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Combined radiocarbon and CO_2 flux measurements used to determine *in situ* chlorinated solvent mineralization rate†

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A series of combined measurements was made at the Naval Air Station North Island (NASNI) Installation Restoration Site 5, Unit 2 during July and August 2013. Combined measurements included CO_2 respiration rate, CO_2 radiocarbon content to estimate chlorinated hydrocarbon (CH) mineralization and a zone of influence (ZOI) model. CO_2 was collected continuously over 2 two-week periods by recirculating monitoring well headspace gas through NaOH traps. A series of 12 wells in the main CH plume zone and a background well with no known historical contamination were sampled. The background well CO_2 was used to determine radiocarbon content derived from respired natural organic matter. A two end-member mixing model was then used to determine the amount of CH-derived carbon present in the CO_2 collected from plume region wells. The ZOI model provided an estimate for the soil volume sampled at each well. CH mineralization rates were highest upgradient and at the plume fringe for areas of high historical contamination and ranged from 0.02 to 5.6 mg CH carbon per day. Using the ZOI model volume estimates, CH–carbon removal ranged from 0.2 to 32 mg CH–carbon m^{-3} per day. Because the rate estimates were based on a limited sampling (temporally), they were not further extrapolated to long-term contaminant degradation estimates. However, if the site manager or regulators required them, estimates – subject to long-term variability uncertainties – could be made using volume and rate data determined over short timescales. A more comprehensive seasonal sampling is needed to constrain long-term remediation models for the entire impacted area and identify environmental conditions related to more rapid turnover times amongst the wells.

Environmental impact

CO_2 radiocarbon analysis has proved extremely useful in definitively demonstrating on-site hydrocarbon (fuels, industrial chemicals, *etc.*) remediation to a non-toxic end-product. Vadoze-zone and groundwater CO_2 which is radiocarbon-depleted relative to background CO_2 confirms fossil-fuel or industrial chemical degradation. Combining CO_2 radiocarbon analysis, on-site CO_2 production rate, and a hydrogeologic Zone of Influence (ZOI) model for each collection well allows calculating contaminant degradation per unit time and unit area. Combining these measurements allows an environmental manager to estimate time-to-remediate for specific regions within a site – or the entire site. This information aids in evaluating remediation alternatives and can be used throughout the life-cycle of site analysis to assess remediation.

Introduction

The Department of Defense (DoD), Department of Energy (DOE), other federal agencies and civilian entities are faced with billion dollar expenditures for environmental cleanup in the United States. Prohibitive cleanup costs make treatment strategies such as monitored natural attenuation (MNA), enhanced passive remediation (EPR) or low cost engineered solutions attractive remediation alternatives for reaching Response Complete (RC) status. Historically, lines of converging evidence are used to establish the occurrence of *in situ* bioremediation, abiotic contaminant conversion, or other forms of natural attenuation. It is often accepted that no single analysis or combination of *ex situ* laboratory tests provides an accurate contaminant turnover confirmation or rate information for contaminant degradation under *in situ* conditions.[1–4] Similarly, reports sponsored by DoD, DOE and Environmental Protection Agency (EPA) advocate collection of a wide array of data to confirm contaminant attenuation and predict timescale(s) for remediation.[5–7]

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Multiple lines of evidence provide a means for refining what occurs on-site and in some instances, may provide indirect contaminant degradation rate estimates. However, site managers are under considerable pressure to decrease costs while still obtaining the most realistic and complete site conceptual model data. A clear need exists for relatively inexpensive methods that are able to provide compelling evidence for contaminant turnover while also offering realistic rate estimates for obtaining cleanup goals. Combining natural abundance $^{14}CO_2$ measurements with CO_2 production (contaminant respiration) rates offers a method for simultaneously determining the amount of CO_2 generated from the contaminant pool and that CO_2's generation rate (be it biodegradation or abiotic conversion).[8]

Because of the very distinct fossil carbon signatures (devoid of ^{14}C) relative to contemporary carbon (modern), $^{14}CO_2$ analysis has recently been applied to tracking fossil fuel-derived contaminant degradation products.[8–14] Analytical resolution between the two end members (fossil and contemporary) is over 1100 parts per thousand (standard measurement scale) and can be accurately measured on contemporary AMS systems. Living biomass, atmospheric CO_2, and soil organic matter-derived CO_2 are all analytically distinct from fossil-derived CO_2. Petroleum and petroleum-sourced industrial chemicals have a distinct radiocarbon signature (0% modern) and the absence of ^{14}C is evenly distributed throughout the contaminant pool – offering a built-in tracer. As radioactive decay rates are unchanging, the only potential bias in this measurement is toward the conservative (for example, if some atmospheric CO_2 contaminates a sample the measurement will be more modern and thus will not overestimate degradation rate).

If considerable degradation (contaminant oxidation) is occurring, CO_2 evolution associated with a fossil-fuel based contaminant plume will reflect the carbon source. Up-gradient of the plume (*e.g.* background site), groundwater and soil CO_2 will be primarily derived from respired natural organic matter. Within the plume or at the fringes, biodegrading contaminant will generate CO_2 with 0% modern carbon. This signal can be differentiated from CO_2 from natural organic carbon sources using a two end-member mixing model.[12,13] With one measurement, it is possible to directly link contaminant degradation to the on-site CO_2 pool.

This single measurement technique, applied to several sites, has linked contaminant turnover to fossil-hydrocarbon or industrial chemical oxidation.[5–9] Although this singular analytical method is powerful evidence that contaminants are being degraded to CO_2 *in situ*, it does not readily allow calculating contaminant turnover rates without additional site information. It only defines what percentage of the total respiration CO_2 pool is due to contaminant degradation relative to natural organic matter. A logical next step would be to couple CO_2 source (contaminant *versus* natural organic matter) with CO_2 production rate to estimate intrinsic contaminant biodegradation rate. In previous studies, short-term soil respiration rates were measured at the same site where soil gas CO_2 radiocarbon analysis indicated fossil fuel contributed significantly to the CO_2 pool.[8] The data were scaled to the site's area such that a two dimensional flux measurement for contaminant carbon could be estimated.

