Naval Research Laboratory

Washington, DC 20375-5320

NRL/MR/6110--14-9539

CO_2 Radiocarbon Analysis to Quantify Organic Contaminant Degradation, MNA, and Engineered Remediation Approaches

Thomas J. Boyd
Michael Montgomery

Chemical Dynamics and Diagnostics Branch
Chemistry Division

Richard H. Cuenca
Yutaka Hagimoto

Oregon State University
Corvallis, Oregon

September 22, 2014

Approved for public release; distribution is unlimited.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE *(DD-MM-YYYY)*
22-09-2014

2. REPORT TYPE
NRL Memorandum Report

3. DATES COVERED *(From - To)*
01 October 2012 – 30 September 2013

4. TITLE AND SUBTITLE
CO_2 Radiocarbon Analysis to Quantify Organic Contaminant Degradation, MNA, and Engineered Remediation Approaches

5a. CONTRACT NUMBER
61-5557-E2-5

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Thomas J. Boyd, Michael Montgomery, Richard H. Cuenca,[1] and Yutaka Hagimoto,[1]

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Naval Research Laboratory, Code 6114
4555 Overlook Avenue, SW
Washington, DC 20375-5320

8. PERFORMING ORGANIZATION REPORT NUMBER
NRL/MR/6110--14-9539

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Strategic Environmental Research and Development Program
Attn: Andrea Leeson
4800 Mark Center Drive, Suite 17D08
Alexandria, VA 22350-3605

10. SPONSOR / MONITOR'S ACRONYM(S)
SERDP

11. SPONSOR / MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES
[1]Department of Biological and Ecological Engineering, Oregon State University, Corvallis, OR 97331-3906

14. ABSTRACT

A series of coupled measurements was made at the Naval Air Station North Island (NASNI) Installation Restoration Site 5, Unit 2 during July and August 2013. Preliminary samples were taken in March 2013. Coupled measurements included CO_2 respiration rate, proportion of the CO_2 attributable to chlorinated hydrocarbon (CH) mineralization and a zone of influence (ZOI) model. This coupling led to calculating CH degradation per unit time per unit area. These coupled measurements represent the first analysis where carbon is followed from contaminant to final degradation product (CO_2) directly – without need for inference or "lines of evidence."

In order to determine a mass removal for this study, the average contaminant mineralization rate (0.673 g C m^{-3} d^{-1}) was multiplied by the total area within the sampling grid (1,225 m^2) then multiplied by the ZOI depth to give the total carbon mass removal from the CH pool: 14.5 g C d^{-1}. The wells on site are screened at the groundwater:vadoze zone interface and the vertical ZOI characteristics are likely very different above and below the water table (vadoze versus saturated zone). However, if the assumption is made that the entire surface soil lens (sandy silt) to a depth of approximately 3 meters has similar CH degradation rates, an optimistic estimate of 246 g C d^{-1} over the entire sampled site area can be calculated. In terms of dissolved CH, an estimate of 0.100 g CH carbon L^{-1} was assumed based on reported values (from 2009). Over the site, within the ZOI, residence time for CH averaged just over 4 years, assuming no additional input (desorbing from soils). At the lowest measured turnover rates, residence time was calculated at 2,400 years and the highest measured rate, 11 months.

15. SUBJECT TERMS

Remediation	Natural abundance	Chlorinated hydrocarbons	Flux	Groundwater
Radiocarbon	Contaminant	Carbon dioxide	Time-to-remediate	Soil gas

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
					Thomas J. Boyd
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	Unclassified Unlimited	58	**19b. TELEPHONE NUMBER** *(include area code)*
Unclassified Unlimited	Unclassified Unlimited	Unclassified Unlimited			(202) 404-6424

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

Table of Contents

Abstract 1
Objective 3
Background 4
  SERDP Relevance 4
  Relevant previous work 4
Materials and Methods 8
  Site Selection 8
  Hardware modification and Field sampling 8
  CO_2 Respiration Field Sampling 9
  Water Quality Analyses 9
  CO_2 Production Rate Analysis 10
  Radiocarbon Analysis 10
  Zone of Influence Model/Simulation 10
  Determining the Contaminant Respired 11
Results and Discussion 12
  Historical Contamination 12
  Cation and pH Analysis 13
  CO_2 production rates 13
  CO_2 Radiocarbon Analysis 14
  ZOI model 15
  Contaminant Turnover (Conversion to CO_2) 18
  Site-wide CH Degradation 19
Conclusions and Implications for Future Research 21
Literature Cited 23
Methods and selected raw data 25
Beta Analytic Data Report 28

List of Figures

Figure 1. Typical isotope ratios 5
Figure 2. Field isotope schematic 5
Figure 3. Soil gas CO_2 and radiocarbon 6
Figure 4. NASNI Fuel Farm CO_2. Fraction from fossil source 7
Figure 5. IR Site 5, NASNI 8
Figure 6. Field pumps 8
Figure 7. Power distribution center 9
Figure 8. Well sampling head caps 9
Figure 9. Well sampling schematic 10
Figure 10. Deployed system at NASNI IR-5 U2 10
Figure 11. Historical contamination at NASNI IR-5 U2 12
Figure 12. CO_2 production (μMol CO_2 d^{-1}) on site 14
Figure 13. ZOI model results 16
Figure 14. ZOI model calibrated for CO_2 collection rate 17
Figure 15. ZOI volume related to background CO_2 concentration 18
Figure 16. Contaminant degradation modeled over site 20

List of Tables

Table 1. Water quality parameters, March 2013 13
Table 2. Water quality parameters, July 2013 13
Table 3. Radiocarbon analysis results 14
Table 4. Parameter summary for ZOI model 15
Table 5. Simulated ZOI sizes 18
Table 6. Contaminant degradation rate 19

Abstract

A series of coupled measurements was made at the Naval Air Station North Island (NASNI) Installation Restoration Site 5, Unit 2 during July and August 2013. The objective was to assess CO_2 natural abundance radiocarbon analysis as a means to determine overall site chlorinated hydrocarbon contaminant degradation over time and spatial scales. An additional enabling objective was to develop a zone of influence model for each sampled groundwater well in order to constrain the spatial scale (volume) for each radiocarbon measurement.

The approach involved taking preliminary samples (March 2013) to determine if the site was a good candidate. Cation analysis showed no discernable contribution of caclium carbonates to the groundwater (which might bias the measurements). Existing groundwater wells were fitted with sealed caps and the well headspace sampled over time by trapping CO_2 (with sodium hydroxide). From these samples, CO_2 respiration rate was measured over two, 2-week periods in the dry season (July-August 2013). The proportion of collected CO_2 attributable to chlorinated hydrocarbon (CH) mineralization was determined by radiocarbon analysis - comparing site samples relative to a background well with no known contamination. A zone of influence (ZOI) model was developed for wells based on site-specific hydrologic data and CO_2 measurements. Coupling these data enabled calculating CH degradation per unit time per unit area. These coupled measurements represent the first analysis where carbon is followed from contaminant to final degradation product (CO_2) directly - without need for inference or "lines of evidence."

The following results were obtained: the average contaminant mineralization rate (0.673 g C m^{-3} d^{-1}) was calculated from individual wells over the site. It was multiplied by the total area within the sampling grid (1,225 m^2) then multiplied by the ZOI depth to give the total carbon mass removal from the CH pool: 14.5 g C d^{-1}. While wells on site are screened at the groundwater:vadose zone interface and the vertical ZOI characteristics may differ above and below the water table (vadose versus saturated zone), if the entire surface soil lens (sandy silt) to a depth of approximately 3 meters has similar CH degradation rates, an optimistic estimate of 246 g C d^{-1} over the entire sampled site area can be calculated. If the remaining source is assumed to be 1,500 kg, the measured rate offers approximately 17 years to remediate. In terms of dissolved CH, an estimate of 0.100 g CH carbon L^{-1} was assumed based on reported values (from 2009). Over the site, within the ZOI, residence time for CH averaged just over 4 years, assuming no additional input (desorbing from soils at the source pool area). At the lowest measured turnover rates, residence time was calculated at 2,400 years and the highest measured rate, 11 months. The lowest CO_2 production rates were coincident with the highest historical CH contamination. This is contrary to observations at sites where less recalcitrant compounds (fuels, for instance) serve as energy and carbon sources for the natural bacterial assemblage (rather than as co-metabolic substrate). Degradation rates were are higher at fringing areas. The overall time-to-remediate was assumed to be related to both dissolved CH degradation and dissolution rate(s) from source pools. Assuming a constant dissolution from source pools, an additive estimate of ~21 years to remediate can be calculated.

A reasonable caveat to remember is that rates were measured over only one small portion of the year (one month) and in only one season (dry season). Rates are presumed to be variable over the course of the year, so additional temporal sampling is recommended. Additionally, the calculations presented are integrated over a larger area than can actually be measured (individual wells). While most studies rely on spatial variability attributable to “point source” well screens, in this study, a ZOI was calculated for each well to gather a volumetric estimate for each sample.

Manuscript approved December 17, 2013.

These “volumes” were interpolated for the above estimates. Because ZOIs were calculated using site-specific geochemical data, we presume the interpolation is more accurate than simply scaling a 10 mL water sample (chemical concentration, for instance) between discreet point source wells. There is no evidence in the peer-reviewed literature that the extrapolation approach used in this work is any less accurate than scaling other point source measurements. Calculating a ZOI would seem to offer a spatial improvement over other well-based sample measurement.

With contaminated sites numbering in the thousands, DoD and other activities are faced with considerable survey, investigation and cleanup costs. Application of this methodology will enable activities to calculate the actual rate of contaminant mineralization to harmless CO_2 using the elemental label ^{14}C (or more precisely, its absence). The analytical protocol is analogous to adding ^{14}C-labeled contaminant to the entire site, then monitoring it's transformation. Because the lack of label can be traced into the final degradation product (CO_2), a definitive link can be made between the original contaminant and the CO_2 generated on-site. Because measurements can be made over temporal and spatial scales, a refined estimate can be made for total contaminant removal per unit time and area at actual field sites with relatively low cost and relatively high accuracy - well above what can be made with indirect lines of evidence measures. The method may not be applicable to sites with limestone lenses if there is low pH (< ~5) driving carbonate (ancient) dissolution. The method may under-predict CH degradation rate in sub-regions where methanogenesis is prevalent. In highly reducing regions, CH degradation may lead to CH_4 formation (from the CH carbon backbone). This may be analytically relevant where soil gas is sampled under anaerobic conditions. However, at the soil:air interface, methane is oxidized rapidly outside of wetlands. At all sites studied to date, CH_4 radiocarbon ages were more ancient than CO_2, therefore in future studies, we intend to measure CH_4 fluxes to better constrain CH turnover rate estimates.

Objective

In this "limited scope project," we coupled natural abundance CO_2 radiocarbon content, CO_2 flux measurements and a zone of influence (ZOI) model for well capture volume to quantify complete hydrocarbon-based contaminant (*e.g.* chlorinated hydrocarbons) degradation. This technology relies on the fact that the contaminants of interest (COI) are almost exclusively manufactured from petroleum sources. For example, carbon in TCE is derived from fossil fuel feedstocks (*i.e.* petroleum). With a ~6,000 year half life, the carbon backbone in TCE will have no ^{14}C; it will have completely decayed away. Consequently, CO_2 molecules produced through biological degradation or abiotic TCE oxidation will be devoid of ^{14}C. This provides an immutable elemental tracer for the final contaminant degradation product: CO_2. Radioactive decay is not influenced by physical, chemical or biological processes; therefore this tracer cannot be impacted by natural or engineered on-site activities. As such, this technique is a highly-suitable candidate for obtaining realistic degradation rate estimates under any remediation or natural attenuation scheme.

The objective was to demonstrate proof of concept that coupling on-site respiration rates (g CO_2 produced per unit time), the proportion of respiration product derived from contaminants (fraction of the respired CO_2 from fossil sources - *e.g.* having no ^{14}C), and a ZOI estimate (m^{-3} volume contributing to respiration rate measured at each sampling well), determining the actual contaminant turnover rate is possible (*e.g.* grams CH degraded m^{-3} day^{-1}). Making these coupled measurements over the site and interpolating the degradation values allows calculating the mass removed over the site. The initial objective was to sample seasonally in order to estimate yearly mass removal rate(s).

Background

SERDP Relevance: The Department of Defense (DoD) and Department of Energy (DOE) are faced with billion dollar expenditures for environmental cleanup in the United States. One must understand the interplay between contaminants and natural compounds in complex biogeochemical processes to design and implement effective remediation strategies. 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. Several lines of converging evidence are seen as necessary to establish reasonable evidence for *in situ* bioremediation or natural attenuation. It is generally accepted that no single analysis or combination of *ex situ* or laboratory tests provides an accurate confirmation or rate for biodegradation under *in situ* conditions (*1*). Similarly, reports sponsored by DoD, the DOE and the Environmental Protection Agency (EPA) advocate collection of a wide array of data in order to attempt confirmation of contaminant attenuation and predict timescale(s) for remediation (*2-4*).

Several recent SERDP/ESTCP Expert Panel Workshop reports have outlined current data gaps and research needs for the overall Defense Environmental Restoration Program (DERP) and Installation Restoration Program (IRP) (*5, 6*). Priority responsiveness to science, technology, characterization and monitoring needs were identified as:

- Quantifying natural attenuation capacities;
- Reducing uncertainty;
- Assessing and managing spatial variability;
- Determining side-effects of remediation;
- Optimizing existing technologies;
- Understanding emerging contaminants;
- Improving long-term monitoring;
- Source delineation and characterization and source zone characterization and flux analysis;
- Bioaugmentation and source zone bioremediation; and
- Effects of treatment amendments

Inherent in all of these priorities is the ability to accurately determine parent contaminant conversion to the desired end product, CO_2 – whether the treatment is active (engineered) or passive. Currently, there are around 70 or so "lines of evidence" measures currently used for confirming (or indicating) biodegradation at contaminated sites (*7-9*). These measures vary considerably in analysis cost and difficulty and due to inherent uncertainties, may never fully support decision-making. The ultimate end-product for organic contaminant degradation is CO_2 – representing a complete conversion to a relatively 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. To our knowledge, no methods are routinely applied which can differentiate contaminant-derived CO_2 from natural soil respiration processes. We propose here to refine natural abundance CO_2 radiocarbon measurements with CO_2 flux measurements to quantify contaminant carbon conversion to CO_2 – and thus complete degradation.

Relevant previous work: Isotope ratios have been used for the past 50 years to track carbon through natural biogeochemical cycles. Only recently has commercially available accelerator mass spectrometry (AMS) allowed routine $^{14}CO_2$ measurement at low concentrations.

Because of the very distinct separation between fossil carbon (devoid of ^{14}C) and contemporary carbon (modern), ^{14}C content has very recently been applied to tracking contaminant degradation products (*10-13*). The analytical resolution between the two end members (fossil and contemporary) is over 1,100 parts per thousand (the 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 (Fig. 1). The analysis and technique application are robust (FDA-approved for pharmaceutical studies) and lend themselves perfectly to quantifying and qualifying the cycling of contaminant carbon in complex groundwater and vadose zone systems. As radioactive decay rates are "fixed," 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 never overestimate the degradation rate).

