

Concentrations and Stable Isotope Values of BTEX in Gasoline-Contaminated Groundwater

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This work was undertaken to investigate the usefulness of stable carbon isotopic analysis as a monitoring tool for contaminant remediation. Concentrations and $\delta^{13}\text{C}$ values of BTEX (benzene, toluene, ethylbenzene, and xylenes) were measured at a gasoline-contaminated site in southern California. The BTEX data were determined using a purge-and-trap connected to a gas chromatograph/ion trap mass spectrometer and to an isotope ratio mass spectrometer system. Concentrations ranged from below detection (<0.5 ppb ≈ 0.05 μM C) to about 120 ppm ($\approx 10\,000$ μM C) total BTEX, with toluene generally having the highest concentrations. For BTEX compounds at monitoring wells averaged across all sampling dates, $\delta^{13}\text{C}$ values ranged from -23.8 to -26.6‰ (benzene), -22.9 to -25.2‰ (toluene), from -23.0 to -25.3‰ (p&m-xylenes), and from -22.4 to -25.0‰ (o-xylene). The data strongly suggest two sources of contamination: one with lighter (^{12}C -enriched) $\delta^{13}\text{C}$ values emanating from the area near monitoring wells 1 and 2, and the other containing higher MTBE concentrations, an additive of unleaded gasoline, with heavier (^{13}C -enriched) $\delta^{13}\text{C}$ values coming from the vicinity of monitoring wells 8 and 9. The isotope data suggest that the leaded and unleaded gasoline at this site are isotopically distinct.

Introduction

Gas chromatography/mass spectroscopy (GC/MS) analyses for fingerprinting sources of petroleum hydrocarbons have been used for many years (e.g., ref 1). GC/MS has been used to quantify hydrocarbon losses as well as to determine class compositional changes in degraded oils (2). By using markers within the fuel products that are resistant to degradation, oil depletion (3) and biodegradation losses in soil (4) have been quantified.

Another type of fingerprinting involves the use of stable isotope values. Ratios of $^{13}\text{C}/^{12}\text{C}$, reported as $\delta^{13}\text{C}$ values, have been used to determine carbon sources that are

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assimilated by bacteria and higher trophic levels, while $\delta^{15}\text{N}$ values have been used to analyze food web dynamics (see ref 5). Combining both concentration and stable isotope data of contaminant compounds may provide a powerful tool in determining sources, degradation pathways, and transport from the contaminant site.

However, little is known about the $^{13}\text{C}/^{12}\text{C}$ composition of BTEX compounds. Previous studies have used the $\delta^{13}\text{C}$ of BTEX components of oils and condensates to determine maturation and correlations of oils (6, 7). Recently, the use of stable carbon isotopes of CO_2 has been suggested as an approach for monitoring the effectiveness of bioremediation (8–10). Laboratory work was successful in isotopically tracing the aromatic hydrocarbon fluoranthene into bacterial biomass and respired CO_2 (11). This approach of following the contaminant $\delta^{13}\text{C}$ signature into bacterial biomass and respired CO_2 has yet to be tested under field conditions. The objective of the present study was to measure BTEX concentrations and stable carbon isotope ratios under *in situ* bioremediation conditions at a gasoline-contaminated site. Overall, we hope to use these values in addition to the $\delta^{13}\text{C}$ signatures of the other major carbon pools (dissolved inorganic carbon, carbon dioxide, and methane) to obtain a carbon mass balance and to determine the efficacy of the bioremediation treatment (see ref 12). This paper describes only the BTEX concentration and isotope data.

Materials and Methods

The gasoline contamination at the Naval Construction Battalion Center, Port Hueneme, CA, is located at the Naval Exchange (NEX) gasoline service station and is currently trapped in a perched aquifer overlying a clay cap at a depth of about 8 m. In March 1985, a leak in the NEX gas station storage tanks was found. Inventory records indicate that between September 1984 and March 1985 approximately 10 800 gal (40 880 L) of gasoline leaked from the tanks. It is not known whether there were leaks before September 1984. The groundwater in the aquifer is brackish to saline; the sediment is coarse to fine sands.

In 1994, an *in situ* bioremediation strategy was initiated. Vertical groundwater circulation wells (GCWs) were installed in December 1994. One, GCW400-1, was placed near the main leakage area. Twelve monitoring wells radiated out from it at right angles, three wells to a leg (MW1–MW12). Three GCWs (GCW200-1, GCW200-2, GCW200-3) were installed downstream from the gas station to form a "biocurtain." The biocurtain was positioned to prevent the plume of dissolved hydrocarbons from migrating in the groundwater past this plane. Eight monitoring wells (MW13–MW20) were installed around these GCWs (Figure 1).

