Unsaturated Zone CO$_2$, CH$_4$, and $\delta^{13}$C-CO$_2$ at an Arid Region Low-Level Radioactive Waste Disposal Site


Elevated tritium, radiocarbon, Hg, and volatile organic compounds associated with low-level radioactive waste (LLRW) at the USGS Amargosa Desert Research Site (ADRS) have stimulated research on factors and processes that affect contaminant gas distribution and transport. Consequently, we examined the sources, mixing, and biogeochemistry of CO$_2$ and CH$_4$, two additional important species in the unsaturated zone at ADRS. In spring 2015 and 2016, shallow unsaturated zone gas samples were collected from the 1.5-m depth both inside and outside the LLRW disposal area. Samples also were collected from two 110-m-deep multi-level gas-sampling boreholes and a distant background site. These samples were analyzed for CO$_2$ mole fraction ($x$CO$_2$) and C isotopic composition ($\delta^{13}$C-CO$_2$) and CH$_4$ mole fraction ($x$CH$_4$). Graphical analysis of the results indicates mixing of CO$_2$ characteristic of the root zone ($\delta^{13}$C −18 to −19‰), deep soil gas of the capillary fringe (−13 to −15‰), and CO$_2$ produced by microbial respiration of organic matter disposed in the LLRW trenches (−22 to −25‰). Distribution of CH$_4$ overall reflects atmospheric sources and production in anaerobic microzones in the LLRW area and methanotrophy in the undisturbed shallow subsurface outside the LLRW area. Although $x$CH$_4$ reflecting lateral transport from the LLRW area is decreasing with time in the deep profiles, deep unsaturated zone $x$CO$_2$ has changed little in recent decades. The results imply that CH$_4$ and $\delta^{13}$C-CO$_2$ may serve as good tracers of anthropogenic effects in the unsaturated zone even when CO$_2$ primarily reflects natural processes.

Understanding gas transport in arid, unsaturated zones is critical to addressing challenges related to waste disposal and storage, including chemical and radioactive waste facilities. Such facilities often are sited in desert environments because they tend to be in remote areas and because deep water tables and low levels of precipitation minimize contaminant mobility and groundwater vulnerability. Yet contaminant transport, particularly in the gas phase, is far from negligible in these systems. Characterizing this transport through the unsaturated zone can be complicated by anisotropic flow and preferential flow paths—limited information and few studies exist for unconsolidated sediments in deep unsaturated zones (Green et al., 2015). Therefore, recent unsaturated zone studies in arid environments have focused on investigating and refining transport models (Green et al., 2015; Monger et al., 2014; Walvoord et al., 2014). Information from gas isotopes and environmental tracers offer important guidance for these refinements. In this study, we examined CO$_2$ and CH$_4$ at the USGS Amargosa Desert Research Site (ADRS), which includes the Beatty, NV, low-level radioactive waste (LLRW) site, adjacent land, and a distant natural background site. Our general purpose was to understand sources and transport of subsurface CO$_2$ and CH$_4$ in the unsaturated zone adjacent to and within the LLRW area.

The distribution of CO$_2$ and CH$_4$ in the arid unsaturated zone can generally be considered as resulting from atmosphere–soil exchange, shallow subsurface microbial sources and sinks, and in some cases deep sources originating at or immediately above
the water table (Bacon and Keller, 1998; Tokunaga et al., 2016; Walvoord et al., 2005; Wood and Petratis, 1984). Natural profile studies at ADRS have shown two primary subsurface sources of CO$_2$; one shallow source that is related to microbial respiration in the root zone, and one deep source that is at least in part related to calcite precipitation (Walvoord et al., 2005). The relative production of these sources and upward diffusion of CO$_2$ from the deep source was determined using C isotopic composition ($\delta^{13}C$) and geochemical gas diffusion modeling. Methane in shallow arid unsaturated zones is predominantly a balance of downward diffusion of atmospheric CH$_4$ and consumption by soil methanotrophs, with soil moisture being an important factor in this balance (Angel and Conrad, 2013; Hou et al., 2012; Striegl et al., 1992). Low soil moisture can cause microbial stress through desiccation and thus results in lower methanotrophy and higher $\delta^{13}CH_4$, whereas higher soil moisture can limit CH$_4$ gas transport from the atmosphere to the soil by reducing air-filled porosity (Angel and Conrad, 2013; Czepiel et al., 1996a; Hou et al., 2012; Striegl et al., 1992). Thus, there is an optimal window for microbial CH$_4$ oxidation (Czepiel et al., 1996a). At landfill sites, another consideration is that soil moisture can facilitate formation of anaerobic microzones in waste, promoting microbial methanogenesis, and water infiltration can displace gas from waste pore spaces (Czepiel et al., 1996a; Striegl and Ishii, 1989). Efflux of CO$_2$ from arid landfills can be substantial, but that efflux is not necessarily influenced by changes in soil moisture or temperature (Koerner and Kloepke, 2002). Arid climate conditions result in minimal formation of CH$_4$ in landfills compared with those in other climate types; however, limited data suggest that a relatively high proportion of that CH$_4$ is oxidized within the landfill footprint (Chanton et al., 2011).