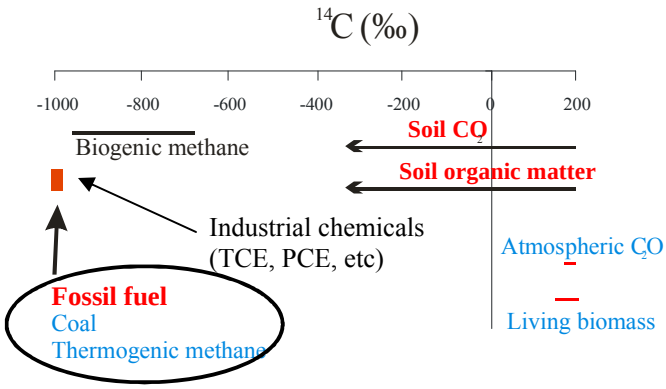


Figure 1. Typical carbon isotope ratios ($\Delta^{14}C$) on the per mil scale showing analytical resolution between soil CO_2 and petroleum-derived CO_2

If considerable degradation (contaminant oxidation) is occurring, CO_2 evolution associated with a fossil-fuel based contaminant plume will reflect the carbon source (Fig. 2). Up-gradient of the plume, soil CO_2 will be largely derived from respired natural organic matter. In the "Background area," CO_2 is primarily modern at +50 ‰ (analogous to 105 percent modern carbon - pMC). Over the plume, if the contaminant is being degraded, the CO_2 radiocarbon ratio will be -999 ‰ (analogous to 0 pMC). Down-gradient, the CO_2 radiocarbon content will reflect the microbial consortium's carbon source. In the example below, CO_2 has a radiocarbon ratio of -450 ‰ (analogous to

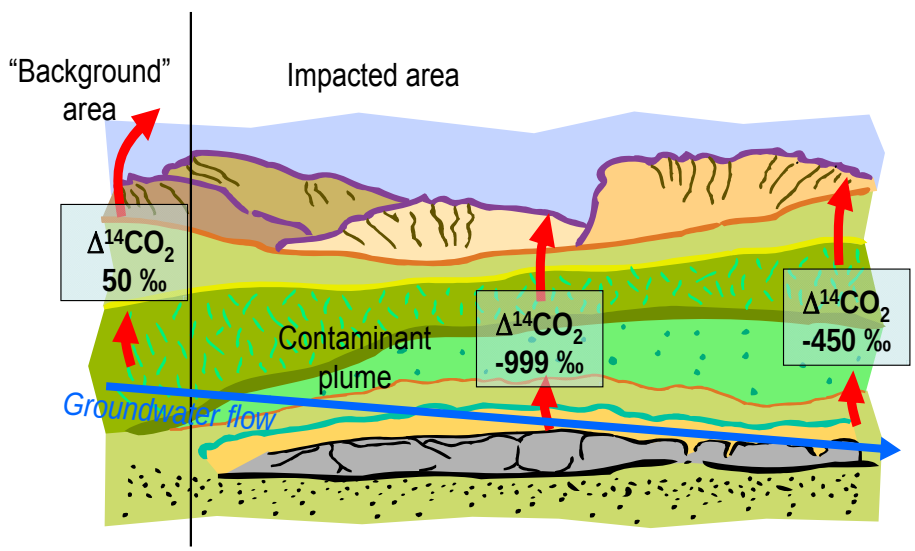


Figure 2 Projected CO_2 radiocarbon isotope ratios up-gradient, mid-gradient, and down-gradient of a contaminant plume - assuming considerable biological degradation.

55 pMC). We can calculate the contribution of fossil carbon to the CO_2 soil gas using a relatively straightforward isotopic mixing equation:

$$(1)\ \Delta^{14}CO_2 = (\Delta^{14}C_{\text{petroluem}} \text{ X } \mathit{fraction}_{\text{petroleum}}) + [\Delta^{14}C_{\text{natural organic matter}} \text{ X } (1 - \mathit{fraction}_{\text{petroluem}})]$$

We know that $\Delta^{14}C_{\text{petroleum}}$ is -999 ‰ and the $\Delta^{14}C_{\text{natural organic matter}}$ is the value measured at background wells. One only then needs to solve for $\mathit{fraction}_{\text{petroleum}}$. This allows calculating the percent of the ambient CO_2 on-site coming from the fossil end-member (*i.e.* the contaminant).

Sampling, processing and analysis of soil gas $^{14}CO_2$ and $^{14}CH_4$ has been performed for several years (*14, 15*). Most ^{14}C measurements have been related to age-dating materials and only recently have been applied to tracking fossil fuel-derived carbon . Isotope techniques are not only useful for monitoring natural attenuation, but also for evaluating *in situ* remediation strategies. Aelion et al., (*11*) showed the effectiveness of a soil vapor extraction (SVE) system installed at a former South Carolina gasoline service station having fuel-contaminated soil and groundwater. The SVE system ran for ~3 months prior to sampling. Soil gas and groundwater samples were taken and the CO_2 analyzed for $\delta^{13}C$, and $\Delta^{14}C$ content (presented as pMC). Background (uncontaminated) soil gas had a ^{14}C age of ~118 pMC – demonstrating significant infusion of atmospheric CO_2 to the vadose zone. However, samples taken from wells within the fuel plume demonstrated soil gas CO_2 ages between 20 and 80 pMC – indicating a fossil source of carbon contributing to the soil gas CO_2. The same was observed for the groundwater dissolved inorganic carbon (DIC – or dissolved CO_2); radiocarbon ages were between 25 and 50 pMC.

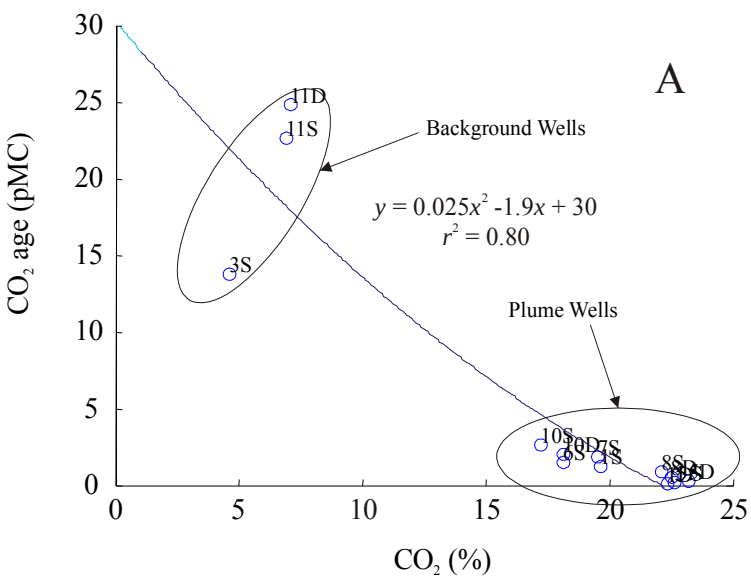


Figure 3. CO_2 radiocarbon age (pMC) and soil gas CO_2 percent, Norfolk Navy Base (2007-2008)

Recently stable and radiocarbon measurements of chlorinated solvents and their degradation products were used to assess remediation at the Savannah River Site (*12*). A soil vapor extraction system was operated at the site prior to sampling. The vadose zone gas was sampled over the course of 120 days and the CO_2 analyzed for $\delta^{13}C$ ratios and ^{14}C content. As with the fuel hydrocarbon studies, a systematic "aging" of soil gas CO_2 was observed over the course of the sampling. SVE systems create a drawdown of atmospheric gas into the vadose zone, so right after shutdown one would expect soil gas CO_2 to be relatively modern (*i.e.* reflect atmospheric CO_2). Over time, however, if biodegradation occurs, the CO_2 in the vadose zone should become progressively older – reflecting the "signature" of the fossil-derived source.

To concretely confirm on-site biodegradation it is necessary to source apportion the CO_2 to modern (*i.e.* background organic matter) or truly fossil sources. Soil gas was sampled above and adjacent to a fuel hydrocarbon plume at the Norfolk Navy Base in Virginia by NRL. The site has a parking lot with asphalt overlying the plume (which greatly restricts any air-soil gas exchange. Soil gas CO_2 was assayed for radiocarbon content and CO_2 concentration (Fig. 3). Background wells (circled area) had a CO_2 age from ~15 to 25 pMC. This is a function of the natural organic matter age (soil organic matter can be 1,000s of years old) and the relative lack modern atmospheric CO_2 influx. Note that sample wells (enclosed by lower ellipse) are less than 5 pMC indicating the CO_2 was derived from a fossil source. The concentration dependence potentially indicates higher fuel respiration relative to background organic matter - confirming enhanced biodegradation relative to background wells (*10*). Most recently, NRL has applied radiocarbon analysis to the fuel farm site at the Naval Air Station North Island, CA. Groundwater DIC samples were collected over a known fuel plume. The DIC was analyzed for ^{14}C using a commercial AMS facility (Beta Analytic). A background site with no known contamination was used in determining the fraction DIC from petroleum sources (see equation above). Over the plume areas ("hot pink" in Fig. 4), the respiration product (DIC) was primarily (>90%) derived from petroleum sources. Moving toward San Diego Bay (Northwest), petroleum contamination was absent (from 2010 surveys) and the DIC was found to be primarily from natural sources (~90% modern downgradient of the plume). These measurements confirm biological hydrocarbon degradation – complete to CO_2 - in areas where fuel contamination still exists (*16*).

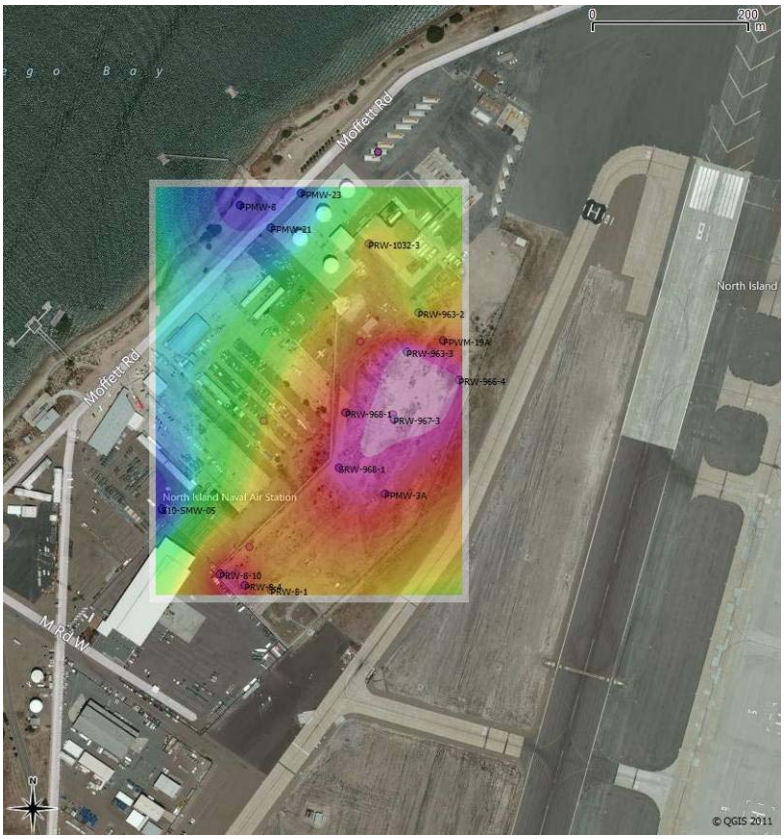


Figure 4. North Island Naval Air Station. Fuel Farm sampling area. CO_2 fraction from petroleum source (light pink highest at ~95%; blue lowest at ~10%)

Materials and Methods

Site Selection: Groundwater from pre-existing monitoring wells at a site with on-going remediation and investigation efforts was the target for this study. IR Site 5 at North Island, CA was identified as a prime candidate 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. An estimated 1-2,000 tons of hazardous wastes were disposed at the site before 1970. Waste was then transferred off-site using the area before it 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. The current site maintenance includes monitoring, inspection and maintenance of the landfill cover. Groundwater well monitoring has shown that groundwater adjacent to IR 5 Unit 1 has virtually no residual organic contamination (TCE, *cis*-DCE, and VC were detected in one well adjacent to IR-5, Unit 2). Within Unit 2, monitoring has been conducted semi-annually and the plume of chlorinated solvent material (in some wells over 1 g L^{-1}) appears to be stable, but receding over time. The presumed attenuation mechanism is biological degradation. The site is heavily vegetated (for the region) within Unit 1 (the golf course region, while Unit 2 consists of more natural vegetation (Fig. 5). Wells within Unit 1 were sampled for dissolved CO_2 radiocarbon when searching for a suitable background site during the fuel farm project outlined in the Background section above. We found ^{14}C depleted CO_2 within the two wells sampled (only ~42% modern) indicating a potential fossil source in the region.

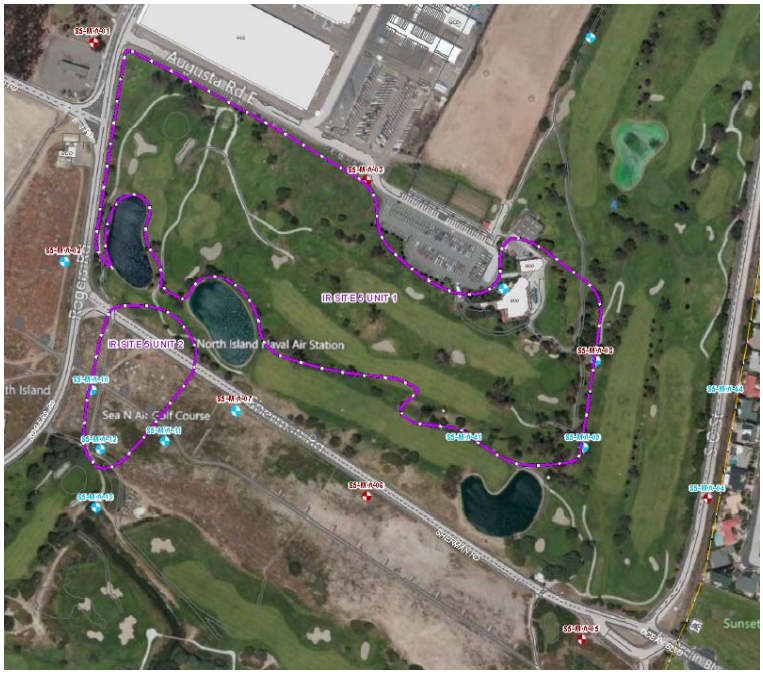


Figure 5. IR Site 5, NAS North Island

Figure 6. Modified pumps (sealed sample and return lines)

Hardware modification and Field sampling*:* Initial efforts immediately upon fund transfer revolved around fabricating field sampling equipment. Low power (battery operated) pumps were purchased and modified to accept power via an external source (directly wired) and fitted with incoming and outgoing non-permeable tubing -

sealed in place with silicone sealant (Fig. 6). "Power distribution" systems were also fabricated so that each well pump could receive the appropriate voltage to keep it running optimally (wiring to each pump had different length due to different distance(s) from the main solar:battery power center). Each potentiometer was monitored using a voltage logging system (Hobo data logger) and a step-down transformer was installed to provide the appropriate ~3V from the solar:battery system to each pump (Fig. 7). Many methods currently exist for measuring CO_2 flux across the air:soil interface (*17*). Because we sampled existing wells and did not want to collect surface soil respiration (which would likely represent predominantly natural organic matter respiration), a closed-system sampling apparatus was used. Briefly, each well head space was sealed with a modified well cap - fitted with two gas lines: one long enough to pull gas samples in the vicinity of the groundwater head; the other fitted near the cap. Gas lines were sealed with vacuum grease along with the cap threads and sealing flange (Fig. 8). Gas was drawn from the lower gas line, bubbled through a sodium hydroxide trap (saturated NaOH - with additional pellets added to each vial) to collect CO_2. The scrubbed gas was recirculated into the top of the well casing to minimize any pressure differential (Fig. 9). A "cluster" of wells was so outfitted in the region around the highest historical contamination. One background well (identified and used in an earlier study, S5-MW-01) was sampled to obtain the respiration rate and radiocarbon age for natural organic matter (*16*).