At each sampling location, a deep (approximately 6.1 m below ground surface) and a shallow (approximately 3.0 m before ground surface) well were installed. Groundwater at each of the monitoring wells was sampled through 1/4 in. stainless steel tubes using a vacuum pump. Before sampling, the wells were purged by pumping out three times the volume of water contained in the well. Approximately 200 and 500 mL of water was purged from shallow and deep wells, respectively. All BTEX samples were collected in 40-mL VOA vials, overflowing the vials with three volumes, and then preserved with HCl. The wells were sampled in January, March, August, and December 1995 and March 1996. The GCWs were turned on after the March 1995 sampling date, although the GCW400-1 did not operate on a continual basis until after the August sampling.

Samples and standards were analyzed using EPA Method 8260 [Volatile Organic Compounds by Gas Chromatography/

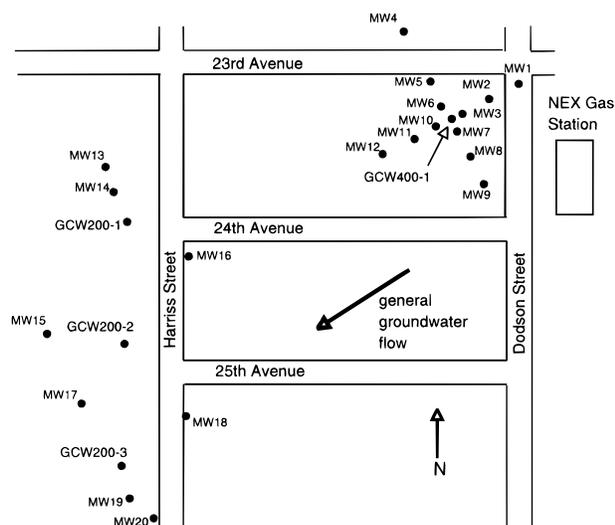


FIGURE 1. GCW and monitoring well placement near the NEX gasoline service station located at the Naval Construction Battalion Center, Port Hueneme, CA.

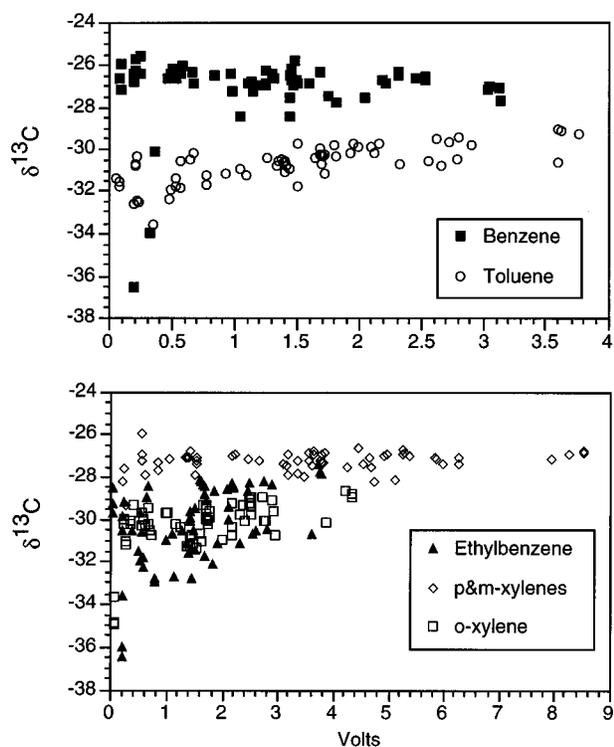


FIGURE 2. Isotopic composition of individual standard BTEX compounds versus the voltage measured on the isotope ratio mass spectrometer; the voltage was varied by diluting the BTEX standard. These data were collected throughout 1995 and the beginning of 1996 using the same BTEX standard. Mean and standard deviations of all measurements ($n = 62$) were $-27.2 \pm 1.7\text{‰}$ for benzene, $-30.8 \pm 0.9\text{‰}$ for toluene, $-30.3 \pm 1.9\text{‰}$ for ethylbenzene, $-27.3 \pm 0.5\text{‰}$ for p&m-xylenes, and $-30.3 \pm 1.2\text{‰}$ for o-xylene. When greater than 1 V was measured, the $\delta^{13}\text{C}$ values of the BTEX compounds were as followed: benzene, $-27.0 \pm 0.6\text{‰}$ ($n = 39$); toluene, $-30.4 \pm 0.6\text{‰}$ ($n = 41$); ethylbenzene, $-29.8 \pm 1.5\text{‰}$ ($n = 42$); p&m-xylenes, $-27.1 \pm 0.2\text{‰}$ ($n = 53$); o-xylene, $-30.0 \pm 0.8\text{‰}$ ($n = 43$).