Many techniques exist for determining CO_2 flux within soil horizons. Generally, methods may have open- or closed-system designs.[15] Most recently, flux chambers (a type of closed-system) and gas flux models were used to estimate net respiration in contaminated soils.[8,14,16,17] These techniques applied over a range of sub-sites (*e.g.* over a contaminant plume and background areas) estimate increased CO_2 production attributable to organic contaminants. Although the two-dimensional flux at the air:soil interface can estimate contaminant turnover, it provides only a net flux two-dimensional estimate (m^2 per day). Scaling to 3-D required a soil flux model. Another means to obtain a 3-dimensional CO_2 gas production rate is to trap CO_2 from a "known" volume over unit time. This also requires modeling the system to determine the volume within the collection sphere. Collecting CO_2 from soil gas or groundwater is relatively easy and inexpensive, however, the ability to confirm that CO_2 produced is definitively linked to the contaminant on-site requires radiocarbon analysis – which may be sample limited ($\sim$1 mg CO_2 needed).

In this study, the goal was to collect CO_2 produced at a predominately TCE-contaminated groundwater site over time to both assess CH to CO_2 conversion rates and synchronously collect ample CO_2 for confirmatory radiocarbon analysis. An additional goal was to produce a ZOI model to calculate TCE conversion to CO_2 on a per unit volume and per unit time basis.

Materials and methods

Site description

IR Site 5, Unit 2 at North Island, CA (Fig. 1) was identified as a prime candidate to couple radiocarbon and CO_2 flux measurements due to a rich archive of existing data on contaminant levels, hydrogeology and the need for site closure information. The site is a former landfill with an estimated 2000 tons of hazardous wastes disposed at the site prior to 1970. Waste was then transferred off-site. The area was converted to a golf course in 1983. Two pits were associated with Unit 2 (Eastern and Western). Only the Eastern pit was excavated (2001). Waste deposited at IR-5 included trash, solvents, oils, caustics, hydraulic fluid, contaminated solid waste, sludge and paints.

Current site activity includes monitoring, inspection and maintenance of the landfill cover. Within Unit 2, monitoring was conducted semi-annually until mid-2008 and the plume of chlorinated solvent material (in some wells over 1 g L^{-1}) appears to be slowly receding over time. The presumed attenuation mechanism is biological degradation. Unit 2 consists of mostly natural vegetation (Fig. 1). Wells within the adjacent IR Site 5 Unit 1 were sampled for dissolved CO_2 radiocarbon when searching for a suitable background site during a previous study at NASNI and found to be relatively depleted in ^{14}C.[13]

The site is fitted with numerous groundwater sampling wells installed from 2000–2005, made from 4″ PVC pipe and screened

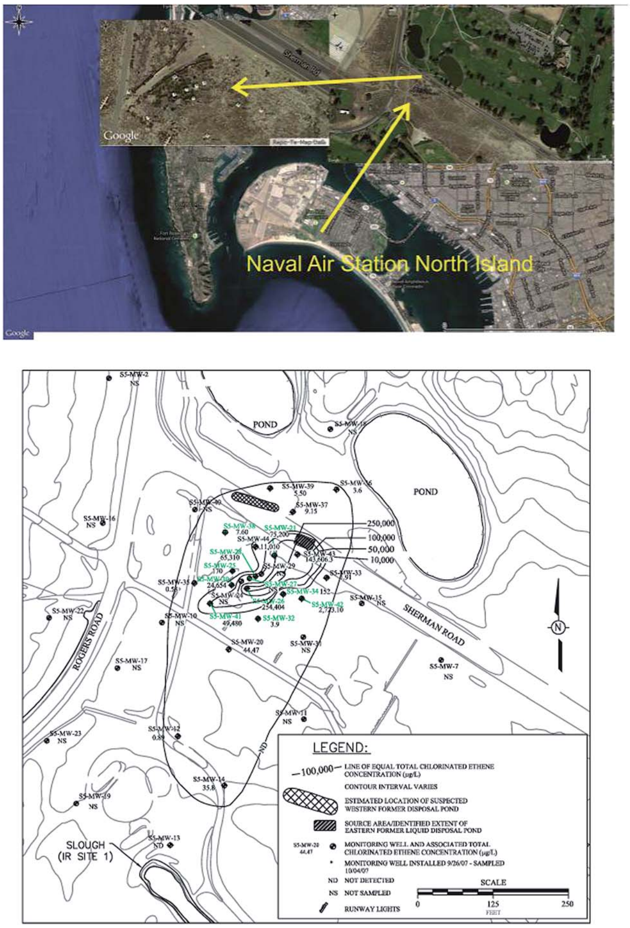

Fig. 1 Sample site. Engineering diagram shows central well cluster. Sampled wells in green text.

across the groundwater:vadose transition. It is seldom disturbed being in the approach path to a runway. Twelve wells within a central cluster were used for CO_2 collection. A background well upgradient of any known contamination was used for background CO_2 radiocarbon age and flux measurements.[13]

San Diego has a Mediterranean-like climate with two major seasonal patterns (wet and dry season). The limited sampling event described here was conducted during June and August 2013 – during the dry season. Rain total prior to sampling was 11.2 cm for the calendar 2013 year. At the site, historical contamination from chlorinated hydrocarbons was elevated within the central well cluster (MW-25–MW-30) and on the Northern portion of the site near Sherman Road (Fig. 1 – largest zoom). Contaminated soil was removed from the historical landfill site in 1983 and the Eastern waste pit of Unit 2 in 2001. Since that time, regular monitoring has revealed decreasing CH concentrations with persistently high contamination at the central well cluster. According to site managers, seasonal rains (Dec–Feb) typically elute CHs off soils in the vadose zone which transiently increases groundwater CH concentrations.[18] Soils have been identified as primarily sands (from dredging operations last century). No significant sources of $CaCO_3$ have been identified.