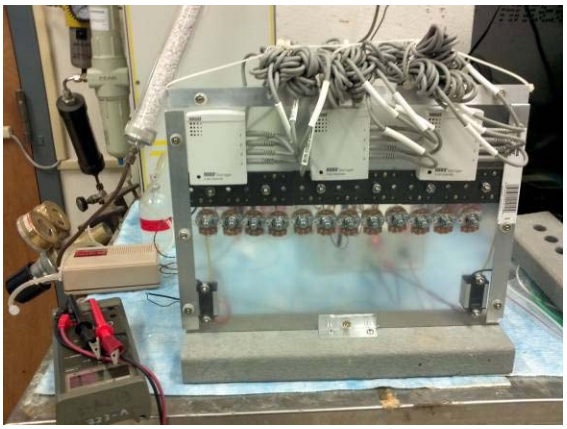


Figure 7. Power distribution system

Figure 8. Modified well caps (sealed sample and return lines)

CO_2 Respiration Field Sampling:

An initial equilibrium period (>30 well casing volumes - 14 hours) was allowed to elapse. After equilibration, the CO_2 trap was changed and collection commenced for two weeks. Gas samples were collected from 16 July through 2 August 2013, then again from 3-16 August 2013 (Fig. 10). Trapped CO_2 samples were shipped back to NRL for CO_2 concentration analysis,

Water Quality Analyses: While almost all sources of potential CO_2 contamination bias radiocarbon measurements toward the modern (and are thus conservative), in soils with considerable carbonates (limestone), high organic carbon biodegradation rates (associated with electron acceptor injection for instance) could lead to decreased *in situ* pH - and thus carbonate dissolution (pH < 5.5). Carbonate carbon would be ancient relative to background carbon and might thus bias the measurement. While IR-5 Unit 2 has not been augmented with electron acceptors to stimulate biodegradation (potentially lowering pH), we collected samples to evaluate possible dissolved carbonate influence. Water samples were taken in pre-cleaned 40 mL vials for pH, cation, and any additional chemical analyses (VOCs will be run if funding permits

to elucidate the plume dimensions). A small additional groundwater sample was taken and its pH measured (using a standard meter). The sample was assayed for K^+, Ca^{++}, Mg^{++} and Na^+ ions using a Dionex DX120 ion chromatograph with a CS12A cation column. Using Na^+ as a conservative tracer, the influx of seawater to the groundwater can be calculated. 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 indicate no limestone soil lenses so it should not be an issue. However, if this method is to be increasingly applied to contaminated sites, this best practice check should be applied.

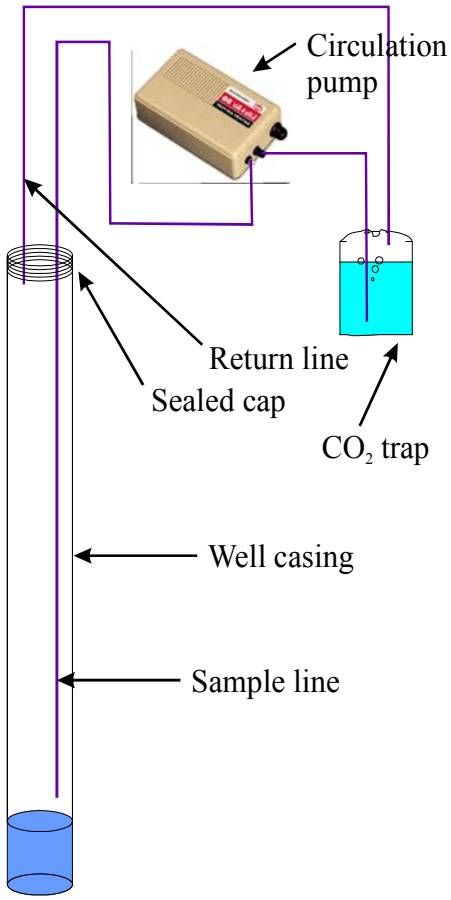


Figure 9. Well casing CO_2 collection system

CO_2 Production Rate Analysis: Collected CO_2 samples (from ~2 week samplings) were diluted until all residual solid NaOH was dissolved. Samples were appropriately diluted and analyzed by acidifying the CO_2 out of solution and measuring by coulometry (*18*). CO_2 was quantified relative to a certified reference material. Samples were run in duplicate and values were averaged for reporting. Production rate was calculated by the total recovered CO_2 divided by the time of collection (nominally 2 weeks – but annotated for each well). Respiration rates were averaged between the two collection periods to obtain a representative "dry season" respiration value.

Radiocarbon Analysis: CO_2 in NaOH left over after coulometric analysis was sent to Beta Analytic for radiocarbon dating. Beta analyzed each sample using accelerator mass spectrometry (AMS). Samples were also analyzed for $\delta^{13}C$ ratio of the CO_2.

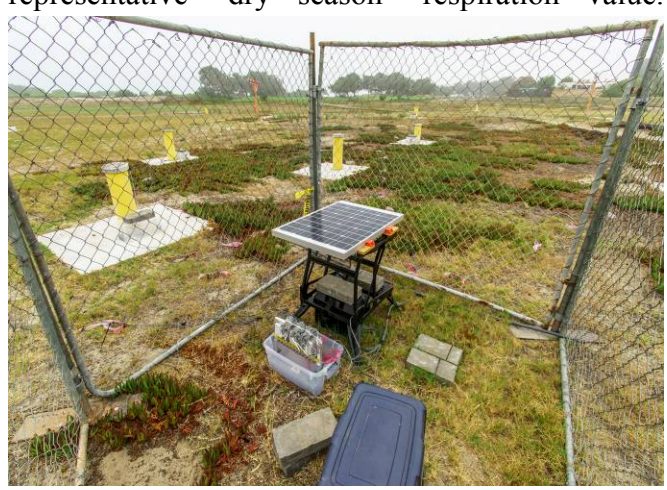


Figure 10. System deployed on-site

Zone of Influence Model/Simulation: A ZOI model was created based on the 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 model of the site. This information was coupled with CO_2 equilibrium simulation models to create the ZOI model. The ZOI model

was developed using MT3DMS (*19*) and MODFLOW-2005 (*20*). MT3DMS is the biodegradation model capable of simulating multi-solute transport and reaction, and 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 is 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 (*21*). In this study, ModelMuse was used to link and interface the two models (*22*).

The target for this study is CO_2 produced from chlorinated solvents (*e.g.* DCE and VC). Among different biodegradation models studied (*e.g.* MT3DMS, RT3D, Biosereen, Biochlor, and SEAM3D), there is no model that is capable of coupling a groundwater simulation model and simulating this complex CO_2 system while tracking individual CO_2 solutes. This project treats all CO_2 with different origins together - and the radiocarbon content was used to uniquely distinguish CO_2 derived from chlorinated solvents.

Determining the Contaminant Respired: The isotopic mixing model was applied to each sample using the radiocarbon value for CO_2 collected at MW-01 as the appropriate site-wide background value. The background $\Delta^{14}C$ was -162 ‰ (MW-01) and $\Delta^{14}C_{petroleum}$ was assigned the value -999 ‰. The $fraction_{petroleum}$ was solved for each well at IR-5 Unit 2:

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

^{14}C-content measurements were thus to determine the proportion of vadose zone CO_2 derived from COI (*10*). These values were then coupled with the hydrogeologic model data to determine the flux of COI through microbial cycles or abiotic oxidation processes to CO_2. Comparing in-plume measurements with reference site(s) measurements allows source apportioning *in situ* microbial assemblage carbon demand and determining biodegradation rate. Methods used in this report are summarized in Appendix A.

Results and Discussion

Historical Contamination: Historical contamination from chlorinated hydrocarbons was high within the central well cluster (MW-25-MW-30) and on the Northern portion of the site

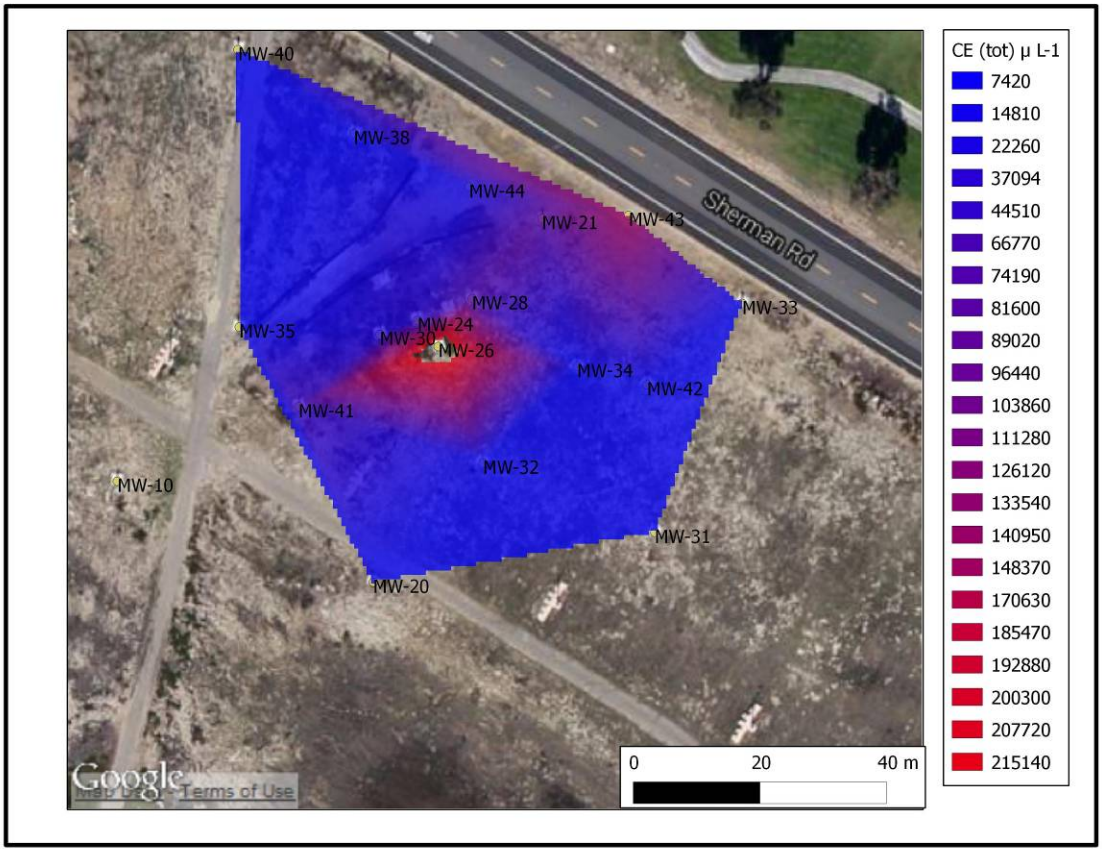


Figure 11. Historical chlorinated hydrocarbon contamination (µg L^{-1})

near Sherman Road (Fig. 11). Contamination was removed from the historical landfill site and soil was remediated as possible in 1983 in the upgradient Unit 1 and in 2001 for 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 "wash" CHs off soils in the vadose zone which transiently increases groundwater CH concentrations (personal communication). Soils have been identified as primarily sands (from dredging operations). No significant sources of $CaCO_3$ have been identified.

Table 1. Water quality parameter for March 2013 sampling

Well	Na^+ (mg L^{-1})	K^+ (mg L^{-1})	Mg^{2+} (mg L^{-1})	Ca^{2+} (mg L^{-1})	pH
MW-01	131	18	32	58	7.34
MW-10	320	104	54	45	6.71
MW-11	430	24	62	32	7.84
MW-12	774	45	109	50	7.76
MW-14	212	19	53	53	7.72
MW-17	427	30	54	27	8.00
MW-20	535	50	56	26	7.69
MW-21	168	41	40	44	7.76
MW-24	385	73	48	29	7.74
MW-26	404	101	39	14	7.46
MW-28	299	44	43	18	7.75
MW-30	492	87	47	17	7.67
MW-31	269	22	43	32	7.92
MW-32	258	76	40	32	7.42
MW-33	128	14	40	62	7.92
MW-34	377	48	47	30	7.35
MW-35	80	26	21	30	7.58
MW-38	178	23	40	51	7.82
MW-40	77	10	18	38	7.78
MW-41	165	88	25	14	7.81
MW-42	487	30	56	17	7.58
MW-43	136	18	37	74	7.60
MW-44	130	19	32	48	7.61

Cation and pH Analysis: Samples for cation and pH were analyzed for both March 2013 and July 2013 samplings. The primary concern driving this analysis was that low pH might promote carbonate dissolution which could bias radiocarbon analysis (see M&M section). pH was near neutral for all wells sampled (Tables 1 and 2). Wells on the site's Southern side generally had a higher Na^+ content, but were not in a range which indicated significant seawater intrusion. Calcium ion concentrations ranged from 8.0 to 58 mg L^{-1} (Tables 1 and 2) 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.

Table 2. 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 production rates: CO_2 production rates ranged from 0.75 to 28 µMol h^{-1} (0.01 to 0.31 g d^{-1}). CO_2 production was lowest in the central well cluster where historical contamination was highest (Fig. 12). CO_2 production in well MW-01 (background well) was the highest measured at 30 µMol CO_2 h^{-1} (0.32 g CO_2 d^{-1}). Standard error for duplicate analyses averaged less than 1% (0.98) and ranged from 0.03 to 6%. CO_2. The two 2-week periods were sampled during the same season therefore they were averaged for subsequent calculations (preliminary time-to-remediate). DIC measurements

were very similar between individual 2-week periods. The standard error between periods for DIC was less than 1% on average and ranged from 0.03 to 6%.

