

Carbon Isotopic Evidence for Biodegradation of Organic Contaminants in the Shallow Vadose Zone of the Radioactive Waste Management Complex

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ABSTRACT

Waste material buried in drums in the shallow subsurface at the Radioactive Waste Management Facility (RWMC) of the Idaho National Engineering and Environmental Laboratory (INEEL) contained significant amounts of organic compounds, including lubricating oils and chlorinated solvents. Carbon dioxide concentrations in pore gas samples from monitoring wells in the vicinity of the disposal pits are three to five times higher than the concentrations in nearby background wells. The stable C isotope ratios ($\delta^{13}\text{C}$ values) of CO_2 from the disposal pits averaged 2.4‰ less than CO_2 from the background wells, indicating that the elevated CO_2 concentrations around the pits were derived from source materials with $\delta^{13}\text{C}$ values in the range of -24 to -29 ‰. These $\delta^{13}\text{C}$ values are typical of lubricating oils, but higher than most solvents. The radiocarbon (^{14}C) contents of CO_2 across most of the site were significantly elevated above modern concentrations due to reactor blocks buried in a subsurface vault at the site. However, several samples collected from the high- CO_2 zone on the far side of the RWMC from the reactor blocks had very low ^{14}C contents (<0.13 times modern), confirming production from lubricating oils manufactured from fossil hydrocarbons. The magnitude of the CO_2 anomaly observed at the site is consistent with intrinsic biodegradation rates on the order of 0.5 to 3.0 t C yr $^{-1}$.

INTRINSIC BIOREMEDIATION—the use of naturally occurring microorganisms to convert organic contaminants to harmless forms—is gaining widespread acceptance as a viable method for remediating sites contaminated with hydrocarbon compounds. In an extensive study of groundwater sites impacted by leaking underground fuel tanks, Rice et al. (1995) demonstrated that natural processes, especially under aerobic conditions, quickly degrade most petroleum hydrocarbons. Wiedemeier et al. (1999) identified a range of conditions that are favorable for biodegradation of chlorinated solvents (e.g., trichloroethene, carbon tetrachloride). For the most part, however, these studies have been focused on groundwater contamination, leaving the potential for intrinsic biodegradation of organic contaminants in the unsaturated zone poorly understood.

One of the primary challenges for determining the efficacy of intrinsic bioremediation as a remediation option is monitoring its progress in the subsurface. One technique is to try to detect changes in the concentrations of metabolic byproducts of the biologic activity.

For aerobic metabolism of organic compounds, the primary product is CO_2 . Increased CO_2 concentrations in the vicinity of organic contaminants can indicate that biodegradation of the contaminants is occurring. However, this interpretation can be complicated by other potential sources of CO_2 , such as plant root respiration, biodegradation of natural soil organic matter, and dissolution of carbonate minerals. To further constrain the origin of subsurface CO_2 , the $\delta^{13}\text{C}$ value of the CO_2 can be analyzed. Hydrocarbon compounds are generally relatively depleted in ^{13}C (low $\delta^{13}\text{C}$ values) relative to most other sources of C (Schoell, 1984). Therefore, microbial metabolism of compounds manufactured from hydrocarbons tends to produce soil gas CO_2 with low $\delta^{13}\text{C}$ values where significant degradation of hydrocarbons is occurring. A number of field studies of aerobic hydrocarbon bioremediation have noted this effect above groundwater plumes (Suchomel et al., 1990; Ostendorf and Kampbell, 1991; Aggarwal and Hinchee, 1991; Feng et al., 2000).

However, $\delta^{13}\text{C}$ analyses alone may lead to ambiguous results because there can be significant overlap between the stable C isotope ratios of the contaminants and background organic matter. In addition, microbial processes such as methanogenesis and methane oxidation can cause the isotopic compositions of CO_2 produced to be enriched rather than depleted in ^{13}C (Revesz et al., 1995; Landmeyer et al., 1996; Conrad et al., 1999). One method of resolving most of the uncertainties associated with stable C isotopic measurements is to measure the ^{14}C content of the metabolic byproducts (Suchomel et al., 1990; Conrad et al., 1997; Aelion et al., 1997). The ^{14}C content of natural organic matter in near surface environments is usually at or near modern atmospheric levels, whereas fossil fuels have no measurable ^{14}C . Further, the variations in $^{14}\text{C}/^{12}\text{C}$ ratios are sufficiently large that they are not significantly affected by isotopic fractionation attending microbial processes.

In this paper, we present data on the concentrations, $\delta^{13}\text{C}$, and ^{14}C values of CO_2 in pore gas samples collected from the vadose zone in and around the RWMC at INEEL. These data clearly indicate that extensive biodegradation of organic contaminants in the shallow vadose zone is occurring at the site.

MATERIALS AND METHODS

Site Background

The RWMC is located in the southwest section of the INEEL on the Snake River Plain in eastern Idaho (inset of

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Abbreviations: CAMS, Center for Accelerator Mass Spectrometry; INEEL, Idaho National Engineering and Environmental Laboratory; RWMC, Radioactive Waste Management Facility; SDA, Subsurface Disposal Area; TSA, Transuranic Storage Area.

