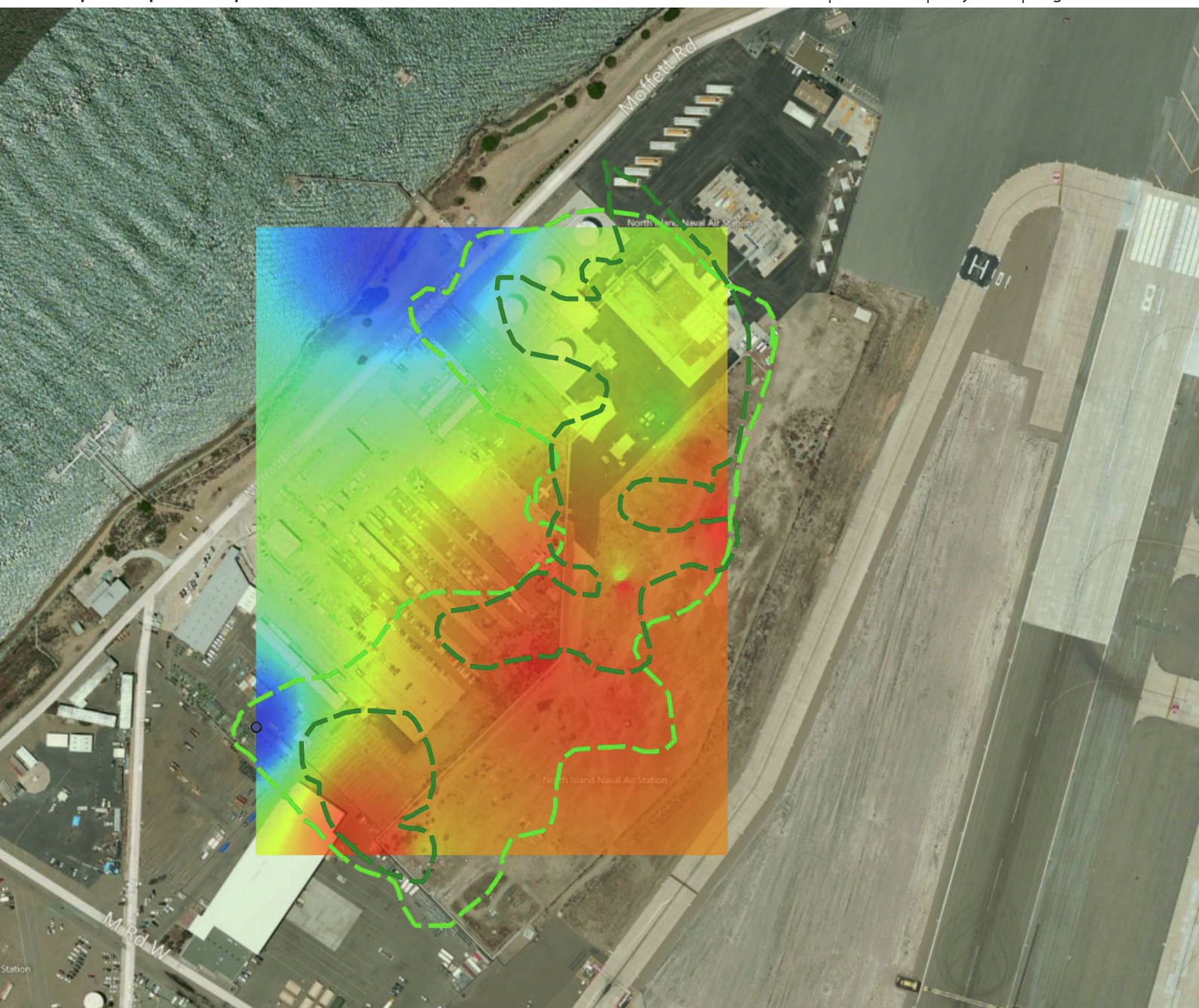


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## PAPER

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Radiocarbon-depleted CO<sub>2</sub> evidence for fuel biodegradation at the Naval Air Station North Island (USA) fuel farm site



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## PAPER

### Radiocarbon-depleted CO<sub>2</sub> evidence for fuel biodegradation at the Naval Air Station North Island (USA) fuel farm site

