those included in the contractor's chromatograms.

Thus, the results of my collaborator's work supported the conclusion that at least twenty-one of the twenty-five shallow groundwater samples collected and analyzed in 1998 by the site's contractor contained MTBE. Since MTBE-amended fuel had not been used at the site by the prior owner, it was clear that a release or releases of MTBE-amended fuel had occurred from the new owner's facility at one or several points in time after they began operations. It was also clear that the contoured areas for shallow groundwater contamination in Figure 1 contained significant amounts of MTBE, although the actual concentrations could not be estimated since the response factor for MTBE had not been determined via calibrations.

4 MTBE Appeared at Deep Wells from Releases by the New Owners

Consultants to the new owners asserted that the migration rate of groundwater and thus MTBE at the site was slow. They argued that it was too slow to allow MTBE released from the site to reach the most downgradient deep monitoring well unless it had been released before the new owners began operation. However, their arguments were not supported by facts. Instead, analysis of the available data showed that MTBE released by the new owner could migrate downward to the permeable strata containing the plume of concern and then laterally to the most downgradient of the monitoring wells. In effect, the conceptual model assumed by the consultants was too simplistic. Figure 4 compares the conceptual model initially proposed by consultants for the new owner to the conceptual model I felt was more defensible, as I discuss in some detail below.



a) Consultant's proposed 3-layer stratigraphy 0-25 ft (0-8 m) bgs: silt/clay aquitard separating two permeable sandy layers. Downward water flow assumed to be very slow.

b) My conceptual model for the stratigraphy and water flow in the vertical interval 0-25 ft (0-8 m) bgs. Sand lenses in the intervening layer serve as preferred flow paths and allow much faster water flow than imagined by consultants.

Figure 4 - Comparison of conceptual models: a) the assumptions of the consultants to the new owners, and b) the conceptual model more consistent with boring logs and other issues discussed in Section 4.1. A two-dimensional drawing does not convey the connected lenses well because they are a three-dimensional object with this video link↗ providing a better conceptualization of the connections. Consultants for the new owner assumed very slow vertical downward flow through a uniform aquitard driven by a vertical hydraulic gradient. In my opinion, a more reasonable conceptual model assumes preferred flow through interconnected sand lenses within the otherwise low permeability layer separating the sandy layers and much faster vertical flow than assumed by the consultants to the new owner.

4.1 Vertical Migration of MTBE from the Shallow to Deeper Permeable Strata

Consultants to the new owners referred to the subsurface as being comprised of shallow and deep aquifers (permeable strata) that were hydraulically distinct, as conceptualized in Figure 4a. The implied assumption is that the two permeable zones were separated by a laterally continuous aquitard (relatively impermeable stratum). This conceptualization was the basis for their assertion that, despite the known downward hydraulic gradient between the sand layers, it would take a very long time for MTBE that was released to the shallow permeable strata to penetrate the aquitard and thus enter the deeper permeable strata.

However, a variety of lines of evidence suggested that water and thus MTBE could flow from the shallow permeable strata to the deeper permeable strata in a much shorter time than the consultants assumed. The primary line of evidence was that MTBE, which was never received, stored, or sold at the site prior to the new owner's operations, had reached the deeper permeable strata. So there must have existed one or more pathways to allow MTBE-contaminated groundwater to move downward at a rate faster than assumed possible by the new owner's consultants. In the following, I review the evidence that such a pathway or pathways existed.

The site was in a region known to have interbedded sands and finer-grained materials. It is relatively close to a large water body and thus likely to have been impacted by water flows towards the larger water body before the area was developed and the terrain leveled. Figure 5 is a site map showing the locations of cross sections presented in subsequent figures, as well as other site features. I created what I called cross section A–A′ and cross section B–B′ by using boring logs provided to me. As I did not have electronic versions of boring logs that I could manipulate in 2001, I resorted to creating the cross sections by cutting and pasting from printouts of cross sections that were available. I then scanned the resulting paste-ups, which produced the somewhat crude images that are shown as Figure 6 and Figure 7. Although hand-made, these images told a story that was clear enough to convince others that the original conceptual model in Figure 4a was incorrect.