Mass Spectrometry (GC/MS): Capillary Column Technique]. Low concentration groundwater (<200 ppb ≈ 15 μM C) samples were loaded directly onto the purge-and-trap multisampler. Five milliliters of groundwater was used. For high concentration groundwater samples, an appropriate dilution, generally 1:1000, was made in 5 mL of deionized water. A mixture of four different internal standards (chlorobenzene-

d_5 ; 1,4-dichlorobenzene- d_4 ; 1,4-difluorobenzene; pentafluorobenzene; concentrations of 40 ppb each) was added before analysis. BTEX standards were linear in the range from 0.8 to 200 ppb. The limit of detection was 0.5 ppb. In addition to the internal standards, a surrogate standard, 4-bromofluorobenzene (10 ppb), was added to each sample; 4-bromofluorobenzene was used as a tuning standard for the ion trap mass spectrometer and to determine the recovery efficiency of the purge-and-trap. At least 10% of all samples were analyzed in duplicate for concentration determination. The concentration of duplicate samples were generally within 10% of each other. The xylenes are reported as p&m-xylenes and o-xylene; the p&m-xylenes were unresolved by the chromatographic column.

Contaminant concentrations were first determined using an ion trap mass spectrometer. Then $\delta^{13}\text{C}$ values were obtained from replicate samples using a gas chromatograph/combustion/isotope ratio mass spectrometer system. For isotopic composition, duplicate samples were analyzed in either duplicate or triplicate resulting in four to six isotope numbers for each reported data point. Standard deviations were generally less than 0.5‰. Analysis of all BTEX samples was completed within 2–4 weeks of field work. We observed no age problems with our samples.

A full suite of BTEX standards was analyzed before each set of isotope samples. From this, it was found that lower concentrations (i.e., lower voltages on the mass 44 ion beam) tended to give $\delta^{13}\text{C}$ values enriched in the lighter isotope (Figure 2). A cutoff of 1 V was arbitrarily implemented, and isotope values below this cutoff were discarded. By using only isotope values obtained from voltages greater than 1 V, the standard deviation around the mean was significantly reduced (Figure 2). A voltage on the mass 44 ion beam of 1 V corresponded to a BTEX concentration of 200–300 ppb (15–23 μM C). Because of the need to have concentrations greater than about 200 ppb, isotope data were only obtained from shallow wells 1–12 and 15–17 on each of the sampling dates. Sample concentrations of ethylbenzene were generally less than 1 V; because of these low concentrations and the high variability of the isotope values of the ethylbenzene standard (Figure 2), $\delta^{13}\text{C}$ values of groundwater ethylbenzene have not been reported.

Concentrations of methyl *tert*-butyl ether (MTBE) were determined for the December and March 1996 samplings. Standards of BTEX mixtures containing MTBE were used to quantify the MTBE that eluted from the GC column before benzene. We were not able to obtain MTBE concentrations for the first sampling periods because we did not have the standards available at that time. The $\delta^{13}\text{C}$ values of the MTBE in the standard ranged from -27 to -37‰ . Because of this large range of isotopic values for the standard, we report no sample $\delta^{13}\text{C}$ values of MTBE. MTBE is an additive of unleaded gasoline.

Results

Total dissolved BTEX concentrations (sum concentration of benzene, toluene, ethylbenzene, and the xylene isomers) in groundwater collected at the shallow monitoring wells are shown in Figure 3 for the five sampling dates. Lowest concentrations in the shallow wells occurred at monitoring wells 13, 14, 18, 19, and 20 surrounding the biocurtain. The placement of these monitoring wells around the biocurtain was chosen to be outside the contaminant plume. Highest BTEX concentrations occurred in the shallow wells near the leakage site (monitoring wells 1, 2, 8, and 9), up to about 10 000 μM C, and then decreased both downgradient and away from the plume. High concentrations were also observed at three wells surrounding the biocurtain, MW15–MW17. These wells were within the contaminant plume, determined from historical data. No temporal trend was observed among the shallow wells.