Materials and Methods

Overview of Amargosa Desert Research Site

The ADRS and Beatty LLRW disposal facility are located in the Amargosa Desert, approximately 150 km northwest of Las Vegas, NV (Fig. 1). Nearby features include Death Valley National Park and Yucca Mountain, the latter a location previously considered for a high-level nuclear waste repository that is located within the Nevada National Security Site, which was once used for nuclear weapons testing. The shallow geologic framework of the site, described in detail by Taylor (2010), consists of Quaternary alluvium from the adjacent Bare Mountain Range and the Amargosa River. The unsaturated zone is characterized by sediments deposited by transport-limited braided fluvial systems typically showing repeated fining-upward sequences, 5 to 8 m thick, of unconsolidated sand and gravel down to the water table at approximately 110 m below the land surface.

Fig. 1. Location of the USGS Amargosa Desert Research Site (ADRS) and Beatty low-level radioactive waste (LLRW) facility. The Amargosa Desert is highlighted within its hydrographic boundary.
Climate

The climate of the area is generally very dry—one of the driest areas in the United States (Stonestrom et al., 2007)—with precipitation at the ADRS averaging 104 mm/yr (Kauble et al., 2018) but with potential evaporation in the region greatly exceeding precipitation on an annual basis (Nichols, 1987; Stonestrom et al., 2007). The majority of annual precipitation in the region arrives in frontal systems during December to March, and daily average temperatures range from around 35°C in summer to around 5°C in winter (Nichols, 1987; Stonestrom et al., 2007; Walvoord et al., 2004). The samples for this study were collected before and after an anomalously wet autumn. October 2015 was characterized as one of the wettest months ever recorded in the region, with 29 mm of precipitation in nearby Death Valley, approximately 16 times the long-term average for that month and roughly half of the typical annual precipitation (NOAA, 2015). Micrometeorological data from the ADRS showed 71 mm of precipitation for October 2015 (Kauble et al., 2018).

Unsaturated Zone Hydrology

The shallow unsaturated zone at ADRS is characterized by low volumetric water content and low (strongly negative) matric potential. Soil moisture profiles are regularly monitored at four experimental sites at ADRS (Andraski, 1997; Arthur et al., 2012; Johnson et al., 2007). One of these sites represents a naturally vegetated native soil profile, and another is a devegetated native soil profile. In addition, there are two devegetated simulated waste trenches designed to simulate solid LLRW burial and unvegetated surface conditions. In vegetated areas, water contents in the upper 1 m vary in response to precipitation and range between 0.02 and 0.14 m³/m³ (Andraski, 1997). The penetration of precipitation below 1 m is limited by efficient desert plant water uptake and a laterally extensive gravelly layer (about 1 m thick) that underlies the surface soil and impedes downward percolation of liquid water. The simulated waste trenches showed enhanced moisture accumulation and penetration below the 1-m depth due to the homogenizing effects of trench construction and maintenance of a vegetation-free surface (Andraski, 1997). In the deep unsaturated zone, water content is temporally invariant and ranges from 0.05 to 0.14 m³/m³. Matric potential and temperature gradients support upward thermal and isothermal water vapor fluxes, although the magnitude of these fluxes is relatively low (Mayers et al., 2005; Walvoord et al., 2004, 2005, 2014).

Beatty Facility Operation

The disposal site consists of both a closed LLRW area and an active hazardous waste disposal area (Fig. 2). The LLRW area, described in detail elsewhere (Idaho National Engineering Laboratory, 1994), was the first commercial LLRW operation in the United States, and operated between 1962 and 1992. The hazardous waste disposal area has operated from 1970 to the present. More than 133,929 m³ of LLRW was buried at the facility. The LLRW came from a variety of sources, predominantly industrial, utility, and government but also academic and medical. This waste contained about 24 PBq (640,000 Ci) of byproduct material, 1.8 million kg of source material, and 274 kg of special nuclear material. The LLRW area has 22 trenches of various sizes—about 90 to 240 m long, 1 to 110 m wide, and 2 to 15 m deep (Fig. 3). Burial-trench construction entailed excavation of native sediment, emplacement of waste, and backfilling. Lining of LLRW trenches was not required; however, lining of hazardous waste trenches was required beginning in 1988. When the LLRW site closed, the trench area was capped with at least 2 m of stockpiled sediment. Early commercial LLRW disposal practices (1960–1980) included disposal of some waste in degradable packaging (such as cardboard), wastes often mixed with other chemical or chemical agents that enhanced waste degradation, and less attention to compaction of waste and slumping or subsidence of trench covers compared with more recent practices (Conference of Radiation Control Program Directors, 1996; Idaho National Engineering Laboratory, 1994).

