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C_2 and C_3 hydrocarbon gases associated with highly reducing conditions in groundwater

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Abstract. This study investigates the presence and concentration of light hydrocarbon gases in soil vapor located immediately above the capillary fringe of a petroleum-contaminated aquifer. A correlation was observed for the linear regression plot of redox potential versus detectable C_2+C_3 alkane concentrations for a limited number of sampling points. C_2+C_3 alkanes were not detected at points were redox potentials in groundwater exceeded –260 millivolts. The predominance of methanogenic processes in this redox range, as well as the observed C_2+C_3 concentration ratios, suggest that ethane and propane gases in soil vapor may be biogenically produced as well as a result of volatilization from NAPL.

Introduction

The analyses of hydrocarbon and biogenic gases in groundwater and soils are commonly being used as an indicator of redox conditions and of petroleum-based contamination in subsurface environments. Biogenic gases are those produced during biological processes such as respiration and photosynthesis. Ludvigsen et al. (1995) have related redox conditions in groundwater down-gradient of a landfill to the presence of specific biogenic gases and electron acceptors, while Robbins et al. (1995) have correlated carbon dioxide and hydrogen sulfide levels in soil vapor with gasoline contamination in the underlying groundwater. Similarly, ratios of methane, oxygen and carbon dioxide in soil gas have been used to predict redox potentials in groundwater contaminated with a mixture of petroleum distillates (Marrin 1994).

Due to its production via a limited set of biochemical reactions, methane production has been used as a spatial indicator of reducing conditions in a variety of subsurface environments (Marrin 1991). Low molecular weight hydrocarbon gases, besides methane, are known to be produced by microbial consortia (Graedel 1978); however, their presence in soil gas overlying contaminated groundwater has rarely been reported. The authors have noted the presence of C_2 and C_3 hydrocarbon gases at a limited number of petroleum release sites (<10%) where highly contaminated soils or groundwater are present (unpublished data); however, the significance of their presence at such sites is not known. While C_2 and C_3 gases are not components of liquid petroleum distillates such as gasoline and diesel fuel, they have been reported to be present in the vapor above these products (Graedel 1978). In addition, C_2 and C_3 hydrocarbon gases have been shown to be produced biogenically under methanogenic conditions in both marine and freshwater sediments (Wiesenburg et al. 1985; Oremland et al. 1987). Finally, these gases have been identified as components of gas seeps that overlie natural petroleum reservoirs.

The objectives of this paper are two-fold. The first is to report the presence of C_2 and C_3 hydrocarbon gases in the vapor above petroleum-contaminated groundwater at a limited number of sites. Adding these compounds to the more common suite of soil gas analytes may be useful for interpreting data sets and for screening potentially explosive gases. Secondly, the paper presents data on co-occurring biogenic and hydrocarbon gases because of their applicability to researchers focusing on either the forensic or mechanistic aspects of soil vapor analysis.

Experimental section

Research site. The release of gasoline from tanks and piping underlying a Southern California service station had resulted in the presence of both dissolved petroleum product and non-aqueous phase liquid (NAPL) in a majority of the groundwater monitor wells that had been installed over a period of eight years. At the time of this study, dissolved gasoline constituents had been detected in wells located as far as 250 meters from the source in a direction corresponding to the regional hydraulic gradient. All groundwater monitor wells were constructed of PVC (5.1 cm diameter) and were screened over a vertical depth interval that ranged from approximately 1.0 meter above to 3.5 meters below the static water level. During the present study, groundwater table elevations varied vertically from 2.9 to 3.5 meters below ground surface (bgs) over the study site. Unsaturated soils are composed predominantly of well-drained sands and silty-sands that are overlain by asphalt pavement.

All of the wells included in this study were located at a sufficient distance from the source so that soil contamination, if any, was related to aqueous or non-aqueous phase hydrocarbons in the capillary fringe. Groundwater underlying this site is characterized by a moderate TDS (total dissolved solids) concentration of about 1,200 mg/L, a near neutral pH, and a year-round temperature of 17° to 20° Celsius. Inorganic analyses of regional groundwater (as distinguished from groundwater within the hydrocarbon plume) indicate that the major cation is calcium at about 300 mg/L, while the major anions are sulfate and bicarbonate at about 400 mg/L each. Neither soluble iron nor nitrate were detected above the 0.5 mg/L detection limit.