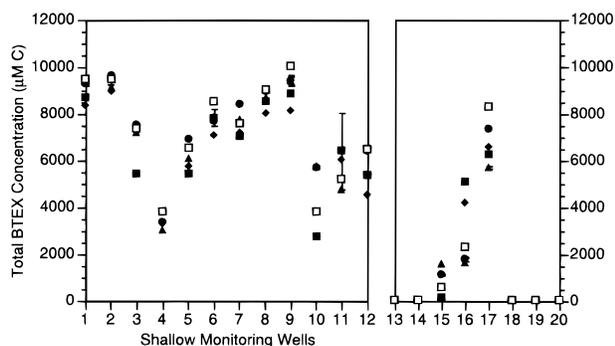


FIGURE 3. Total BTEX concentrations for the shallow monitoring wells (approximately 3.0 m below ground surface) for January 1995 (closed square), March 1995 (closed circle), August 1995 (closed triangle), December 1995 (closed diamond), and March 1996 (open square). The left side of the figure represents the wells around the main GCW (MW1–MW12). The right side represents the monitoring wells surrounding the biocurtain (MW13–MW20). Total BTEX includes concentrations of benzene, toluene, ethylbenzene, and the three isomers of xylene.

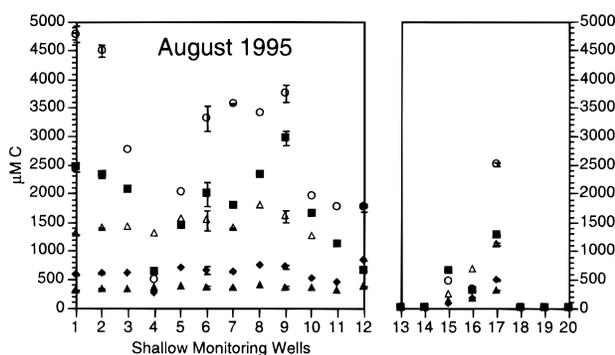


FIGURE 4. Concentrations of individual BTEX compounds measured in August 1995. Symbols are as follows: benzene (closed square), toluene (open circle), ethylbenzene (closed triangle), p&m-xylenes (open triangle), and o-xylene (closed diamond). Error bars represent $\pm 1/2$ range of duplicate samples.

Concentrations in all the deep monitoring wells were near the detection limit of each compound, except in one case. During the January sampling, before the GCWs began operation, the sum BTEX concentration at MW17 was 160 μM ; however, once the biocurtain GCWs were operational, the concentration at this well below 1 μM .

Individual BTEX concentrations for the August 1995 sampling at the shallow wells are shown in Figure 4. Among the individual BTEX compounds, toluene generally had the highest concentrations. In order of descending concentrations, toluene was followed by benzene, p&m-xylenes, o-xylene, and ethylbenzene. The most obvious exception to this general trend in concentration occurred at MW4. At this well, the p&m-xylenes had the highest concentration, followed by benzene, toluene, ethylbenzene, and o-xylene.

The isotopic composition of the BTEX compounds had similar values and patterns for each of the sampling dates. Averaging across all sampling dates, the $\delta^{13}\text{C}$ values ranged from -23.8 to -26.6‰ (benzene), from -22.9 to -25.2‰ (toluene), from -23.0 to -25.3‰ (p&m-xylenes), and from -22.4 to -25.0‰ (o-xylene). The individual compound $\delta^{13}\text{C}$ values for August 1995 are shown in Figure 5 as an example. The xylenes and toluene had similar $\delta^{13}\text{C}$ values and were the heaviest (^{13}C -enriched) of the BTEX compounds. Benzene was generally lighter. In their evaluation of oils of different maturities, Clayton and Bjorøy (7) also found toluene to be the heaviest of the BTEX components. Shallow wells 8 and 9 had heavier $\delta^{13}\text{C}$ values for all the compounds than did the surrounding wells, accounting for the range in isotope values

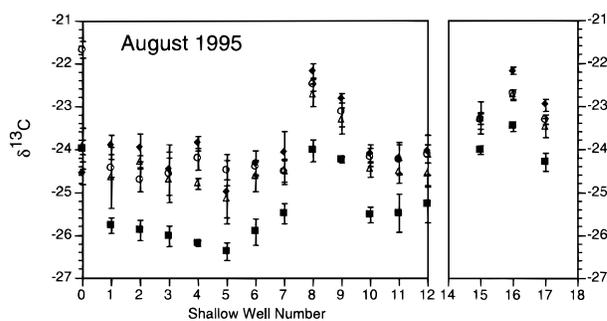


FIGURE 5. $\delta^{13}\text{C}$ values of individual BTEX compounds measured in August 1995. Only shallow wells 1–12 and 15–17 had BTEX concentrations high enough to obtain $\delta^{13}\text{C}$ data. Symbols are as follows: benzene (closed square), toluene (open circle), p&m-xylenes (open triangle), and o-xylene (closed diamond). Error bars represent ± 1 SD.