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Dissolved CO<sub>2</sub> radiocarbon and stable carbon isotope ratios were measured in groundwater from a fuel contaminated site at the North Island Naval Air Station in San Diego, CA (USA). A background groundwater sampling well and 16 wells in the underground fuel contamination zone were evaluated. For each sample, a two end-member isotopic mixing model was used to determine the fraction of CO<sub>2</sub> derived from fossil fuel. The CO<sub>2</sub> fraction from fossil sources ranged from 8 to 93% at the fuel contaminated site, while stable carbon isotope values ranged from −14 to +5‰<sub>VPDB</sub>. Wells associated with highest historical and contemporary fuel contamination showed the highest fraction of CO<sub>2</sub> derived from petroleum (fossil) sources. Stable carbon isotope ratios indicated sub-regions on-site with recycled CO<sub>2</sub> (δ<sup>13</sup>C<sub>CO2</sub> as high as +5‰<sub>VPDB</sub>) – most likely resulting from methanogenesis. Ancillary measurements (pH and cations) were used to determine that no fossil CaCO<sub>3</sub>, for instance limestone, biased the analytical conclusions. Radiocarbon analysis is verified as a viable and definitive technique for confirming fossil hydrocarbon conversion to CO<sub>2</sub> (complete oxidation) at hydrocarbon-contaminated groundwater sites. The technique should also be very useful for assessing the efficacy of engineered remediation efforts and by using CO<sub>2</sub> production rates, contaminant mass conversion over time and per unit volume.

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#### Environmental impact

CO<sub>2</sub> radiocarbon analysis has proved extremely useful in demonstrating on-site fossil fuel-derived contaminant remediation to a non-toxic end-product (CO<sub>2</sub>). In contaminated regions, vadoze-zone and groundwater CO<sub>2</sub> which is radiocarbon-depleted relative to background CO<sub>2</sub> confirms fossil-fuel or industrial chemical degradation. The analysis coupled with a straightforward two end-member mixing model, allows an environmental manager to readily determine the proportion of on-site CO<sub>2</sub> derived from the contaminant. This information aids in evaluating remediation alternatives and can be used throughout the life-cycle of site analysis to assess remediation. Coupling this analysis with CO<sub>2</sub> production rate and hydrologic models could lead to accurate overall mass balance remediation calculations.

#### Introduction

Subsurface hydrocarbon contamination is a common environmental issue at many US civilian and military sites. Considerable costs are incurred in assessing contaminant extent, contaminant fate and residence time, site geology, geochemistry and credible cleanup alternatives. Inherent in all alternatives is the ability to accurately determine parent contaminant conversion to the desired end product – whether the treatment is active (engineered) or passive. There are around 70 or so “lines of evidence” measures currently used for confirming or

indicating hydrocarbon biodegradation at contaminated sites.<sup>1–3</sup> These measures vary considerably in cost, analytical difficulty, and complexity, and due to uncertainties, may never fully support decision-making.

The ultimate end-product for organic contaminant degradation is CO<sub>2</sub> – representing a complete conversion to harmless product. A main methodological limitation for all current technologies is the inability to conclusively link contaminants, daughter products, electron acceptors, hydrogeological parameters, and in some cases biological activities to actual contaminant removal. No methods are routinely applied which can differentiate contaminant-derived CO<sub>2</sub> from natural soil respiration processes. Recent methods have targeted the contaminant's carbon backbone using isotopic analyses – the most common being stable carbon analysis. One can use the Rayleigh distillation equation to estimate contaminant biodegradation given the starting contaminant stable carbon isotope ratio, published fractionation factors, and the down-gradient

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contaminant stable carbon isotope ratio.<sup>4,5</sup> In general, if the contaminant pool stable carbon isotope ratio becomes <sup>13</sup>C-enriched while decreasing in concentration, biodegradation can be confirmed. Two scenarios can make it especially difficult to apply stable carbon isotope analysis to estimate biodegradation rates, (1) if the fractionation factor(s) are variable (for instance, an aquifer with both aerobic and anaerobic regions) or unknown from the literature, but more commonly, (2) if the source is mixed, for instance chronic underground storage tank (UST) leakage with fuels of varying isotopic compositions. For instance, in a chronically leaking UST, the benzene isotope ratio could vary  $\pm 5$ –10‰ over time solely due to natural variation in fuel stocks. A “discreet” spill is needed to have a single contaminant source stable carbon isotope value.

Natural abundance radiocarbon analysis is a complementary and often more definitive approach for tracing carbon assimilation and respiration through the microbial assemblage or through abiotic oxidation processes. <sup>14</sup>C-content can be used to distinguish between carbon sources with different ages.<sup>6–9</sup> With a radiocarbon half-life of approximately 5700 years, petroleum sources are radiocarbon-free and thus provide a known end-member when analyzed against relatively recent photosynthetic-based carbon sources (plant material, contemporary soil organic carbon) which contain modern CO<sub>2</sub> from the atmosphere. CO<sub>2</sub> is continually produced in the atmosphere by cosmic radiation. The percentage modern carbon (pMC) of living photosynthetic biomass is approximately 110% because of nuclear bomb tests, which peaked before 1965.<sup>10</sup> In contrast, petroleum carbon and CO<sub>2</sub> derived from its biodegradation have no <sup>14</sup>C and are thus 0 pMC. Given the two extreme end-members, one can readily differentiate the relative contributions of petroleum and plant biomass degradation in the total respired CO<sub>2</sub> pool.