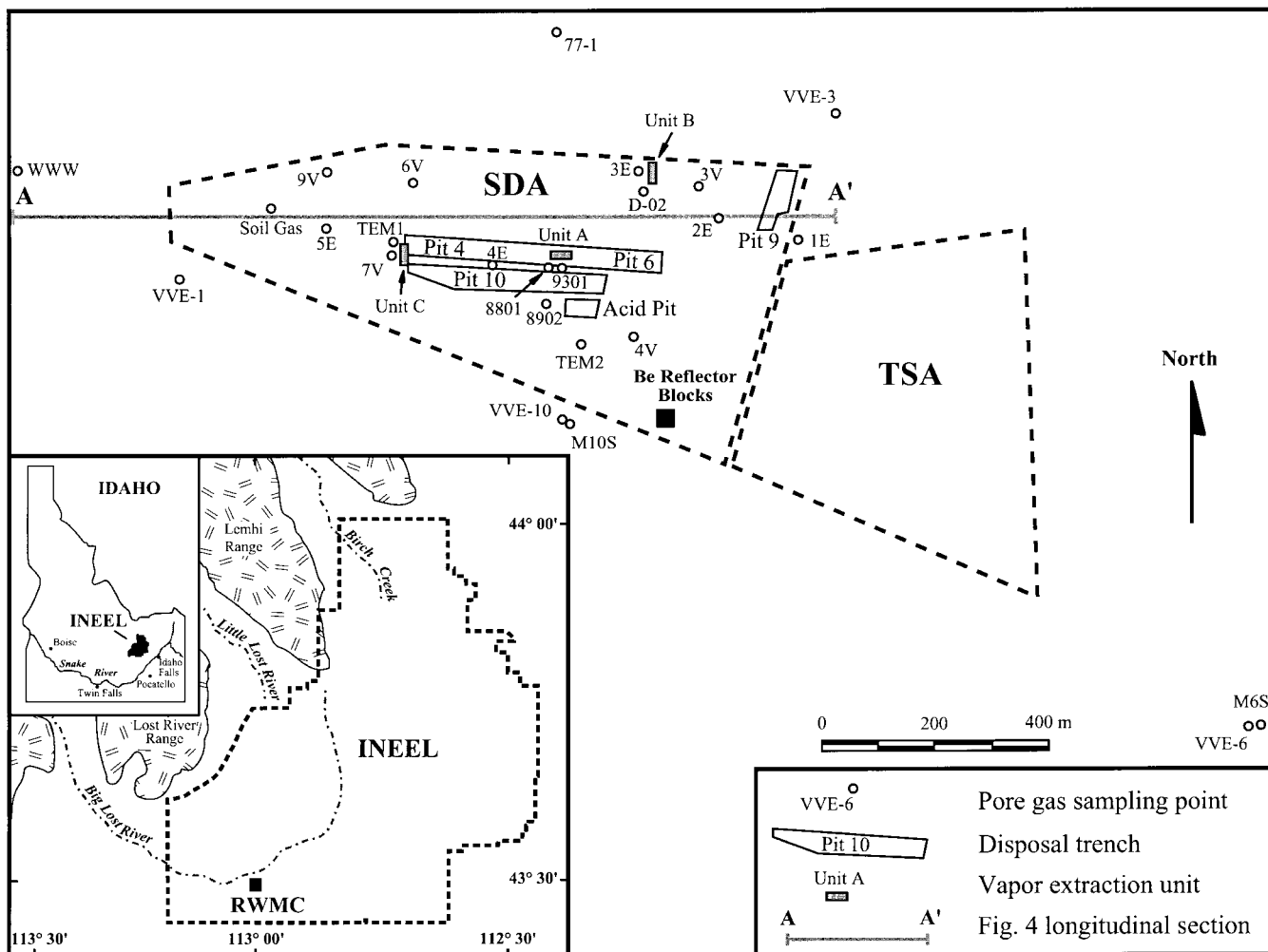


Fig. 1. Map of the Radioactive Waste Management Facility (RWMC) site showing the location of the wells sampled for this study and the Subsurface Disposal Area (SDA) and Transuranic Storage Area (TSA). Also plotted are the locations of the waste disposal pits, the soil vault containing the Be reactor blocks, the vapor extraction units, and the A-A' longitudinal cross section in Fig. 4. The inset shows the location of the RWMC within the INEEL and the state of Idaho.

Fig. 1). The geology of the upper 200 m at the RWMC site consists of 10 basalt-flow groups with seven major sedimentary interbed units ranging in age from 100 000 to 600 000 yr. Each basalt group is made up of one to five separate flows erupted from a common source during periods of volcanic activity lasting <200 yr (Anderson and Lewis, 1989). The sedimentary interbeds consist of river and lake sediments, paleosols, and wind-blown dust deposited during periods of volcanic quiescence. These interbeds are up to 10 m thick, constituting approximately 10% of the total stratigraphic section (Anderson and Lewis, 1989). The unsaturated zone is approximately 180 m thick and contains perched water horizons above some of the interbeds.

Significant amounts of radioactive waste resulting from USDOE activities are stored at the RWMC. Figure 1 contains a map of the site, with the locations of the wells sampled for this project. The site is divided into two sections, the Subsurface Disposal Area (SDA) and the Transuranic Storage Area (TSA). Most of the waste in the SDA is contained in drums buried in shallow pits (approximately 1.5 m deep) that are shown on Fig. 1. In addition to the radionuclides, the waste drums also contain significant amounts of organic compounds. The total amount of organics originally deposited into the pits is estimated at approximately 148 t of carbon tetrachloride,

138 t of other chlorinated solvents (e.g., perchloroethene, trichloroethene and trichloroethane), and 125 t of lubricating oils (Anderson and Lewis, 1989). Leakage from the drums has resulted in a vapor-phase, chlorinated solvent plume in the vadose zone and low levels of organics in the groundwater. In addition, various other waste materials are stored in the SDA, including six Be reflector blocks from the Advanced Test Reactor at the INEEL buried in a soil vault in the southeast section of the SDA (Fig. 1). The waste at the TSA is all stored in temporary, aboveground containers.

To remediate the solvent plume emanating from the disposal pits in the SDA, a vapor extraction system was installed at the site and began operation shortly before this project began (Fall of 1996). The system originally consisted of three treatment units, but after continuing problems with one of the units (Unit C on Fig. 1), that unit was shut down. The other two units also had significant periods of down time for repairs and maintenance.

During operation, the vapor extraction units pump pore gas out of extraction wells. The chlorinated solvents are stripped from the pore gas using activated charcoal, and the air is released to the atmosphere. The extent of influence of the system on subsurface processes is poorly understood. The contaminant levels in the extracted vapors drop to very low levels

when the extraction units are in operation, but rebound quickly when the units are shut down. One of the secondary goals of this project was to determine the extent of influence of the extraction wells.

Methods

To determine the extent of natural biodegradation of organic contaminants at the RWMC, more than 200 gas samples were collected from 57 sampling ports in 24 different monitoring wells during a 2-yr period (October 1996–November 1998). These samples were taken from a combination of shallow soil gas probes and deep gas sampling ports (to almost 180 m below ground surface) installed in monitoring wells in and around the RWMC. The details of the installation and subsurface characteristics for the deep vapor sampling ports are in a report by Parsons Engineering Sciences (1995) and summarized here. The vapor sampling ports were installed on the outside of the well casing. The sampling intervals are filled with size 4–6 sand. Intervals with only vapor ports are typically about 1.5 m long, but intervals where the well casing are screened for vapor extraction are as long as 10 m. The sand-filled intervals are sealed above and below with bentonite layers ranging from 0.6 to 2.0 m thick. The rest of the casing was grouted in place. The vapor ports were constructed of approximately 9.5-mm (3/8")-o.d. stainless-steel tubing with approximately 3.2-mm (2 1/8")-diameter perforations every 7.6 cm. The ports were connected to the surface with 1-cm (3/8") tubing and are kept sealed when not being used. Several of the vapor sampling ports were sealed and could not be used, and at least one port (9V-2) became sealed during this study.

The samples were collected in 1- or 3-L Tedlar bags from selected vapor ports using a portable diaphragm pump after purging the port for a specified time period (approximately equal to the time required to pump three times the volume of the sample tubing). The concentrations of N₂, O₂, and CO₂ in the samples were analyzed by gas chromatograph. These analyses are accurate to ±0.1%. Samples containing low concentrations of CO₂ (<0.2%) were analyzed using an infrared gas analyzer (Li-Cor, Lincoln, NE) and are accurate to within ±1% of the measured values. Carbon dioxide concentrations measured by both techniques are given in Table 1. The CO₂ concentrations measured for duplicate samples collected during the same sampling trip were within ±10% of each other.