Table 3. Radiocarbon Analysis

Well	$\delta^{13}C$ (‰$_{VPDB}$)	$\Delta^{14}C$ (‰)	Conventional Age (ybp)	Percent Modern C (pMC)
MW-01	-34	-147	1280	85
MW-21	-28	-663	8730	34
MW-25	-23	-153	1340	85
MW-26	-25	-298	2845	70
MW-27	-18	N.D.*	N.D.*	N.D.*
MW-28	-25	-190	1695	81
MW-30	-35	-254	2365	75
MW-32	-20	N.D.*	N.D.*	N.D.*
MW-34	-32	-283	2670	72
MW-35	-25	-598	7320	40
MW-38	-32	-354	3515	65
MW-41	-28	-232	2125	77
MW-42	-23	-482	5280	52

*N.D. No data - pump leaking

CO_2 Radiocarbon Analysis: A total of 13 NaOH-trapped CO_2 samples were sent to Beta Analytic for analysis. Two wells (MW-27 and MW-32) had pump issues (became unsealed) and were suspect but sent for analysis anyway. The background well (MW-01) was 1280 years before present (ybp) or 85 percent modern (pMC). This well was used as the background for the isotopic mixing model. The two sampling period samples were averaged for subsequent calculations similar to the DIC measurements. Again, because we were unable to sample through the year, we used two

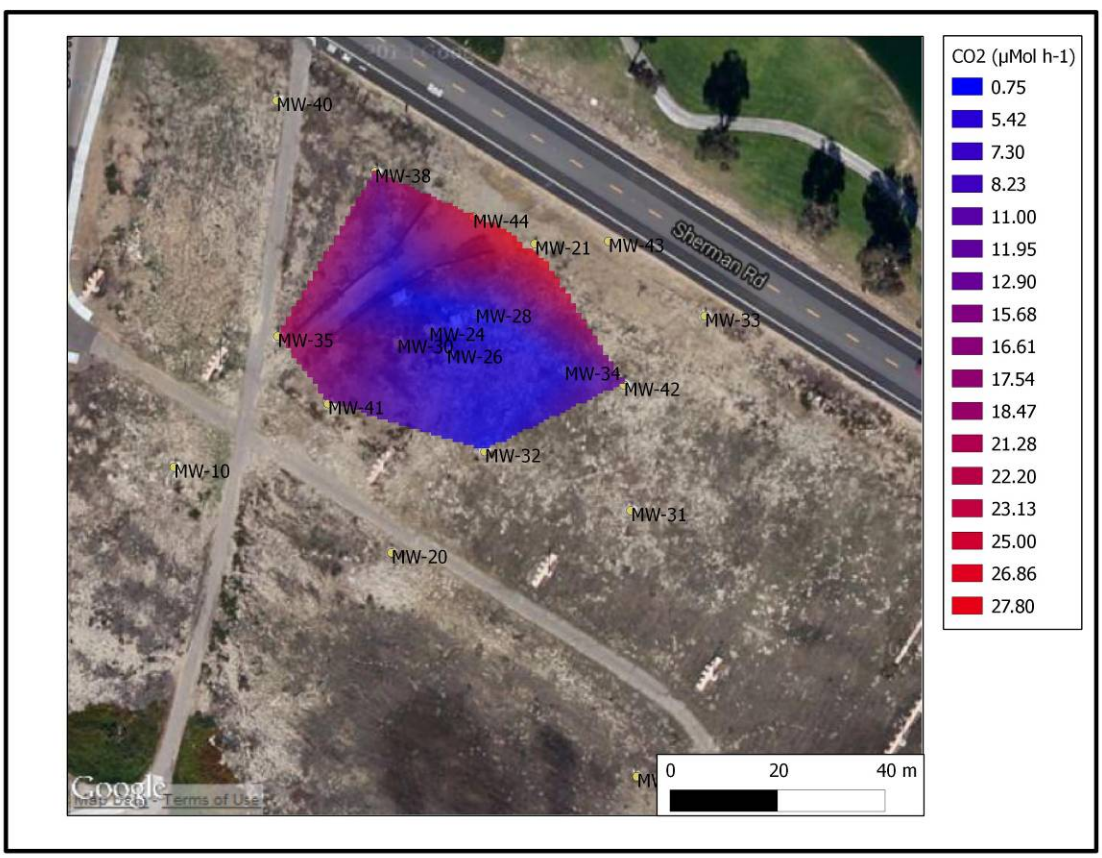


Figure 12. CO_2 production (µMol CO_2 d^{-1})

back-to-back periods during the same season to "represent" the dry season. As with DIC production rates, radiocarbon measurements were very similar between individual 2-week periods. The standard error between periods averaged 6% and ranged from 0.25 to 18%.

The average radiocarbon data were converted to standard $\Delta^{14}C$ notation (*23*) before applying the two-end member mixing model (eq (*1*)). Stable carbon isotope ratios for CO_2 indicated potential contamination with atmospheric CO_2 (typically -7 $‰_{VPDB}$) for MW-27 and MW-32. Overall, radiocarbon CO_2 ages ranged from ~1340 to 8,700 ybp or from 34 to 85 pMC (Table 3). The suspect wells (MW-27 and MW-32) had modern radiocarbon values and were thus confirmed as compromised. These samples were not included in further analysis. The Beta Analytical data report is included as Appendix B.

ZOI model: Groundwater hydraulic and CO_2 solute properties for the study site were obtained from previous reports (*24, 25*). Three years of weather data (2007, 2011 and 2012) were obtained from the CIMIS San Diego station (Station ID 184) to estimate the recharge rate of the aquifer. 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 on the Northeastern side of the area (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 (*e.g.* daily and weekly periods) changes in sea level around the peninsula on groundwater flow at the study site were not significant. This result agrees with the previous report from Wiedemeier and Associates (personal communication, April, 2013). The groundwater hydrology at the study site is usually steady between late summer and fall. Therefore, the groundwater flow during the CO_2 collection periods (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 the value estimated from the groundwater elevation map in June 2011 (*24*). Parameters obtained from literature sources are outlined in Table 4.

Table 4. Parameter summary for the ZOI model.

Parameter	Units	Value
Hydrology		
Hydraulic Conductivity	(m/hr)	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)	0.015
CO_2 Solute Transport		
Diffusion Coefficient (CO_2)	(m^2/hr)	6.77×10^{-6}
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 collection periods in 2013 were 2 weeks in duration. Prior to the CO_2 sampling, the initial distribution of solute CO_2 in the aquifer around the sampling well was assumed in equilibrium with the CO_2 supplied from the overlying soil gas and mineralization; therefore, the 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 the CO_2 collection was defined as the volume of aquifer that has a CO_2 concentration of 95% or less of the initial concentration. Using Henry's law, the 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 at the time of the CO_2 collection was unknown, the ZOI model assumed constant and conservative mineralization rates for the chlorinated solvents (*e.g.* half-life of DCE and VC = 3.8 and 9.5 years, respectively). The CO_2 production rate from the chlorinated solvents was estimated using this assumption, and appeared to be negligibly small (< 0.001 g m^{-3} d^{-1}) compared to the observed CO_2 collection rate at the site which ranged from 0.01 - 0.31 g d^{-1}. The ZOI model was thus simplified by not accounting for mineralization during the 2-week CO_2 collection period (Fig. 13). However, mineralization has certainly accumulated CO_2 in the aquifer over time as CO_2 radiocarbon ages were older than the background value (Table 3).

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 x 4.5 m x 10.0 m deep. The horizontal spatial resolution is set to 0.09 m x 0.09 m, which makes one grid area equal to 0.0081 m^2, the same as the well area. The vertical

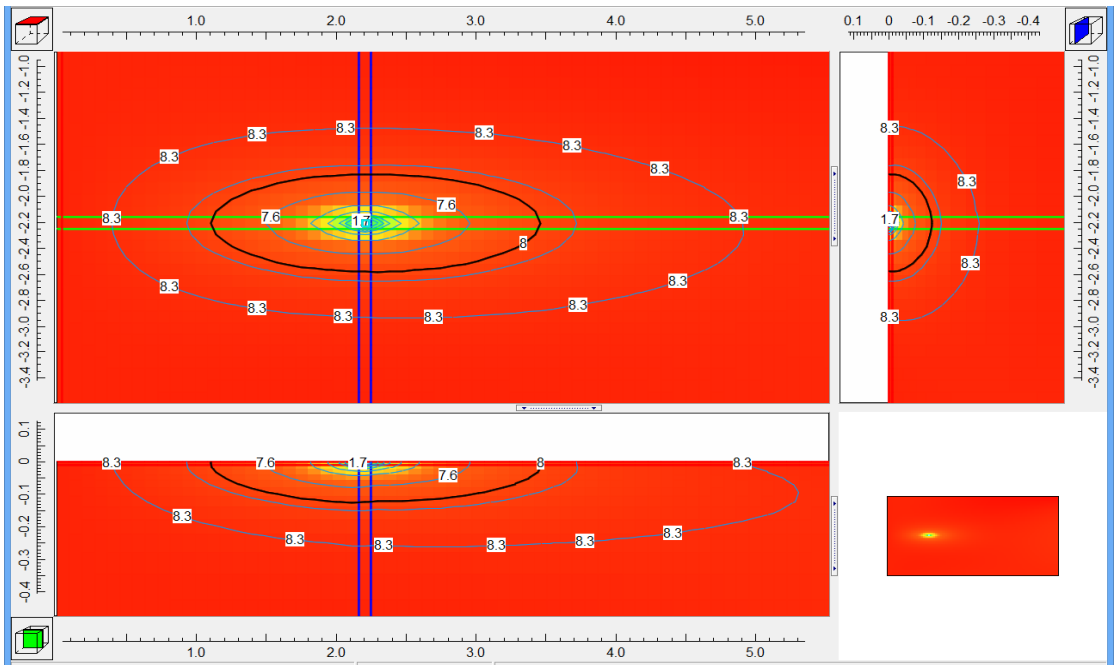


Figure 13. Top (top) and side (bottom) views of simulated CO_2 distribution assuming the hydraulic gradient of 0.015 (m m^{-1}). The side view is exaggerated by 2.5 times in vertical direction to show the CO_2 concentration gradient.

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 the two boundaries, which allowed groundwater to flow in the left to right direction (Fig. 14).

The ZOI model described above was then coupled with the observed CO_2 collocation rates. The collection rate was averaged at 0.0048 g CO_2 h^{-1} m^{-3}, and varied from 0.0003 to 0.0131 g h^{-1}.

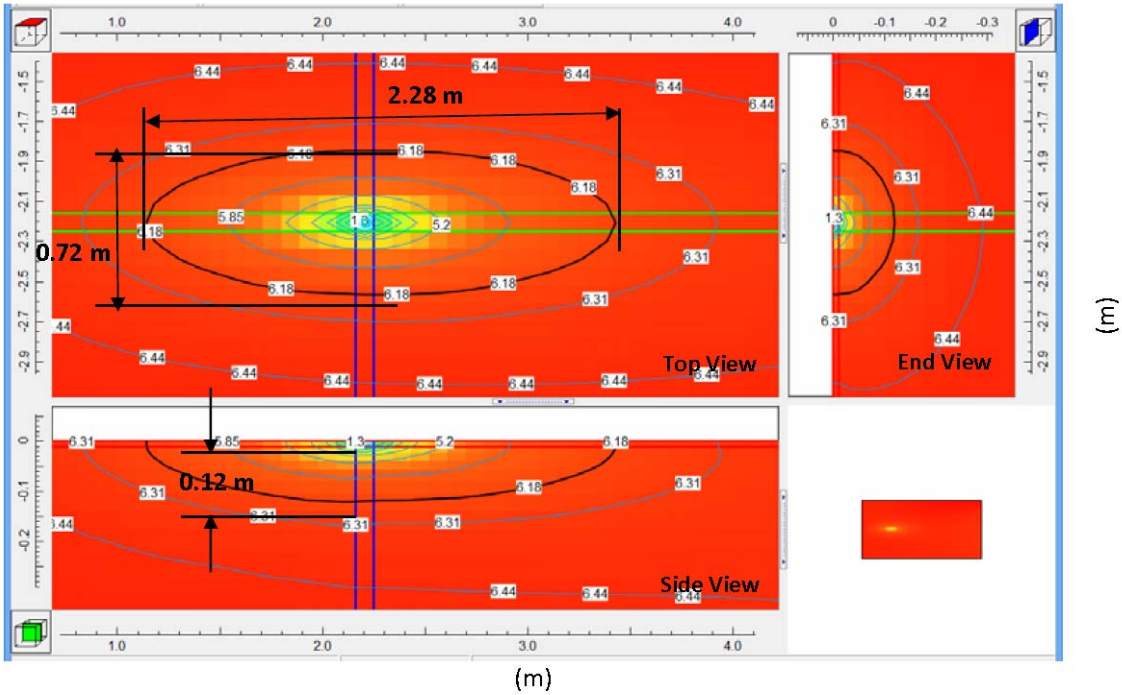


Figure 14. Calibrated ZOI model for the average CO_2 collection rate (0.0048 g m^{-3}). The calibrated background CO_2 concentration was 6.5 g m^{-3}, and the ZOI threshold concentration was 6.18 g m^{-3} (solid black line). Longitudinal and transverse diameters of the ZOI were 2.28 m and 0.72 m, respectively. Depth of the ZOI was 0.12 m.

The calibration assumed that the collection rate was constant during the collection period. The calibration also assumed the equilibrium between the CO_2 output (*i.e.* collection) and supply (*i.e.* diffusion) at the water table in the well at the end of the collection period. In other words, the CO_2 concentration of the water surface in the well was assumed to be decreased to 0.0 g CO_2 m^{-3} by the end of the simulation.

Taking the CO_2 collection rate into account, the ZOI calibration varied. The calibration result indicated a strong linear correlation between the observed collection rate and the calibrated background CO_2 concentration (Fig. 15). Also, estimated ZOI volume indicates a strong linear correlation with background CO_2 concentration and thus CO_2 collection rate. Assuming the partial pressure of the atmospheric CO_2 of 0.04 %, the equilibrium CO_2 concentration of non-contaminated aquifer exposed to the atmosphere would be 0.60 g m^{-3}. The estimated background CO_2 concentration for all collection rates was higher than this value which suggests groundwater contamination with chlorinated solvents (*e.g.* DCE and VC) and their active mineralization. However, the estimated background CO_2 concentrations are below solubility of CO_2 (1,450 g m^{-3} at 25 °C) and do not indicate saturation of CO_2 in the aquifer.

The calibration assumes a steady hydraulic gradient and constant collection rates. A supplemental simulation for the average CO_2 collection rate indicated approximately 50 % increase in the 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 the average CO_2 collection rate indicated approximately 46 % increase in the estimate background CO_2 concentration (*i.e.* increased 6.5 to 9.5 g m^{-3}) if the collection rate changed from 0.00530 (+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 the chlorinated solvents. After accounting for the small difference in the first and second CO_2 collection rates, the 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.

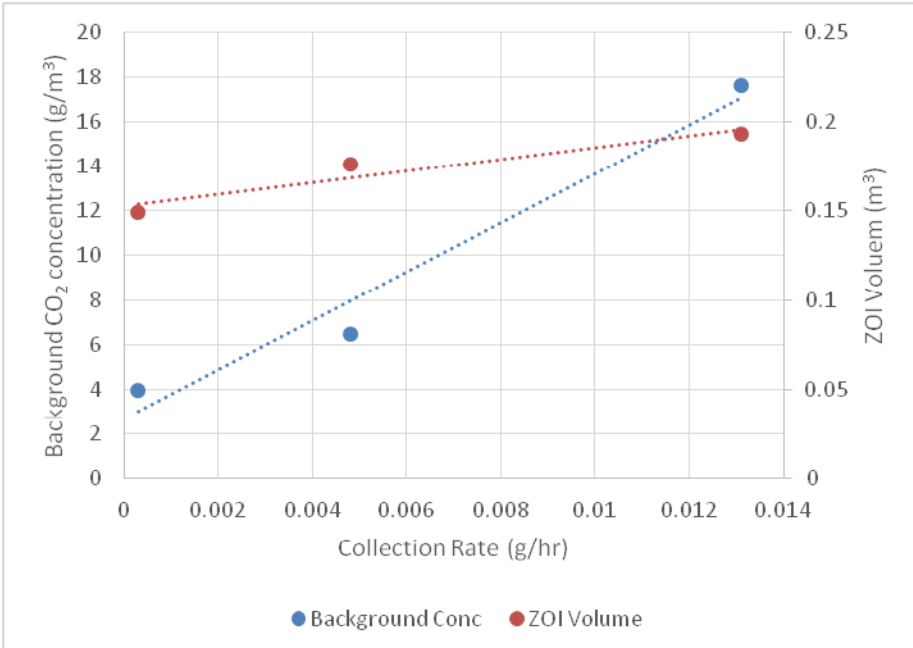


Figure 15. Estimated background CO_2 concentration and ZOI volume versus collection rate

Table 5. Estimated background CO_2 concentrations and simulated ZOI sizes with different CO_2 collection rates.