Soil gas CO<sub>2</sub> radiocarbon content was originally used to study contaminant degradation and migration in the vadose zone of an aquifer contaminated with organic solvents by Suchomel *et al.*<sup>11</sup> The results demonstrated distinct CO<sub>2</sub> radiocarbon signatures from control and contaminated sites. In a subsequent study, radiocarbon was used to investigate petroleum degradation in groundwater and soil gas.<sup>12</sup> In this study, petroleum biodegradation could not be verified by stable carbon isotope due to on-site methanogenesis – which drastically alters the CO<sub>2</sub> stable carbon isotope ratio. Radiocarbon analysis, however, was able to confirm petroleum biodegradation. Radiocarbon was also used to survey groundwater contaminant degradation at a gasoline-contaminated site undergoing remediation with an air sparging/soil vapor extraction system.<sup>10</sup> The CO<sub>2</sub> radiocarbon signature in the soil gas and groundwater dissolved inorganic carbon (DIC) suggested aerobic petroleum biodegradation produced 59–87% of the total CO<sub>2</sub>. The approach was then applied to a chlorinated solvent plume wherein biodegradation was confirmed through observing the fossil end-member in soil gas CO<sub>2</sub>.<sup>13,14</sup> Additionally, a study combining stable and radiocarbon soil gas CO<sub>2</sub> analysis confirmed >90% of the soil gas CO<sub>2</sub> was derived from petroleum sources.<sup>15</sup> These studies provide strong support for applying and coupling stable carbon and radiocarbon analyses to confirm and quantify natural attenuation.

The CO<sub>2</sub> radiocarbon technique has demonstrated biodegradation in field settings with analytical certainty. This measurement ultimately provides a value for the petroleum-derived CO<sub>2</sub> within the CO<sub>2</sub> pool of a given sample using a simple isotopic mixing model.<sup>15</sup> Background sites are used to determine the natural <sup>14</sup>C age for CO<sub>2</sub> on site (accounting for aging natural organic matter and root respiration) and used in the model. In this study, CO<sub>2</sub> radiocarbon analysis was used to confirm if natural attenuation is a significant factor leading to the removal of fuel hydrocarbons at a US Navy facility.

## Materials and methods

### Site description

The Naval Air Station North Island (NASNI) is located adjacent to Coronado Island to the northwest. Most of the facility is comprised of hydraulic dredge fill from San Diego Bay – started in the 1930s. The soils are primarily well sorted, fine-grained silty sand. About 10 m below ground surface (bgs) consists of the Bay Pont formation which is silty fine- to medium-grained sand with coarser clayey material. The groundwater is approximately 4–5 meters bgs and has a very flat hydraulic gradient (0.0002–0.0005) toward the north-northwest. The original fuel farm site had 34 USTs ranging from ~40 000 to 2 400 000 L which contained primarily gasoline, diesel and aviation gasoline. Currently, all fuel tanks are above-ground and the free-phase hydrocarbon layer encountered on-site in 1992 is thought to be largely from historical UST leakage. Initial estimates placed the subsurface hydrocarbon volume between 400 000 and 2 560 000 L. Operations commenced to remove underground tanks, underground piping, and initiate fuel recovery remediation efforts.

Pilot-scale and full-scale fuel recovery operations commenced from 1994–2005 using groundwater and light non-aqueous phase liquid (LNAPL) pumping systems augmented with vacuum-enhanced recovery, skimmer pumps, submersible pumps and an expanded extraction well network. In total, 116 monitoring and former recovery wells are installed on-site and after the system was shut down, an estimated 1 120 000 L of fuel had been recovered. As the recovery system reached diminishing returns (fuel to groundwater ratio reached 0.17%), shut down was followed by an assessment of plume migration, product rebound, and natural attenuation. Initial investigations determined that there was insufficient data to assess natural attenuation. Previous to and concurrent with the described study, RORE Environmental conducted several investigations to determine the fuel plume extent, LNAPL thickness and plume attenuation. Changes in these parameters indicated that ~16% of the remaining LNAPL had been attenuated to ~4% over three years (since the recovery system was shut down).