Field and Sampling Methods

Sampling Locations

All samples were collected during 2- to 3-d annual sampling events in April 2015 and 2016. Gas samples were collected from shallow transects that extended outside and across the LLRW area and from two deep boreholes (Fig. 2). For the shallow transects, representing the shallow unsaturated zone, samples were collected from 1.5-m-depth soil gas tubes. The tubes were 2-m lengths of...
black steel pipe (10.29 mm o.d., 5.47 mm i.d.) that were hand driven vertically to sampling depth (Andraski et al., 2003). These shallow samples were collected from locations near the edge of the area and directly over trenches (Fig. 3). Shallow transect samples were generally collected along east–west and north–south trends, with location names (e.g., X-215, Y-650) designating the x, y distance in meters away from the southwest corner of the ADRS study area perimeter. Locations X-488, Y-480 and X-418, Y-456 are off the main transects, but represent locations by creosote bushes known to have elevated plant water tritium activity. Samples from the deep unsaturated zone were collected from the two deep boreholes (UZB2 and UZB3, 100 and 33 m outside the LLRW area, respectively) instrumented with nested, vertical sampling wells extending to depths of just over 100 m (Prudic et al., 1997; Walvoord et al., 2005). Samples were also collected from a site 3 km south of the LLRW area, consisting of both air samples (about 1 m above ground level) and samples from another nested, vertical sampling well (JFDB). Sampling points in UZB2 and UZB3 were 30-cm-long stainless steel screened intervals connected to 6-mm-diameter nylon tubing that extended to the surface. At JFDB, sampling points used 60-cm-long polyvinyl chloride screen and 6-mm polyethylene tubing (Baker et al., 2012).

Sample Collection

Samples from the unsaturated zone and air were pumped into 1-L multilayer foil bags (Restek Corporation) using a portable, battery-powered peristaltic pump (Masterflex L/S, Cole-Parmer) at a rate of 1000 mL/min. To minimize CO₂ carryover between sampling points, the pump sample line used a minimal length of C-Flex tubing connected to short lengths of Teflon fluorinated ethylene propylene (FEP) tubing. In addition, sampling in 2016 used a small rigid, negative pressure sampling box (Vac-U-Chamber, SKC, Inc.) that allowed direct filling of sample bags without passing through the pump. A purge time of 1 or 2 min per 10 m of well depth (minimum time 2 min) was used to circulate each well and condition the tubing before sampling. The shorter 1-min purge time was used if the well was recently (<4 h) sampled for another analyte as part of complementary ongoing studies at ADRS (e.g., tritium analysis). The volume of well tubing was 0.03 L/m, so purge time and pumping rate correspond to three to seven well volumes. Prior to the field sampling campaign, the stability of analytes in sampling bags was tested by performing repeated measurements on bags of reference gas for xCO₂ and δ¹³C-CO₂ (average 9000 mol/mol and −40‰, respectively), which showed no change for 10 d.

Analysis

Instrumental Analysis

Gas sample bags were transported and analyzed within 4 d of sampling at USGS, Menlo Park, CA, by direct injection into a Picarro G2101-i cavity ring-down spectrometer (CRDS). The CRDS sampling rate was 25 mL/min for 3 min, with xCO₂, δ¹³C-CO₂, and xCH₄ data representing the average and standard deviation during 1 min of stable reading. Stability was assessed using the instrument-reported linear slope of data during the 1-min period as well as relative standard deviation of the data. The normal operating range of the G2101-i is 200 to 3500 mol/mol CO₂ for determinations of xCO₂ and δ¹³C-CO₂. All samples were above the specified minimum of this range. Higher xCO₂ and all xCH₄ results were verified against in-house standards up to 20,000 mol/mol CO₂ and 35 mol/mol CH₄. Calibration of the CRDS for δ¹³C-CO₂ was performed by combustion of powdered samples with a known δ¹³CVPDB (i.e., values use the Vienna Peedee Belemnite scale), covering the full range of sample result xCO₂ and δ¹³C-CO₂. Drift of the δ¹³C-CO₂ instrument response was monitored using gas samples prepared in the laboratory of –6, –14, and –30‰ δ¹³C-CO₂ or by periodic determinations on a reference gas using an uncalibrated commercial CO₂ source (1% CO₂ in N₂, δ¹³C-CO₂ of –40‰). Because calibration standards were prepared in N₂ rather than air, sample data were corrected for gas matrix differences using literature values. We used a δ¹³C offset of 5.1 for the difference between pure N₂ and pure air, as discussed by Friedrichs et al. (2010). For further information on isotope fundamentals and causes of isotopic variation, see Kendall et al. (2014).

Quality Assurance and Control

Duplicate analyses performed on sample bags (n = 6) showed a difference of <0.2% for δ¹³C-CO₂, a relative percentage difference (RPD) of typically <0.5% on xCO₂, and typically <0.7% for xCH₄ (median 0.3%). Duplicate samples collected in the field (n = 12) showed a difference of <0.4% for δ¹³C-CO₂ (median difference 0.2%), a RPD of typically <3% for xCO₂ (median 0.4%), and typically <6% for xCH₄ (median 0.8%). The RPD on one set of field-collected duplicates, from our highest xCO₂ site (X-488, Y-480) was 6% for xCO₂ and 12% for xCH₄—we attribute the differences to the relatively high amounts of CO₂ and CH₄ and
to the shallow depth of sampling and a partial blockage noted in this particular well.