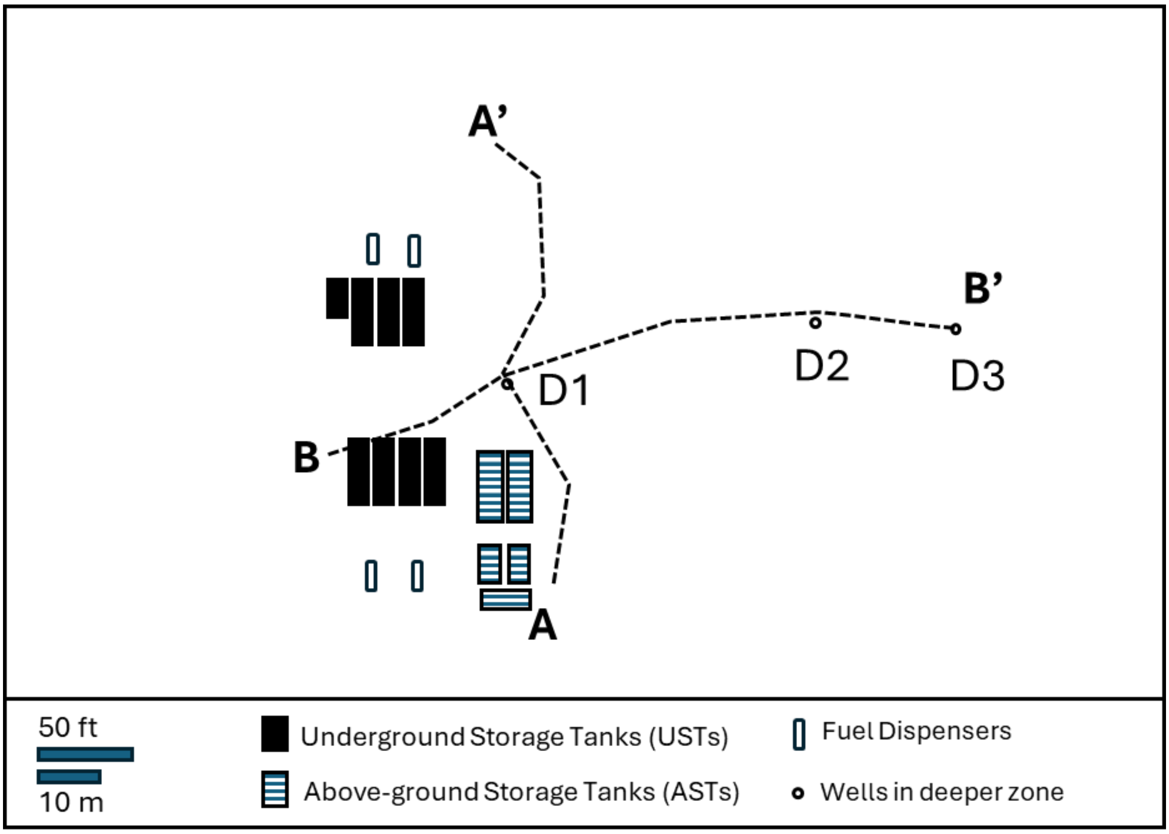


Figure 5 - Map of the site showing locations of underground storage tanks (USTs), above ground storage tanks (ASTs), fuel dispensers, the locations of cross-sections discussed in the text (dashed black lines), and three wells (black circles) monitoring what was called the deep aquifer.

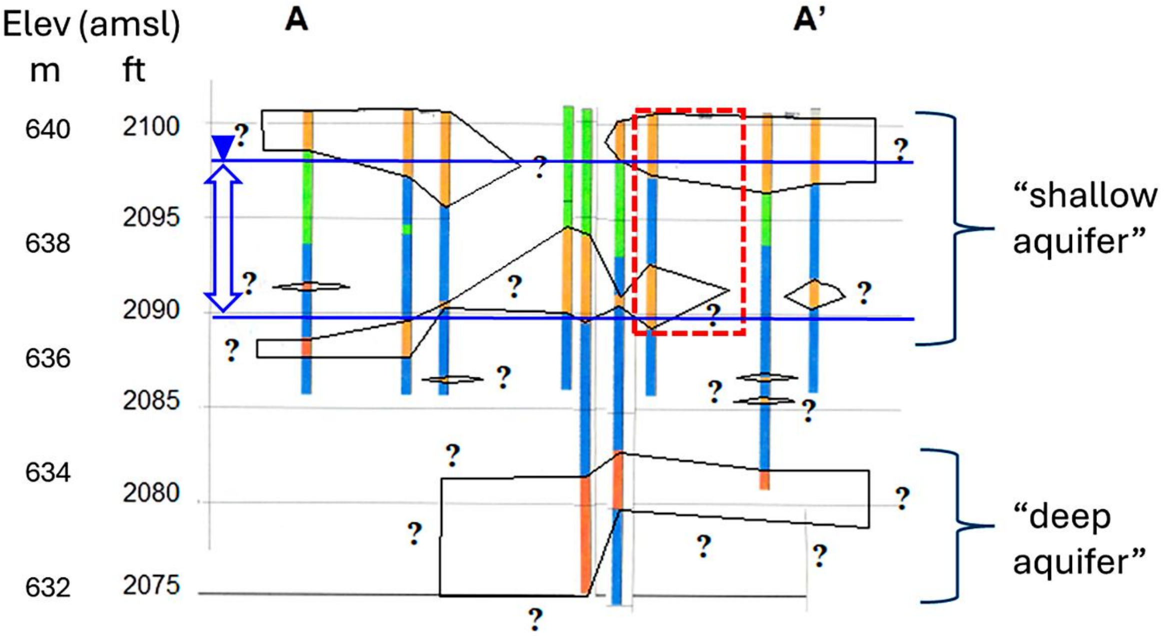


Figure 6 - Cross-section created along A–A' created from printed boring logs by cutting and pasting. Vertical exaggeration is a factor of 10. The approximate vertical intervals referred to by the new owner's consultants as the shallow and deep aquifers are indicated by brackets. The brown strata are logged as sands; the green are logged as silts or silty sand or clayey silt; and the blue are logged as silty clays. The red dashed rectangle is a projection of the estimated excavation depth of one of the USTs onto A–A' illustrating that it may have connected two sets of sand layers in the "shallow" aquifer. The black lines are my interpretations of possible connections between permeable sands. Horizontal blue lines show the range of water table depths for the shallow aquifer. D1 indicates the boring into which the deep well D1 was installed.

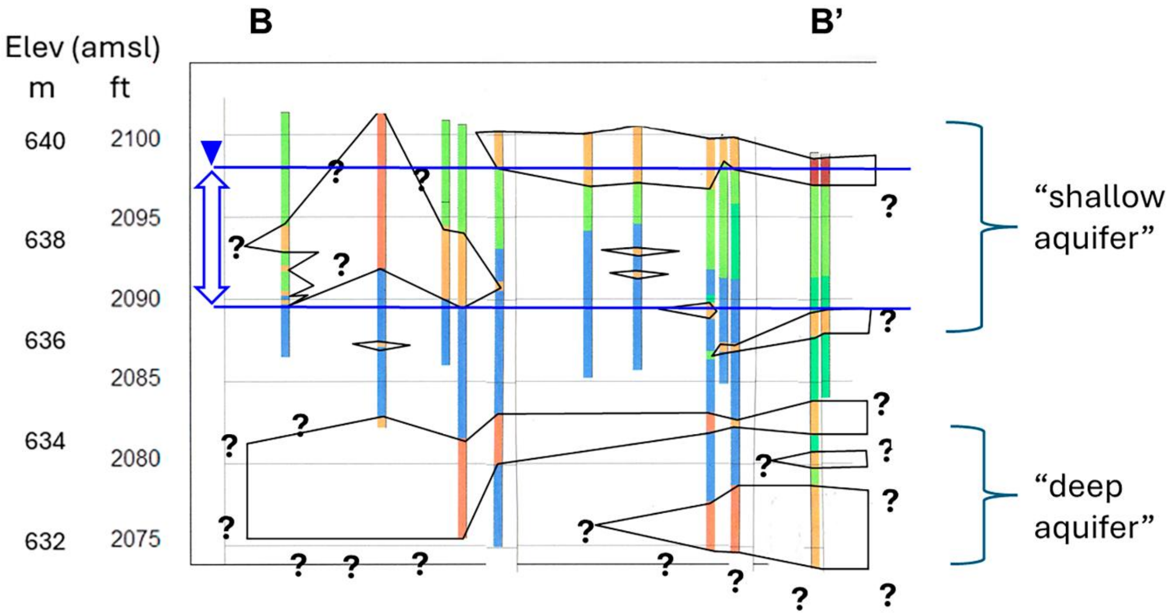


Figure 7 - Cross-section along B–B' created from printed boring logs by cutting and pasting. Vertical exaggeration is a factor of 10. Color scheme is the same as in Figure 6. The black lines are my interpretations of possible connections between permeable sands. Horizontal blue lines show the range of water table depths for the shallow aquifer. D1, D2, and D3 indicate the borings into which the deep wells D1, D2 and D3 were installed.