For isotopic analyses, the CO₂ was extracted from the gas samples by bubbling it through a solution of 5 M NaOH. Aliquots of the CO₂ were then released from the NaOH solutions by acidifying them with 100% H₃PO₄ in evacuated tubes. The evolved CO₂ was then separated from the water by passing it through a trap with a –90°C methanol slush and freezing it into a tube at liquid N₂ temperature. This technique was more time consuming than standard cryogenic techniques used to separate CO₂ from air samples, but was necessary to avoid trapping vapor-phase hydrocarbon compounds with the CO₂. The stable C isotope ratios of the samples were determined using the VG Prism Isotope Ratio Mass Spectrometer at the Center for Isotope Geochemistry at the Lawrence Berkeley National Laboratory. The isotope ratios are reported relative to Vienna PeeDee Belemnite using the per mil notation (‰), where

$$\delta^{13}\text{C}_{\text{VPDB}} = \left[\frac{(^{13}\text{C}/^{12}\text{C})_{\text{sample}} - (^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}}{(^{13}\text{C}/^{12}\text{C})_{\text{VPDB}}} \right] 1000 \quad [1]$$

Variations between the δ¹³C values of separately prepared aliquots of the NaOH solution were generally within ±0.2‰. Duplicate samples collected in the field were within ±0.5‰.

The δ¹³C values are given in Table 1 (where duplicate analyses were done, only an average value is reported).

The ¹⁴C content of CO₂ aliquots split from the stable isotope samples were analyzed at the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory. Carbon dioxide was converted to graphite following the procedures documented by Lloyd et al. (1991). The ¹⁴C content of the graphite was then analyzed using the CAMS accelerator. The results from these analyses are reported as a fraction of modern (pre-1950) C (values >1 represent samples containing radiocarbon produced during aboveground testing of nuclear weapons). The precision of the analyses is ≤0.01 times modern C.

RESULTS AND DISCUSSION

Table 1 contains a compilation of the data collected for this study. Carbon dioxide concentrations ranged from 66 μL L⁻¹ (considerably less than the ≈380 μL L⁻¹ concentration in the atmosphere) to 2.1% by volume. The measured δ¹³C values were between –24.3 and –9.8‰, and the ¹⁴C concentrations ranged from below the lower detection limit of the CAMS accelerator (<0.01 times modern) to more than five times modern (the upper detection limit of the CAMS accelerator).

Background Carbon Dioxide

Samples were collected from three sites to determine the background CO₂ signal in the vicinity of the RWMC. Boreholes VVE-6 and M6S are located approximately 400 m southeast of the TSA and more than 1 km from the SDA on a knoll overlooking the site (≈20 m in elevation above the level of the SDA). Twenty-nine samples from five depths were collected from these wells during the project. The WWW boreholes are located about 300 m west of the SDA and 700 m from the nearest burial pit. Eleven samples from four different depths were collected from this site during the second year of the study. In addition, a single sample was collected from Port 6 in Borehole 77-1 during the early part of the project. This borehole is located about 250 m from the SDA and 500 m from the nearest burial pit.

The CO₂ concentrations and isotopic compositions measured for the samples from the background wells are plotted with the data for samples from the SDA on Fig. 2. The CO₂ concentrations were variable, but generally decreased from approximately 0.3% in the shallow subsurface (<5 m) to <0.1% below 100 m. This is consistent with higher levels of biologic activity (e.g., root respiration, microbial degradation of organic matter) in the shallow soils. These data establish that background CO₂ concentrations between 10 and 70 m deep are between 0.1 and 0.4% and average about 0.2%.

The δ¹³C values of the CO₂ from the background wells ranged from –12.1 to –22.1‰, but most (35 of 40 samples) were between –17 and –21‰. The CO₂ in the shallowest samples were slightly more depleted in ¹³C than the deeper samples, which is consistent with increased biologic activity in the shallow soils. Between the 10- and 70-m depths, the average δ¹³C value is –18.2‰, with a 1σ standard deviation of 1‰.

The ¹⁴C contents of four samples from the VVE-6/

Table 1. Continued

Well (depth, m)	Date	CO ₂	CO ₂	δ ¹³ C CO ₂	¹⁴ C CO ₂
		%	ppm		
WWW-1 (73.2)	July 1998	0.1	1309	-22.1	
VVE-10-3 (22.9)	Feb. 1997	0.4		—	
	June 1997	0.3	2475	-20.6	
	Aug. 1998	0.2		-21.1	
VVE-10-2 (42.1)	June 1998	0.2	2661	-21.1	
VVE-10-1 (59.7)	June 1997	0.0	438	—	
	June 1998		365	-11.9	
	Oct. 1996	0.0	134	-21.3	
M10S-4 (89.9)	Feb. 1997	0.0	185	-11.2	
	Feb. 1998	0.0	259	—	
	June 1998		481	—	
M10S-3 (108.8)	July 1998	0.0	785	-18.4	
	Aug. 1998		66	-11.7	
	Oct. 1996	0.0	160	-16.0	
M10S-2 (138.7)	Feb. 1997	0.0	219	-18.8	
	June 1998		211	-13.4	
	Oct. 1996	0.0	376	-9.8	
VVE-3-3 (28.0)	June 1998	0.2	1720	-20.9	
	Aug. 1998	0.2	1947	-21.2	
	Oct. 1998		2264	-20.8	
VVE-3-2 (47.2)	June 1998	0.2	2292	-21.2	
VVE-3-1 (61.0)	June 1998	0.2	2383	-20.8	
	Oct. 1998		2378	-20.6	
	Feb. 1997	0.0	963	-14.8	
VVE-6-3 (32.9)	Mar. 1997	0.2	1499	-17.0	
	June 1997	0.2	2050	-19.6	
	Nov. 1997	0.2	1551	-17.1	
	June 1998		1491	-19.4	
	Aug. 1998	0.1		-19.2	
	Oct. 1998		1535	-18.8	
VVE-6-2 (57.0)	Feb. 1997	0.2	1520	-19.2	
	Mar. 1997	0.1	1327	—	
	Nov. 1997	0.2	1366	-18.3	>5
	Feb. 1998	0.0	1302	-18.6	
	June 1998		1289	-18.5	
	Aug. 1998	0.2		-18.7	
VVE-6-1 (97.5)	Oct. 1998		3981	-17.7	
	Nov. 1996	0.0	464	-12.4	1.11
	Nov. 1996	0.0	684	-17.1	1.80
M6S-3 (111.6)	Feb. 1997	0.0	709	-18.9	
	Mar. 1997	0.0	710	-17.7	
	June 1997	0.0	750	-18.3	
	Nov. 1997	0.0	706	-18.9	
	Aug. 1998		634	-19.7	
	Oct. 1998		722	-18.4	
M6S-2 (149.4)	June 1998		978	-19.0	
M6S-1 (179.2)	Nov. 1996	0.0	805	-19.3	0.98
	Feb. 1997	0.0	832	-21.2	
	Mar. 1997	0.0	833	-18.1	
	Feb. 1998	0.0	812	-19.9	
	June 1998		722	-19.7	
	Aug. 1998	0.3		-20.5	
1E-1 (18.4)	July 1998	0.3		-19.6	
77-1-6 (19.5)	Aug. 1998	0.2		-17.7	
	Feb. 1997	0.2	2331	-19.7	
VVE-1-3 (19.8)	Feb. 1997	0.3		-22.5	