Results and Discussion

Overview

A three-dimensional understanding of $x_{CO_2}$ and $x_{CH_4}$ distribution and related biogeochemical processes is gained by evaluating data collected from the two deep boreholes and numerous shallow gas tubes in and near the LLRW area and from samples collected from the remote reference site JFDB. The $\delta^{13}C$-$CO_2$ data help elucidate the mixed sources of $CO_2$ throughout the site. The limited time-series data from locations sampled more than once shed some light on changing gas composition during a short time interval, especially as related to changing moisture conditions caused by precipitation variability in different years. These points are discussed in detail below.

Background and Deep Borehole Profiles of $x_{CO_2}$, $\delta^{13}C$-$CO_2$, and $x_{CH_4}$

The background air measured 1 m above the ground at JFBD was about 407 $\mu$mol/mol $CO_2$, $\delta^{13}C$-$CO_2$ $\approx -10\%$, and 1.9 $\mu$mol/mol $CH_4$, which is consistent with typical background atmospheric values. The profiles at UZB2 showed the distribution of $x_{CO_2}$, $\delta^{13}C$-$CO_2$, and $x_{CH_4}$ in relatively unperturbed conditions near the LLRW area (100 m away) compared with UZB3, which is closer in proximity (33 m) to the LLRW boundary (Fig. 4). As noted by Walvoord et al. (2005), the $x_{CO_2}$ in UZB2 showed a consistent increase with depth, suggestive of a deep natural source of $CO_2$ near the water table. At the deepest JFDB background sampling point (28.7 m), the $x_{CO_2}$ was only slightly less than the equivalent depth in the $x_{CO_2}$ profile at UZB2, and that was consistent with the relatively natural profile of $x_{CO_2}$ at UZB2.

However, a comparison $\delta^{13}C$-$CO_2$ at that same point shows that UZB2 was about 3‰ lower than JFBD. In addition, $x_{CH_4}$ was also greater in the UZB2 profile than the deep sampling point at JFDB and showed a broad increase, with a peak at about 60 m. The distribution of $x_{CH_4}$ in the UZB2 profile, which was similar to its UZB3 profile, was in excess of atmospheric values, which, as discussed in detail below, shows that the $CH_4$ was derived from microbial methanogenesis related to the decomposition of organic waste buried at the waste site.

A contaminant $x_{CO_2}$ peak, $x_{CH_4}$ peak, and lower $\delta^{13}C$-$CO_2$ at UZB3 than UZB2 are all consistent with UZB3 being closer to the LLRW area. In contrast to UZB2, the $x_{CO_2}$ profile at UZB3 showed elevated values between 5 and 60 m, with a peak of >20,000 $\mu$mol/mol between the 15- and 35-m depths (Fig. 4A). Associated with this $x_{CO_2}$ peak were lower values for $\delta^{13}C$-$CO_2$ to about $-22\%$ (Fig. 4B). The $x_{CH_4}$ profile showed a linear increase from the surface to about the 35-m depth, then a more gradual decrease from that peak to about the 80-m depth, and then a sharp reduction in $x_{CH_4}$ below 80 m (Fig. 4C). The $x_{CH_4}$ profile somewhat mirrored the $x_{CO_2}$ profile, but the peak values were at different depths and $x_{CH_4}$ decreased more gradually with depth. The occurrence of peak $x_{CO_2}$ and $x_{CH_4}$ at or below the depth of the deepest trenches (15 m) was consistent with the observed contaminant peaks at 20 to 40 m in UZB3 of volatile organic compounds (VOCs), tritium, and Hg vapor (Baker et al., 2012; Mayers et al., 2005; Walvoord et al., 2008). This difference in peak contaminant occurrence and the lowest trench depth has been attributed both to anisotropic transport in laterally extensive gravel layers (Mayers et al., 2005) and to downward buoyant forces on relatively dense gas contaminants during lateral transport (Baker et al., 2012). Differences in $CO_2$ and $CH_4$ distributions can be explained by the relatively higher solubility and complex chemistry between $CO_2$ and pore water via $CO_2$–$CO_3$ system chemistry compared with the relatively unreactive and less soluble $CH_4$ (Striegl and Ishii, 1989). This difference in chemical properties explains the sharper decline of $x_{CO_2}$ in profiles compared with the more gradual changes in the $x_{CH_4}$ profile.