In Figure 6 and Figure 7, the brown strata (sands) are much more permeable than the green or blue strata (silts, etc.). Certainly, these figures do not conform with the assertion of the new owner's consultants that there was a simple three-layer configuration of strata (shallow permeable strata, underlain by less permeable strata, underlain my deeper permeable strata). Furthermore, as illustrated in Figure 6, the native media would have been disturbed by the excavations required to install the underground storage tanks (USTs) and the permeable backfill normally used around the USTs. I did not have access to specific details regarding the excavations for the USTs and backfills, but it is possible to make a reasonable estimate of the total depths for the larger USTs. According to consultant reports, the capacity of each of the three larger USTs in the area of the shallow contamination shown in Figure 1 was 12,000 gal (45,400 L). Based on plan views in those reports and information easily accessible online, those USTs were likely 10 ft (3 m) in diameter and 29 ft (8.8 m) long. Assuming the tanks were installed 2 to 3 ft (0.6 to 0.9 m) below ground surface and were placed on anchor pads that were 0.5 to 1 ft (0.15 to 0.3 m) thick, the total depth of the excavation would have been 12.5 to 14 ft (3.8 to 4.3 m) below ground surface. Figure 6 shows that the UST excavations could have connected the two sandy layers within what the consultants called the shallow aquifer.

Figure 6 and Figure 7 suggest that, given a downward vertical hydraulic gradient, water in the shallow aquifer could have migrated to the deeper aquifer through interconnected lenses and layers of permeable media on the order of 0.5 to 1 ft (0.15 to 0.3 m) thick. However, it was conceivable that thicker and thinner lenses could have existed in that interval, but were not detected by the sparse sampling. In addition, there may have been an old, unused, and improperly abandoned well at the site that was screened across the two sandy layers but not identified in the site sampling. Such wells have been discovered to function as permeable conduits between water bearing strata in many towns and cities that expanded into formerly agricultural areas. Reports I reviewed, but cannot cite without identifying the site location, described some wells in the area that had been hand-dug because they did not have to be deep. Such wells would have had large diameters compared to drilled wells. There was no discussion, in any report I could find, of the means of abandoning such wells. In any case, Figure 6 and Figure 7 suggest that there was only a 5 to 10 ft (1.5 to 3 m) vertical separation between the intercepted shallow and deeper permeable media.

A downward vertical gradient was confirmed as shown in Figure 8, which is a plot of water levels measured over time in several wells screened within the shallow strata and one screened within the deeper strata. These wells were relatively close together and located in the vicinity of the hypothesized important permeable pathways between the shallow and deeper permeable strata. This is near the area of high contaminant concentration in the shallow zone shown in Figure 1. At the time of this writing, I no longer have information on the screened intervals of the wells nor the consultant's explanation for the yearly decreases, though it is likely the water levels decreased during the drier summer/fall seasons. As evident in Figure 8, the measured water levels in wells in the shallow strata and the deeper strata are consistently different but follow a remarkably similar trend with time. The fact that the trends are very similar suggests a permeable flow path and thus hydraulic connection between the shallow permeable strata and the deeper permeable strata, though the specific location of such a connection is not known. Figure 8 indicates the measured water level differences range from 5 to 7 ft (1.5 to 2.1 m).

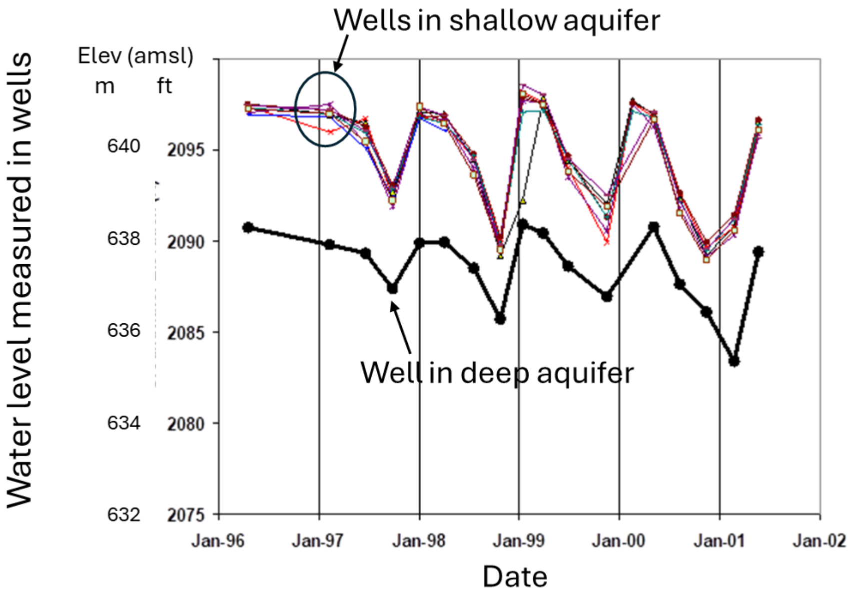


Figure 8 - Variation in water level over time for several shallow wells (thin lines) and one deep well (bold black line and filled symbols). All the wells were located close to the zone of elevated contaminant concentrations shown in Figure 1.