CO_2 collection

A CO_2 collection system consisting of solar power cells, battery banks, voltage controllers, sealed pumps, tubing, well caps, and NaOH traps was developed and deployed on-site. Battery-powered pumps (Won Brothers LifeAir 50) were modified to intake only from a glued Teflon tubing connection and output through a separate tube (1/16″). Tubing was glued into place using epoxy and sealed with silicone sealant. Battery powered pumps were modified by the manufacturer to accept 3 V from a wired connection. Solar panels were used to recharge deep-cycle batteries and appropriate step-down transformers were used to deliver ~3 V to each pump. For the main well cluster and a background well, a pump and associated sampling infrastructure was installed. The sample cluster for pumps was limited to wells within the range of the solar panel and wiring. Initial samples (groundwater only) collected previous to pump deployment (March 2013) covered a larger area. It was not possible given flight path restrictions and solar power requirements to cover a wider sampling area for CO_2 collection.

Sealable well caps (Dean Bennett Supply, Denver, CO) were modified with thru-tubes to allow removal of gas from the well headspace and return CO_2-scrubbed gas to the same headspace (thus producing no net "draw" from the well). The draw tube was approximately 2 meters and pushed down toward – but above – the groundwater level while the return tube extended only ~10 cm from the well cap. A CO_2 trap consisting of ~50 g NaOH pellets was made from a 100 mL serum bottle and Teflon-lined septum (Fig. 2).

Before CO_2 was captured, each well pump was run for ~48 hours (at least 60 well casing volumes) and trapped CO_2 – presumed to be a mixture of in-well CO_2 and CO_2 drawn in from opening the well – was discarded. A fresh CO_2 trap was installed

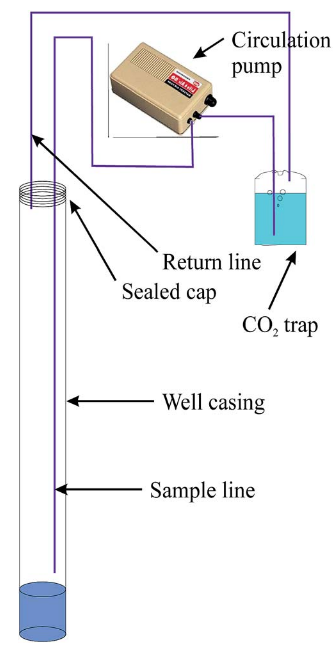

Fig. 2 Well sampling schematic.

and pumps were run continuously for two 2 week periods (one set of traps per 2 weeks). Traps were shipped to NRL for subsequent analysis.

Pump operation was monitored using a voltage sensor for each pump (Hobo U-12 data loggers, Onset, Bourne, MA). Pumps were generally operational for the full period, however, towards the end of each 2 week period, early morning operation became limited as solar cells could not keep up with the constant current draw. Several pumps did not survive the full 4 week collection period (dead motor, disintegrated plastic, *etc.*). These issues are addressed in the results section. No uncompromised pumps were non-operational for more than 4 h during any 24 h period.

CO_2 production analysis

Serum bottle contents with trapped CO_2 were carefully transferred to a large graduated cylinder and diluted with purified water (MilliQ > 18 MΩ resistance) until all NaOH pellets were dissolved. Triplicate sub-samples from each 2 week collection were then transferred to 20 mL serum bottles. Samples were appropriately diluted and analyzed by acidifying the CO_2 out of solution and measuring by coulometry.[19] CO_2 was quantified relative to a certified reference material.[20] Samples were run in duplicate and values were averaged for reporting. Production (collection) rate was calculated dividing the total recovered CO_2 by the time of collection (annotated for each well). Because trapping CO_2 from the well headspace could introduce an equilibrium CO_2 transfer from the adjacent volume to the well head-space, CO_2 collection rates were converted to CO_2 production rates by subtracting the average collection value for the lowest value well (see Results section). The CO_2 flux from this well was assumed to be solely driven by equilibrium (even though organic matter and contaminating mineralization may have occurred). CO_2 collection and production rates were averaged between the two collection periods to obtain a representative "dry season" values.

Radiocarbon analysis

CO_2 trapped in aqueous NaOH (left over after coulometric analysis) was sent to Beta Analytic (Miami, FL) for radiocarbon dating using accelerator mass spectrometry (AMS). Samples were also analyzed for $\delta^{13}CO_2$ ratios using methods previously described.[13]

Water quality analysis

In order to rule out any sources of potential CO_2 contamination which might bias radiocarbon measurements, cations potentially associated with carbonate dissolution, fertilizer use (potassium carbonates) and seawater intrusion were measured. Carbonate carbon could be ancient relative to background. Water samples were taken in pre-cleaned 40 mL vials for pH and cation concentrations. Samples were assayed for K^+, Ca^{++}, Mg^{++} and Na^+ ions using a Dionex DX120 ion chromatograph with a CS12A cation column as previously described.[13] Stoichiometric differences between seawater and groundwater $Na^+ : Ca^{++}$ ratios coupled with low pH relative to background wells were evaluated as a potential indication of carbonate dissolution. Soil characterization data from borehole studies at two sites on North Island indicated no limestone soil lenses.

Zone of influence model/simulation

A ZOI model was created based on well and local soil characteristics. These included well construction (casing dimensions, depth to water) temperature, atmospheric pressure and soil permeability values. Analysis of well logs and prior well tests in the project area was used to develop a hydrogeologic site model. This information was coupled with CO_2 equilibrium simulations to create the ZOI model. The ZOI model was developed using MT3DMS[21] and MODFLOW-2005.[22] MT3DMS is the biodegradation model capable of simulating multi-solute transport and reaction, and was used to simulate CO_2 solute transport as a part of the ZOI model. MODFLOW-2005 is the hydrogeological model considered as the reference code to simulate groundwater dynamics and was used to simulate groundwater flow in the unconfined aquifer at the study site. The two models have been used together as the standard package for multi-species contaminant transport simulations.[23] In this study, ModelMuse linked and interfaced the two models.[24]

The study target was CO_2 produced from chlorinated solvents (*e.g.* TCE and its breakdown products DCE and VC). Among different biodegradation models studied (*e.g.* MT3DMS, RT3D, Biosereen, Biochlor, and SEAM3D), a groundwater simulation model and a complex CO_2 transformation system tracking CO_2 solutes from different sources was needed. ModelMuse was able to adequately couple models for this purpose. Simulations treated all CO_2 with different origins together – radiocarbon content was then used to uniquely distinguish CO_2 derived from chlorinated solvents.