Interannual and Decadal Trends in Deep Borehole $x_{CO_2}$, $\delta^{13}C$-$CO_2$, and $x_{CH_4}$

When comparing 2015 and 2016 results at a given site and depth, samples from UZB2 and UZB3 at depths below 5 m showed little difference in $x_{CO_2}$, $\delta^{13}C$-$CO_2$, and $x_{CH_4}$ (Fig. 4). The relative difference [= (absolute difference)/mean] of $x_{CO_2}$ in samples below 5 m was typically <5%, and changes in $\delta^{13}C$-$CO_2$ were usually <0.5‰. Somewhat greater differences were observed in $x_{CH_4}$ but were <10% in the deeper samples. The differences in deep unsaturated zone $x_{CO_2}$, $\delta^{13}C$-$CO_2$, and $x_{CH_4}$ are similar
to those observed in field-collected duplicates, suggesting generally little difference between 2015 and 2016 sampling results. However, some larger differences were observed in deeper samples. In UZB3 from 35.1 to 56.6 m there was an increase in xCO₂, with a maximum change from 4460 to 8300 μmol/mol at 48.6 m (Fig. 4A), and a decrease of 5.6‰ in δ¹³C-CO₂ (Fig. 4B). This shift is unlikely to be explained by seasonal or interannual changes in soil respiration because such effects are limited to the upper 30 m (Walvoord et al., 2005). In addition, a xCO₂ increase from 3760 to 5280 μmol/mol was observed in UZB3 just above the water table (103.9 m), with a corresponding 1.1‰ decrease in δ¹³C-CO₂. This change could be related to an increase in the deep production rate (Walvoord et al., 2005), but the exact mechanism for this change is not clear, and intuitively such changes usually occur over a longer time frame.

The xCO₂ profile at UZB2 strongly resembled the 1994 to 2003 data presented by Walvoord et al. (2005), suggesting little change in the deep xCO₂ profile in more than a decade (Fig. 5A). However, δ¹³C-CO₂ in roughly the 30– to 50-m interval appeared to show a slight (1‰) increase between 1998 and 2015 to 2016 (Fig. 5B). As at UZB2, the xCO₂ profile at UZB3 in this study was consistent with data from previous sampling back to 2000 (Baker et al., 2012; Stonestrom et al., 2004). Thus, although there was some year-to-year variability of xCO₂ in the borehole profiles, there was apparently not a long-term increase or decrease in xCO₂ or a change in profile shape. This lack of a long-term decrease or increase is consistent with approximately steady-state VOC concentration profiles from 2000 to 2009 (Baker et al., 2012), although VOC concentrations show a greater year-to-year variability.

In contrast to xCO₂, xCH₄ appears to have decreased at both UZB2 and UZB3 during the past two decades (Fig. 5C). At UZB2, a decrease was observed between 1997, when values up to 9 μmol/mol were measured (Stonestrom et al., 2004), and 2015 to 2016 (this study) with a peak value of 4.7 μmol/mol. Similarly, xCH₄ at UZB3 has decreased substantially from a profile maximum of 18 μmol/mol in 2000 (Stonestrom et al., 2004) to 12 μmol/mol in 2015 to 2016 (this study). These decadal-scale xCH₄ decreases are greater than the observed 2015 to 2016 variability and may represent a long-term trend for xCH₄ in the deep unsaturated zone. We note, however, that sampling and analytical methods were similar in many ways (e.g., well purging times, pumping rates) but not identical (e.g., sampling containers, instrumental analysis) for 1997 to 2000 and 2015 to 2016. Nonetheless, the consistency of xCO₂ data using these different sampling and analytical methods is reassuring for xCH₄ data comparison.

### Spatial Variability of Shallow xCO₂, δ¹³C-CO₂, and xCH₄

There were substantial changes in xCO₂, δ¹³C-CO₂, and xCH₄ at the 1.5-m-depth sampling locations moving from 400 m outside the LLRW area and onto and across the trench cover along the Y-650 line (Fig. 6). The most apparent change along the transect was at X-375, 25 m outside the LLRW area, where δ¹³C-CO₂ becomes lower and xCH₄ increases. This transition around 25 m was consistent with the observed difference between UZB3 and UZB2, which are located 33 and 100 m outside the LLRW area, respectively. Other transects across the trench cover showed similarly elevated xCO₂ and xCH₄, and lower δ¹³C-CO₂ (Fig. 7 and 8). Peak values of xCO₂ were observed over Trench 20 near the X-500 line at X-488, Y-480 (50,000–60,000 μmol/mol), while other peak values were observed over Trench 16 along the X-700 and X-800 lines (30,000–50,000 μmol/mol). Over and near the trenches, δ¹³C-CO₂ was typically in the range of −23 to −25‰. In the relatively undisturbed southwestern corner (no trench) and near the edges of the LLRW area (which includes X-600 along the Y-650 transect), δ¹³C-CO₂ was slightly higher: −18 to −19‰.

The distribution of xCH₄ was generally similar to that of xCO₂; however, there were exceptions. For example, the north–south transect on the western part of the LLRW area (X-500 line) appeared to demonstrate a northward increase in xCH₄, whereas xCO₂ appears to peak around Y-550. This same feature was shown along the Y-650 transect at the X-500 coordinate. It is unlikely that this uncoupling was caused by subsurface migration of CH₄ from the active hazardous waste area to the north into the LLRW area because the bottom and sidewalls of this hazardous waste trench are lined and impermeable to CH₄ migration (Stark and Choi, 2005). Previous work has demonstrated distinctly different composition of VOCs from
the LLRW area and closed hazardous waste area to the east (Baker et al., 2012), which suggests that the uncoupling may have resulted in part from source variations. Consistent with that suggestion is

the observation that emission patterns of CH₄ from landfill covers characteristically feature hotspots (Czepiel et al., 1996b).