Sampling and analysis. Groundwater samples were collected from a total of 24 groundwater wells that had been previously sampled and analyzed for total petroleum hydrocarbons (TPH according to EPA Method 8015-modified). After minimal purging, groundwater samples were bailed from wells and an aliquot was analyzed according to the specifications in ASTM Method D-1498 (*Standard Practice for Oxidation-Reduction Potential of Water*). Redox potential and pH were quantified using an Orion model 240 instrument.

Soil gas samples were collected by hydraulically driving a 2.5 cm diameter (1.3 cm inner diameter) probe to depths of 2 to 3 meters below ground surface. The objective of the variable depth sampling was to collect soil gas within a 0.5-meter vertical distance of the water table and at a horizontal distance less than 3 meters from existing groundwater wells. Subsurface vapor samples were obtained via a two-stage evacuation chamber, permitting the extraction of exactly 0.5 liters of soil gas and the collection of samples under ambient pressure.

Gas samples were analyzed on site for oxygen (O_2) and hydrocarbon gases in the carbon range of C_1 through C_{10} using Hewlett-Packard model 5890 and Varian model 3400 gas chromatographs. These instruments were equipped with flame ionization (GC/FID) and thermal conductivity (GC/TCD) detectors. Separation of the C_4–C_{10} hydrocarbon analytes was achieved by using a DB-624 megabore capillary column (J&W Scientific), while the C_1–C_3 fraction was separated using a Unibeads-A packed column (Alltech Associates). Oxygen was separated using a CTR-1 dual packed column (Alltech Associates).

Results and discussion

Groundwater and soil gas chemistry. Table 1 presents redox and pH measurements, as well as TPH concentrations in groundwater, for individual wells included in this study. The results indicate that redox potentials ranged from –360 to +180 millivolts and that pH values were in the neutral range of 6.6 to 7.3 for all of the wells tested. TPH concentrations in the 24 groundwater wells varied from <0.1 mg/L (representing the analytical detection limit) to 220 mg/L, as measured by a commercial analytical laboratory. Over the past

Table 1. Groundwater and soil gas parameters associated with each of 24 subsurface monitoring locations. The groundwater parameters include total petroleum hydrocarbon (TPH) concentrations, pH and redox potential (Redox), while the soil gas parameters include the concentrations of methane (CH_4), ethane plus propane (C_2+C_3), C_4–C_{10} hydrocarbon gases (C_4–C_{10}) and oxygen (O_2). An asterisk (*) beside the TPH values denotes the wells at which NAPL had been detected at least once in the eight-year period preceeding this study

Well	TPH (mg/L)	pH	Redox (mv)	CH_4 (ppmv)	C_2+C_3 (ppmv)	C_4–C_{10} (ppmv)	O_2 (%)
A	45*	7.2	−170	12,000	<5	28,000	4.8
B	7.7*	7.3	−360	5,700	6300	57,000	5.7
C	8.1*	7.1	−260	810	340	34,000	3.5
D	29*	7.0	−30	1,500	<5	18,000	8.4
E	220*	6.8	−120	<10	<5	340	8.0
F	190*	7.2	−140	11,000	<5	23,000	2.6
G	82*	7.0	−250	6,200	<5	59,000	2.0
H	53	7.1	−30	1,500	<5	74,000	5.5
I	0.2	7.1	−330	<10	<5	<10	15.9
J	16*	6.6	−310	18,000	4500	57,000	2.6
K	98*	6.9	−150	14,000	3500	76,000	2.8
L	7.5*	7.1	−150	6,100	<5	37,000	4.9
M	2.2	6.8	−310	6,600	<5	82,000	2.9
N	0.2	6.9	−80	<10	<5	22	11.8
O	140*	7.0	−310	17,000	<5	39,000	2.0
P	4.8*	6.9	−50	1,700	<5	4,900	5.7
Q	1.6	7.1	−60	<10	<5	<10	13.1
R	<0.1	7.0	+140	<10	<5	<10	19.3
S	<0.1	7.2	+170	<10	<5	<10	20.0
T	<0.1	7.2	−80	<10	<5	<10	17.7
U	<0.1	7.1	+10	<10	<5	20	17.9
V	<0.1	7.2	+170	<10	<5	<10	19.1
W	<0.1	7.1	+160	<10	<5	75	15.7
X	<0.1	7.1	+180	<10	<5	<10	19.5

eight years, NAPL was detected during at least one quarterly sampling event at approximately half of the groundwater wells listed on Table 1.