Determining contaminant respired

Radiocarbon data were converted to $\Delta^{14}C$ notation as needed for further calculations using standard methods.[25] An isotopic mixing model was applied to each sample using CO_2 radiocarbon value collected at MW-01 as the site-wide background value.[12] MW-01 is roughly 400 meters northwest of the main contamination. There is no known contamination at this well (planned background well). Background $\Delta^{14}C$ was $-162‰$ (MW-01) and $\Delta^{14}C_{petroleum}$ was assigned the value $-999‰$. The $fraction_{petroleum}$ was solved using eqn (1):

$$\Delta^{14}CO_2 = (\Delta^{14}C_{petroleum} \times fraction_{petroleum}) + [\Delta^{14}C_{natural\ organic\ matter} \times (1 - fraction_{petroleum})] \quad (1)$$

^{14}C-content measurements were used to determine the proportion of vadose zone CO_2 derived from contaminants of interest (CH).[12] These values were then coupled with hydrogeologic model data to determine contaminant flux through oxidation processes to CO_2. The CO_2 production rate at well MW-01 was not used for this correction – only to calculate fraction petroleum. Comparing in-plume measurements with reference site(s) measurements allowed source apportioning *in* *situ* microbial assemblage carbon demand and determining COI degradation rate.

Results and discussion

Cation and pH analysis

Samples for cation and pH were analyzed for March 2013 and July 2013 samplings. pH was near neutral for most wells except for MW-01 (background) and MW-38 (Table 1). Wells on the site's Southern side generally had a higher Na^+ content, but were not in a range which indicated significant seawater intrusion. pH was elevated in the pre-sampling (March 2013 – see ESI†), but cation concentrations were not significantly different. We speculate seasonal rains (typically January through March) impact groundwater pH. Calcium ion concentrations ranged from 8.0 to 66 mg L^{-1} (Table 1) but did not inversely correlate with pH to indicate significant carbonate dissolution during either sampling ($r^2 < 0.3$). We performed a trend analysis with the water quality data using principal components analysis (PCA). Bi-plots showed no strong loadings with any variable (Ca^{2+} being of most concern). We thus assumed any possible interferences were minimal and would be encapsulated within the background well's radiocarbon ratio(s).

CO_2 collection and production rates

CO_2 collection rates ranged from 0 (see equilibrium subtraction below) to 34 mg CO_2 per day (Table 2). CO_2 collection was lowest in the central well cluster where historical contamination was highest. Because CO_2 was constantly scrubbed from the well casing, a physical equilibrium-driven "draw" of CO_2 should have occurred in each well (in addition to CO_2 driven into the well headspace due to active respiration). There was no correlation between the dissolved CO_2 in the groundwater collected immediately before the wells were sealed and pumping started (data in ESI†). The lowest collection rate (MW-25) was used to estimate the CO_2 trapped only from physical equilibrium kinetics. This well coincidentally also had CO_2 with the youngest radiocarbon age relative to the background well (Table 2). The collection rate at this well was conservatively estimated as the physical CO_2 equilibrium influence and was subtracted (as proportion of starting DIC − raw CO_2 collection − (DIC × MW-25 collection rate/MW-25 DIC)) from all other collection rates to calculate CO_2 production rate in each well. MW-01 (background well) had high CO_2 production rate at ~31 mg CO_2 per day. Standard error for duplicate analyses averaged 0.98% and ranged from 0.03 to 4%. Two 2 week periods were sampled during the same season and averaged for subsequent calculations (*e.g.* preliminary time-to-remediate). Standard error for CO_2 ranged from <1 to 51% between the two collection periods. However, most standard errors were relatively low and averaged ~13% (Table 2). While introducing additional error, averaging allowed a single calculation for volume removed during a one month period.

Table 2 CO_2 production rates and isotopic values

Well	CO_2 production (mg per day)	$\delta^{13}CO_2$ (‰VPDB)	$\Delta^{14}CO_2$ (‰)
MW-01[a]	31 ± 0.85	−34	−147
MW-21	34 ± 4.3	−28	−663
MW-25	0.0[c]	−23	−153
MW-26	3.4 ± 0.79	−25	−298
MW-27	0.0[b]	−18	M[b]
MW-28[a]	1.3 ± 0.03	−25	−190
MW-30	9.7 ± 5.1	−35	−254
MW-32	1.6 ± 0.01	−28	M[b]
MW-34	2.1 ± 0.04	−32	−283
MW-35	25 ± 1.9	−25	−598
MW-38	21 ± 11	−25	−354
MW-41	16 ± 0.68	−28	−232
MW-42	16 ± 0.080	−23	−482

[a] Based on single 2 week collection (pump failure). [b] Modern value (1950+) – indicated pump leak. [c] Assumed to be purely equilibrium-driven.

Table 1 Water quality parameter for July 2013 sampling

Well	Na^+ (mg L^{-1})	K^+ (mg L^{-1})	Mg^{2+} (mg L^{-1})	Ca^{2+} (mg L^{-1})	pH
MW-01	134	11	33	66	5.87
MW-21	190	44	20	33	6.74
MW-25	569	43	59	22	6.69
MW-26	465	64	52	22	6.40
MW-27	513	80	62	25	6.66
MW-28	611	78	54	13	6.80
MW-30	359	70	42	29	6.54
MW-32	936	39	78	13	6.76
MW-34	462	55	48	8	6.97
MW-38	283	29	41	30	5.13
MW-41	306	120	45	29	6.49
MW-42	665	34	64	13	6.78

CO_2 carbon isotope analysis

Twenty six NaOH-trapped CO_2 samples were analyzed for radiocarbon. Two wells (MW-27 and MW-32) had pump issues (became unsealed allowing atmospheric CO_2 intrusion) and were suspect but sent for analysis anyway. Stable carbon isotope ratios for CO_2 indicated potential contamination with atmospheric CO_2 (typically −7‰VPDB) for MW-27. MW-32, which also leaked at the inlet line, had a $\delta^{13}CO_2$ value similar to other wells. $\delta^{13}CO_2$ values were in a range to indicate respiration from natural organic matter sources (Table 2). Many values were lighter than ~−25‰VPDB. This might indicate removal of isotopically-lighter contaminant source or daughter products. In a previous studies, several wells were sampled for compound-specific stable carbon isotope values (MW-21, MW-41, MW-42, and MW-43). In wells where *cis*-1,2-DCE concentrations decreased between the two time-points studied (about 1 year apart), there was a concomitant ^{13}C enrichment in the remaining *cis*-1,2-DCE pool.