Variability of Shallow xCO₂, δ¹³C-CO₂, and xCH₄ in 2015 and 2016

In contrast to the generally invariant short-term xCO₂ in the deep unsaturated zone, shallow samples (<5-m depth) compared for similar site and depth in boreholes and shallow transects showed an increase in xCO₂ between the 2015 and 2016 samplings. Outside the LLRW area, including along the Y-650 transect and 1.5-m samples at the boreholes, mean values of xCO₂, δ¹³C-CO₂, and xCH₄ were significantly different in 2015 than 2016 (Wilcoxon signed-rank test, p < 0.05). There was a mean relative change [=(x_{2016} - x_{2015})/x_{2015}] of 35% in xCO₂, with an accompanying decrease (depletion) of 1 to 2‰ in δ¹³C-CO₂. There was a consistent decrease in xCH₄, with a relative change of 30 to 79%. Inside the LLRW area, a paired difference test showed greater mean xCO₂ in 2016 (Wilcoxon signed-rank test, p < 0.05), with a mean relative increase of 24% in xCO₂ in paired samples but little change in paired δ¹³C-CO₂ values and no significant difference in means. There were both increases and decreases in sample pairs of xCH₄ inside the LLRW area, with a range of relative change from −13 to 47% but overall a slightly and significantly greater mean in 2016 (Wilcoxon signed-rank test, p < 0.05).

The higher xCO₂, lower δ¹³C-CO₂, and lower xCH₄ values outside the LLRW area in 2016 than 2015 are consistent with increased soil moisture related to the October 2015 rain event. Previous observations in the Amargosa Desert and at Yucca Mountain showed that greater soil moisture and warmer temperatures are associated with higher xCO₂ and lower δ¹³C-CO₂, and xCO₂ is highest in the spring, when δ¹³C-CO₂ is likewise at its lowest (McConnaughey et al., 1994; Riggs et al., 2009). Both observations are consistent with increased contributions of CO₂ from respiration. Precipitation enhances CH₄ consumption in arid soils (Hou et al., 2012; Striegl et al., 1992). Depth profile soil
moisture monitoring at ADRS covering 2015 to 2016 showed that soil moisture increased substantially at shallow depths to about 0.5 m following the October 2015 rain event, with effects lasting through the spring 2016 sampling (Kauble et al., 2018). The effects were greatest in experimental sites with the unvegetated native soil profile. At the 0.75-m depth and below, there appears to have been little influence from that precipitation and little indication of any temporal trends. The deep profiles of $xCO_2$, $\delta^{13}C-CO_2$, and $xCH_4$ would not be expected to respond to rainfall events because of the negligible percolation of infiltrated precipitation below the 1- to 2-m depth (Andraski, 1997).

The large amount of rain in October 2015 triggered an industrial fire incident at the LLRW site. Infiltrating rainwater reacted with metallic sodium waste in corroded steel drums at the eastern edge of Trench 14 (Fig. 3), causing a deflagration and release of NaOH in that area (Nevada Department of Public Safety, 2015). Although no sampling points in this study were over Trench 14, the most proximal set of samples, about 60 m away (X-800, Y-500 and X-800, Y-550), showed little or no difference between 2015 and 2016 in $xCO_2$, $\delta^{13}C-CO_2$, or $xCH_4$ (Fig. 8).

**Sources and Biogeochemistry**

Graphical analysis of the results using Keeling plots (Fig. 9) indicates mixing of $CO_2$ from several sources, including the atmosphere, soil root zone, deep unsaturated zone, and decomposition of buried organic waste. Deep sources may include both biogenic “georespiration” and abiotic $CO_2$ from precipitation of carbonate or degassing groundwater (Walvoord et al., 2005). Although source partitioning of many sources ($\geq 4$) is impossible using only one isotopic system ($\delta^{13}C$), insight can be gained by examining the Keeling plots.

Sources of $CO_2$ from the root zone, waste, and atmosphere are illustrated by a Keeling plot of the shallow sampling sites (Fig. 9A). Samples along the Y-650 line that are outside the LLRW and 1.5-m samples from UZB2 and UZB3 (i.e., “buffer zone” locations) show mixing predominantly between the atmosphere (roughly $-8\%$) and respiration in the root zone ($-18$ to $-19\%$), as determined by the $\delta^{13}C$ intercept of ordinary least-squares regression of all buffer zone data. Samples from within the LLRW area show a cluster of data with high $xCO_2$ and $\delta^{13}C$ in the range of $-22$ to $-25\%$. This represents $CO_2$ predominantly from decomposition of organic waste. A small number of samples from the LLRW area are outside that cluster, and those samples represent sites along the edge of the LLRW area (Fig. 3: X-400, Y-650; X-600, Y-650) and from the unexcavated...
part of the LLRW area (X-500, Y-425). This smaller set of LLRW area samples, which is intermediate between buffer zone samples and the cluster of other LLRW area samples, appear to be a mix of CO₂ from decomposition of organic waste and respiration in the root zone. It is important to consider that vegetation in the buffer zone is more nearly in a “natural” state, including the presence of soil crust and creosote bush scrub plant community, whereas the LLRW area is engineered surface that in the past was regularly cleared of vegetation, although less so along the edges and in the unexcavated portion in the southwestern corner.