Collection Rate Level	Collection Rate	Background Concentration	ZOI Size			
			Longitudinal	Transverse	Depth	Volume
	(g/hr)	(g/m³)	(m)			(m³)
Maximum	0.0131	17.6	2.47	0.77	0.13	0.193
Average	0.0048	6.5	2.28	0.72	0.12	0.176
Minimum	0.0003	4.0	2.16	0.68	0.11	0.149

Contaminant Turnover (Conversion to CO_2): Using the CO_2 production rate, the proportion of CO_2 attributable to CH degradation, and the ZOI model, we calculated the mass CH removal at each well per unit time. The two end-member mixing model (eq *(1)*) was used with data from Table 3 to solve for f_{pet} at each well. The f_{pet} varied from 1 to 60 % over the sampled wells (Table 6). This proportion was multiplied per carbon basis with the CO_2 production rate to obtain the contaminant (CH) degradation rate (Table 6). Finally, using the ZOI volume (Table 5), the contaminant degradation rate per unit time and volume was calculated (Table 6). The contaminant degradation rate per unit area varied between 1 mg to 287 mg C m^{-3}

d^{-1} (Table 6). In areas with the highest historical contamination (MW-25 - MW-30), CH degradation was lowest, potentially indicating toxicity or lack of necessary co-metabolic substrates driving CH turnover. CH degradation rates measured at the site periphery (near Sherman Road) appear to be higher relative to the central well cluster (MW-38, MW-21, MW-42). Historical contamination is higher in this region (although not as high as the central well cluster). Higher rates in this region might indicate greater co-metabolic substrate availability. CO_2 production was higher in this area, while f_{pet} indicated significant CH turnover (Fig. 16).

Table 6. Contaminant Degradation

Well	f_{pet} (%)	CO_2 production (g CO_2 d^{-1})	Contaminant degradation rate (g C d^{-1})	Contaminant degradation (g C m^{-3} d^{-1})
MW-21	60	0.306	0.0504	0.2865
MW-25	1.0	0.0107	0.000020	0.0001
MW-26	18	0.0388	0.00187	0.0106
MW-28	5.0	0.0124	0.00017	0.0010
MW-30	12	0.101	0.00342	0.0194
MW-34	16	0.0311	0.00135	0.0077
MW-35	53	0.222	0.0321	0.182
MW-38	24	0.179	0.0118	0.0672
MW-41	10	0.145	0.00393	0.0224
MW-42	39	0.124	0.0133	0.0755

Site-wide CH Degradation: A major focus for this study was to couple rate measurements, proportion mineralization from contaminant and ZOI estimates to determine overall site CH degradation. While any estimate along these lines is subject to error, each method in this study offers direct measurements of the relevant analyte. This methodology does not rely on indirect measures (electron acceptors, nutrients, dissolved oxygen, etc). Instead we are able to directly measure the 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). As mentioned in the background section, there are currently around 70 “lines of evidence” measures used for confirming (or indicating) contaminant turnover at impacted sites (*7-9*). None of these techniques directly measure the complete degradation product (CO_2) in order to explicitly link original contaminant to degradation product. While many measures "indicate" remediation is occurring, issues such as treatment dilution, remediation alternatives, aquifer recharge, etc all impact the process of determining mass removal (*26-28*).

In order to determine a mass removal for this study, the average contaminant mineralization rate (0.0673 g C m^{-3} d^{-1}) was multiplied by the total area within the sampling grid (*c.f.* Fig. 12) giving 82.4 g C m^{-2} d^{-1}. This value was then multiplied by the ZOI depth to give the total carbon mass removal from the CH pool: 9.9 g C d^{-1}. The wells on site are screened at the groundwater:vadose zone interface and the vertical ZOI characteristics are likely very different above and below the water table (vadose versus saturated zone). However, if we make the assumption that the entire surface soil lens (sandy silt) to a depth of approximately 3 meters (*24*) has similar CH degradation rates, an optimistic estimate of 250 g C d^{-1} over the entire sampled site area can be calculated. Extrapolating for the estimated total mass (1,500 kg CH; Todd Wiedemeier, personal communication), gives a full removal rate of 16 years. For dissolved contaminants, an average range of 0.100 g L^{-1} (combined TCE, *cis*-DCE and VC from 2011 report) may be used to estimate dissolved CH. Using porosity and estimates (Table 4), the ZOI over the sampled site should hold ~70.5 m^3 of water. At measured rates, within the ZOI, CH degradation will take an average 4.1 years (assuming no additional CH "washing" off soils and

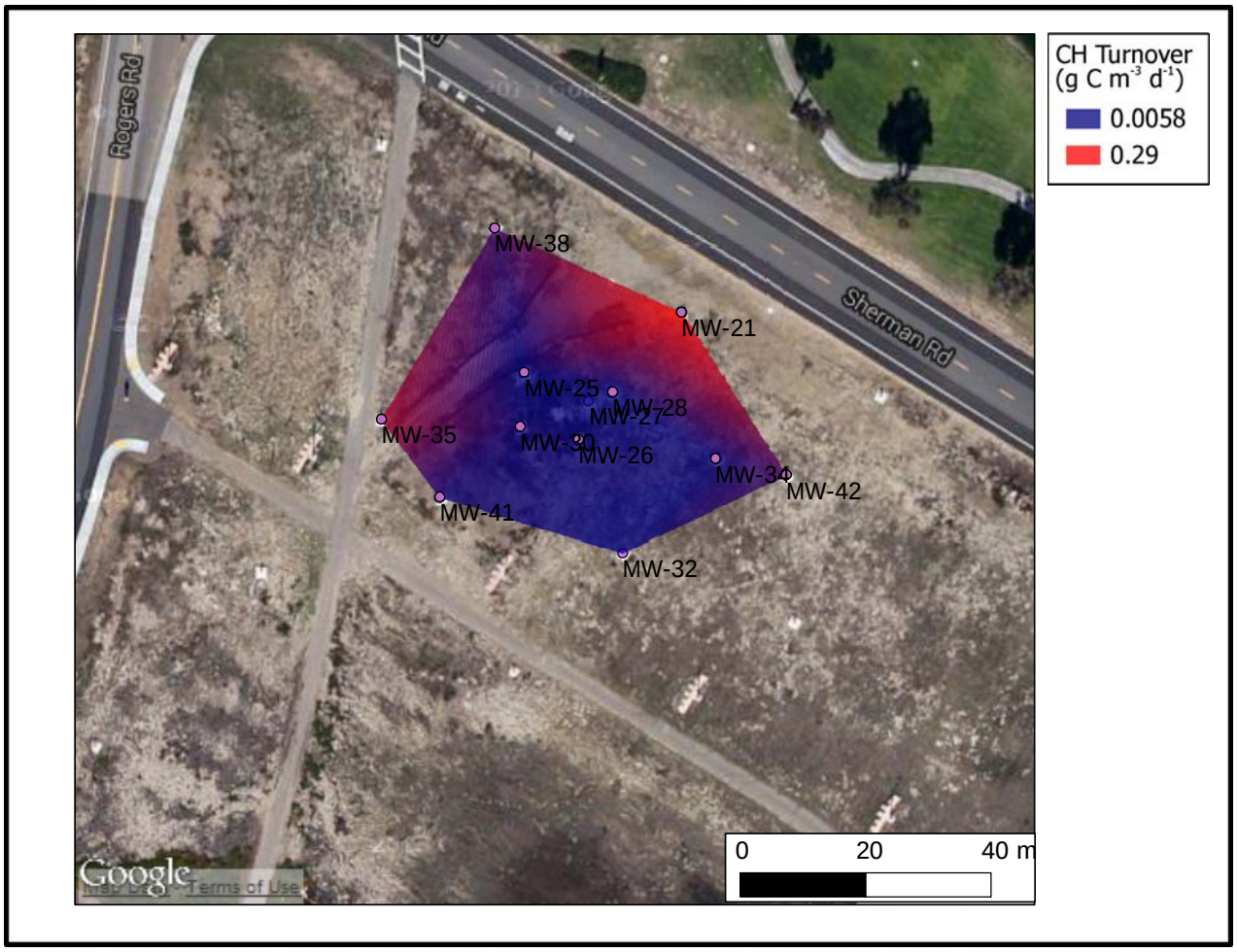


Figure 16. Contaminant degradation rate per unit time per unit area

entering the groundwater). This initial estimate doesn't take into account the lower mineralization rates measured where contamination is highest. Using these rates, remediation time becomes close to 2,400 years. At the highest mineralization rate, one could estimate a 11 month residence time for CH in groundwater.

We are unaware of any previous study with similar goals - and in which similar methods were coupled. Typically, soil respiration measurements are made using flux chambers and rates are expressed per square unit area (to indicate soil-atmosphere exchange). In a recent report, CO_2 flux measurements were made using flux chambers while discreet soil gas samples were collected for $^{14}CO_2$ measurements (*29*). Along with soil respiration data from an earlier study, 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 (*29, 30*). In this study, collected CO_2 from the well screen region was used exclusively for the coupled measurements.

Conclusions and Implications for Future Research

In this study, we were able to couple CO_2 respiration measurements, radiocarbon age for the same collected CO_2 and an estimate of the ZOI for each well in order to determine contaminant mineralization rate(s). ZOIs were calculated using site-specific geochemical data, therefore represent a refined estimate of the sampled area relative to a single point source water sample for instance. The peer-reviewed 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 before extrapolating. Calculating a ZOI would seem to offer a spatial improvement over other well-based sample measurement. The ultimate goal was to determine the contaminant to CO_2 conversion rate per unit area (m^{-3}) per unit time (d^{-1}). With this successful Limited Scope effort, we completed the following:

- Measured respiration rate(s) as CO_2 collected over one month period (the average of two, 2-week collections)
  - -CO_2 collection rates ranged from 0.75 to 28 μMol h^{-1} (0.01 to 0.31 g d^{-1})
  - -CO_2 collection rates were lowest where CH contamination was highest
- Measured radiocarbon content for CO_2 respired on-site
  - -Respired CO_2 ages ranged from ~1340 to 8,700 ybp or from 34 to 85 pMC
  - -CO_2 was primarily derived from non-fossil sources in areas with the highest CH contamination
- Determined respiration from contaminants by fraction petroleum-derived over the site Contaminant mineralization to CO_2 ranged from 0.00002 to 0.032 grams carbon per day
  - -Rates were lowest over the central well region (area of highest CH contamination)
- A zone of influence (ZOI) model was created to determine per unit volume for collected CO_2 (grams per unit volume)
  - -The average ZOI was 2.28 X 0.72 X 0.12 meters with an average volume of 0.176 m^{-3}
- Determined the total CH removed per unit area per unit time for each well sampled
  - -Contaminant turnover ranged from 0.0001 to 0.29 g carbon m^{-3} d^{-1}
  - -This rate was lowest over the region of highest historical CH contamination.
- Total volume removed per unit time was calculated as 9.9 g CH d^{-1} over the collection area
- Total volume removed by integrating average results vertically (3 meter depth of unconsolidated layer) was calculated at ~250 g CH d^{-1} over the collection area.
- When calculated with groundwater within the site-wide ZOI, time to degradation ranged between 9 months and 1,700 years with an average of ~4 years. This estimate assumes no additional input (desorbed from soils)

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 contaminant concentrations and CH utilization. CO_2 collected above the high historical contamination region had the greatest pMC indicating less relative contribution from CH than natural organic matter. 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 . At present, it is unknown why CH conversion appears lowest where substrate concentrations are highest. 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.

Future research to advance this technology and expand the scope in which it can be applied should focus on the present site in order to expand seasonality and branch out to more challenging sites where engineering approaches are in place (zero valent iron curtains, addition of electron acceptors, chemical oxidation additions, etc). Finally, the method should be tested in aquifers with limestone influences - so that potential biases can be accurately accounted for and the technology validated. Overall, future proposed activities should include:

- Additional seasonal samplings (Four suggested but possibility only "wet" and "dry" needed for the current site)
- Allocate funding for contaminant concentration analyses from samples collected during the study
- Procure and deploy more robust pumps (non-mechanical). Prototype in-hand - about 3 times the cost of current pumps - but far better
- Refine ZOI model by collecting and calibrating CO_2 collection rates with groundwater concentrations. Expand collection duration?
- Utilize this technology to understand carbon flow at an engineered remediation site (OU-24)
  - -Do added electron acceptors increase respiration of organic matter (contaminants?) to CO_2?
  - -Do added electron acceptors increase the fraction of contaminant carbon in the respired CO_2 pool?
- Do actual measurements of CO_2 derived from contaminants reflect estimates based on non-direct rate estimates?
  - -Evaluate results from ongoing studies with literature - several recent of which are similar in terms of attempting to couple respiration rates with radiocarbon analysis
- Validate technology at site(s) with significant seasonal variability
- Sample during or at least under the influence of rain events
- Determine the response due to temperature variation(s)
- Refine time to degrade models

Literature Cited

1. C. National Research, "In situ bioremediation: When does it work?," (National Academy of Sciences, Washington, DC, 1993).
2. 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).
3. 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, F. H. Chapelle, "Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water," (USEPA Office of Research and Development, Washington, DC, 1998).
4. J. T. Wilson, D. H. Kampbell, M. Ferrey, 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).
5. SERDP/ESTCP, "SERDP/ESTCP Expert Panel Workshop on Research and Development Needs for Cleanup of Chlorinated Solvent Sites," (2002).
6. A. Leeson, H. F. Stroo, "SERDP and ESTCP workshop on investment strategies to optimize research and demonstration impacts in support of DoD restoration goals," (SERDP/ESTCP, Arlington, VA, 2011).
7. Parsons Engineering, "Natural Attenuation of Fuel Hydrocarbons Performance and Cost Results from Multiple Air Force Demonstration Sites," (Parsons Engineering Science, Inc., Denver, CO, 1999).
8. Parsons Engineering, "Natural Attenuation of Chlorinated Solvents Performance and Cost Results from Multiple Air Force Demonstration Sites," (Parsons Engineering, Inc., Denver, CO, 1999).
9. Parsons Engineering, "Principles and practices of enhanced anaerobic bioremeidation of chlorinated solvents," (2004).
10. R. B. Coffin, J. W. Pohlman, K. S. Grabowski, D. L. Knies, R. E. Plummer, R. W. Magee, T. J. Boyd, Radiocarbon and Stable Carbon Isotope Analysis to Confirm Petroleum Natural Attenuation in the Vadose Zone. *Environmental Forensics* **9**, 75-84 (2008).
11. C. M. Aelion, B. C. Kirtland, P. A. Stone, Radiocarbon assessment of aerobic petroleum bioremediation in the vadose zone and groundwater at an AS/SVE site. *Environ. Sci. Technol.* **31**, 3363-3370 (1997).
12. B. C. Kirtland, C. M. Aelion, P. A. Stone, D. Hunkeler, Isotopic and Geochemical Assessment of in Situ Biodegradation of Chlorinated Hydrocarbons. *Environ. Sci. Technol.* **37**, 4205-4212 (2003).
13. B. C. Kirtland, C. M. Aelion, P. A. Stone, Assessing in situ mineralization of recalcitrant organic compounds in vadose zone sediments using $\delta^{13}C$ and $\Delta^{14}C$ measurements. *J. Contam. Hydrol.* **76**, 1-18 (2005).
14. H. Haas, D. W. Fisher, D. C. Thorstenson, E. P. Weeks, $^{13}CO_2$ and $^{14}CO_2$ Measurements on Soil Atmosphere Sampled in the Western Great Plains of the US *Radiocarbon* **25** 301-314 (1983).