The background well (MW-01) had a $\Delta^{14}C$ ratio of −147‰. This equates to 1280 years before present (ybp) or 85% modern (pMC). This well was used as the background for the isotopic mixing model. Radiocarbon ratios ranged from −147‰ to −663‰ at the fringe of the removed source area (Sherman Road) with wells near the central cluster of high residual contamination showing relatively modern values (*e.g.* close to 0 – Table 2). As with CO_2 production, the two sampling period samples were averaged for subsequent calculations. Radiocarbon ratio measurements were very similar between individual 2 week periods. Standard error between periods averaged 6% and ranged from 0.25 to 18%.

ZOI model

Groundwater hydraulic and CO_2 solute properties for the study site were obtained from previous reports.[26,27] Three years of weather data (2007, 2011 and 2012) were obtained from CIMIS San Diego station (Station ID 184) to estimate aquifer recharge rate. Tidal data for the same three years were obtained from the NOAA San Diego Station (Station ID: 9410170) to define boundary conditions. From the aerial photo, surface water pools (*e.g.* ponds and creeks) were identified adjacent to the site (in the golf course and park). A constant head equal to the elevation of these surface water bodies was assigned to the boundary.

The areal model indicated that the effects of short term (daily and weekly periods) changes in sea level around the peninsula on groundwater flow at the study site were insignificant. This agrees with the previous reports[18] and cation analysis presented here. Groundwater hydrology at the study site is usually steady between late summer and fall, therefore, flow during CO_2 collection (July–August 2013) was assumed steady (*i.e.* constant hydraulic gradient). The hydraulic gradient estimated by the areal model was 0.009 m m^{-1}, which was reasonably close to that estimated from the groundwater elevation map in June 2011.[26] Other parameters were obtained from the literature (Table 3).

Initial solute CO_2 distribution in the aquifer around the sampling well was assumed in equilibrium with the CO_2 supplied from overlying soil gas and mineralization; therefore,

Table 3 Parameter summary for ZOI model

Parameter	Units	Value
Hydrology		
Hydraulic conductivity	mL h^{-1}	0.44 (aquifer) 10 (well)
Porosity (aquifer)		0.48 (aquifer) 0.99 (well)
Bulk density	g cm^{-3}	1.4
Specific yield	cm^3 cm^{-3}	0.2
Hydraulic gradient	m m^{-1}	0.015
CO_2 solute transport		
Diffusion coefficient	m^2 h^{-1}	5.77×10^{-5}
Longitudinal dispersivity	m	6.1
Horizontal transverse dispersivity	m	0.61
Vertical transverse dispersivity	m	0.061
Soil gas CO_2	%	0.56

CO_2 distribution was assumed uniform. Any CO_2 gradient observed at the end of the 2 week simulation period was assumed to be attributable to CO_2 collection in the well. With uniform CO_2 distribution, the ZOI associated with CO_2 collection was defined as the volume of aquifer that had a CO_2 concentration 95% or less of the initial concentration. Using Henry's law, CO_2 equilibrium concentration at the groundwater table with the CO_2-rich soil gas was estimated as 8.4 g CO_2 m^{-3}. Because biochemical conditions in the unconfined aquifer during CO_2 collection was unknown, the ZOI model assumed constant mineralization rates for chlorinated solvents (*e.g.* DCE and VC half lives = 3.8 and 9.5 years, respectively). The ZOI model was thus simplified by not accounting for mineralization during the 2 week CO_2 collection period. However, mineralization has certainly accumulated CO_2 in the aquifer over time as CO_2 radiocarbon ages were older than background (Table 4).

The calibrated ZOI model was run with the estimated hydraulic gradient (0.015 m m^{-1}) and hypothetical background CO_2 concentration (8.4 g CO_2 m^{-3}). The entire model domain for this scenario was 9.0 m × 4.5 m × 10.0 m deep. Horizontal spatial resolution was set to 0.09 m × 0.09 m, which makes one grid area equal to 0.0081 m^2, the same as the well area. Vertical spatial resolution varied from 0.05 m at the surface to 1.7 m at the bottom. The hydraulic gradient was applied to the ZOI model by setting the constant head condition along two boundaries allowing groundwater to flow left to right (Fig. 3).

The ZOI model described above was then coupled with measured CO_2 collection rates. Calibration assumed that collection rate was constant during the collection period. Calibration also assumed an equilibrium between CO_2 output (*i.e.* collection) and supply (*i.e.* diffusion) at the well water table. In other words, CO_2 concentration at the well water surface was assumed to decrease to 0.0 g CO_2 m^{-3} by the end of the simulation.

ZOI calibration varied when taking CO_2 collection rate into account. Measured collection rate linearly correlated with the calibrated background CO_2 groundwater concentration (r^2 = 0.96). Also, estimated ZOI volume was linearly correlated with background CO_2 concentration (r^2 = 0.98) and thus CO_2 collection rate. Assuming 0.04% partial pressure of atmospheric CO_2, equilibrium CO_2 concentration of non-contaminated aquifer exposed to the atmosphere would be 0.60 g m^{-3}. Estimated background CO_2 concentration for all collection rates was higher than this value suggesting groundwater contamination with chlorinated solvents (*e.g.* TCE, DCE, VC) and their active mineralization. However, estimated background CO_2 concentrations are below solubility of CO_2 (1450 g m^{-3} at 25 °C) and do not indicate CO_2 saturation in the aquifer.