reported above. Shallow well 16 also had heavier $\delta^{13}\text{C}$ values. These three wells had statistically heavier $\delta^{13}\text{C}$ values than the other wells around the GCW400-1 (Students t , $p < 0.01$). This isotopic difference among wells, with MW8, MW9, and MW16 being heavier, was seen at all sampling dates.

Discussion

Very little change in concentration of the BTEX compounds occurred through time (Figure 3). The difference in relative concentrations of the BTEX compounds at MW4, a monitoring well located across the street from the main study site, may be due to a different source of contamination. However, it may simply be related to the rate and ease of degradation of the compounds. Toluene is the easiest BTEX compound to degrade, followed by the xylenes, with benzene and ethylbenzene being the most difficult to degrade (13–15). If degradation were occurring, toluene concentrations would be the first to decrease, as is seen at MW4.

The heavier $\delta^{13}\text{C}$ values observed at monitoring wells 8, 9, and 16 (Figure 5) suggest that something is different at these wells. Either there is another heavier source of BTEX or there is higher degradation of the contaminants occurring at these wells with an associated isotopic fractionation. During normal isotopic fractionation, the molecules with the lighter isotope (^{12}C) react at slightly faster rates, causing the residual molecules to become heavier (^{13}C -enriched). If degradation is the cause, then isotopic fractionation associated with this degradation needs to occur in all the compounds to account for all compounds having heavier $\delta^{13}\text{C}$ values at these wells.

In a laboratory incubation experiment with this groundwater, Morin et al. (16; unpublished) found a slight isotopic effect (fractionation factor of about 1.002) associated with toluene degradation under anaerobic conditions. No isotopic fractionation was observed with concentration decreases of any of the isomers of xylene and since little benzene was degraded, an accurate fractionation factor could not be calculated. Because no isotopic fractionation was observed in the xylenes, the heavy $\delta^{13}\text{C}$ values of the xylenes at MW8, MW9, and MW16 cannot be due strictly to greater degradation at these wells. Instead these data strongly suggest another contaminant source.

Support of another source of contamination at these wells comes in the form of MTBE concentration data. In December 1995 and March 1996, along with BTEX concentrations, methyl *tert*-butyl ether (MTBE) concentrations were also determined. As noted above, MTBE is an additive in unleaded gasoline. Figure 6 shows the relationship between the isotopic composition of toluene, used as an example, and MTBE concentrations. Concentrations of MTBE were fairly high at a number of monitoring wells, although MW8, MW9, and MW16 (a well downstream from 8 and 9) separate themselves from

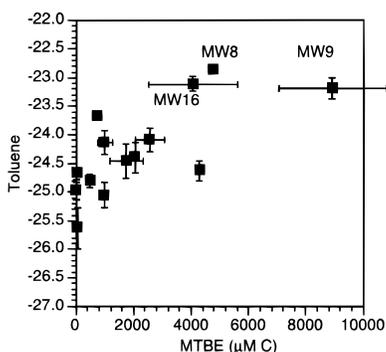


FIGURE 6. Average toluene $\delta^{13}\text{C}$ values versus average MTBE concentrations for the December 1995 and March 1996 sampling dates. Error bars represent $\pm 1/2$ range.

most of the other wells, having both high MTBE concentrations and heavy $\delta^{13}\text{C}$ values. Although approximately equally high concentrations of BTEX are observed at MW1 and MW2 and MW8 and MW9, wells 8 and 9 also have high MTBE concentrations and heavy $\delta^{13}\text{C}$ values. All these data together strongly suggest two sources of gasoline contamination. Further, the data suggest that the leaded and unleaded (containing MTBE) gasoline leaked at this site are isotopically distinct.

By using fingerprinting techniques taken from both concentration and stable isotopic analyses, we believe that at least two sources of gasoline contamination occurred at the Port Hueneme site. The heavier $\delta^{13}\text{C}$ values and higher concentrations of MTBE at MW8, MW9, and MW16 suggest a predominance of leaded versus unleaded gasoline at these wells.

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