The mixing of CO₂ from deep sources and the waste is illustrated by a Keeling plot of the borehole data (Fig. 9B). The bottom of UZB2, near the water table, had a δ¹³C-CO₂ of around −13‰, which is characteristic of gas in isotopic equilibrium with UZB2 groundwater (Walvoord et al., 2005). The lowest part of the UZB3 profile had a wider range of δ¹³C-CO₂ and was slightly lower (−14 to −15‰) compared with UZB2. This may represent the contribution of deep microbial respiration at UZB3, which is supported by reports of elevated coliform counts in the capillary fringe of UZB3 (Walvoord et al., 2005) and groundwater contamination by acetone and toluene (Baker et al., 2012). Regardless, samples at the lowest part of UZB3 (103.9 m) may not have been close enough to the water table (about 110 m) to show C isotopic equilibrium with the groundwater. Both UZB2 and UZB3 showed a mid-depth excursion of increasing xCO₂ and C isotope values toward a δ¹³C-CO₂ of −22 to −24‰, which probably represents lateral transport of CO₂ generated by microbial respiration of disposed waste. The upper parts of the borehole profiles show a trend toward the atmospheric endmember.

Consideration of previous data on fixed gas composition provides insight into the microbial processes generating CO₂ and CH₄. Previous sampling at UZB2 and UZB3 has shown that the mole fraction of oxygen (xO₂) was lower at depth compared with atmospheric values, especially in UZB3 (17.5% O₂) at depths (23.5 m) that have high concentrations of VOCs (Baker et al., 2012). This depletion of xO₂ corresponds to elevated xCO₂ and xCH₄. The changes in xCO₂ and xO₂ are far greater than changes in xCH₄, and this suggests that aerobic microbial respiration was predominant. Presumably CH₄ is produced by obligate anaerobic methanogens, which in aerobic vadose zones would typically only be active in anoxic microenvironments facilitated by the accumulation of water in and on waste containers (Striegl and Ishii, 1989). However, methanogenesis has been observed to occur in the presence of O₂ in biological soil crusts of arid regions using CO₂ as a terminal electron acceptor (Angel et al., 2011). Differences in the peak values and depth profiles of xCO₂ and xCH₄ noted above (Fig. 4) may have resulted to some extent from differences in the distribution of microbial processes and local conditions generating CO₂ and CH₄.

The consumption of CH₄ by soil methanotrophs is also a key process in controlling xCH₄. The xCH₄ in the air at JFDB was 1.9 μmol/mol, but subsurface xCH₄ at JFBD and shallow xCH₄ measurements outside the LLRW area were typically <0.6 μmol/mol. In these areas, CH₄ is probably atmospheric in origin and depleted by soil methanotrophs relative to atmospheric values. The xCH₄ values observed in this study were similar in magnitude to those observed in unsaturated glacial and eolian deposits adjacent to a LLRW facility near Sheffield, IL (Striegl and Ishii, 1989). An arid climate and low precipitation can result in minimal formation of leachate and anaerobic microzones in landfills, and thus relatively low generation of CH₄ compared with landfills in other climate types (Chanton et al., 2011; Goldsmith et al., 2012). Within the LLRW area, xCH₄ in the shallow subsurface was typically above background atmospheric values, which reflects both the CH₄ produced in the waste zone but also potentially the engineered trench surface and thus the lack of a well-developed root zone supporting soil methanotrophs as CH₄ consumers. A similar effect occurred along the Y-650 transect at X-215, where xCH₄ was 1.0 to 1.5 μmol/mol. This sampling site is in another mechanically disturbed area with a surface devoid of vegetation (Fig. 2). Sampling locations along the transect on either side of X-215 had xCH₄ < 0.3 μmol/mol. A lack of soil methanotrophs in disturbed arid soils was also observed in the Negev Desert, Israel (Angel and Conrad, 2009). In contrast to that result, however, a relatively high fraction of landfill-produced CH₄ was oxidized in landfill covers in arid climates compared with other climate types (Chanton et al., 2011)