### Sample locations

Three general locations were sampled (Fig. 1). Two sites were chosen to as potential “background” areas with conditions matching the fuel farm. One site (background well site) had some extant vegetation and was largely devoid of concrete or



Fig. 1 Sampling locations.

asphalt covering. This site was close to a golf course on base. This is a former landfill area, with current remedial activities. One well is located upgradient of any known contamination (S5-MW-01) – closest to the arrow (Fig. 1). The second potential background site (base center) was chosen near the center of the base – and the proposed highest water table region. This area consisted of mixed asphalt covered parking lots with interspersed vegetation. A hazardous waste collection activity was located at the Northeast region of the area. This was unknown at the time of sampling. At the fuel farm (principal sample location for this study), samples were collected in vegetated, non-vegetated and asphalt-covered regions. Wells outside the estimated zone of contamination (down-gradient) were also sampled at the fuel farm site.

### Groundwater sampling

Groundwater was pumped from existing wells using a peristaltic pump fitted with C-flex tubing (Cole Parmer) within the pump head. Teflon-lined polypropylene tubing was used for reaching the groundwater within the well and for transfer into glass bottles. Approximately 1 L of groundwater was purged before filling the bottle from the bottom up – and allowing approximately 500 mL of overflow to occur. The samples were immediately poisoned with 10 mL saturated  $\text{CuSO}_4$  solution, capped and sealed with no headspace. Sub-samples were collected for pH and cation measurements. Sample bottles (1 L) were sent to Beta Analytic for  $\text{CO}_2$  radiocarbon analysis.

### Radiocarbon analysis

Radiocarbon analysis was conducted using cryogenic  $\text{CO}_2$  purification, followed by graphitization and accelerator mass

spectrometry. Beta Analytic (Miami, FL) modified their gas stream  $\text{CO}_2$  stripping and purification procedure to include a  $\text{MgClO}_4$  and activated carbon trap to keep any LNAPL from freezing out with  $\text{CO}_2$  in the cryogenic trap. We have confirmed through GC/MS analysis that this is sufficient for removing any hydrocarbon (including vinyl chloride) which might not freeze out of the gas stream using a dry ice slurry pre-trap. Beta Analytic provided both radiocarbon content (in  $\Delta^{14}\text{C}$  and pMC notation) and stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) for all samples.

In order to estimate the  $\text{CO}_2$  proportion derived from fossil sources (e.g. the fuel), published conversion factors<sup>16</sup> and a two end-member mixing model (1) was used:<sup>15</sup>

$$\Delta^{14}\text{CO}_2 = (\Delta^{14}\text{C}_{\text{pet}} \times f_{\text{pet}}) + [\Delta^{14}\text{C}_{\text{NOM}} \times (1 - f_{\text{pet}})] \quad (1)$$

where  $\Delta^{14}\text{CO}_2$ ,  $\Delta^{14}\text{C}_{\text{pet}}$ , and  $\Delta^{14}\text{C}_{\text{NOM}}$  are the groundwater  $\text{CO}_2$ , petroleum and natural organic matter (NOM)  $\Delta^{14}\text{C}$  values, respectively.  $f_{\text{pet}}$  is the  $\text{CO}_2$  fraction derived from petroleum sources. The background well (S5-MW-01)  $\Delta^{14}\text{CO}_2$  ( $-234\text{‰}$ ) was used as  $\Delta^{14}\text{C}_{\text{NOM}}$ . The  $\Delta^{14}\text{CO}_2$  was the given well measurement and  $\Delta^{14}\text{C}_{\text{pet}}$  was assumed to be  $-1000\text{‰}$ .

### Cation and pH analysis

Cation concentrations ( $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$ ) were measured using a Dionex (Sunnyvale, CA) DX-120 ion chromatograph equipped with an AS-40 autosampler, ionPac® CS-12A Cation Exchange Column, and a Cation Self-Regenerating Suppressor (CSRS®-ULTRA). A 5 mL sample (1 : 1 dilution v/v) was injected *via* autosampler. A 20 mM methanesulfonic acid eluent was used at a  $\sim 0.7 \text{ mL min}^{-1}$  flow rate. Samples were run against a series of 5 calibrations standards. IAPSO standard seawater (50 : 1 v/v) was used as a reference with an analytical precision of  $\pm 2\text{--}3\%$ . Three samples were run in triplicate to obtain an average standard error. pH was measured using Fisher Accumet Basic pH meter calibrated with 4, 7, and 10 pH solutions (Fisher Scientific).

## Results

### Carbon isotopes

$\text{CO}_2$  radiocarbon content ranged from 6.0 to 77 pMC – with the highest value representing the NOM on site (Table 1).  $\text{CO}_2$  stable carbon isotope ratios ( $\delta^{13}\text{C}$ ) ranged from  $-14.6$  to  $+5.1\text{‰}_{\text{VPDB}}$  (Table 1). The 77 pMC sample (S5-MW-01) was used as  $\Delta^{14}\text{C}_{\text{NOM}}$  for the two end-member mixing model (eqn (1)) giving a range of fraction petroleum ( $f_{\text{pet}}$ ) values from  $-4$  to 93% of the  $\text{CO}_2$  derived from a fossil source (Table 1).