The difference in measured water levels between the shallow and deep permeable strata resulted in a strong downward hydraulic gradient (on the order of 0.5 to 1) that provided a driving force for downward flow of water. The rate at which water would flow from the shallow strata to the deeper strata would have depended on many things, and in any case, was likely to have been variable laterally given the heterogeneity of the subsurface at the site. But the main point for this case study was that the water did not have to go far, perhaps only 5 to 10 ft (1.5 to 3 m) or so, and there were very likely interconnected permeable pathways to allow that to happen.

For the purpose of this summary, a simple conceptual model can be used to explore the consequences of the hypothesized permeable interconnections. Although probably not physically reasonable, let us assume that an unidentified vertical permeable sandy pathway existed that was one square foot (1 ft^2, or 0.093 m^2) in horizontal cross-sectional area with water flowing downward through it from the shallow to the deeper permeable stratum. Let's also assume the vertical gradient was constant and on the order of 0.5 (e.g., 5 feet of hydraulic head difference over 10 vertical feet of the permeable pathway, as implied by Figure 6, Figure 7, and Figure 8) and the pathway was composed of a clean sand with hydraulic conductivity on the order of $3\text{x}10^{-4}$ ft/s ($1\text{x}10^{-4}$ m/s), the middle of the range tabulated by Freeze and Cherry (1979). Based on Darcy's Law, we would estimate a volumetric flowrate for groundwater through the pathway of approximately 13 ft^3/day (97 gal/day, 0.4 m^3/day, or 400 L/day).

Assuming a typical value for the porosity of the sand of 0.3, this would correspond to an average linear groundwater velocity of 43 ft/day (14.4 m/day), which means the water would take about five hours to move vertically from the shallow permeable strata to the deeper permeable strata. Even if we assumed the sands were much less permeable (hydraulic conductivity 100 times lower, which Freeze and Cherry (1979) indicate is in the middle of the range for silty sand), we would estimate the volumetric flowrate through the pathway as 0.1 gal/day (4 L/day) and the average linear groundwater velocity about 0.4 ft/day (0.14 m/day). This would mean the time for flow from the shallow to deeper permeable strata would be about 21 days.

To push these estimates a bit further, we could assume that the flow path was not perfectly vertical, as conceptualized in Figure 4b, thus elongating the total distance the water would have to travel to span the 10-ft (3-m) vertical separation between strata. As just one example, if the length of the actual flow path was 20 times the vertical separation between the permeable strata (200 feet, or 61 m), the time to traverse the circuitous flow path would be on the order of 20 times the estimates above, on the order of 4 to 400 days. The point of this exercise was not to create unassailable estimates of flow rates and volumes, but simply to show that reasonable assumptions based on core logs and tabulated data suggested that interconnected permeable sandy pathways could have allowed significant water flow between the shallow and deeper permeable aquifers. The flow could have traversed the vertical distance between the permeable strata in about a year or less.

Next, I estimated how much time might have been required to move enough MTBE mass from the shallow permeable zone to the deeper permeable zone to account for all the MTBE that appears to be in the deeper zone. I made an estimate of the total amount of MTBE mass in the deeper permeable zone using an approach I used in my previous research and for peer-reviewed publications (Mackay & Cherry, 1989). I made assumptions that I believe almost certainly led to an overestimate of the total mass. Here I modify those assumptions slightly from the 2001 work. I believe the new assumptions used here are more reasonable. The calculation assumes that the MTBE plume in the deep aquifer was 500 ft (152 m) long, 150 ft (46 m) wide, and 10 ft (3 m) in vertical extent. This is likely to be much more laterally extensive than the plume was at that time, and it is likely that the total thickness of the deeper permeable strata was less than assumed, as suggested by Figure 6 and Figure 7. I assume the porosity of the sandy aquifer was 0.3. I also assume that MTBE did not sorb significantly, consistent with its physicochemical properties (Squillace et al., 1997), so that all MTBE mass in the deeper aquifer was dissolved in groundwater. Finally, I assume the concentration of MTBE within the hypothesized plume averaged 2000 ug/L (i.e., about half of what I believe was the highest concentration ever detected in the deep aquifer). This leads to an estimate of approximately 13 kg of MTBE dissolved in the deep aquifer at the time of the 2001 study. The true MTBE mass in the deeper aquifer was probably far less than 13 kg for many reasons, including that the plume was certainly not rectilinear in shape. I did not then, nor now, offer this as an accurate estimate. But only as one to be used in the following calculations.

First, 13 kg of MTBE corresponds to the mass that would be present in approximately 176 kg (176 L or 46 gal) of MTBE-containing gasoline, assuming that the fuel averaged 10% MTBE by volume over the time the fuel releases occurred. Thus, it was possible that the MTBE plume detected in the deep aquifer arose from a single release or series of spills or releases of MTBE-amended fuel totaling no more than 176 L (46 gal). It could even have been much less if my estimate of total MTBE mass in the deep aquifer was a significant overestimate.

The water concentration of MTBE in equilibrium with gasoline containing 10% MTBE is 5000 mg/L at 25 °C (Squillace et al., 1997). At a lower temperature, the equilibrium concentration would have been higher. If we assume that the MTBE concentration in groundwater moving from the shallow to deeper aquifer averaged, for some period of time, on the order of 20% of the maximum possible in equilibrium with gasoline, which is 1,000 mg/L, then the 13 kg of MTBE estimated to be within the deeper strata could have been transported by approximately 13,000 L (34,354 gal) of water. If the flow rate was between 4 to 400 L/day, as estimated above for two perhaps extreme sets of assumptions, it would have taken approximately 32 to 3230 days (0.09 to 8.9 yr) to transfer the total MTBE mass to the deeper aquifer. The total mass of MTBE in the lower aquifer may well have been considerably less than 13 kg since the plume may not have been as large nor had as high an average concentration as I assumed. Thus, I thought it probable that the MTBE mass detected in the deeper aquifer was introduced to that stratum within the 15-year period prior to my study (i.e., during the time the new owner operated the service station). We know that such water flow had to have occurred, since an MTBE plume had been created by that vertical flow into the deeper aquifer. The main question was whether it was possible to estimate the time the MTBE reached the deeper aquifer. Monitoring data from the deeper aquifer yielded an answer.