M6S site were measured. Two of the samples had ¹⁴C contents close to or slightly less than atmospheric CO₂ (currently at about 1.12 times modern due to production of ¹⁴C from aboveground nuclear testing). Two of the samples, however, had ¹⁴C contents above atmospheric values. The Be-reflector blocks buried in the southeast corner of the SDA, more than 1 km from the VVE-6 and M6S, are the most likely source of the ¹⁴CO₂ (Fig. 1). Transuranics are also stored in the TSA, but these are all in aboveground containers. This clearly indicates that VVE-6 and M6S have been influenced by the activities at the site. However, concentrations of radiocarbon in soil gas CO₂ from adjacent to the vault containing the Be-reflector blocks are up to 4000 times modern (Ritter and McElroy, 1999). Therefore, the total input of CO₂

from the SDA required to produce the ¹⁴C content measured in VVE-6 is small ($\approx 0.1\%$).

Carbon Dioxide in the Subsurface Disposal Area

The CO₂ concentrations measured for pore gas samples from the vicinity of the SDA were generally significantly higher than the CO₂ concentrations in the background wells. The highest CO₂ concentration measured in any of the background samples was 0.4%. Within the SDA, nearly one-half of the samples (74 of 151) contained more than 0.4% CO₂, and a significant number (25) were 1.0% or higher (Fig. 2). There were some very high concentration samples (to >2% CO₂) in the shallow subsurface (<10 m depth). Samples from the same sample locations were highly variable, with a weak seasonal correlation related to the growing season of surface plants. Concentrations tended to be higher during the spring and early summer and lower during the late summer and fall. More significantly, there was a zone of highly elevated CO₂ concentrations between the 15- and 35-m depths. The relationship between these samples and the waste material in the disposal pits is discussed below.

Location of Elevated Carbon Dioxide Zone

The highest CO₂ concentrations in the deeper vadose zone of the SDA were concentrated in the vicinity of the burial pits. Figure 3 contains a series of maps with the average CO₂ concentrations for samples from between depths from 10 to 25, 25 to 40, and 40 to 70 m. There is an area of elevated CO₂ just to the north of Pit 4 and 6, especially at the 10- to 25-m depth. Figure 4 is an east-west longitudinal section passing through the center of the high CO₂ zone (all data from sampling points within 100 m of the section have been projected onto the section). Also shown on this figure are the extent of surficial alluvium and the sedimentary interbeds. Most of the higher CO₂ concentrations (>0.3%) were measured for samples taken from the vicinity of the burial pits, above the B-C interbed (one of the more continuous interbed units in the RWMC subsurface). Within this area, however, there were some distinctive fluctuations in the depth of the CO₂ contours. Most of this variability is probably the result of the vapor extraction units that began operating at the site shortly before the beginning of this study.

Impact of the Vapor Extraction Units

The effect of the vapor extraction units on the CO₂ concentrations is clearly illustrated in Fig. 5. Borehole 8801 is immediately adjacent to Vapor Extraction Unit A. When in operation, the unit pulls pore gas from ports in several wells, including 8901, which is located approximately 20 m from 8801. Operation of this unit began during 1996, but it was shut down for repairs and maintenance from March through the beginning of July in 1997. During that time, the concentrations of CO₂ increased in all three sampling ports in Borehole 8801. After the unit began regular operation in July, the CO₂ concentra-

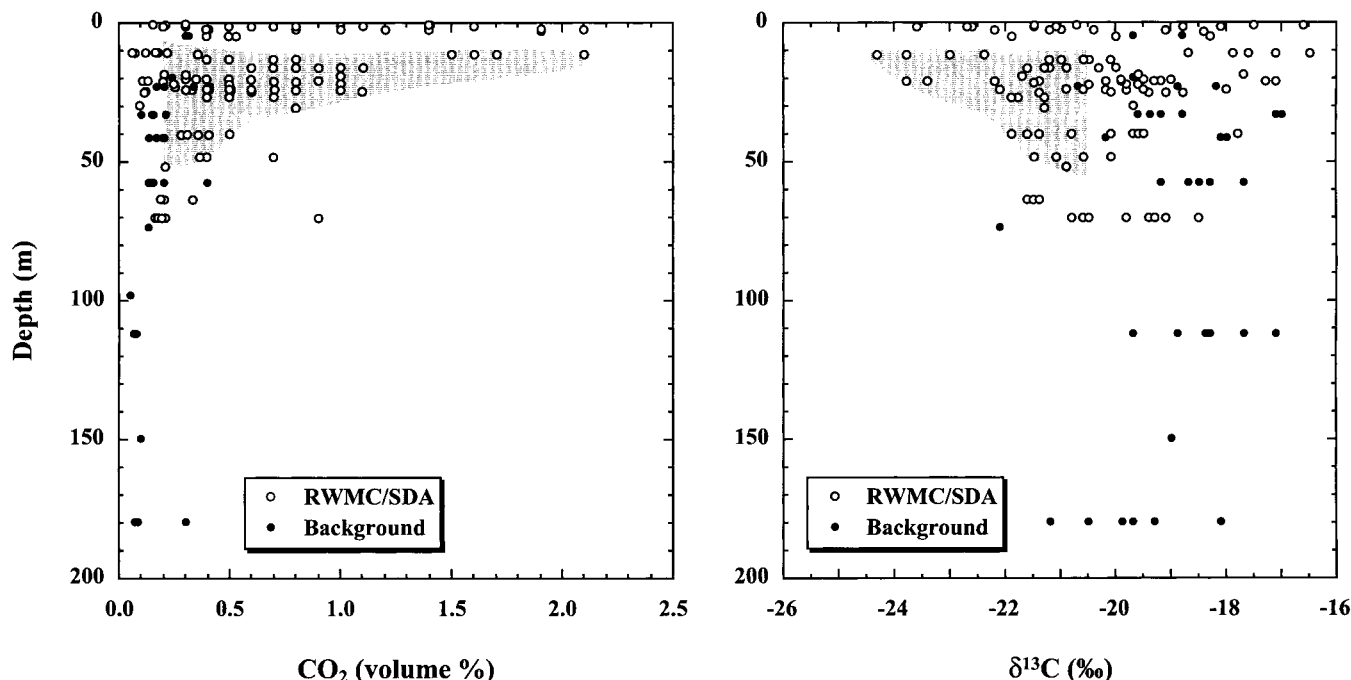


Fig. 2. Carbon dioxide concentrations and $\delta^{13}\text{C}$ vs. versus depth for samples from the Subsurface Disposal Area (SDA) and from background wells. The main depth interval of elevated concentrations is between 10 and 30 m (shown shaded). Slightly elevated values occur down to the 75-m depth. Soils from the TEM1 locality and from farther to the west of that locality have particularly high CO_2 values within a few meters of the surface. These values require very high local production rates of CO_2 (from root respiration).

tions of all three ports decreased significantly. There was another period of extended downtime during the spring and early summer of 1998 that also resulted in a rebound in the CO_2 concentrations in 8801. It is clear that the CO_2 concentrations in the subsurface immediately adjacent to the vapor extraction units are drawn down when the units are in operation. The CO_2 concentration in 8801-4 (the shallowest port in 8801) would have probably averaged close to 1% CO_2 without the influence of the vapor extraction units.