### Cations and pH

Major cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{++}$  and  $\text{Ca}^{++}$ ) primarily fell within groundwater ranges aside from well FPMW-8 which was closest to San Diego Bay and had sodium ion concentrations approaching seawater levels (Table 1). Both monovalent and divalent cations had the lowest concentrations at the mid-base sampling site (near the hazardous waste collection facility). Higher sodium and potassium values were found near the golf

**Table 1** Groundwater parameters for each well

Well	Na <sup>+</sup> (mg L <sup>-1</sup> ±4%)	K <sup>+</sup> (mg L <sup>-1</sup> ±5%)	Mg <sup>++</sup> (mg L <sup>-1</sup> ±3%)	Ca <sup>++</sup> (mg L <sup>-1</sup> ±5%)	pH	δ <sup>13</sup> C (‰ ± 0.2‰)	pMC (±0.01%)	f <sub>pet</sub>
S11-MW-13 <sup>c</sup>	179	2.4	37.7	19.1	5.4	-10.7	40.0	40.0
S11-MW-24 <sup>c</sup>	32.8	1.2	51.6	21.8	4.9	-12.5	68.8	4.0
S11-MW-25 <sup>c</sup>	568	5.9	95.7	62.5	5.4	-10.2	36.9	44.0
S11-MW-3 <sup>c</sup>	145	1.4	15.3	— <sup>a</sup>	4.9	-13.4	38.1	42.0
S5-MW-01 <sup>bc</sup>	570	63.9	123.9	182.2	4.9	-12.7	76.6	0
S5-MW-39 <sup>c</sup>	215	43.7	108.5	121.0	5.1	-14.6	38.2	42.2
S5-MW-44 <sup>c</sup>	366	54.4	128.8	152.9	1.9	-4.0	55.8	16.0
FPMW-8	5874	233.1	480.4	243.4	4.8	-10.0	60.3	8.9
FPMW-03A	35.7	14.9	60.9	304.4	4.8	-14.2	9.0	86.5
FPMW-19A	56.7	26.9	79.0	135.7	4.9	-7.3	13.2	80.0
FPMW-21	375	80.8	152.3	118.0	5.5	-5.6	55.0	17.0
FPMW-23	523	60.6	123.7	167.2	5.4	-13.7	55.8	15.7
PRW-1032-3	63.3	15.3	84.7	172.4	5.1	-5.8	24.3	63.3
PRW-8-1	59.9	16.7	56.8	137.9	4.6	0.5	21.0	68.3
PRW-8-10	36.1	25.0	87.6	148.8	5.1	5.1	9.4	85.8
PRW-8-4	26.1	12.6	40.8	134.0	5.1	-2.0	9.0	86.5
PRW-963-2	65.1	34.2	75.3	114.3	5.1	-10.2	28.8	56.6
PRW-963-3	111	40.5	87.7	450.2	5.1	-7.7	4.56	93.1
PRW-966-4	54.1	32.5	89.9	296.3	6.1	-9.7	6.0	90.9
PRW-967-3	67.1	34.3	74.0	116.1	4.5	-2.1	27.6	58.4
PRW-968-1	86.2	24.6	89.0	178.4	5.1	-11.8	9.8	85.2
S10-SMW-5	36.8	22.6	43.3	108.3	4.9	-7.7	60.5	8.7
SRW-968-1	70.7	36.5	96.1	184.3	5.0	-14.5	7.3	89.0

<sup>a</sup> Poor peak shape negated analysis. <sup>b</sup> Background well. <sup>c</sup> These wells were distinct from the fuel farm site.

course site (including the chosen background well S5-MW-01) indicating possible marine influence in the groundwater (Table 1). At the fuel farm, cations were most variable indicating potential seawater influence. Sodium and potassium cation concentrations correlated moderately ( $r^2 = 0.84$ ) and each correlated with magnesium ( $r^2 = 0.91$  for Na<sup>+</sup> and  $r^2 = 0.95$  for K<sup>+</sup>). Calcium cation concentrations did not correlate with any other cation. Neither calcium or magnesium cation concentrations correlated with CO<sub>2</sub> pMC indicating a non-systematic, if any, calcium carbonate influence on the CO<sub>2</sub> radiocarbon ages.