4.2 Horizontal Transport of MTBE in the Deeper Aquifer

Consultants to the new and prior owners made widely varying estimates of the groundwater velocity in the deeper aquifer, based on applications of Darcy's Law, ranging from 1 to 1400 ft (0.3 to 430 m) per year. This was of little help in answering the question about the date MTBE entered the deeper aquifer. They both relied on estimates of the hydraulic conductivity of the sandy media, the hydraulic gradient in the deeper aquifer, and the porosity. Since to my knowledge there were no measurements of the most important parameter, hydraulic conductivity, the consultants' estimates ranged primarily due to variations in assumptions regarding the hydraulic conductivity. At research sites, scientists generally estimate groundwater velocity more directly through tracer tests involving monitoring of the migration of a chemical introduced into the natural groundwater flow. Typical tracers are water soluble, do not degrade during the duration of the test, and do not sorb to the geologic media. Thus, they are thought to migrate at the same rate as groundwater. Tracer migration can be determined by monitoring its movement over space or its migration past a given sampling point over time. In the latter case, the results are plotted as tracer concentration versus time at the monitoring point. The arrival time of the tracer peak can be used to estimate the time it took for the tracer to move from the point of injection or release to the point of monitoring. Given the distance traversed, the groundwater velocity can be calculated as the distance traversed divided by the time taken to traverse it.

In practical cases such as the investigations related to this site, conduct of tracer tests is rare. However, sometimes the known properties and observed behavior of one of the regularly monitored species allow it to serve as a tracer for groundwater flow. At this site, it is reasonable to assume MTBE behaved as a tracer since it is thought to migrate with little to no impact of sorption to the geologic media (Squillace et al., 1997). Therefore, the results of MTBE monitoring in the deeper aquifer could be used to generate reliable estimates of the groundwater velocity therein. Figure 9 shows MTBE concentration versus time for three of the deep wells (D1, D2, and D3) with locations depicted in Figure 1 and screened sections within the deeper permeable stratum as depicted schematically in Figure 4 and evident in Figure 6 and Figure 7.

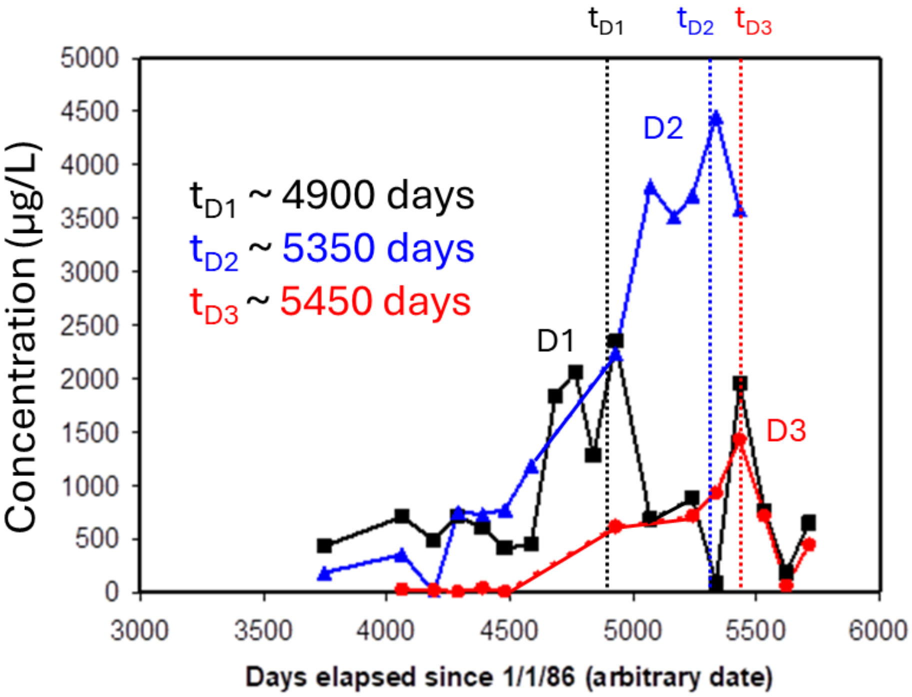


Figure 9 - Concentrations of MTBE over time in three wells monitoring the deeper zone (D1, D2, and D3). The vertical dashed lines mark the arrival times of the initial peaks (t_{D1}, t_{D2}, t_{D3}) for the three wells, in my opinion. The estimated arrival times are listed in the frame (in days elapsed after 1/1/1986).

For plotting and interpretation convenience, I calculated and plotted time as days elapsed after 1/1/1986, an arbitrary date; although, it marks the beginning of the year the new owners began operation of the site. The data for each well shows concentration over time reaching a peak followed by a decline. These are called breakthrough curves. For each well, the MTBE concentrations rose over time to form a main peak and appear to have declined thereafter for wells D2 and D3. This is analogous to a peak in gas chromatography, suggesting that the initial input of MTBE to the aquifer may have been a pulse, analogous to the injection of a sample into a gas chromatograph but with the pulse of MTBE-containing groundwater driven by downward flow from the surface to the lower permeable stratum. There is some indication from the D1 data that a second pulse of MTBE was injected into the deeper strata on the order of two years after the first, but we do not have enough information for wells D2 and D3 to confirm a second release.

If these wells were aligned perfectly along the flow direction, the maximum concentration observed in the wells should decline with distance along the flow direction as a result of longitudinal dispersion. The fact that the highest peak is observed for D2 suggests that the wells are not aligned perfectly along the flow direction and thus each well monitored the migration of a different portion of the plume. This concept is illustrated in Figure 1, depicting a hypothesized plume at an angle to the orientation of the three wells. Therefore, D2 appeared to be closer to the middle of the plume while D1 and D3 monitored the opposite lateral edges of the plume. As indicated by Figure 4b, the MTBE plume was assumed to originate in the deeper aquifer from one or more preferred pathways from the shallow aquifer to the deeper aquifer beneath the zone of elevated contaminant concentrations detected in the shallow monitoring wells, near the uppermost set of dispenser islands. For the following calculations, I assumed the source of the MTBE-contaminated water to the deeper aquifer (the outlet of the downward vertical flow) was located below the shallow zone of elevated contaminant concentrations.