The calibration assumes a steady hydraulic gradient and constant collection rates. A supplemental simulation for average CO_2 collection rate indicated approximately 50% increase in estimated background CO_2 concentration (*i.e.* increased from 6.5 to 9.7 g m^{-3}) with 10% increase in hydraulic gradient (*i.e.* increased from 0.0150 to 0.0165 m m^{-1}). Another supplemental simulation for average CO_2 production rate increased background CO_2 concentration by 46% (*i.e.* increased 6.5 to 9.5 g m^{-3}) if the collection rate changed from 0.00530

Table 4 Site-scaled contaminant degradation[a]

Well	f_{pet} (%)	Contaminant degradation rate (mg C per day ± 10%)	Contaminant degradation per unit time and volume (mg C m^{-3} per day ± 15%)
MW-01	0	N.A.	N.A.
MW-21	60	5.6	32
MW-25[b]	1.0	0	0
MW-26	18	0.18	1.0
MW-28	5.0	0.017	0.098
MW-30	12	0.34	1.9
MW-34	16	0.10	0.58
MW-35	53	3.6	20
MW-38	24	1.4	8.1
MW-41	10	0.44	2.5
MW-42	39	1.7	9.8

[a] N.A. not applicable – MW-01 used as the background (*i.e.* no contamination). [b] Assumed to be purely equilibrium-driven (*e.g.* no respiration).

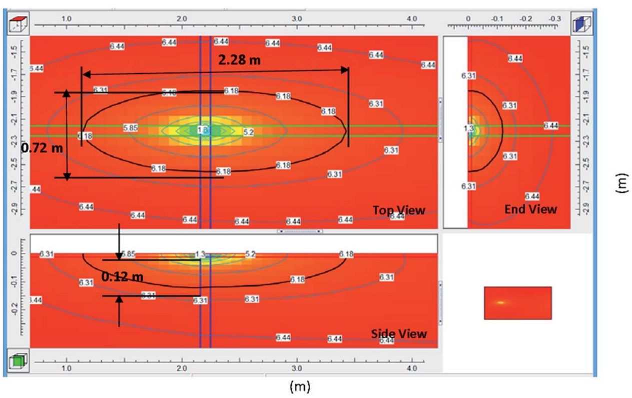

Fig. 3 Calibrated ZOI model for the average CO_2 collection rate (0.0048 g m^{-3}). Calibrated background CO_2 concentration was 6.5 g m^{-3}, and ZOI threshold concentration was 6.18 g m^{-3} (solid black line). Longitudinal and transverse diameters of ZOI were 2.28 m and 0.727 m, respectively. Depth of ZOI was 0.12 m.

(+10%) to 0.00434 g h^{-1} (−10%) over the 2 week collection period. Furthermore, the ZOI model assumed constant and conservative reaction rate for chlorinated solvents. After accounting for the small difference in the first and second CO_2 collection rates, reaction rate appeared to be underestimated for the study site. Therefore, it is important for ZOI estimation to collect and account for these aquifer and operation parameters for better accuracy and reliability.

Contaminant turnover

Using CO_2 collection rate, proportion of CO_2 attributable to CH degradation, and the ZOI model, we calculated mass CH removal at each well per unit time. The two end-member mixing model (eqn (1)) was used with data (Table 2) to solve for f_{pet} at each well. The f_{pet} varied from 1 to 60% over the sampled wells (Table 4). This proportion was multiplied per carbon basis with the CO_2 production rate to obtain the contaminant (CH) mineralization rate (Table 4). Finally, using the ZOI volume (average – 0.176 m^3), contaminant mineralization rate per unit time and volume was calculated (Table 4). Contaminant degradation rate per unit area was highest at MW-21 (32 mg C m^{-3} per day). In areas with highest historical contamination (MW-25–MW-30), CH mineralization rate was slowest, potentially indicating toxicity or lack of necessary co-metabolic substrates driving CH turnover. CH mineralization rates measured at the fringing periphery (near Sherman Road) appear to be most rapid relative to the central well cluster (MW-38, MW-21, MW-42) which supports the plume fringe biodegradation concept observed in other systems.[28] Historical contamination was higher in this region before excavation. Higher rates here (at the fringe) might indicate greater co-metabolic substrate availability or decreased toxicity. CO_2 production was high in the fringing area, while f_{pet} indicated significant CH turnover (Fig. 4).

A major focus for this study was to combine rate measurements, proportion mineralized from contaminants and ZOI estimates to determine site CH mineralization spatially and temporally. While any estimate is subject to error, each technique in this study offers direct *in situ* measurements of relevant

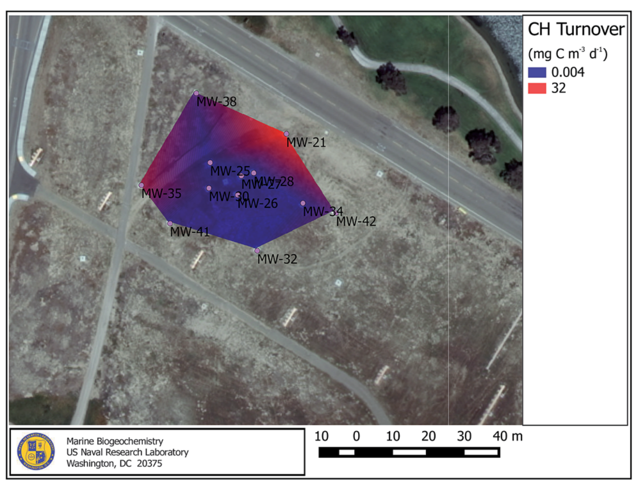

Fig. 4 Contaminant mineralization rate per unit time and area (g C m^{-3} per day).

analytes rather than more common indirect measures (electron acceptors, nutrients, dissolved oxygen, *etc.*). Instead, carbon mineralized specifically from the contaminant of interest (in this case CH, but the method is applicable to any carbon-based chemical produced from fossil fuel stocks) is analyzed. There are currently many "lines of evidence" measures used for confirming (or indicating) contaminant turnover at impacted sites.[29–31] However, these techniques do not directly target the complete degradation product (CO_2) linking original contaminant to degradation product. While many measures indirectly suggest remediation is occurring, they cannot readily be used to determine mass removal (as most do not directly relate to carbon mineralized).[32–34]

To determine mass removal, one could extrapolate the data in the time and volume domains as required. As only one month of data were collected in this study, it would be difficult to extrapolate into accurate long-term degradation rate – or time-to-remediate estimates. Methods do exist for interpolating the collected data to the site, for instance finite-difference estimations and inverse weighting interpolation. For this initial demonstration combining concurrent CO_2 radiocarbon and flux measurements with ZOI modeling, this type of modeling could be done. One would have to assume that the annual CO_2 flux and proportion derived from the CH, were similar throughout the year. Additionally, seasonal weather patterns (winter rains which significantly increase contaminant desorption from soil particles[18]) would have to be ignored. Continued sampling over longer periods capturing seasonal variation would allow a far more robust modeled time-to-remediate estimates.