Other wells used for vapor extraction while samples were collected include 7V, 4E, 3V, and 2E. The average CO_2 concentrations in the vicinity of all of these wells plotted on Fig. 4 were significantly lower than in the other wells. In fact, the vapor extraction units had no perceptible affect on the CO_2 concentrations in ports at any significant distance from the units (e.g., 3E and D-02, which are located ≈ 80 m from the nearest extraction wells), suggesting that the extraction units had limited lateral areas of influence.

Subambient Carbon Dioxide Concentrations

There were also several samples collected from Ports 3 and 4 in Borehole M10S that had CO_2 concentrations below atmospheric levels ($\approx 380 \mu\text{L L}^{-1}$). This is most likely caused by exchange with pore water dissolved inorganic C. At higher pHs, the equilibrium concentration of dissolved inorganic C compounds in water shifts from dissolved CO_2 to carbonate and bicarbonate ions, resulting in lower CO_2 pressures in the gas phase. The existence of such low CO_2 concentrations in the samples from M10S suggests that chemical trapping of

CO_2 must be occurring in the vicinity of those sampling ports.

Source of Elevated CO_2 in the Subsurface Disposal Area

The concentration data clearly indicate that the elevated CO_2 in the SDA is associated with the disposal trenches. There are a variety of potential sources for the additional CO_2 , such as degradation of the lubricating oils and/or chlorinated solvents in the waste, degradation of other organic matter buried with the waste, and differences in plant cover at the surface. The origin of the CO_2 cannot be determined from the concentration data alone; however, the C isotope data help place additional constraints on the source of the CO_2 .

The average $\delta^{13}\text{C}$ value of CO_2 in samples from between the 10- and 70-m depths in the high- CO_2 zone of the SDA (defined by the area within the 0.3% contour on Fig. 3a) is -20.6‰ . This is 2.4‰ lower than the average $\delta^{13}\text{C}$ value of CO_2 in samples from the same depth range in the background wells (-18.2‰). This relationship is further demonstrated on Fig. 6, which is a plot of the inverse CO_2 concentration vs. the $\delta^{13}\text{C}$ values of CO_2 in samples from the high- CO_2 zone. Allowing for C isotopic fractionation of 4.4‰ resulting from diffusive loss of CO_2 to the atmosphere (Cerling, 1984), this indicates that the source of the CO_2 has a $\delta^{13}\text{C}$ value between -24 and -29‰ . Carbon dioxide produced from aerobic biodegradation of organic compounds is generally 1 to 3‰ lower than the substrate, suggesting that the source of the CO_2 in the SDA was between -21 to -28‰ . This is within the range of $\delta^{13}\text{C}$ values that would be expected

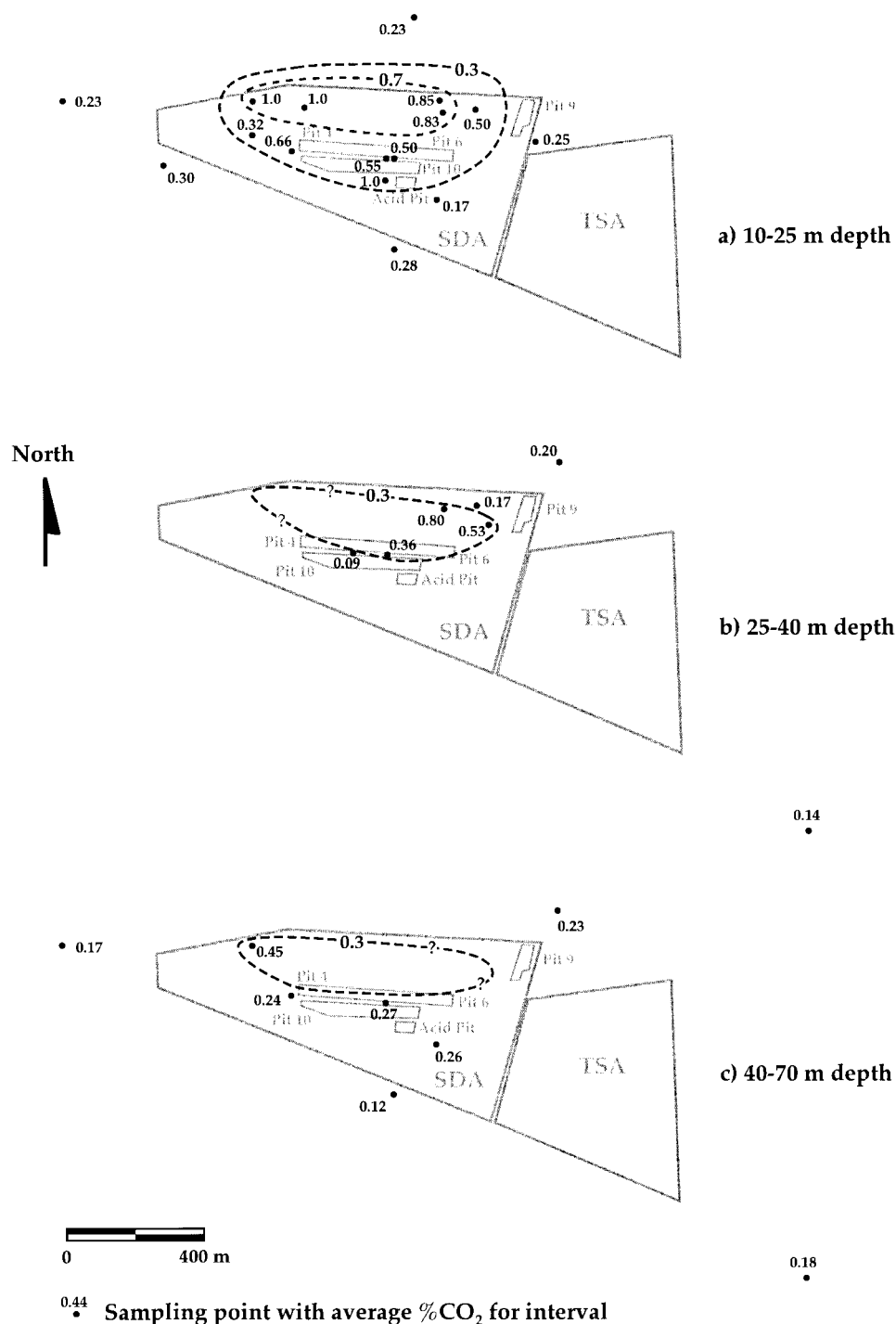


Fig. 3. Average CO₂ concentrations (in volume %) in pore gas samples collected from different depth intervals in and around the Radioactive Waste Management Facility (RWMC) site.

for petroleum hydrocarbons (e.g., the lubricating oils). However, plant respiration and/or microbial degradation of natural organic matter could also produce CO₂ with δ¹³C values in this range. Although there is no obvious increase in the amount of natural organic matter in the vicinity of the disposal pits, it is possible that the activities at the site (e.g., wetting down the ground for

dust abatement) might have caused enhanced biological activity in the near surface.