The data in Figure 9 can be used to generate an estimate of the groundwater flow rate in the deeper aquifer. First, an estimate of the approximate arrival time of each well's peak must be made. Because the data are noisy and sparse, I chose to estimate the arrival times based on my professional judgement, having done so numerous times with experimental data in the past. As indicated by the colored vertical bars on Figure 9 and the list of days within the graph area, the peaks arrived at approximately 4900 days, 5350 days, and 5450 days after 1/1/1986 at D1, D2, and D3, respectively. By examining site maps, I estimated the following approximate distances from the assumed source to each well in the direction of flow: 100 feet for D1; 250 feet for D2; and 320 feet for D3. The groundwater velocity can be estimated for each well by the distance from the source divided by the difference between the estimated arrival time of the MTBE peak and the time the MTBE entered the deep groundwater. Although the time the peak entered was not known, it could be estimated by assuming the groundwater velocities were the same for migration to each of the wells. Thus, there were three equations for the velocity (ft/day), each containing the unknown time (t_0) when the MTBE reached the deep aquifer—Equations (1), (2), and (3).

$$v_{D1} = {}^{100\,ft}\Big/_{(4900\,days - t_0\,days)} \tag{1}$$

$$v_{D2} = {}^{250\,ft}\Big/_{(5350\,days - t_0\,days)} \tag{2}$$

$$v_{D2} = {}^{320\,ft}\Big/_{(5450\,days - t_0\,days)} \tag{3}$$

Solving different pairs of those equations by assuming the velocities are equal allows for three estimates of the time (t_0) that MTBE first impacted the deeper aquifer. Solving the first two, the last two, and the first and last yields the following estimates of t_0: 4546 days, 4993 days, and 4612 days (for elapsed time after 1/1/86). These are quite consistent, with an average estimated initial impact time of 4717 days and a standard deviation of only 5%. The groundwater velocities calculated from the average estimated impact time, the peak arrival times, and distance to the monitoring wells range from 144 ft/yr to 220 ft/yr. These velocities are at the low end of the range estimated by the original consultants (1 to 1400 ft/yr).

Thus, the date of first arrival of MTBE to the deeper sands was on the order of 4717 days after the arbitrary start date of the axes (1/1/86), or approximately 12/1/1998. While these calculations cannot be considered rigorous, they nonetheless make it very clear that the MTBE must have been introduced to the deep sand aquifer on the order of 13 years after the site was sold to the new owners in 1986. The estimated date of the first arrival of MTBE to the deep aquifer is, perhaps not surprisingly, less than a year after the shallow zone of elevated contaminant concentrations had been identified in spring of 1998 and, therefore, within the range of estimates I made for travel time from the shallow to deeper permeable strata (under 400 days).

5 Conclusion

A careful review of analytical and groundwater monitoring data showed the MTBE contamination of groundwater beneath—or downgradient of—the service station arose solely from the operations of the new owner after they began operations on the property. Key to these conclusions was realizing that the shallow monitoring in 1998 detected MTBE but the analysts had not calibrated for MTBE and thus could not and did not report MTBE. So, a spill of MTBE-amended fuel had occurred at the site. Consideration of the migration behavior of the MTBE in the deeper aquifer allowed definition of peak arrival times at different distances from the source area, from which the likely date of entry of the MTBE to the deeper aquifer could be derived. This arrival time was long after the new owner started operations.

The implications of this case study are: 1) although analytical methods have improved significantly since the time of this case study, all contaminants of concern must be identifiable by the analytical methods being applied; and 2) site data can often be used to make estimates of the timing of spills and leaks of gasoline (or other types of contaminants).

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7 Boxes

Box 1 – General Reasons to Conclude the New Owners Released MTBE

It was likely that the new owners, who acquired the site in the mid-1980s, dispensed MTBE-amended fuel. This is especially likely given introduction of MTBE as a fuel oxygenate in 1979 (State Water Resources Control Board of CA, 2017) and its increasing use thereafter. MTBE-amended products could have been released to the environment by the new owner as early as their purchase of the site in the mid-1980s or at any time thereafter. Consultants to the new owner prepared a report in 1997, which noted that in the mid-1980s the new owner made improvements to the property that included new underground and above-ground fuel tanks. That report also summarized a statement by the new owner that "*all tanks had leak and overfill detection equipment installed in 1990*." This implies that there was a period of several years during which no such detection facilities were in place. This suggests that leaks, overfills of USTs or ASTs or other types of spills (e.g., overfills of vehicles, damage to pumps and hoses caused by customers driving off without removing the hose from their fill spout) could have occurred and not been detected by any specific apparatus during that time. Overfills and the other types of spills have occurred at other fuel stations and there is no reason to assume that they did not occur at the subject site, perhaps even without the knowledge of the employees or owners of the service station.

Based on the information made available to me during my work in 2001, the new owner had the underground storage tanks (shown in Figure 1) and some or all of the associated piping pressure tested in 1991, 1992, 1993, and 1997. In each instance, they received confirmation that the systems passed the tests. The new owners asserted that this testing of their tanks and piping proved that no significant leaks could have occurred. However, having tanks and piping pass leak tests is no guarantee that fuel products or their constituents have not escaped into the subsurface environment. There are many reasons for this, as summarized in the previous paragraph.

Although the tanks passed the leak tests in 1997, the report by the leak assessment consultant noted that two tanks had leak rates of 0.01359 gal/h and 0.02173 gal/h (0.05 and 0.08 L/h). These tanks likely contained regular unleaded or super unleaded fuels, both of which were MTBE-amended. Such leak rates may conceivably have been an artifact of the measurement method. However, if they were accurate and the leaks continued for considerable periods of time, the estimated leak rates would have corresponded to about 120 gal and 180 gal (450 L and 680 L) per year. Spills or leaks of such volumes of MTBE-amended fuel would have been sufficient to create the contested MTBE plume migrating in groundwater. Although an estimate, analysis of the volume and concentrations of the plume in the deeper aquifer suggests it may have contained about 13 kg of MTBE, which would have been present in 170 L (45 gal) of gasoline amended with 10% MTBE.

Return to where text linked to Box 1↥

Box 2 – Overview of Gas Chromatography Applied to Site Groundwater Samples

I no longer have the report from the owner's contractor who conducted the shallow groundwater sampling. However, I have excerpts from the report that prove that 1) a table-top GC from a well-known manufacturer was used for the analyses and 2) describe the configuration of their GC. As explained in the report, the contractors collected water samples in 40 mL glass vials, then emptied half of the water, shook the sample, then used a syringe to take a sample of the air-filled headspace and inject it into the GC's injection port.