15. D. C. Thorstenson, E. P. Weeks, H. Haas, D. W. Fisher, Distribution of Gaseous $^{12}CO_2$, $^{13}CO_2$, and $^{14}CO_2$ in the Sub-Soil Unsaturated Zone of the Western Great Plains *Radiocarbon* **25** 315-346 (1983).
16. T. J. Boyd, M. J. Pound, D. Lohr, R. B. Coffin, Radiocarbon-depleted CO_2 evidence for fuel biodegradation at the Naval Air Station North Island (USA) fuel farm site. *Environmental Science: Processes & Impacts* **15**, 912-918 (2013).
17. J. M. Norman, C. J. Kucharik, S. T. Gower, D. D. Baldocchi, P. M. Crill, M. Rayment, K. Savage, R. G. Striegl, A comparison of six methods for measuring soil-surface carbon dioxide fluxes. *J. Geophys. Res.* **102**, 28771-28777 (1997).
18. K. M. Johnson, J. M. Sieburth, P. J. l. B. Williams, L. Brändström, Coulometric total carbon dioxide analysis for marine studies: Automation and Calibration. *Mar.Chem.* **21**, 117-133 (1987).
19. C. Zheng, 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).
20. 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).
21. H. Prommer, D. A. Barry, C. Zheng, MODFLOW/MT3DMS-based reactive multicomponent transport modeling. *Ground Water* **41**, 247-257 (2003).
22. R. B. Winston, in *Ground Water - Book 6*. (U.S. Geological Survey, Reston, VA, 2009), vol. Techniques and Methods 6-A29, chap. 29.
23. M. Stuiver, H. A. Polach, Discussion: Reporting of ^{14}C Data. *Radiocarbon* **19**, 355-363 (1977).
24. 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).
25. Geosyntec Consultants, "Annual Progress Report October 2010 to December 2011, Operable Unit 24," (Columbia, MD, 2012).
26. F. H. Chapelle, P. M. Bradley, C. C. Casey, Behavior of a chlorinated ethene plume following source‐area treatment with Fenton's reagent. *Ground Water Monitoring & Remediation* **25**, 131-141 (2005).
27. F. J. Krembs, R. L. Siegrist, M. L. Crimi, R. F. Furrer, B. G. Petri, ISCO for groundwater remediation: Analysis of field applications and performance. *Ground Water Monitoring & Remediation* **30**, 42-53 (2010).
28. M. L. Brusseau, V. Rohay, M. J. Truex, Analysis of Soil Vapor Extraction Data to Evaluate Mass‐Transfer Constraints and Estimate Source‐Zone Mass Flux. *Ground water monitoring & remediation* **30**, 57-64 (2010).
29. N. J. Sihota, K. Ulrich Mayer, Characterizing vadose zone hydrocarbon biodegradation using carbon dioxide effluxes, isotopes, and reactive transport modeling. *Vadose Zone Journal* **11**, (2012).
30. N. I. Sihota, O. Singurindy, K. U. Mayer, CO_2-Efflux Measurements for Evaluating Source Zone Natural Attenuation Rates in a Petroleum Hydrocarbon Contaminated Aquifer. *Environ. Sci. Technol.* **45**, 482-488 (2011).

Analysis	Sample type	Instrument	Reference
Cations	Groundwater	Dionex IC	Boyd et al. 2013. Environ. Sci. Proc. Impacts 15(5): 912.
Dissolved inorganic carbon (DIC)	Groundwater / trapped CO_2	Coulometer	Johnson et al. 1987. Mar. Chem. 21(2): 117.
Radiocarbon	Trapped CO_2	Accelerator Mass Spectrometery	Stuiver and Polach. 1997. Radiocarbon 19(3):355.

Sample	Comments	Counts	µMol CO2	Average µM CO2	S.E.	S.E. (%)
S5-MW-01		85620	3138.36	3119	19	0.622809
S5-MW-11		115315	4226.82	4216	11	0.26223
S5-MW-12		227412	8642.71	8646	4	0.041578
S5-MW-14		122732	4498.68	4522	23	0.517131
S5-MW-17		157014	5967.26	6001	34	0.564559
S5-MW-20		322779	11960.81	11886	75	0.632444
S5-MW-21		265565	9840.7	9902	61	0.614349
S5-MW-24		183700	6981.45	6936	45	0.648964
S5-MW-26		212066	8059.49	8094	35	0.429625
S5-MW-28		229475	8411.29	8411		
S5-MW-30		190132	7225.9	7434	208	2.794528
S5-MW-31		241324	8845.61	8778	67	0.767638
S5-MW-32		245311	8991.76	9023	31	0.340814
S5-MW-33		247075	9155.54	9050	106	1.168368
S5-MW-34		175513	6433.34	6465	32	0.488482
S5-MW-35		138665	5269.91	5272	2	0.035756
S5-MW-38		189312	6939.14	6920	20	0.283691
S5-MW-40		26883	996.17	1027	30	2.963208
S5-MW-41		64242	2441.49	2298	144	6.245512
S5-MW-42		282776	10500.92	10514	13	0.125735
S5-MW-43		253399	9288.22	9324	36	0.385611

S.E. (%) max	6.245512
S.E. (%) min	0.035756
S.E. (%) ave	0.996652

Sample#	Well ID	Beta Number	Beta calibrated	d13C	Apparent	Conventior	D14C	D14C	pMC	fPet	fPet_Av	d13C_Av	pMC_Av
1	1-t1-MW-01	1420 +/- 30 BP	1280 +/- 30 BP	-33.7	1420	1280	-162	-147	85	0			
2	2-t1-MW-21	8670 +/- 40 BP	8490 +/- 40 BP	-36.1	8670	8490	-660	-652	35	59			
3	3-t1-MW-25	1050 +/- 30 BP	1080 +/- 30 BP	-23.4	1050	1080	-123	-126	87	-3			
4	4-t1-MW-26	3040 +/- 30 BP	3050 +/- 30 BP	-24.1	3040	3050	-315	-316	68	20			
5	5-t1-MW-27	105.2 +/- 0.3 pMC	103.9 +/- 0.3 pMC	-18.9					104	-17			
6	6-t1-MW-28	1680 +/- 30 BP	1730 +/- 30 BP	-21.9	1680	1730	-189	-194	81	5			
7	7-t1-MW-30	2840 +/- 30 BP	2870 +/- 30 BP	-23.4	2840	2870	-298	-300	70	18			
8	8-t1-MW-32	130 +/- 30 BP	90 +/- 30 BP	-27.2	130	90	-16	-11	99	-16			
9	9-t1-MW-34	2830 +/- 30 BP	2670 +/- 30 BP	-34.8	2830	2670	-297	-283	72	16	16	-35	72
10	10-t1-MW-35	7270 +/- 30 BP	7350 +/- 30 BP	-20.3	7270	7350	-595	-599	40	53			
11	11-t1-MW-38	3730 +/- 30 BP	3650 +/- 30 BP	-29.8	3730	3650	-371	-365	63	26			
12	12-t1-MW-41	2060 +/- 30 BP	2030 +/- 30 BP	-26.6	2060	2030	-226	-223	78	9			
13	13-t2-MW-21	8900 +/- 40 BP	8970 +/- 40 BP	-20.5	8900	8970	-670	-673	33	62	60	-28	34
14	14-t2-MW-25	1550 +/- 30 BP	1600 +/- 30 BP	-21.8	1550	1600	-175	-181	82	4	1	-23	85
15	15-t2-MW-26	2670 +/- 30 BP	2640 +/- 30 BP	-26.7	2670	2640	-283	-280	72	16	18	-25	70
16	16-t2-MW-27	104.8 +/- 0.3 pMC	104.2 +/- 0.3 pMC	-22					104	-17	-17	-20	104
17	17-t2-MW-28	1670 +/- 30 BP	1660 +/- 30 BP	-25.6	1670	1660	-188	-187	81	5	5	-24	81
18	18-t2-MW-30	1880 +/- 30 BP	1860 +/- 30 BP	-26	1880	1860	-209	-207	79	7	12	-25	75
19	19-t2-MW-32	108.4 +/- 0.3 pMC	109.2 +/- 0.3 pMC	-28.8					109	-17	-17	-28	104
20	20-t2-MW-35	7100 +/- 30 BP	7290 +/- 30 BP	-13.7	7100	7290	-587	-596	40	53	53	-17	40
21	21-t2-MW-38	3520 +/- 30 BP	3380 +/- 30 BP	-33.5	3520	3380	-355	-343	66	23	24	-32	65
22	22-t2-MW-41	2200 +/- 30 BP	2220 +/- 30 BP	-23.5	2200	2220	-240	-241	76	11	10	-25	77
23	23-t2-MW-42	5400 +/- 30 BP	5280 +/- 30 BP	-32.4	5400	5280	-489	-482	52	39	39	-32	65

Well ID	Average D14C	S.E.	S.E. (%)
1	-147		
21	-663	10	1.52127
25	-153	27	17.88435
26	-298	18	6.010055
28	-190	4	1.854782
30	-254	47	18.48262
34	-283		
35	-598	2	0.251083
38	-354	11	3.062417
41	-232	9	3.90631
42	-482		
			average S.E. (%)
			6.621611

Loose (unglued) input!!! (See field notes)
Check pump - loose valve? Anomously young (See field notes)

Beta Analytic Inc.
4985 SW 74 Court
Miami, Florida 33155 USA
Tel: 305 667 5167
Fax: 305 663 0964
Beta@radiocarbon.com
www.radiocarbon.com

Consistent Accuracy . . .
. . . Delivered On-time

Darden Hood
President

Ronald Hatfield
Christopher Patrick
Deputy Directors

October 22, 2013

Mr. Thomas J. Boyd
Naval Research Lab
Code 6114, US NRL
4555 Overlook Avenue, SW
Washington D.C, 20375
USA

RE: Radiocarbon Dating Results For Samples 1-t1-MW-01, 2-t1-MW-21, 3-t1-MW-25, 4-t1-MW-26, 5-t1-MW-27, 6-t1-MW-28, 7-t1-MW-30, 8-t1-MW-32, 9-t1-MW-34, 10-t1-MW-35, 11-t1-MW-38, 12-t1-MW-41, 13-t2-MW-21, 14-t2-MW-25, 15-t2-MW-26, 16-t2-MW-27, 17-t2-MW-28, 18-t2-MW-30, 19-t2-MW-32, 20-t2-MW-35, 21-t2-MW-38, 22-t2-MW-41, 23-t2-MW-42

Dear Mr. Boyd:

Enclosed are the radiocarbon dating results for 23 samples recently sent to us. They each provided plenty of carbon for accurate measurements and all the analyses proceeded normally. As usual, the method of analysis is listed on the report with the results and calibration data is provided where applicable.

You will notice that Beta-361724, 361735, 361738 (5-t1-MW-27, 16-t2-MW-27, 19-t2-MW-32) are reported with the units “pMC” rather than BP. “pMC” stands for "percent modern carbon". Results are reported in the pMC format when the analyzed material had more ^{14}C than did the modern (AD 1950) reference standard. The source of this "extra" ^{14}C in the atmosphere is thermo-nuclear bomb testing which on-set in the 1950s. Its presence generally indicates the material analyzed was part of a system that was respiring carbon after the on-set of the testing (AD 1950s). On occasion, the two sigma lower limit will extend into the time region before this "bomb-carbon" onset (i.e. less than 100 pMC). In those cases, there is some probability for 18th, 19th, or 20th century antiquity.

All results reported are accredited to ISO-17025 standards and all analyses were performed entirely here in our laboratories. Since Beta is not a teaching laboratory, only graduates trained in accordance with the strict protocols of the ISO-17025 program participated in the analyses. When interpreting the results, please consider any communications you may have had with us regarding the samples.

Our invoice has been sent separately. Thank you for your prior efforts in arranging payment. As always, if you have any questions or would like to discuss the results, don’t hesitate to contact me.

Sincerely,

Darden Hood

Digital signature on file

BETA ANALYTIC INC.
DR. M.A. TAMERS and MR. D.G. HOOD
4985 S.W. 74 COURT
MIAMI, FLORIDA, USA 33155
PH: 305-667-5167 FAX:305-663-0964
beta@radiocarbon.com

REPORT OF RADIOCARBON DATING ANALYSES

Mr. Thomas J. Boyd — Report Date: 10/22/2013

Naval Research Lab — Material Received: 10/11/2013

Sample Data	Measured Radiocarbon Age	13C/12C Ratio	Conventional Radiocarbon Age(*)
Beta - 361720	1420 +/- 30 BP	-33.7 o/oo	1280 +/- 30 BP
SAMPLE : 1-t1-MW-01			
ANALYSIS : AMS-Standard delivery			
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification			
2 SIGMA CALIBRATION : Cal AD 660 to 780 (Cal BP 1290 to 1170)			
Beta - 361721	8670 +/- 40 BP	-36.1 o/oo	8490 +/- 40 BP
SAMPLE : 2-t1-MW-21			
ANALYSIS : AMS-Standard delivery			
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification			
2 SIGMA CALIBRATION : Cal BC 7590 to 7510 (Cal BP 9540 to 9460)			
Beta - 361722	1050 +/- 30 BP	-23.4 o/oo	1080 +/- 30 BP
SAMPLE : 3-t1-MW-25			
ANALYSIS : AMS-Standard delivery			
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification			
2 SIGMA CALIBRATION : Cal AD 890 to 1020 (Cal BP 1060 to 930)			
Beta - 361723	3040 +/- 30 BP	-24.1 o/oo	3050 +/- 30 BP
SAMPLE : 4-t1-MW-26			
ANALYSIS : AMS-Standard delivery			
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification			
2 SIGMA CALIBRATION : Cal BC 1410 to 1260 (Cal BP 3360 to 3210) AND Cal BC 1230 to 1220 (Cal BP 3180 to 3170)			

Dates are reported as RCYBP (radiocarbon years before present, "present" = AD 1950). By international convention, the modern reference standard was 95% the 14C activity of the National Institute of Standards and Technology (NIST) Oxalic Acid (SRM 4990C) and calculated using the Libby 14C half-life (5568 years). Quoted errors represent 1 relative standard deviation statistics (68% probability) counting errors based on the combined measurements of the sample, background, and modern reference standards. Measured 13C/12C ratios (delta 13C) were calculated relative to the PDB-1 standard.

The Conventional Radiocarbon Age represents the Measured Radiocarbon Age corrected for isotopic fractionation, calculated using the delta 13C. On rare occasion where the Conventional Radiocarbon Age was calculated using an assumed delta 13C, the ratio and the Conventional Radiocarbon Age will be followed by "*". The Conventional Radiocarbon Age is not calendar calibrated. When available, the Calendar Calibrated result is calculated from the Conventional Radiocarbon Age and is listed as the "Two Sigma Calibrated Result" for each sample.