The ¹⁴C contents of a limited number of CO₂ samples were analyzed to address the issue of whether or not the source of the high CO₂ was derived from the organic contaminants or from augmented natural activity. Interpreting this data was complicated by the Be reflector

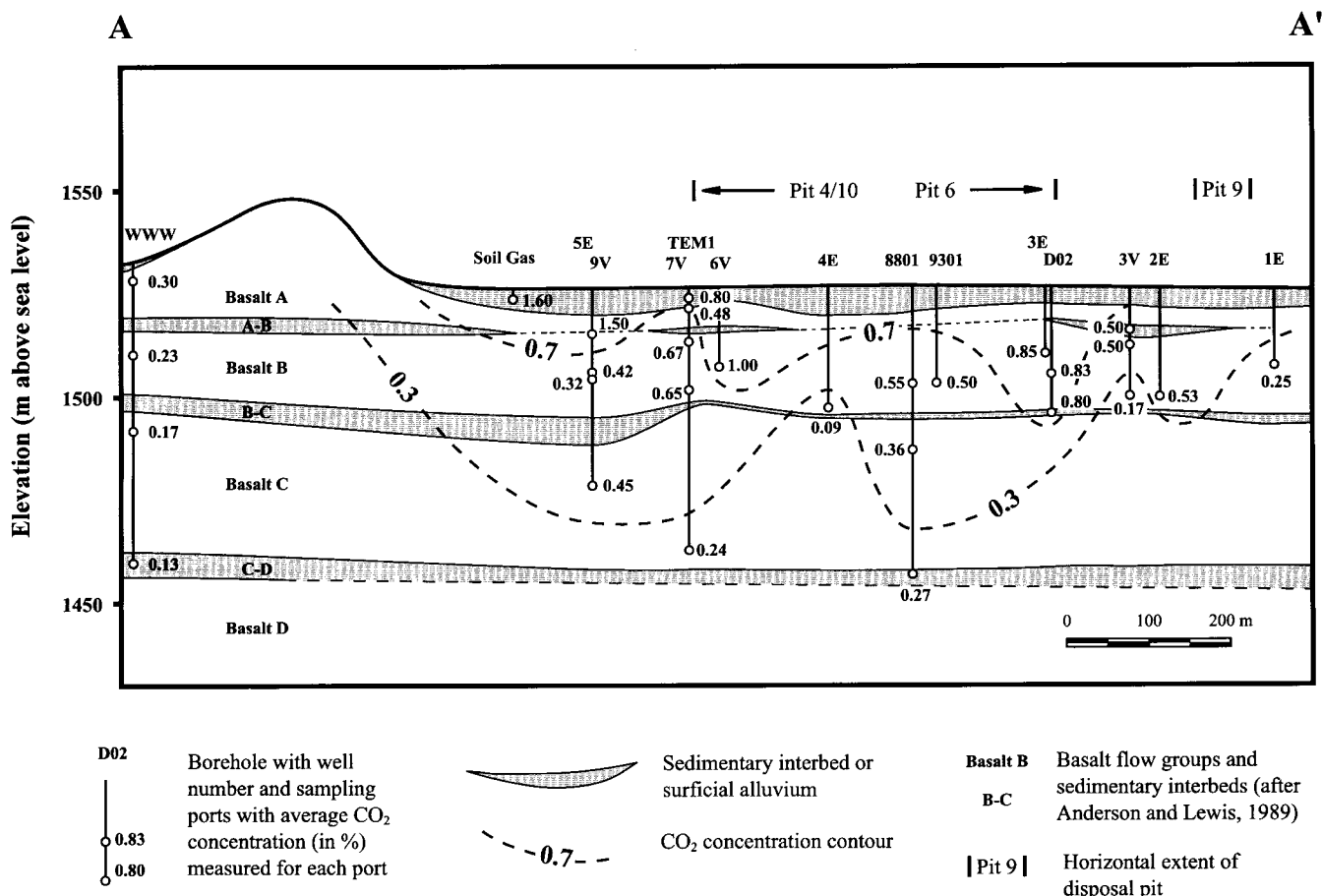


Fig. 4. Longitudinal cross section A-A' (Fig. 1) passing through the high-CO₂ zone in the Radioactive Waste Management Facility, with contours of the labeled average CO₂ concentrations measured for pore gas samples collected from different sampling port in wells within 100 m of the section. The approximate extent of the surficial sediments and the sedimentary interbeds are shown as shaded areas on the section.

blocks buried in the soil vault in the southeast corner of the SDA, which are a source for high ¹⁴C CO₂. Because that source is so high (>4000 times modern; Ritter and McElroy, 1999), relatively small inputs from the reflector blocks will dominate the measured ¹⁴C signal, as was observed for the samples from VVE-6 (one of the background wells). Figure 7 is a map of the site with all of the available radiocarbon data. Most of the samples from the SDA have ¹⁴C contents greater than five times modern (the upper detection limit of the CAMS accelerator). However, three samples taken from two of the monitoring wells (7V and 9V) have ¹⁴C contents between 0.00 and 0.13 times modern. These wells are on the opposite side of the disposal trenches from the Be reflector blocks and are most likely to be representative of the ¹⁴C contents of the elevated CO₂ source.

The only possible sources of such low ¹⁴C CO₂ in the SDA are organic compounds derived from fossil hydrocarbons (e.g., lubricating oils, chlorinated solvents) and "old" carbonates in the sedimentary interbeds. If the source of the low-¹⁴C CO₂ was dissolution of carbonates, the δ¹³C values of the CO₂ should be much higher. No measurements have been made of calcite from the RWMF site, but calcite from the TAN site at the INEEL has δ¹³C values ranging from -3 to -7‰ (Tobin et al., 1997). Assuming that calcite at the RWMF has a similar

range, the δ¹³C value of CO₂ produced from dissolution of the calcite would be between -9 and -15‰, depending on the temperature and pH of the pore waters at the time of dissolution (Wigley et al., 1978). As discussed above, the source of the CO₂ was significantly more depleted in ¹³C (between -24 and -29‰), ruling out the possibility of a large contribution of CO₂ from carbonate dissolution. Furthermore, the ¹⁴C contents of the samples from the background wells that were not impacted by the high-¹⁴C CO₂ were close to atmospheric concentrations, implying that dissolution of carbonates is not a significant source of subsurface CO₂.