Soil respiration measurements have recently been made using flux chambers and rates are expressed per square unit area (to indicate soil–atmosphere exchange). Additionally, collecting soil gas at different depths has allowed modeling carbon flux from contaminants in the volume domain. In a recent report discreet soil gas samples were collected for $^{14}CO_2$ measurements.[8] The authors conclude that it is possible to both underestimate and overestimate contaminant degradation rates when soil gas is collected from a separate "pool" than the CO_2 accounted for in flux chamber respiration measurements and advocate coupling rate measurements with radiocarbon analysis on the same sample.[8,14] In the present study, collected CO_2 from the well screen region was used exclusively for the combined measurements. Follow-on work is pending to extend the study over the course of one year. In this manner, it is hoped that variation over time (seasonal, extreme weather, static conditions, *etc.*) can be captured and directly related to radiocarbon content in order to directly determine total CH conversion to CO_2 on-site.

No measurement scaled to an entire site is free from inherent uncertainty. Hydrogeologic parameters, such as porosity, specific yield, *etc.* are taken as single values and used in models to describe entire sites. These parameters are measured in subsamples assumed to be homogenous – but in reality are heterogeneous at the macro- and microscales. The ZOI model, for instance, had variation on the order of 35%. It is difficult to propagate this error as the uncertainty inherent in the simulation is unknown. Furthermore, at IR-5, Unit 2, there has been mixed contamination (*cf.* (ref. 18)). In the region North of the study area, there was considerable fuel hydrocarbon contamination. In the most recent surveys, the region sampled for this study are virtually free of fuel hydrocarbons – with the major contaminant source being CH.[18] As the groundwater flow is from the North, it is possible CO_2 respired from the region upgradient of the study area is a source for ancient CO_2. As natural abundance radiocarbon analysis is non-specific for source (actual compound, not fossil origin), it cannot be ruled out that some of the CO_2 used to calculate CH mineralization could be from fuel hydrocarbons. As fringe wells (like MW-38 and MW-21) have been free of fuel hydrocarbons in recent samplings,[18] we make the assumption that CO_2 captured as respiration product is derived from NOM and CH at these wells.

Conclusions

In this study, we were able to combine CO_2 production measurements, radiocarbon age for that same CO_2 and estimated ZOI for each well to determine contaminant mineralization rate(s). ZOIs were calculated using site-specific geochemical data, and therefore represent a refined estimate of the sampled area relative to a single point source water sample. The literature has numerous examples of extrapolation between groundwater sampling wells to parameterize and visualize site characteristics. In this work, we modeled the zone around each well in three dimensions but did not further extrapolate – believing seasonal differences would likely introduce considerable error. A follow-on study in which CO_2 fluxes will be measured for an entire year has been proposed. The ultimate goal for this initial study was to determine the contaminant to CO_2 conversion rate per unit area (m^{-3}) per unit time (per day) at a group of wells spanning the contaminant plume. While this effort only represents a short temporal sampling (one month), we initially conclude:

• CO_2 production rate(s) collected over one month period (the average of two, 2 week collections) ranged from 0.001 to 5.6 $\pm$ 10% mg per day and CO_2 collection rates were lowest where CH contamination was historically highest.

• Radiocarbon content for CO_2 respired *in situ* ranged from ~1340 to 8700 ybp or from 34 to 85 pMC. CO_2 was primarily derived from non-fossil sources (natural organic matter) in areas with highest historical CH contamination (well cluster MW-28–MW-30).

• A zone of influence (ZOI) model was created to determine per unit volume for collected CO_2 (grams per unit volume). Average ZOI was 2.28 $\times$ 0.72 $\times$ 0.12 meters with an average volume of 0.176 m^{-3}.

• Contaminant turnover ranged from 0.004 to 32 mg carbon m^{-3} per day. This rate was lowest over the region of highest historical CH contamination (MW-25–MW-30).

Of particular interest were the findings that the lowest apparent CH utilization was coincident with regions of highest historical contamination. There was no direct correlation ($r^2 < 0.50$) between historical contaminant concentrations and CH utilization. CO_2 collected above the high historical contamination region had the highest pMC indicating less relative contribution from CH than natural organic matter to the relatively small respiration CO_2 pool. This finding was contrary to the previous study at NASNI in which the contamination was fuel hydrocarbons and CO_2 collected within the fuel plume was distinctly from the fossil end-member.[13] At present, it is unknown why CH conversion appears lowest where substrate concentrations are highest. The plume fringe concept has become widely accepted (*cf.* (ref. 28)) as a model for this phenomenon. We speculate lack of cometabolic substrates coupled with the fact that CH degradation is usually a co-metabolic process (not offering direct carbon and energy gains to the assemblage) as likely reasons. Processes that spatially enhance the plume fringe (*e.g.* fluctuating water table) may be important to increasing contaminant mineralization rates at these types of sites. For instance, during rain events, nutrients, electron acceptors, and additional substrates may be "released" into the groundwater.

Future research to advance this combined methodology and expand the scope will focus on the present site to expand seasonality and refine the spatial approach by scaling well measurements to individual well ZOIs. The approach is particularly appropriate for sites where engineering approaches are in place (zero valent iron curtains, addition of electron acceptors, chemical oxidation additions, *etc.*). Future planned activities at this site include:

• Additional seasonal samplings (currently planning subsampling every two weeks to gather "wet" and "dry" season total CO_2 production)

• Deploy more robust pumps (non-mechanical). While the pumps utilized in this study worked well in the laboratory for extended periods, they were not robust enough for field use. Magnetic oscillating pumps, while drawing more power, have been procured for additional temporal sampling.

• Refine ZOI model by collecting and calibrating CO_2 collection rates with groundwater concentrations.

• Sample during, or, at least under the influence of rain events.

• Given estimates of source size (kg), refine time to degrade estimates.