BETA ANALYTIC INC.
DR. M.A. TAMERS and MR. D.G. HOOD
4985 S.W. 74 COURT
MIAMI, FLORIDA, USA 33155
PH: 305-667-5167 FAX:305-663-0964
beta@radiocarbon.com

REPORT OF RADIOCARBON DATING ANALYSES

Mr. Thomas J. Boyd

Report Date: 10/22/2013

Sample Data	Measured Radiocarbon Age	13C/12C Ratio	Conventional Radiocarbon Age(*)
Beta - 361724	105.2 +/- 0.3 pMC	-18.9 o/oo	103.9 +/- 0.3 pMC

SAMPLE : 5-t1-MW-27
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification
COMMENT: The reported result indicates an age of post 0 BP and has been reported as a % of the modern reference standard, indicating the material was living about the last 60 years or so ("pMC" = percent modern carbon).

Beta - 361725	1680 +/- 30 BP	-21.9 o/oo	1730 +/- 30 BP

SAMPLE : 6-t1-MW-28
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification
2 SIGMA CALIBRATION : Cal AD 240 to 390 (Cal BP 1710 to 1560)

Beta - 361726	2840 +/- 30 BP	-23.4 o/oo	2870 +/- 30 BP

SAMPLE : 7-t1-MW-30
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification
2 SIGMA CALIBRATION : Cal BC 1130 to 970 (Cal BP 3080 to 2920) AND Cal BC 960 to 940 (Cal BP 2910 to 2890)

Beta - 361727	130 +/- 30 BP	-27.2 o/oo	90 +/- 30 BP

SAMPLE : 8-t1-MW-32
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification
2 SIGMA CALIBRATION : Cal AD 1680 to 1730 (Cal BP 270 to 220) AND Cal AD 1810 to 1930 (Cal BP 140 to 20)
Cal AD Post 1950

Dates are reported as RCYBP (radiocarbon years before present, "present" = AD 1950). By international convention, the modern reference standard was 95% the 14C activity of the National Institute of Standards and Technology (NIST) Oxalic Acid (SRM 4990C) and calculated using the Libby 14C half-life (5568 years). Quoted errors represent 1 relative standard deviation statistics (68% probability) counting errors based on the combined measurements of the sample, background, and modern reference standards. Measured 13C/12C ratios (delta 13C) were calculated relative to the PDB-1 standard.

The Conventional Radiocarbon Age represents the Measured Radiocarbon Age corrected for isotopic fractionation, calculated using the delta 13C. On rare occasion where the Conventional Radiocarbon Age was calculated using an assumed delta 13C, the ratio and the Conventional Radiocarbon Age will be followed by "*". The Conventional Radiocarbon Age is not calendar calibrated. When available, the Calendar Calibrated result is calculated from the Conventional Radiocarbon Age and is listed as the "Two Sigma Calibrated Result" for each sample.

BETA ANALYTIC INC.
DR. M.A. TAMERS and MR. D.G. HOOD
4985 S.W. 74 COURT
MIAMI, FLORIDA, USA 33155
PH: 305-667-5167 FAX:305-663-0964
beta@radiocarbon.com

REPORT OF RADIOCARBON DATING ANALYSES

Mr. Thomas J. Boyd

Report Date: 10/22/2013

Sample Data	Measured Radiocarbon Age	13C/12C Ratio	Conventional Radiocarbon Age(*)
Beta - 361728	2830 +/- 30 BP	-34.8 o/oo	2670 +/- 30 BP

SAMPLE : 9-t1-MW-34
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification
2 SIGMA CALIBRATION : Cal BC 890 to 880 (Cal BP 2840 to 2820) AND Cal BC 850 to 800 (Cal BP 2800 to 2750)

Beta - 361729	7270 +/- 30 BP	-20.3 o/oo	7350 +/- 30 BP

SAMPLE : 10-t1-MW-35
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification
2 SIGMA CALIBRATION : Cal BC 6250 to 6210 (Cal BP 8200 to 8160) AND Cal BC 6190 to 6180 (Cal BP 8140 to 8130)
Cal BC 6170 to 6160 (Cal BP 8120 to 8110) AND Cal BC 6140 to 6110 (Cal BP 8090 to 8060)

Beta - 361730	3730 +/- 30 BP	-29.8 o/oo	3650 +/- 30 BP

SAMPLE : 11-t1-MW-38
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification
2 SIGMA CALIBRATION : Cal BC 2130 to 2080 (Cal BP 4080 to 4030) AND Cal BC 2060 to 1940 (Cal BP 4010 to 3890)

Beta - 361731	2060 +/- 30 BP	-26.6 o/oo	2030 +/- 30 BP

SAMPLE : 12-t1-MW-41
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification
2 SIGMA CALIBRATION : Cal BC 110 Cal AD 30 (Cal BP 2060 to 1920) AND Cal AD 40 to 50 (Cal BP 1910 to 1900)

Dates are reported as RCYBP (radiocarbon years before present, “present” = AD 1950). By international convention, the modern reference standard was 95% the 14C activity of the National Institute of Standards and Technology (NIST) Oxalic Acid (SRM 4990C) and calculated using the Libby 14C half-life (5568 years). Quoted errors represent 1 relative standard deviation statistics (68% probability) counting errors based on the combined measurements of the sample, background, and modern reference standards. Measured 13C/12C ratios (delta 13C) were calculated relative to the PDB-1 standard.

The Conventional Radiocarbon Age represents the Measured Radiocarbon Age corrected for isotopic fractionation, calculated using the delta 13C. On rare occasion where the Conventional Radiocarbon Age was calculated using an assumed delta 13C, the ratio and the Conventional Radiocarbon Age will be followed by “*”. The Conventional Radiocarbon Age is not calendar calibrated. When available, the Calendar Calibrated result is calculated from the Conventional Radiocarbon Age and is listed as the “Two Sigma Calibrated Result” for each sample.

BETA ANALYTIC INC.
DR. M.A. TAMERS and MR. D.G. HOOD
4985 S.W. 74 COURT
MIAMI, FLORIDA, USA 33155
PH: 305-667-5167 FAX:305-663-0964
beta@radiocarbon.com

REPORT OF RADIOCARBON DATING ANALYSES

Mr. Thomas J. Boyd

Report Date: 10/22/2013

Sample Data	Measured Radiocarbon Age	13C/12C Ratio	Conventional Radiocarbon Age(*)
Beta - 361732	8900 +/- 40 BP	-20.5 o/oo	8970 +/- 40 BP

SAMPLE : 13-t2-MW-21
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with co2): CO2 extracted via acidification
2 SIGMA CALIBRATION : Cal BC 8280 to 8180 (Cal BP 10230 to 10130) AND Cal BC 8110 to 8090 (Cal BP 10060 to 10040) Cal BC 8070 to 8060 (Cal BP 10020 to 10010) AND Cal BC 8040 to 7990 (Cal BP 9990 to 9940)

Beta - 361733	1550 +/- 30 BP	-21.8 o/oo	1600 +/- 30 BP

SAMPLE : 14-t2-MW-25
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification
2 SIGMA CALIBRATION : Cal AD 400 to 540 (Cal BP 1550 to 1410)

Beta - 361734	2670 +/- 30 BP	-26.7 o/oo	2640 +/- 30 BP

SAMPLE : 15-t2-MW-26
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification
2 SIGMA CALIBRATION : Cal BC 830 to 790 (Cal BP 2780 to 2740)

Beta - 361735	104.8 +/- 0.3 pMC	-22.0 o/oo	104.2 +/- 0.3 pMC

SAMPLE : 16-t2-MW-27
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification
COMMENT: The reported result indicates an age of post 0 BP and has been reported as a % of the modern reference standard, indicating the material was living about the last 60 years or so ("pMC" = percent modern carbon).

Dates are reported as RCYBP (radiocarbon years before present, "present" = AD 1950). By international convention, the modern reference standard was 95% the 14C activity of the National Institute of Standards and Technology (NIST) Oxalic Acid (SRM 4990C) and calculated using the Libby 14C half-life (5568 years). Quoted errors represent 1 relative standard deviation statistics (68% probability) counting errors based on the combined measurements of the sample, background, and modern reference standards. Measured 13C/12C ratios (delta 13C) were calculated relative to the PDB-1 standard.

The Conventional Radiocarbon Age represents the Measured Radiocarbon Age corrected for isotopic fractionation, calculated using the delta 13C. On rare occasion where the Conventional Radiocarbon Age was calculated using an assumed delta 13C, the ratio and the Conventional Radiocarbon Age will be followed by "*". The Conventional Radiocarbon Age is not calendar calibrated. When available, the Calendar Calibrated result is calculated from the Conventional Radiocarbon Age and is listed as the "Two Sigma Calibrated Result" for each sample.

BETA ANALYTIC INC.
DR. M.A. TAMERS and MR. D.G. HOOD
4985 S.W. 74 COURT
MIAMI, FLORIDA, USA 33155
PH: 305-667-5167 FAX:305-663-0964
beta@radiocarbon.com

REPORT OF RADIOCARBON DATING ANALYSES

Mr. Thomas J. Boyd

Report Date: 10/22/2013

Sample Data	Measured Radiocarbon Age	13C/12C Ratio	Conventional Radiocarbon Age(*)
Beta - 361736	1670 +/- 30 BP	-25.6 o/oo	1660 +/- 30 BP

SAMPLE : 17-t2-MW-28
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification
2 SIGMA CALIBRATION : Cal AD 260 to 270 (Cal BP 1690 to 1680) AND Cal AD 330 to 430 (Cal BP 1620 to 1520)

Beta - 361737	1880 +/- 30 BP	-26.0 o/oo	1860 +/- 30 BP

SAMPLE : 18-t2-MW-30
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification
2 SIGMA CALIBRATION : Cal AD 80 to 240 (Cal BP 1870 to 1720)

Beta - 361738	108.4 +/- 0.3 pMC	-28.8 o/oo	109.2 +/- 0.3 pMC

SAMPLE : 19-t2-MW-32
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification
COMMENT: The reported result indicates an age of post 0 BP and has been reported as a % of the modern reference standard, indicating the material was living about the last 60 years or so ("pMC" = percent modern carbon).

Beta - 361739	7100 +/- 30 BP	-13.7 o/oo	7290 +/- 30 BP

SAMPLE : 20-t2-MW-35
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification
2 SIGMA CALIBRATION : Cal BC 6230 to 6070 (Cal BP 8180 to 8020)

Dates are reported as RCYBP (radiocarbon years before present, "present" = AD 1950). By international convention, the modern reference standard was 95% the 14C activity of the National Institute of Standards and Technology (NIST) Oxalic Acid (SRM 4990C) and calculated using the Libby 14C half-life (5568 years). Quoted errors represent 1 relative standard deviation statistics (68% probability) counting errors based on the combined measurements of the sample, background, and modern reference standards. Measured 13C/12C ratios (delta 13C) were calculated relative to the PDB-1 standard.

The Conventional Radiocarbon Age represents the Measured Radiocarbon Age corrected for isotopic fractionation, calculated using the delta 13C. On rare occasion where the Conventional Radiocarbon Age was calculated using an assumed delta 13C, the ratio and the Conventional Radiocarbon Age will be followed by "*". The Conventional Radiocarbon Age is not calendar calibrated. When available, the Calendar Calibrated result is calculated from the Conventional Radiocarbon Age and is listed as the "Two Sigma Calibrated Result" for each sample.

BETA ANALYTIC INC.
DR. M.A. TAMERS and MR. D.G. HOOD
4985 S.W. 74 COURT
MIAMI, FLORIDA, USA 33155
PH: 305-667-5167 FAX:305-663-0964
beta@radiocarbon.com

REPORT OF RADIOCARBON DATING ANALYSES

Mr. Thomas J. Boyd

Report Date: 10/22/2013

Sample Data	Measured Radiocarbon Age	13C/12C Ratio	Conventional Radiocarbon Age(*)
Beta - 361740	3520 +/- 30 BP	-33.5 o/oo	3380 +/- 30 BP
SAMPLE : 21-t2-MW-38			
ANALYSIS : AMS-Standard delivery			
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification			
2 SIGMA CALIBRATION : Cal BC 1740 to 1610 (Cal BP 3690 to 3560)			
Beta - 361741	2200 +/- 30 BP	-23.5 o/oo	2220 +/- 30 BP
SAMPLE : 22-t2-MW-41			
ANALYSIS : AMS-Standard delivery			
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification			
2 SIGMA CALIBRATION : Cal BC 380 to 200 (Cal BP 2340 to 2150)			
Beta - 361742	5400 +/- 30 BP	-32.4 o/oo	5280 +/- 30 BP
SAMPLE : 23-t2-MW-42			
ANALYSIS : AMS-Standard delivery			
MATERIAL/PRETREATMENT : (NaOH with CO2): CO2 extracted via acidification			
2 SIGMA CALIBRATION : Cal BC 4230 to 4190 (Cal BP 6180 to 6140) AND Cal BC 4180 to 4040 (Cal BP 6130 to 5990) Cal BC 4020 to 3990 (Cal BP 5970 to 5940)			

Dates are reported as RCYBP (radiocarbon years before present, "present" = AD 1950). By international convention, the modern reference standard was 95% the 14C activity of the National Institute of Standards and Technology (NIST) Oxalic Acid (SRM 4990C) and calculated using the Libby 14C half-life (5568 years). Quoted errors represent 1 relative standard deviation statistics (68% probability) counting errors based on the combined measurements of the sample, background, and modern reference standards. Measured 13C/12C ratios (delta 13C) were calculated relative to the PDB-1 standard.

The Conventional Radiocarbon Age represents the Measured Radiocarbon Age corrected for isotopic fractionation, calculated using the delta 13C. On rare occasion where the Conventional Radiocarbon Age was calculated using an assumed delta 13C, the ratio and the Conventional Radiocarbon Age will be followed by "*". The Conventional Radiocarbon Age is not calendar calibrated. When available, the Calendar Calibrated result is calculated from the Conventional Radiocarbon Age and is listed as the "Two Sigma Calibrated Result" for each sample.