Generally, TPH concentrations were highest in those wells which were reported to have contained NAPL. The carbon range for TPH in quarterly groundwater samples (i.e., C_6 through C_{12}) suggests that gasoline was the only distillate present. Redox potentials less than zero millivolts (mv) were

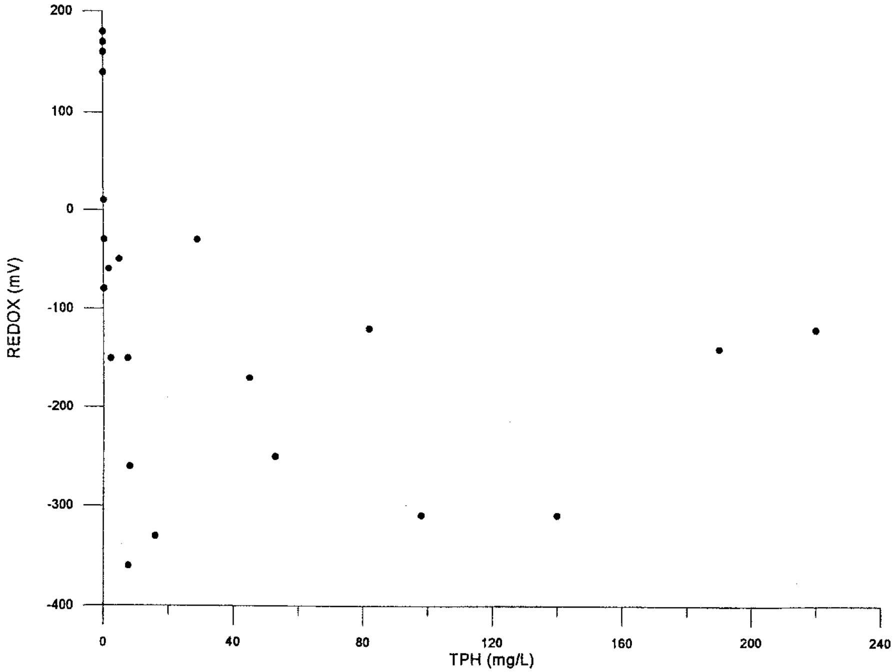

Figure 1. Plot of Redox (redox potential) vs TPH (total petroleum hydrocarbons in the range of C_6 through C_{12}) in groundwater wells.

recorded at all wells where TPH was present, while redox potentials greater than zero were encountered at 6 of the 7 wells in which no aqueous contamination by TPH was detected. TPH concentrations in groundwater are plotted against redox potentials on Figure 1.

The results of analyzing vapor samples from 24 points located adjacent to the groundwater wells are presented on Table 1. Oxygen concentrations in soil vapor, which ranged from 2.0% to 20.0%, did not exceed 16% adjacent to wells in which TPH was detected. Oxygen concentrations in soil gas are plotted against groundwater redox potential on Figure 2. Linear regression analysis indicates an r^2 value of 0.72, suggesting that there is a positive correlation between the two parameters despite a wide scattering of points. Oxygen was analyzed because of its biotic and abiotic demand in the subsurface and, thus, its role in influencing both redox conditions and biodegradation pathways (White et al. 1990). O_2 concentrations are normally quite low in soil vapor immediately above contaminated groundwater due to the abundance of electron donors and the limited re-aeration of highly saturated soils near the capillary fringe (Marrin 1991).

Methane concentrations ranged from less than the 10 ppmv detection limit to as high as 18,000 ppmv (1.8% by volume) in soil gas and were