Groundwater pH was acidic at all wells averaging 4.9. The lowest pH was measured (1.9) at well S5-MW-44 near the golf course. This anomalously low pH value was assumed to be compromised as ample CO<sub>2</sub> was available for radiocarbon measurement in this sample. Groundwater pH was low enough to drive calcium carbonate dissolution.

## Discussion

### Background selection

Probably the most challenging aspect of the reported study – and those of its kind, is selecting an appropriate background which represents unimpacted conditions. For most “established” sites, groundwater wells exist to address potential contamination. We sought a well that was upgradient to known contamination, with mixed vegetative and asphalt covering and representative pH and soil type. Through historical literature review, no wells were thought to exist at the fuel farm which are not impacted by fuel contamination. Wells in the hazardous waste collection area were also thought to have all been

potentially influenced by mixed organic contaminants. The golf course site is an area with a previously decommissioned and capped landfill. The chosen background well has been historically considered upgradient to any known contamination. It is in a partially vegetated – partially asphalt covered area (currently a do-it-yourself carwash). Its pH and cation values are within one standard deviation of the average for the fuel farm wells and it has a “reasonable” CO<sub>2</sub> radiocarbon age (indicative of aged organic matter utilization).

### Potential biasing influences

The presence of considerable CaCO<sub>3</sub> (limestone) in the saturated zone could influence acidic groundwater CO<sub>2</sub>. While there is virtually no limestone on-site, soil geology studies showed silty sands containing shells and shell fragments (presumably from the dredge material used to create much of NASNI). As the shell and shell fragment radiocarbon age is unknown, we were concerned shell dissolution under acidic conditions might bias the CO<sub>2</sub> age measurements – thus justifying cation measurements. There was no correlation between Ca<sup>++</sup> concentrations and pMC for the measurement suite.

To statistically characterize the groundwater geochemistry, we created a principal components analysis (PCA) model using cation measurements and pH. All data were mean-centered and normalized before the model was created (using Eigenvector Toolbox in Matlab®). The model encapsulated 81% of the sample variability within the first two components. Sodium, potassium and magnesium cations loaded strongly along PC1, while pH loaded along PC2 (Fig. 2A). Calcium cation loaded



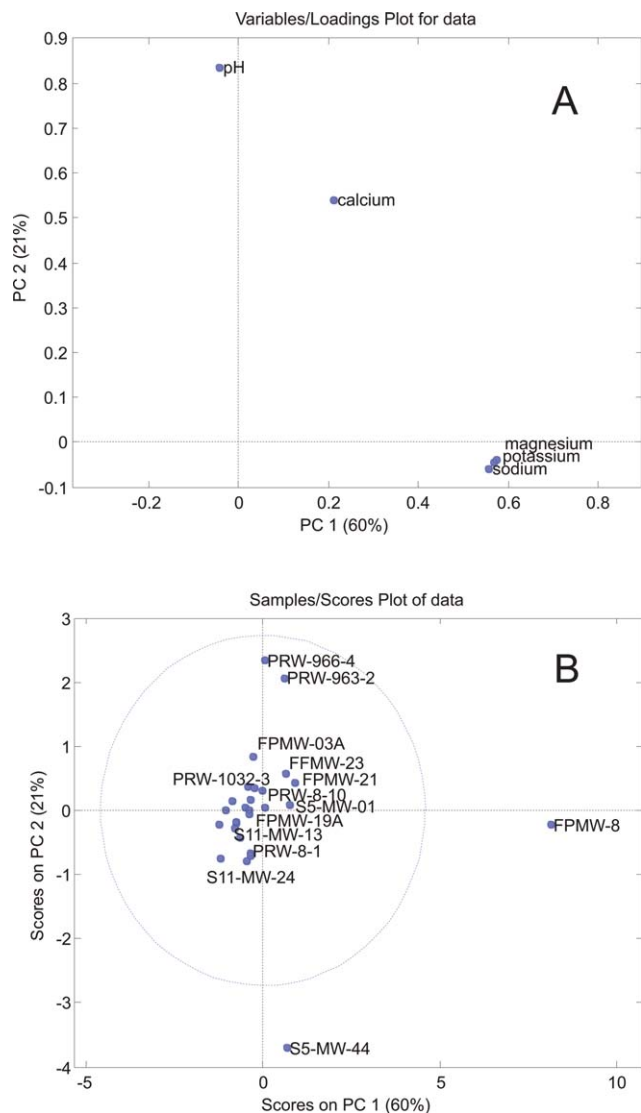


Fig. 2 PCA analysis. A – loadings plot; B – scores plot.

within the data space between pH and the other cations indicating a potential relationship with pH (Fig. 2A). The scores plot reveals that only two wells fall outside the 95% confidence interval of the model (Fig. 2B), FPMW-8 – which is very close to San Diego Bay and obviously influenced by seawater influx, and S5-MW-44 which had an anomalously low pH (1.9) and is scored at  $\sim -4$  on PC2 (loaded heavily by pH). The two wells scoring highest along PC2, PRW-963-2 and PRW-966-4 had relatively high pH relative to other wells (Table 1, Fig. 2B). Based on the PCA model confidence interval, it appears no wells were statistically influenced by calcium cation which could bias the  $\text{CO}_2$  radiocarbon measurements.