Figure Box 2-1 is a schematic illustrating the key parts of the GC analytical system. The injected gas becomes mixed with the carrier gas, which flows through the column to the detector. The column was in an insulated chamber called an oven, whose temperature is set by the analyst (or a temperature program is established to change the temperature in desirable ways during each analysis). The chemicals in the gas sample were separated as they flowed through the column. The flame ionization detector (FID) sensed the arrival of each chemical and sent a signal to the integrator, which forwarded the chromatogram and various summary information to the printer, as illustrated in Figure Box 2-2. I had access only to examples of the printouts of the analytical results, not to electronic summaries that may have been created during the analyses.

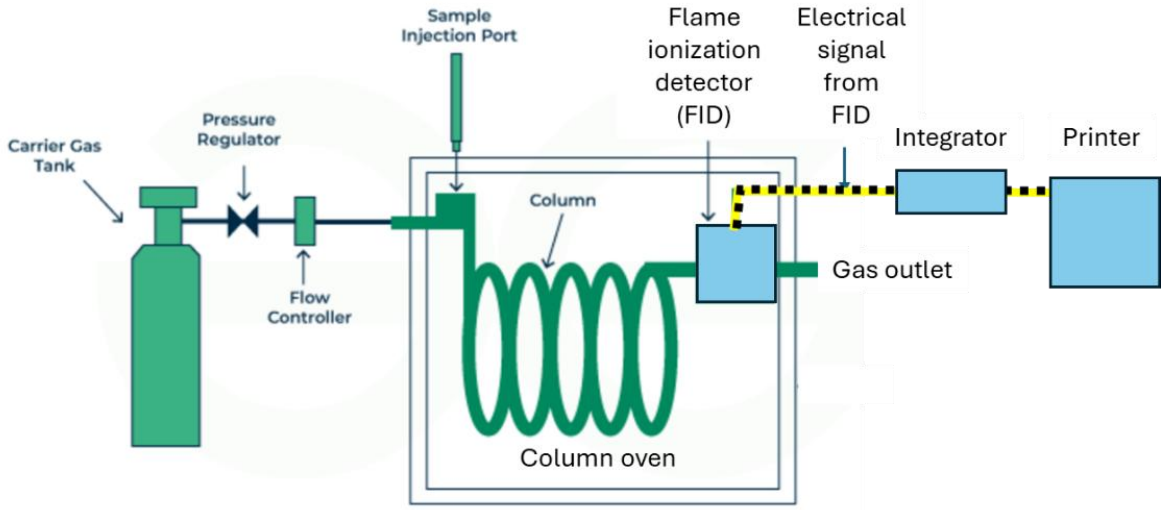
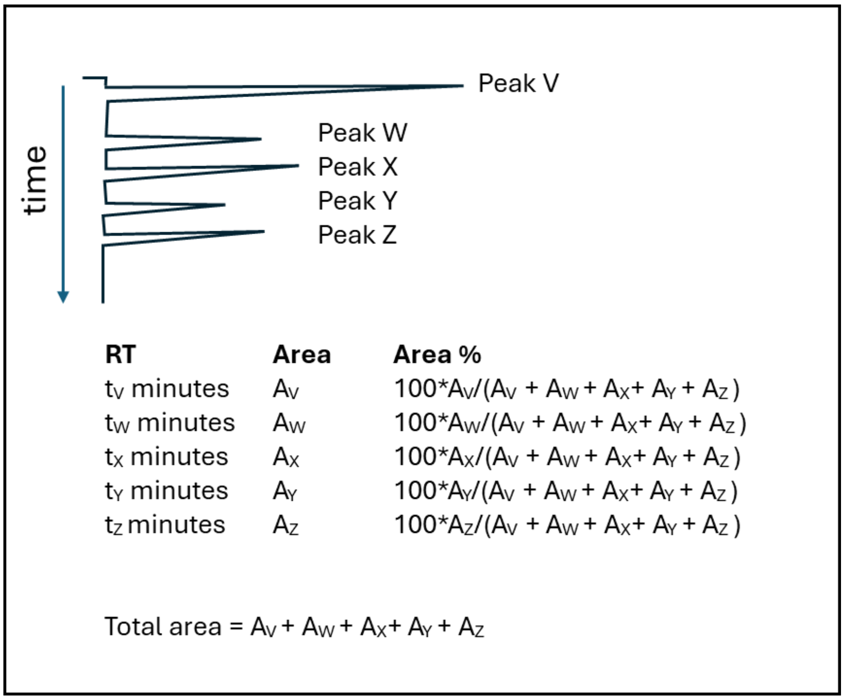


Figure Box 2-1 - Schematic of the key components of the GC used for analyses of shallow groundwater samples from the site in 1998 (Adapted from https://www.geeksforgeeks.org/gas-chromatography/↗).



RT	**Area**	**Area %**
t_V minutes	A_V	$100*A_V/(A_V + A_W + A_X + A_Y + A_Z)$
t_W minutes	A_W	$100*A_W/(A_V + A_W + A_X + A_Y + A_Z)$
t_X minutes	A_X	$100*A_X/(A_V + A_W + A_X + A_Y + A_Z)$
t_Y minutes	A_Y	$100*A_Y/(A_V + A_W + A_X + A_Y + A_Z)$
t_Z minutes	A_Z	$100*A_Z/(A_V + A_W + A_X + A_Y + A_Z)$

Total area = $A_V + A_W + A_X + A_Y + A_Z$

Figure Box 2-2 - Type of printout generated by the GC system used by the new owner's contractor. A strip of thermal printer paper emerged from the analytical system's printer, which was then removed by the analyst for annotation and storage. The following text contains discussion of the features of such printouts.