Of the organic contaminants at the site, the lubricating oils represent a more likely source for the CO₂ than the chlorinated solvents. The δ¹³C values of the CO₂ are in the appropriate range for oil (-24 to -32‰; Schoell, 1984) but are on the high side for chlorinated solvents. δ¹³C values reported in the literature for the chlorinated solvents range from -33 to -47‰ for carbon tetrachloride, -23 to -37‰ for perchloroethene, -28 to -43‰ for trichloroethene, and -26 to -32‰ for 1,1,1-trichloroethane (van Warmerdam et al., 1995; Holt et al., 1997; Beneteau et al., 1999; Hunkeler and Aravena, 2000; Jendrzewski et al., 2001). Furthermore, the stable C isotope ratios of two samples of bulk chlorinated solvents in gas samples collected from the RWMF were

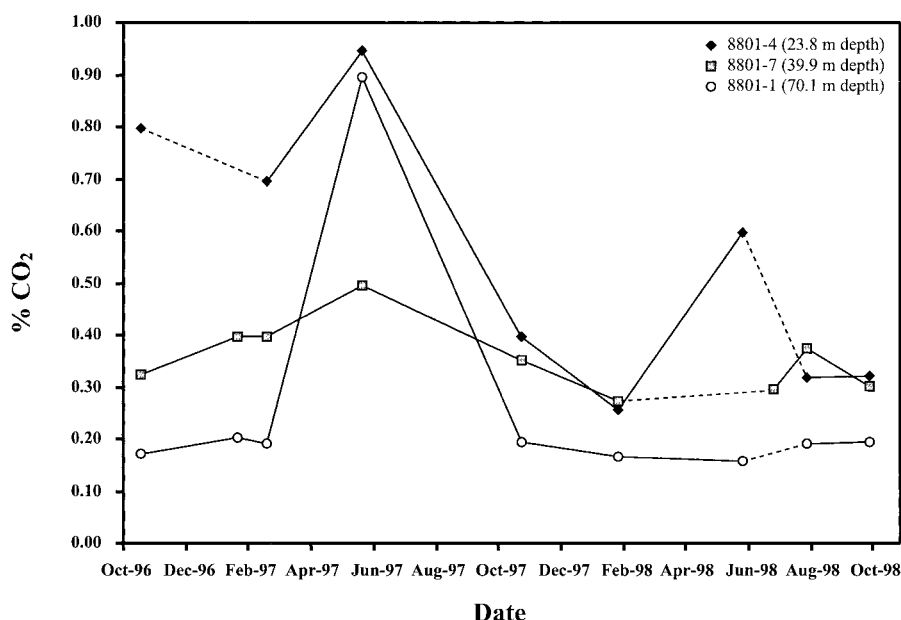


Fig. 5. Carbon dioxide concentrations measured over time in three vapor sampling ports in Borehole 8801, showing the effect of vapor extraction from Borehole 8901 (located approximately 20 m from 8801). Dashed lines indicate intervals where a sampling period was missed.

trapped onto resin columns and analyzed, giving $\delta^{13}\text{C}$ values of -32 and -38% . It is possible that there was preferential degradation of higher $\delta^{13}\text{C}$ solvents (e.g., perchloroethene), but it is unlikely that a significant amount of the CO_2 in the SDA was derived from breakdown of the solvents.

Estimated Rate of Biodegradation of Oils

The rate of degradation of the lubricating oils translates to a rate of production of CO_2 in the subsurface, which can be estimated roughly from the elevated CO_2 concentrations in the pore gas. We derive this estimate from a simplified model of the CO_2 production and transport in the region under the 0.7% contour shown in Fig. 3a. We assume that CO_2 is being produced in a volume of rock that has the areal dimensions of the 0.7% contour (area $\approx 75\,000\text{ m}^2$) and a vertical dimension corresponding to the depth interval 10 to 30 m below the ground surface. The total volume of producing rock is then $1.5 \times 10^6\text{ m}^3$. The CO_2 produced in this volume of rock must diffuse out through the pore space, and with time the CO_2 concentration may reach a steady-state concentration that reflects the balance between production and loss by diffusion into the surrounding low- CO_2 pore air. If the producing volume of rock is modeled as a one-dimensional system, which is reasonable insofar as the lateral dimensions are much greater than the vertical, then the steady-state maximum CO_2 concentration is given by

$$[\text{CO}_2]_{\text{max}} = [\text{CO}_2]_{\text{amb}} + \frac{G_{\text{CO}_2}a}{D_{\text{CO}_2}\phi\tau} \left(d - \frac{a}{2} \right) \quad [2]$$

where the brackets represent concentrations of CO_2 in pore air, G_{CO_2} is the production rate of CO_2 per unit vol-

ume of soil, a is the half-thickness of the CO_2 producing layer in the subsurface, d is the depth to the middle of the producing layer, D_{CO_2} is the diffusivity of CO_2 in air, and ϕ and τ are porosity and tortuosity. Rearranging this equation, we can express the total production of CO_2 as

$$P_{\text{total}} = 2A_{\text{prod}} \frac{D_{\text{CO}_2}\phi\tau}{(d - a/2)} ([\text{CO}_2]_{\text{max}} - [\text{CO}_2]_{\text{amb}}) \quad [3]$$

This equation applies to a layer of thickness $2a$ at depth d , with CO_2 concentration held at the ambient value at the top and bottom boundaries, uniform CO_2 production within the layer, and transport only by diffusion through the pore space (porosity, $\phi \approx 0.1$) in the vertical direction. Substituting the values $D_{\text{CO}_2} = 756\text{ m}^2\text{ yr}^{-1}$, $\phi = 0.1$, $\tau =$

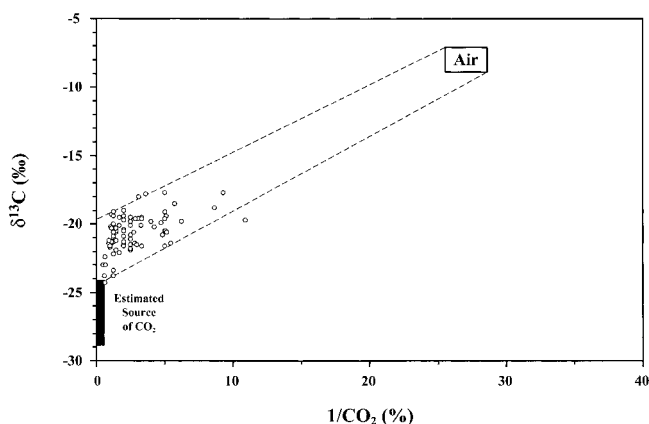


Fig. 6. Inverse concentrations of CO_2 in pore gas samples from between 10 and 70 m depth in the high- CO_2 zone in the Subsurface Disposal Area (SDA). Allowing for a shift of 4.4‰ for diffusive fractionation (Cerling, 1984), this data suggests that the source for the increased CO_2 in the vicinity of the disposal pits has a $\delta^{13}\text{C}$ value of between -24 and -29% .