### Stable carbon isotope ratios

All of the  $\text{CO}_2$  stable carbon isotope ratios were  $^{13}\text{C}$ -enriched relative to what might be expected for respired NOM or hydrocarbon contaminants (Table 1). Typically, soil NOM and fossil hydrocarbons fall within a range of about  $-18$  to  $-30\text{‰}$ VPDB. It

is generally accepted that the microbially respired  $\text{CO}_2$  will isotopically reflect the organic matter source. For instance,  $\text{CO}_2$  respired from glucose with a stable isotope ratio of  $-25\text{‰}$ VPDB will be  $\sim -25\text{‰}$ VPDB. While we did not measure groundwater redox potential, it was clear from sulfurous odors that many wells, especially in the southwestern corner of the fuel farm, were likely anaerobic. There are two possibilities which might explain the enriched  $\delta^{13}\text{C}$  values observed. First, the nominal isotopic ratio of atmospheric  $\text{CO}_2$  is  $\sim -7\text{‰}$ VPDB. It is possible that atmospheric gas has diffused into the groundwater so that a more atmospheric signal ratio was measured. Secondly,  $\text{CO}_2$  may be used as a terminal electron acceptor during methanogenesis in the groundwater. This process is highly specific for the light carbon isotope and thus as  $\text{CO}_2$  is used, the remaining  $\text{CO}_2$  pool becomes  $^{13}\text{C}$ -enriched.

In a previous study, highly  $^{13}\text{C}$ -enriched  $\text{CO}_2$  in soil gas from a known anaerobic fuel plume was observed.<sup>15</sup> Because this site was overlain by asphalt, it was relatively easy to dismiss any atmospheric  $\text{CO}_2$  diffusion and it was relatively straightforward to indicate methanogenesis as the driving force behind the observed  $^{13}\text{C}$ -enriched  $\text{CO}_2$ . Additionally, measured methane concentrations were elevated in wells with  $^{13}\text{C}$ -enriched  $\text{CO}_2$ . The present fuel farm site is not consistently covered by asphalt, so it is possible that some atmospheric diffusion may impact the  $\delta^{13}\text{C}$  values. However, given the inference (sulfur smell) that many wells were anaerobic, we presume that  $\delta^{13}\text{C}$  values more enriched than  $-7\text{‰}$ VPDB (the typical atmospheric  $\delta^{13}\text{C}$  value) are likely the result of methanogenesis.

Of interest at this site is the fact that stable carbon isotope ratios are less enriched at the central plume location (Fig. 3), than at the peripheral plume region(s) – southwest and northwest of the heaviest contamination. From sampling logs, the groundwater over the thickest free product smear zone (darkest blue surface plot region) did not exhibit significant sulfur smell and did not contain any black sulfurous particulates. We suggest possibly the soil vapor extraction system was responsible for potentially oxygenating this region. However, the system was turned off in 2005, so the impact during the

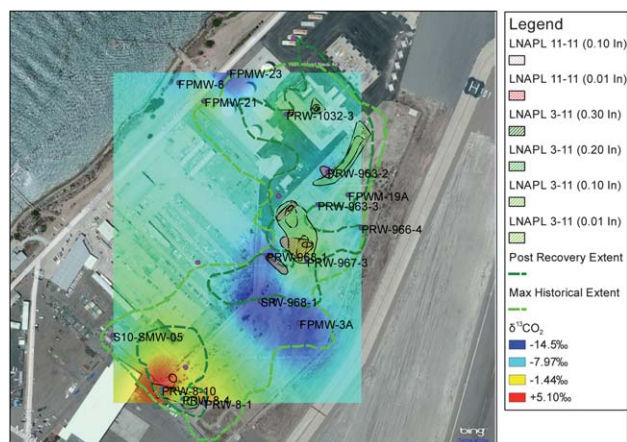


Fig. 3 Stable carbon isotope ratios in relation to historical and current contamination.

described sampling should have been minimal. The wells to the northwest of the main smear area are asphalt/concrete covered (removed from direct atmospheric diffusion) which might explain more anaerobic conditions and  $^{13}\text{C}$ -enriched  $\text{CO}_2$ . The southwest regions was on a sloping hillside (and thus the groundwater was further from the soil surface). This would potentially lower the rate of atmospheric  $\text{CO}_2$  diffusion into the groundwater.