**Carbon-13 Isotopic Composition as an Indicator of Contamination**

As mentioned above, xCO₂ at JFDB was only slightly less than xCO₂ at UZB2 at depth (28.7 m), whereas δ¹³C-CO₂ at UZB2 was about −3‰ lower than at JFDB. This suggests that some portion of the CO₂ at UZB2 was influenced by lateral transport from the LLRW area, and that δ¹³C-CO₂ can be used as a more sensitive indicator of contamination than xCO₂. Walvoord et al. (2005) also suggested that seasonal and annual changes in respiration rate can affect xCO₂ and δ¹³C-CO₂ in the upper 30 m of UZB2. The deflection toward lower δ¹³C-CO₂ in the profile at UZB2 suggests that the depth of influence from the LLRW site was probably from near the surface to roughly 40 m. Contamination of CO₂ from the LLRW is also supported by earlier observations (1994–1995) that the upper part of UZB2 showed ¹⁴C-CO₂ contamination up to 2000‰ modern C, and later sampling (2001) showed ¹⁴C-CO₂ of >600,000‰ modern C in UZB3 at a depth of 23.8 m (Stonestrom et al., 2004). This knowledge complements previous information on subsurface gas studies and provides critical information necessary to understand the distribution and behavior of ¹⁴C as part of CO₂ sources and transport in the subsurface, as CO₂ anomalies associated with waste sites can be a readily detected indicator of ¹⁴C contamination (Bracke and Müller, 2008). Elevated xCH₄ at UZB2 compared with JFDB observed in this study is also consistent with such gas contamination from the LLRW area.

**Future Work**

Estimates of gas flux were not included or modeled in this study. Important opportunities for future work include the use of numerical
models examining specific transport mechanisms, combining with other tracers such as noble gases, and examining potential transport effects on gas fractionation (Ding et al., 2017; Seltzer et al., 2017; Thorstenson and Pollock, 1989; Walvoord et al., 2014).

Conclusions

The amount and C isotopic composition of CO$_2$ and the amount of CH$_4$ measured in shallow and deep unsaturated zone gas samples provide insight on the sources and distribution characteristics of these gases at and near an LLRW facility in an arid region. Important sources of CO$_2$ in shallow and deep samples from the LLRW and surrounding area are aerobic respiration of disposed waste, shallow root zone respiration, and deep sources of CO$_2$, which may include both mineral precipitation and microbial respiration. The xCO$_2$ profile at UZB2 showed equilibrium with root-zone CO$_2$ at the surface, equilibrium with the water table in the deepest parts, and a gradient in between, and showed no influence from waste-generated CO$_2$. The xCO$_2$ profile at UZB3 showed equilibrium in the root zone, no measurements close enough to the water table to assess equilibrium conditions, and a strong signal of waste-generated CO$_2$. This strong CO$_2$ signal was apparently attenuated to non-detectable between UZB3 and UZB2. The $\delta^{13}$C-CO$_2$ profile at UZB2 showed slightly lower values for its entire length. The $-3\%o$ difference between JFDB and UZB2 indicated some influence from waste-generated CO$_2$. Depletion in $\delta^{13}$C-CO$_2$ in the UZB3 profile relative to UZB2 matched the augmentation in the CO$_2$ profile. In contrast to the area outside the LLRW zone, the importance of shallow root microbial processes for the production of CO$_2$ and the consumption of CH$_4$ in the LLRW cover itself may be minimal because it is disturbed from a natural state.

Important sources of CH$_4$ are the atmosphere and anaerobic respiration of disposed waste. Elevated xCH$_4$ was apparent at both UZB2 and UZB3, with values reflecting distances from the LLRW area, as expected. The gradual declining profile for xCH$_4$ in UZB3 compared with the sharper decline with depth for xCO$_2$ can be explained by the interaction between CO$_2$ and pore water in contrast to the non-interaction for CH$_4$, thus resulting in a linear downward profile for CH$_4$ and a more curved profile for the more reactive CO$_2$.

Higher xCO$_2$, lower $\delta^{13}$C-CO$_2$, and lower xCH$_4$ in shallow gas samples in 2016 compared with 2015 springtime samples were consistent with increased soil moisture conditions and subsequent microbial activity in 2016 related to anomalously high precipitation in October 2015. In contrast, the xCO$_2$ in the deep unsaturated zone has not changed appreciably from 2015 to 2016 or changed appreciably in the past decades, but xCH$_4$ is decreasing at depths of 15 to 50 m. The relative proportion of xCO$_2$ to xCH$_4$ suggests that a relatively small fraction of the waste is decomposed anaerobically, and either the available C or anaerobic conditions are diminishing with time, although there are fewer CH$_4$ profiles available from previous sampling (one profile each at UZB2 and UZB3) compared with CO$_2$.

Year-to-year variability in $x$CO$_2$, $\delta^{13}$C-CO$_2$, and xCH$_4$ should be expected in the LLRW area because the processes and rates cannot be expected to be constant with time. Contributing factors may include failure of waste containers with time and potential episodic exposure of degradable materials to water, as demonstrated by the industrial fire incident. Decadal decreases in xCH$_4$ observed in deep boreholes are more pronounced than those for xCO$_2$ because the xCH$_4$ profiles would react faster to decreases at the source because of less interaction with pore water.

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