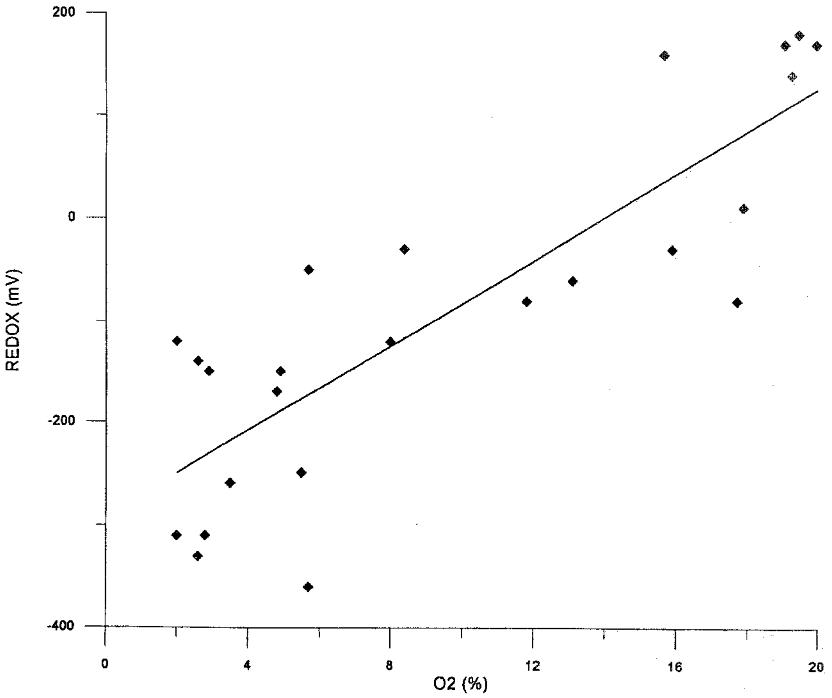

Figure 2. Plot of Redox (redox potential) in groundwater vs O_2 (oxygen) concentrations in soil gas within a 3 meter radius of the well. The curve represents a linear regression fit of the points ($r^2 = 0.72$).

generally highest adjacent to wells in which NAPL or high TPH concentrations were observed. Methane was present above the detection limit only at sampling points where oxygen concentrations were less than 12% and where groundwater redox potentials were less than 0 millivolts. Similar observations for the 'threshold' appearance of methane in soil gas overlying petroleum-contaminated groundwater has been described by Marrin (1991) and is probably related to the spatial dynamics of CH_4 oxidation in the unsaturated zone. A plot of redox potential versus methane concentrations is shown on Figure 3 and suggests a general inverse relationship between the two parameters. Regression analysis indicates this relationship is not statistically significant due to the presence of three points at which relatively low CH_4 levels (<6,000 ppmv) were correlated with redox potentials less than –250 mv.

In addition to methane, both ethane and propane (C_2+C_3 alkanes) were detected in soil gas samples; however, none of these three gases were detected in the headspace above a NAPL sample obtained from the source area. Ethene, propene, and acetylene were analyzed but not detected in any of the

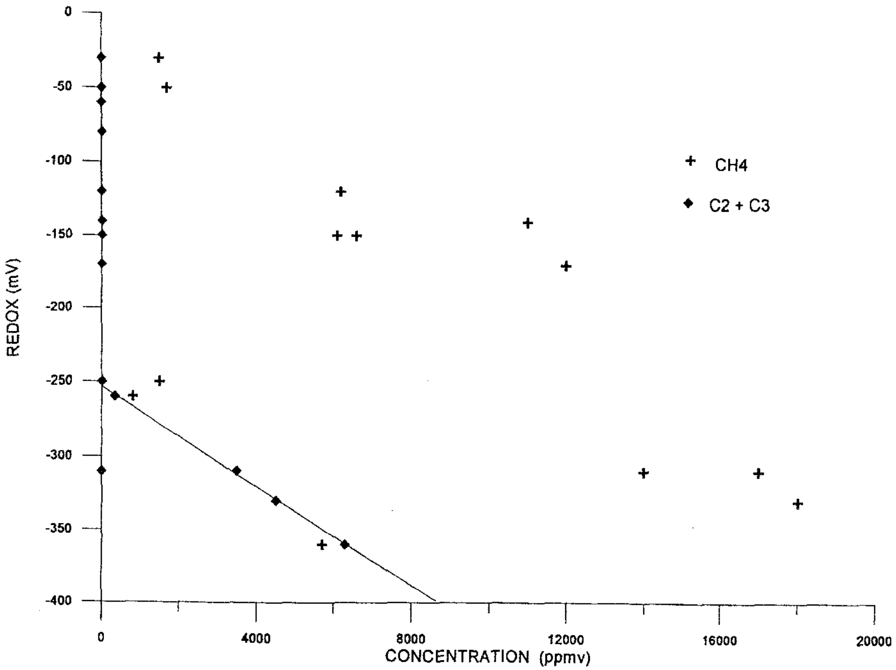

Figure 3. Plot of Redox (redox potential) in groundwater vs CH_4 (methane, as represented by crosses) and C_2+C_3 (ethane plus propane, as represented by diamonds) concentrations in soil gas within a 3 meter radius of the well. The curve represents a linear regression fit of the points ($r^2 = 0.99$) at which C_2+C_3 were present above the analytical detection limit.

vapor samples. Locations at which the C_2+C_3 alkanes were encountered did not correspond to underground sewer or natural gas lines, nor to any other known sources of these compounds (e.g., petroleum deposits or gas seeps). A significant correlation ($r^2 = 0.99$) was calculated for the plot of redox potential versus detectable C_2+C_3 alkane concentrations, as shown on Figure 3. C_2+C_3 alkanes were not present above the 5 ppmv detection limit at points were the redox potential in groundwater exceeded –260 mv. Only one data point in the redox range of –250 to –400 mv lies substantially off the regression line shown on Figure 3. If this point is added to the other five, an r^2 value of 0.87 is calculated for all six data points in this redox range.