### Radiocarbon in groundwater dissolved $\text{CO}_2$ in relation to current and historical fuel contamination

Data for historical and current fuel contamination were provided by RORE in a draft report to the site manager. Those data were visualized along with fraction  $\text{CO}_2$  from petroleum sources across the fuel farm site (Fig. 4). The lowest  $f_{\text{pet}}$  values were “outside” or at the fringe of the historical contamination region. For instance,  $f_{\text{pet}}$  values were  $\sim 10\%$  at S10-SMW-5 and FFMW-8 which are the furthest wells down-gradient to the original source material (Fig. 4). The highest  $f_{\text{pet}}$  values coincide with regions on-site which are within the current free product zone and within zones delineated after the recovery system was stopped in 2005 (Fig. 4). For regions still containing free product, the groundwater  $\text{CO}_2$  is mostly ( $>50\%$ ) derived from fossil sources. This is a direct indication that fuel hydrocarbons are being degraded to  $\text{CO}_2$  on-site.

Based on both radiocarbon and stable carbon isotope analysis, it appears likely that at the site's center, biodegradation is likely occurring *via* aerobic or intermittently aerobic processes ( $\text{CO}_2$  ancient, but  $\delta^{13}\text{CO}_2$  relatively light), while at the southwestern edge and northwestern region; relatively enriched  $\delta^{13}\text{CO}_2$  coincides with ancient  $\text{CO}_2$ . This likely indicates highly recycled  $\text{CO}_2$  (methanogenesis with intermittent methane oxidation – most likely *via* sulfate reduction). This inference is supported by the black sulfur deposits found in the groundwater at the PRW-8-1, PRW-8-4, and PRW-8-10 wells. Although the southwestern corner of the site is not covered by asphalt, considerable  $\text{CO}_2$  recycling was observed during a previous study using stable and radio-carbon isotope analyses.<sup>15</sup>

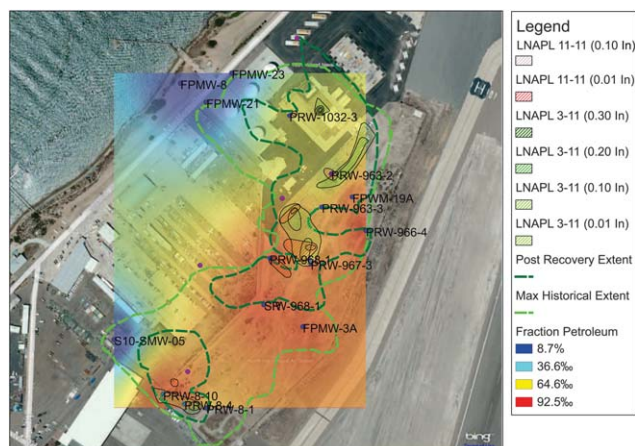


Fig. 4 Fraction  $\text{CO}_2$  from petroleum source related to historical and contemporary contamination.

## Conclusions

This study adds to a growing number of previous efforts which have demonstrated soil gas or groundwater  $\text{CO}_2$  radiocarbon analysis' usefulness in definitively demonstrating on-site hydrocarbon remediation to a non-toxic end-product. Because the end-member radiocarbon signatures are distinctly different between contemporary and fossil  $\text{CO}_2$  (over 1000 units on the per mil scale), radiocarbon-depleted  $\text{CO}_2$  relative to background  $\text{CO}_2$  confirms fossil-fuel degradation. Using a straightforward two end-member mixing model, an environmental manager can readily determine the fraction of respiratory product attributable to the fuel contaminant. This information is critical in evaluating remediation alternatives. The technique can be used during initial site investigations, or as a tool during ongoing site analysis – for instance as a monitoring component for monitored natural attenuation.

Future applications and refinements can be envisioned. Monitoring  $\text{CO}_2$  radiocarbon content could be very useful during time-series samplings to determine if engineered approaches are enhancing remediation efficacy. In this scenario, a shift toward more radiocarbon-depleted  $\text{CO}_2$  might indicate enhanced contaminant oxidation relative to background NOM oxidation (which might be a side effect of adding electron acceptors or co-metabolites). Additionally, measuring  $\text{CO}_2$  production over time in addition to radiocarbon content would allow one to determine the overall contaminant degradation rate using rather simple mathematical relationships (*i.e.*  $\text{CO}_2$  produced over time multiplied by the fraction of  $\text{CO}_2$  derived from the fossil end-member would give the total mass of contaminant degradation per unit time).

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