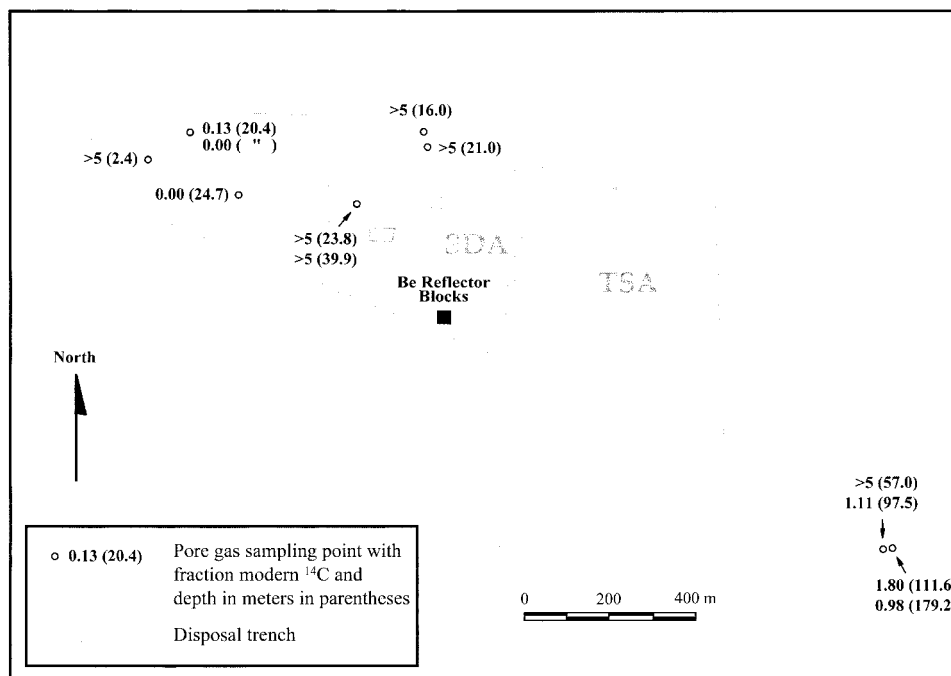


Fig. 7. Radiocarbon contents (in fraction of modern atmospheric C) in CO_2 samples collected for this study. Values in parentheses indicate the depth at which the sample was collected.

0.5, $a = 10$ m, $d = 20$ m, maximum and ambient CO_2 concentrations ($\text{m}^3 \text{m}^{-3}$ air) of 0.011 and 0.002, and the estimated area ($A_{\text{prod}} = 75000 \text{ m}^2$), the resultant value is about $3400 \text{ m}^3 \text{CO}_2 \text{ yr}^{-1}$. This corresponds to the conversion of 1.7 t of C to CO_2 per year. The concentrations predicted by the model are plotted vs. depth with the data on Fig. 8. These calculations are also consistent with the lower $\delta^{13}\text{C}$ values for CO_2 observed within the SDA.

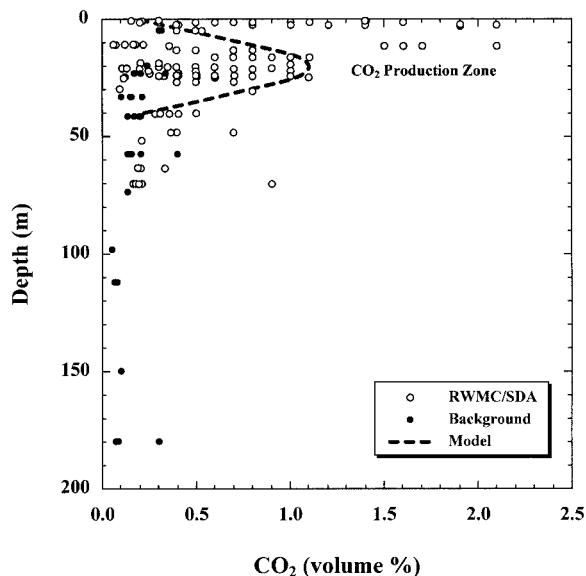


Fig. 8. Comparison of model results for $a = 10$ m and $d = 20$ m and measured CO_2 concentrations vs. depth. This model uses a specific CO_2 production rate of $0.0023 \text{ m}^3 \text{CO}_2 \text{ m}^{-3} \text{ rock yr}^{-1}$ in the producing layer between the 10- and 30-m depths (shown shaded) and gives a total CO_2 production for a 150 by 500 m area equivalent to the degradation of approximately 1.7 t C yr^{-1} .

The simplicity of our model makes this estimate very rough. The actual value could be anywhere from about 0.5 to 3 t C yr^{-1} . Decreasing the concentration gradients at the upper and lower boundaries of the layer would lower the estimated production. Higher estimates would result if lateral transport were accounted for, as well as CO_2 production from rock outside of the core volume used for the calculation.

CONCLUSIONS

The primary goal of this project was to evaluate the levels of intrinsic bioremediation of organic contaminants in the burial pits at the RWMC. The CO_2 concentrations in the subsurface around the burial pits were elevated by three- to fivefold relative to background. The stable C isotope ratios of the CO_2 indicate a source with $\delta^{13}\text{C}$ values between -21 and -28% , and the low ^{14}C contents of several samples confirm that the CO_2 is mainly derived from aerobic biodegradation of fossil hydrocarbons, with the primary source being the lubricating oils and not the chlorinated solvents. The high O_2 content of the pore gas ($>18\%$) and the existence of a subsurface bacterial community at the RWMC dominated by strict aerobes (Colwell, 1989) supports this conclusion.

The CO_2 anomaly corresponds to a biodegradation rate for the lubricating oils of 1.7 t C yr^{-1} . The total amount of lubricating oil in the subsurface at the SDA is estimated at 125 t (Anderson and Lewis, 1989). Assuming that the oils are 80% C by weight, approximately 100 t of C in the form of lubricating oils was buried at the site. If all of the oil has leaked out of the containers and is available to be degraded (which is highly unlikely), this suggests an approximate intrinsic biodegradation rate for the oils of 1 to $2\% \text{ yr}^{-1}$.

The estimated biodegradation rate for the lubricating oils is low relative to rates estimated at other sites. For a production volume of 1.5×10^6 m³ of rock, the degradation rate is $1.15 \text{ g C cm}^{-3} \text{ yr}^{-1}$. By comparison, Baker et al. (2000) measured biodegradation rates for BTEX compounds and gasoline in soil of hundreds to thousands of grams per cubic meter per year. However, lubricating oils tend to have very low vapor pressures, and it is probable that the biological activity within the production zone is limited to areas within close proximity to the oils. Given that the RWMC production zone is hosted in fractured basalts, the distribution of the oils within this zone is undoubtedly highly heterogeneous. Therefore, the actual volume of the rock in which active biodegradation of the oils is occurring could easily be <1% of our production zone.

The results of this study also have significant implications for gas transport in the vadose zone at the RWMC. Elevated ¹⁴C-CO₂ was detected in samples at distances of >1 km from the suspected source. However, the impact of the vapor extraction units on CO₂ concentrations appears to be limited to <100 m. This suggests that advective gas transport is limited to local fracture networks and large-scale transport through the rock matrix is diffusion limited.

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