Possible sources and sinks of C_2+C_3 alkanes. There are two probable sources for C_2+C_3 alkanes present in soil gas at this site. The first is that these compounds are components of the gasoline vapor and are still present at concentrations high enough to be detected at a few of the sampling locations. Mayrsohn et al. (1977) have reported that C_2+C_3 alkanes constitute less than 2% of fresh gasoline vapor, by weight. Although it is possible that NAPL volatilization constitutes the sole source of C_2+C_3 alkanes in soil gas, it is unusual to detect these very "light" hydrocarbon gases above an 8-year old product plume that has migrated as far as 100 meters from the release point. Due to their rapid volatilization and diffusion through soil gas, the lightest fraction ($<C_4$) is normally depleted relative to the intermediate molecular weight fraction (C_5 to C_8) as a function of both time and distance from the release point. At this site, C_2+C_3 alkanes constituted an average of 5.6% of the nonmethane gaseous hydrocarbons, which is actually a higher percentage than that reported for fresh gasoline vapor by Mayrsohn et al. (1977). Additionally, the locations at which C_2+C_3 alkanes were present does not correspond to the highest levels of either C_4–C_{10} hydrocarbon gases in soil vapor or TPH in groundwater (see Table 1), which is an unexpected result if the presence of C_2+C_3 alkanes is due strictly to volatilization.

The other potential source of C_2+C_3 alkanes in soil gas is biogenic, which has been reported to occur under methanogenic conditions (e.g., Wiesenburg et al. 1985, Oremland et al. 1987). The limited presence and spatial distribution of C_2+C_3 alkanes at this site suggest they may be produced under a narrow range of environmental conditions, which are reflected by groundwater redox potentials. In addition, there is always the possibility that small-scale gas seeps could have contributed the C_2+C_3 alkanes. Analysis of carbon isotope ratios in the C_1 to C_3 hydrocarbon gases will be conducted during the next phase of study in order to evaluate this possibility.

Regardless of the source of C_2+C_3 alkanes, the presence or absence of these hydrocarbon gases in soil vapor may also be related to spatial variations associated with their oxidation in the unsaturated zone. It has been shown that methane monooxygenase, the primary enzyme produced by methanotrophic bacteria, is able to catalyze the oxidation of a wide variety of compounds including C_2+C_3 alkanes (Topp & Hanson 1991; Patel et al. 1982). Although data presented in this preliminary study were not designed to answer questions regarding biodegradation pathways, it is interesting to note that the phenomenon of methanotroph-mediated oxidation in soil has been postulated by Marrin (1991) for the observed spatial distribution of methane above petroleum-contaminated groundwater. Based on values of Gibbs free reaction energy for C_1 to C_3 hydrocarbon gases (El-Sebaay et al. 1989), the oxidation of C_2+C_3 alkanes is thermodynamically more favorable than that of methane using all common terminal electron acceptors (e.g., oxygen, nitrate, ferric iron and sulfate). Whatever the contributing mechanisms, methane was detected at higher concentrations and at a greater number of sampling points than were C_2+C_3 alkanes.

The statistically significant correlation between groundwater redox potential and C_2+C_3 alkanes in soil gas may be related, in part, to the relatively few points at which these gases were detected. While the limited data presented in this paper indicate a possible correlation between groundwater redox conditions and C_2+C_3 hydrocarbon gases, further research is required to confirm such a relationship. In particular, the relative contribution of microbial degradation and NAPL volatilization to C_2+C_3 alkane levels in soil gas and the degree to which local variations in the diffusion or oxidation of C_2+C_3 alkanes influence their spatial distribution are unknown. Research is currently being conducted to assess the relationship between multiple indicators of redox conditions and relative concentrations of C_1 to C_3 hydrocarbon gases in both groundwater and the vadose zone.

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