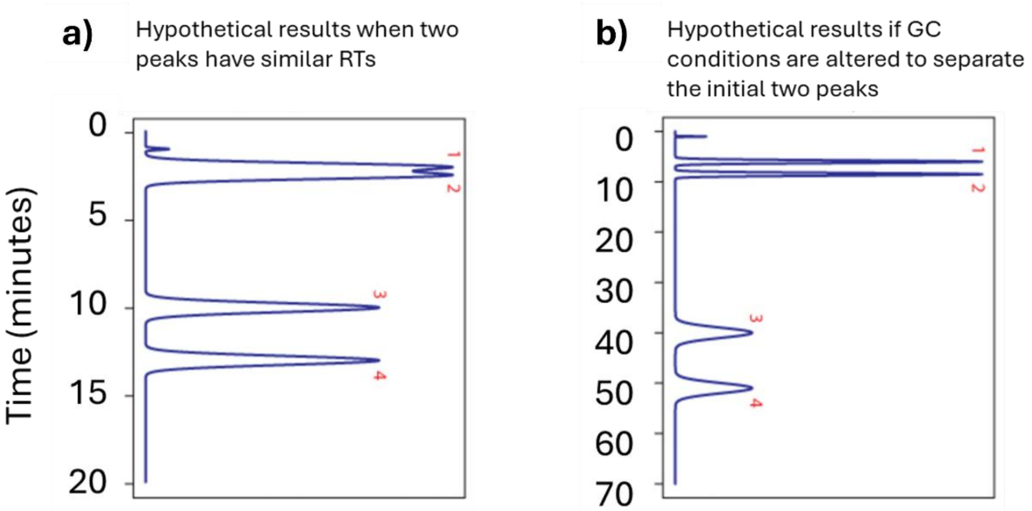
In the hypothetical printout shown in Figure Box 2-2, the top portion depicts the chromatogram, a plot of peaks (detector responses) over time. The higher the peak, the higher the concentration for a given chemical. For this hypothetical example, there are 5 detected peaks, labeled V through Z, arriving over time. The analytes pass through the column at different rates due to their varying affinity for the column contents and thus become separated by their retention time (RT). The integrator summarizes information recorded at the bottom of the printout, including the retention time for the peak, the area enclosed by the peak, and the percent of the total area of all five peaks enclosed within each peak. Other information may also be included in such a printout, but these are the key parts for our purposes.

In gas chromatography, the RT for a given analyte is dependent on the length and type of column used, the flow rate of the carrier gas, the temperature of the column during the analysis, and the age and prior usage of the column.

Return to where text linked to Box 2↥

Box 3 – Need to Optimize GC Conditions to Separate All Analytes

A common problem encountered when analysts utilize short GC run times, is that early eluting peaks can overlap and be barely distinguishable as separate peaks, or perhaps not distinguishable at all, and thus treated and quantified as one peak. This is illustrated hypothetically in Figure Box 3-1a and evident in analyses of site samples shown Figure 3 of Section 3 of this book. Figure Box 3-1b illustrates that the early eluting peaks can be separated if GC conditions are altered (e.g., longer columns, lower temperatures), which can allow identification and quantitation of the two peaks. Changes in analysis protocol can lead to significantly longer total run times (as illustrated in Figure Box 3-1) unless other conditions are altered as well (e.g., ramping up the temperature of the column after the first two peaks elute). An analyst must know all the compounds that may be present in a sample and detectable by a GC in order to set operational conditions to allow all compounds to be separated and quantified. As discussed in Section 3 of this book, in the case study, the contractors did not use conditions that would have allowed clear identification and quantitation of MTBE.



a) Hypothetical results when two peaks have similar RTs

b) Hypothetical results if GC conditions are altered to separate the initial two peaks

Figure Box 3-1 - Illustration of the overlap of early peaks and how to resolve them in principle (Adapted from figures in https://asdlib.org/imageandvideoexchangeforum/the-general-elution-problem-in-chromatography/↗).

Return to where text linked to Box 3↑

Box 4 – RT of MTBE in Analyses Using GC Identical to Contractor's

To test the hypothesis that MTBE would have had a retention time of approximately 0.4 minutes in the analyses conducted by the site's contractor, a collaborator of mine configured a gas chromatograph essentially identical to that of the site's contractor. They did so by using an FID, a new column of the type used by the contractor, and the same operating conditions the contractor had reported (e.g., oven temperature, flow rates). My collaborator conducted analyses of a standard containing MTBE and BTEX. They found the RT of MTBE to be approximately 0.323 minutes. The analyses by my collaborator provided additional support to the assertion that the site's consultant had detected MTBE in some or most of its shallow groundwater samples collected in 1998. Although my collaborator found a somewhat lower RT for MTBE than the site consultants had for their unidentified peak(s) (approximately 0.3 minutes versus 0.4 minutes), it is known that the RT of an analyte can vary as a result of slight changes in GC operating conditions (e.g., temperature and gas flow rate) or as a result of changes in the performance of the column as it ages. Thus, given that the column used by the site's consultants may have been used for some time before application to this site in 1998, it is probable that the RT for MTBE had changed from what it had been when the column was new, all other operating conditions being equal. It is also possible that the actual operating conditions employed by the site consultants were slightly different than they reported (e.g., temperature and gas flow rate) either because of operator error or imprecision of the temperature or gas flow controllers.

Return to where text linked to Box 4↥

8 About the Author

Douglas M. Mackay is an Adjunct Professor Emeritus, who retired from the University of California, Davis, in 2017. His research addressed the transport and fate of organic contaminants and their transformation products in the vadose and saturated zones via field, laboratory, and numerical studies. His research team conducted controlled field experiments to explore constraints and opportunities for groundwater remediation technologies including methods for release and mixing of solutes (remediation amendments and tracers) into groundwater. His team also proposed and evaluated methods for estimating total mass discharge of, and thus risk presented by, contaminants flowing in groundwater, and identified a sensitive NAPL-detecting tracer. Field experiments illustrated factors limiting natural attenuation of organic contaminants in the vadose and saturated zones, including crude oil, refined petroleum products, ethanol-blended gasoline, MTBE, and other gasoline oxygenates, pesticides, and halogenated solvents. In 2024, with Professors R. Allen-King and W. Rixey, he published *Properties of Organic Contaminants*, a book available for free download from the GW-Project website that is intended for use as a reference or in teaching (https://gw-project.org/books/properties-of-organic-contaminants/↗).

Please consider signing up for the GW-Project mailing list to stay informed about new book releases, events, and ways to participate in the GW-Project. When you sign up for our email list it helps us build a global groundwater community. Sign up↗.