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Notes and references

1 National Research Council, *In situ bioremediation: When does it work?*, National Academy of Sciences, Washington, DC, 1993.
2 J. V. Weiss and I. M. Cozzarelli, *Ground water*, 2008, **46**, 305–322.
3 W. A. Illman and P. J. Alvarez, *Crit. Rev. Environ. Sci. Technol.*, 2009, **39**, 209–270.
4 P. Bombach, H. H. Richnow, M. Kästner and A. Fischer, *Appl. Microbiol. Biotechnol.*, 2010, **86**, 839–852.
5 K. M. Vangelas, *Summary Document of Workshops for Hanford, Oak Ridge and Savannah River Site as part of the Monitored Natural Attenuation and Enhanced Passive Remediation for Chlorinated Solvents – DOE Alternative Project for Technology Acceleration*, U.S. Department of Energy, Westinghouse Savannah River Company, Aiken, SC, 2003.
6 T. H. Wiedemeier, M. A. Swanson, D. E. Moutoux, E. K. Gordon, J. T. Wilson, B. H. Wilson, D. H. Kampbell, P. E. Hass, R. N. Miller, J. E. Hansen and F. H. Chapelle, *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water*, USEPA Office of Research and Development, Washington, DC, 1998.
7 J. T. Wilson, D. H. Kampbell, M. Ferrey and P. Estuestra, *Evaluation of the Protocol for Natural Attenuation of Chlorinated Solvents: Case Study at the Twin Cities Army Ammunition Plant*, USEPA Office of Research and Development, Washington, DC, 2001.
8 N. J. Sihota and K. Ulrich Mayer, *Vadose Zone J.*, 2012, **11**, DOI: 10.2136/vzj2011.0204.
9 C. M. Aelion, B. C. Kirtland and P. A. Stone, *Environ. Sci. Technol.*, 1997, **31**, 3363–3370.
10 B. C. Kirtland, C. M. Aelion, P. A. Stone and D. Hunkeler, *Environ. Sci. Technol.*, 2003, **37**, 4205–4212.
11 B. C. Kirtland, C. M. Aelion and P. A. Stone, *J. Contam. Hydrol.*, 2005, **76**, 1–18.
12 R. B. Coffin, J. W. Pohlman, K. S. Grabowski, D. L. Knies, R. E. Plummer, R. W. Magee and T. J. Boyd, *Environ. Forensics*, 2008, **9**, 75–84.
13 T. J. Boyd, M. J. Pound, D. Lohr and R. B. Coffin, *Environ. Sci.: Processes Impacts*, 2013, **15**, 912–918.
14 N. I. Sihota, O. Singurindy and K. U. Mayer, *Environ. Sci. Technol.*, 2011, **45**, 482–488.
15 J. M. Norman, C. J. Kucharik, S. T. Gower, D. D. Baldocchi, P. M. Crill, M. Rayment, K. Savage and R. G. Striegl, *J. Geophys. Res.*, 1997, **102**, 28771–28777.
16 R. T. Amos, K. U. Mayer, B. A. Bekins, G. N. Delin and R. L. Williams, *Water Resour. Res.*, 2005, **41**, 1–15.
17 S. Molins, K. U. Mayer, R. T. Amos and B. A. Bekins, *J. Contam. Hydrol.*, 2010, **112**, 15–29.
18 Shaw Infrastructure Inc., *Draft Feasibility Study, Installation Restoration Site 5, Unit 2, Naval Air Station North Island, San Diego*, California SHAW-4302-0075-2318, Shaw Infrastructure, Inc, Concord, CA, 2013.
19 K. M. Johnson, J. M. Sieburth, P. J. l. B. Williams and L. Brändström, *Mar. Chem.*, 1987, **21**, 117–133.
20 A. G. Dickson, *Oceanography*, 2010, **23**, 34–47.
21 C. Zheng and P. P. Wang, *MT3DMS: A modular three-dimensional multispecies transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems; documentation and user's guide*, DTIC Document, 1999.

22 A. W. Harbaugh, *MODFLOW-2005, the US Geological Survey modular ground-water model: The ground-water flow process*, US Department of the Interior, US Geological Survey, 2005.
23 H. Prommer, D. A. Barry and C. Zheng, *Ground Water*, 2003, **41**, 247–257.
24 R. B. Winston, in *Ground Water-Book 6*, U.S. Geological Survey, Reston, VA, Editon edn, 2009, vol. Techniques and Methods 6–A29.
25 M. Stuiver and H. A. Polach, *Radiocarbon*, 1977, **19**, 355–363.
26 Accord Engineering Inc, *Semi-Annual Post-Closure Maintenance Report for Calendar Year 2011 Installation Restoration (IR) Program Site 2 (Old Spanish Bight Landfill), Site 4 (Public Works Salvage Yard), and Site 5, Unit 1 (Golf Course Landfill)*, San Diego, CA, 2011.
27 Geosyntec Consultants, *Annual Progress Report October 2010 to December 2011, Operable Unit 24*, Columbia, MD, 2012.
28 R. D. Bauer, M. Rolle, S. Bauer, C. Eberhardt, P. Grathwohl, O. Kolditz, R. U. Meckenstock and C. Griebler, *J. Contam. Hydrol.*, 2009, **105**, 56–68.
29 Parsons Engineering, *Natural Attenuation of Fuel Hydrocarbons Performance and Cost Results from Multiple Air Force Demonstration Sites*, Parsons Engineering Science, Inc., Denver, CO, 1999.
30 Parsons Engineering, *Natural Attenuation of Chlorinated Solvents Performance and Cost Results from Multiple Air Force Demonstration Sites*, Parsons Engineering, Inc., Denver, CO, 1999.
31 Parsons Engineering, *Principles and practices of enhanced anaerobic bioremeidation of chlorinated solvents*, 2004.
32 F. H. Chapelle, P. M. Bradley and C. C. Casey, *Groundwater Monit. Rem.*, 2005, **25**, 131–141.
33 F. J. Krembs, R. L. Siegrist, M. L. Crimi, R. F. Furrer and B. G. Petri, *Groundwater Monit. Rem.*, 2010, **30**, 42–53.
34 M. L. Brusseau, V. Rohay and M. J. Truex, *Groundwater Monit. Rem.*, 2010, **30**, 57–64.