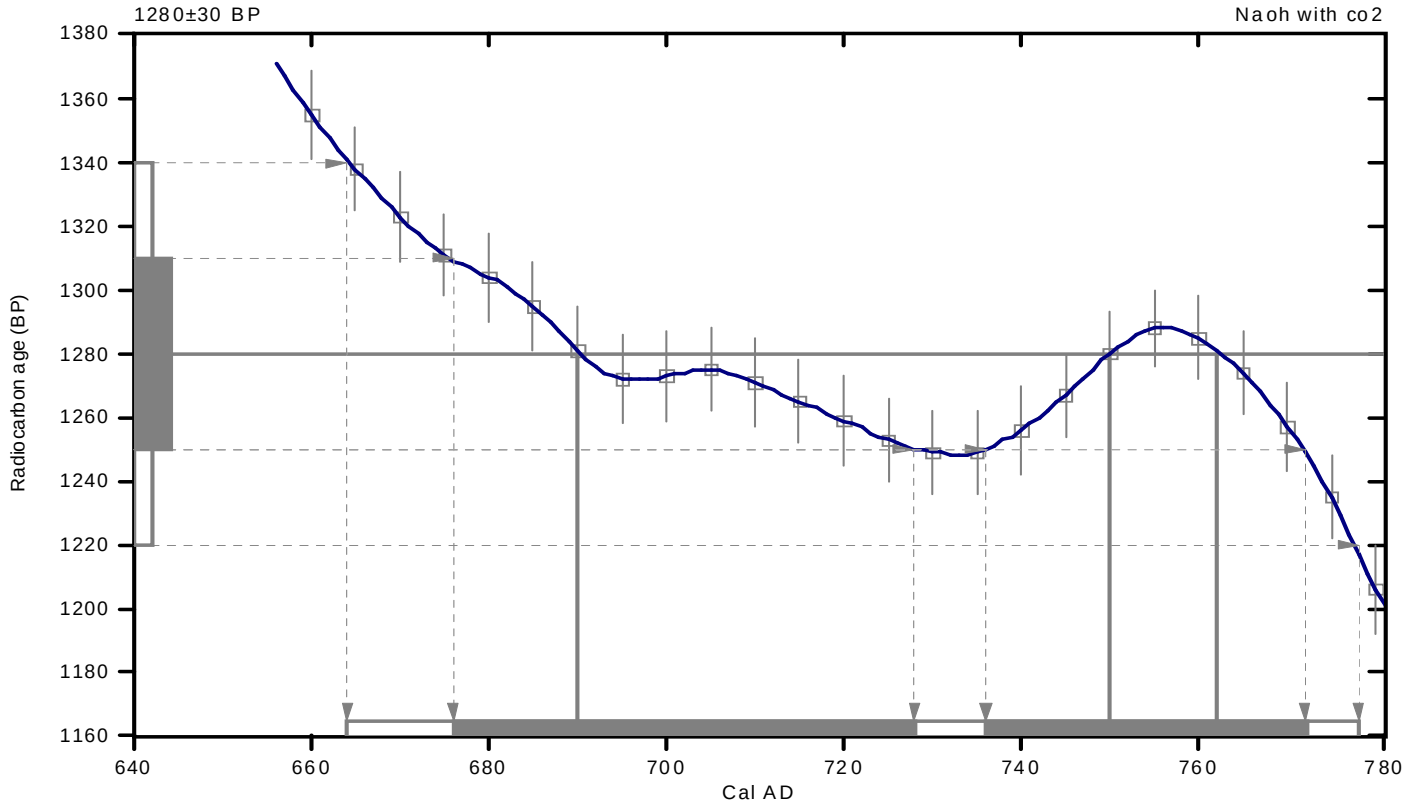
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-33.7:lab. mult=1)

Laboratory number:	**Beta-361720**
Conventional radiocarbon age:	**1280±30 BP**
2 Sigma calibrated result: (95% probability)	**Cal AD 660 to 780 (Cal BP 1290 to 1170)**

Intercept data

Intercepts of radiocarbon age with calibration curve:	Cal AD 690 (Cal BP 1260) and Cal AD 750 (Cal BP 1200) and Cal AD 760 (Cal BP 1190)
1 Sigma calibrated results: (68% probability)	Cal AD 680 to 730 (Cal BP 1270 to 1220) and Cal AD 740 to 770 (Cal BP 1210 to 1180)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):1-244, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

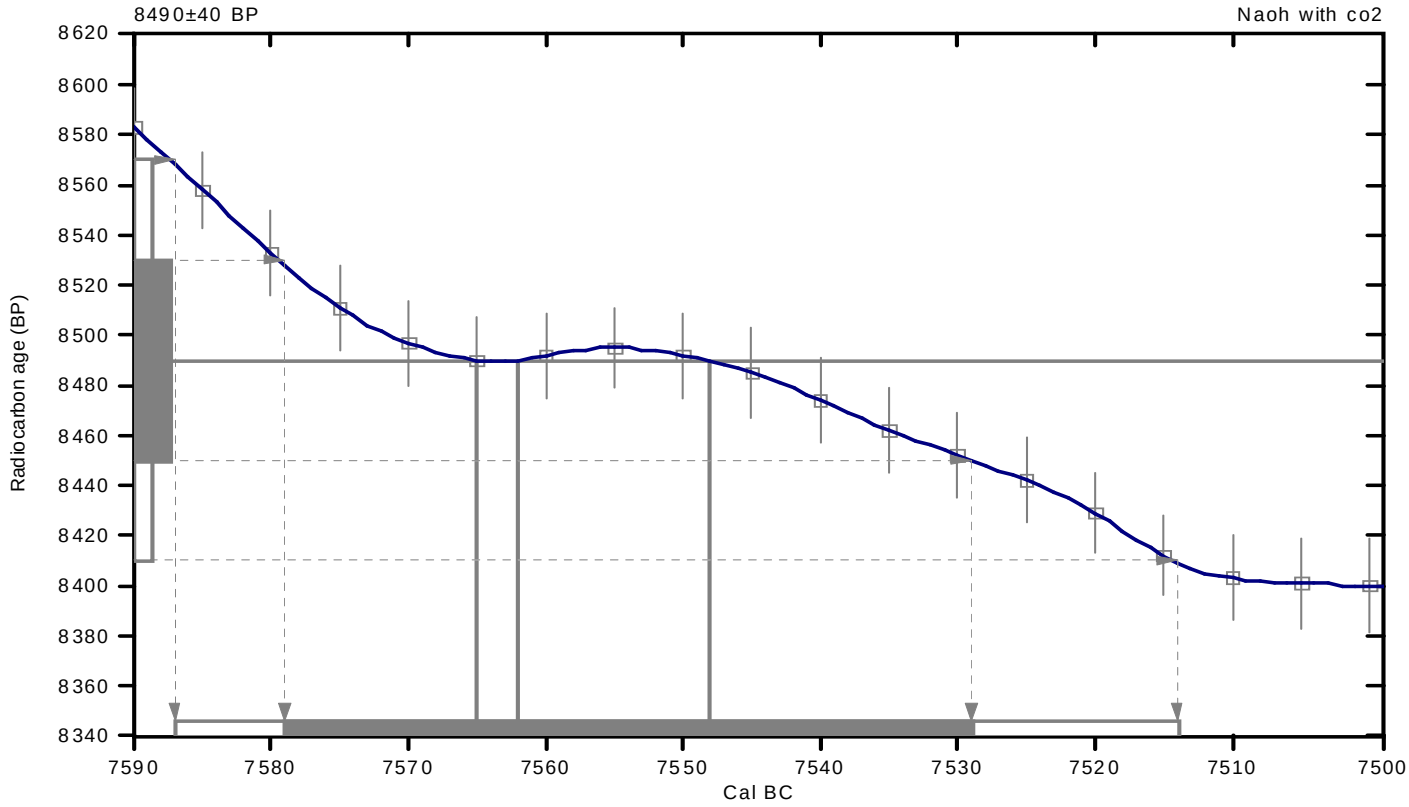
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-36.1:lab. mult=1)

Laboratory number:	**Beta-361721**
Conventional radiocarbon age:	**8490±40 BP**
2 Sigma calibrated result: (95% probability)	**Cal BC 7590 to 7510 (Cal BP 9540 to 9460)**

Intercept data

Intercepts of radiocarbon age with calibration curve:	Cal BC 7560 (Cal BP 9520) and Cal BC 7560 (Cal BP 9510) and Cal BC 7550 (Cal BP 9500)
1 Sigma calibrated result: (68% probability)	Cal BC 7580 to 7530 (Cal BP 9530 to 9480)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

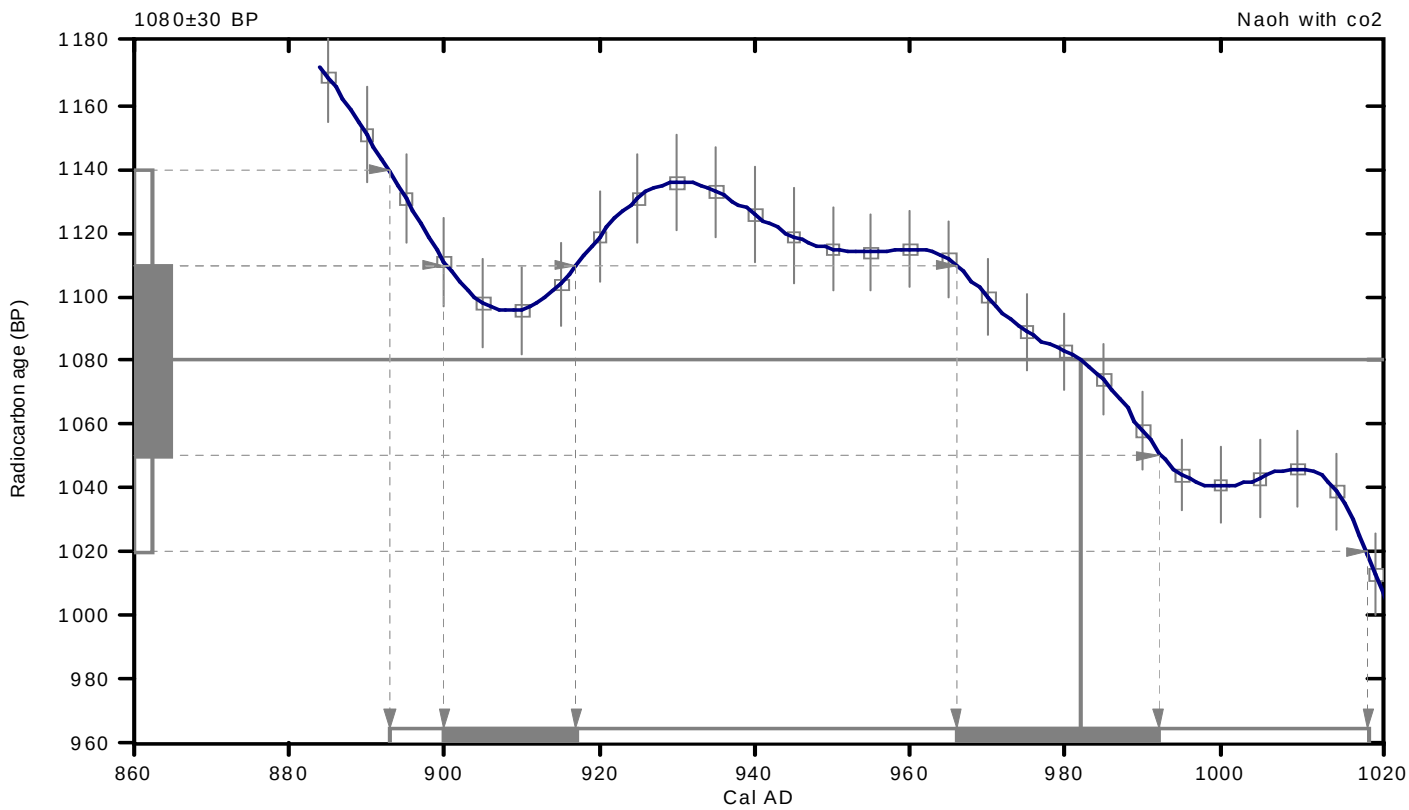
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-23.4:lab. mult=1)

Laboratory number:	**Beta-361722**
Conventional radiocarbon age:	**1080±30 BP**
2 Sigma calibrated result: (95% probability)	**Cal AD 890 to 1020 (Cal BP 1060 to 930)**

Intercept data

Intercept of radiocarbon age with calibration curve:	Cal AD 980 (Cal BP 970)
1 Sigma calibrated results: (68% probability)	Cal AD 900 to 920 (Cal BP 1050 to 1030) and Cal AD 970 to 990 (Cal BP 980 to 960)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

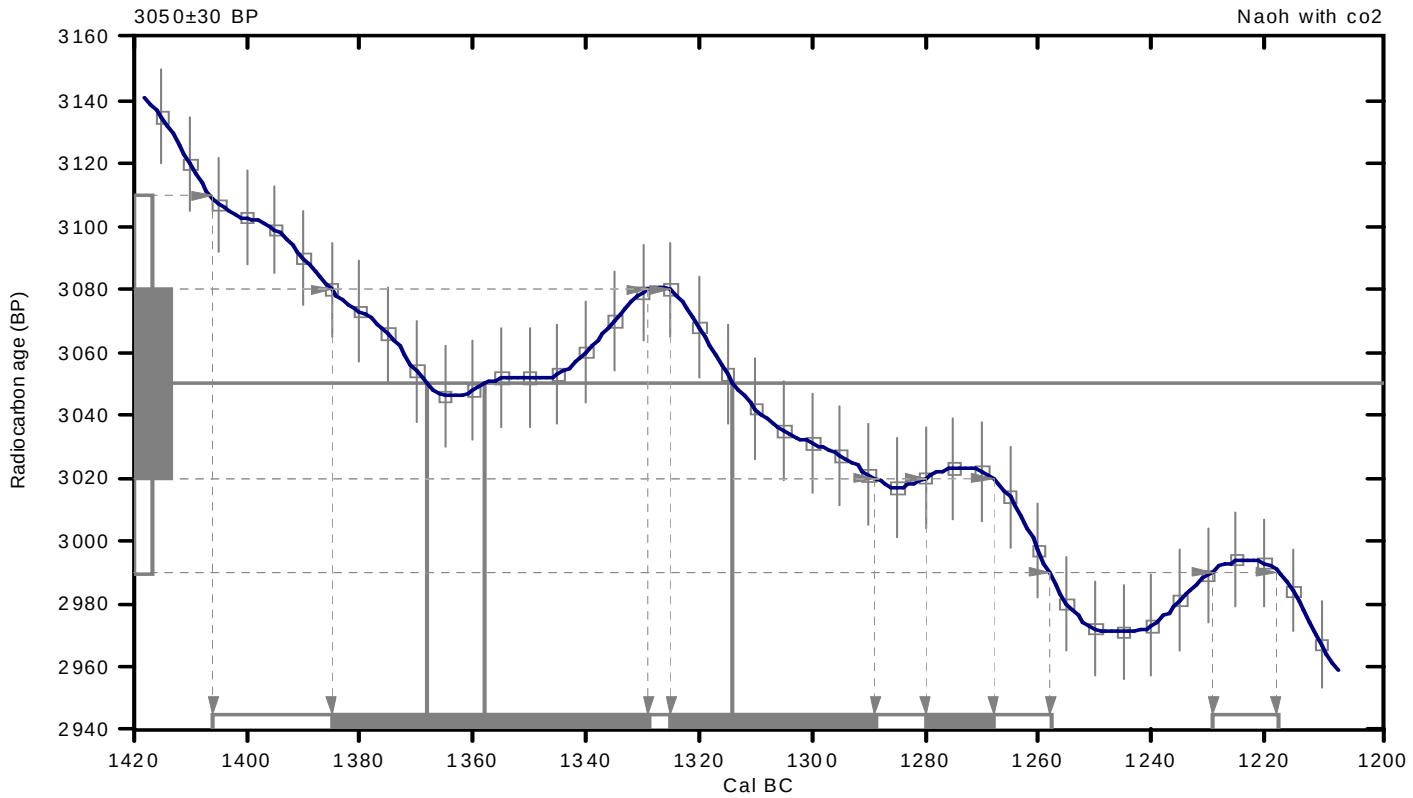
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-24.1:lab. mult=1)

Laboratory number:	**Beta-361723**
Conventional radiocarbon age:	**3050±30 BP**
2 Sigma calibrated results: **(95% probability)**	**Cal BC 1410 to 1260 (Cal BP 3360 to 3210) and** **Cal BC 1230 to 1220 (Cal BP 3180 to 3170)**

Intercept data

Intercepts of radiocarbon age with calibration curve:	Cal BC 1370 (Cal BP 3320) and Cal BC 1360 (Cal BP 3310) and Cal BC 1310 (Cal BP 3260)
1 Sigma calibrated results: (68% probability)	Cal BC 1380 to 1330 (Cal BP 3340 to 3280) and Cal BC 1320 to 1290 (Cal BP 3280 to 3240) and Cal BC 1280 to 1270 (Cal BP 3230 to 3220)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

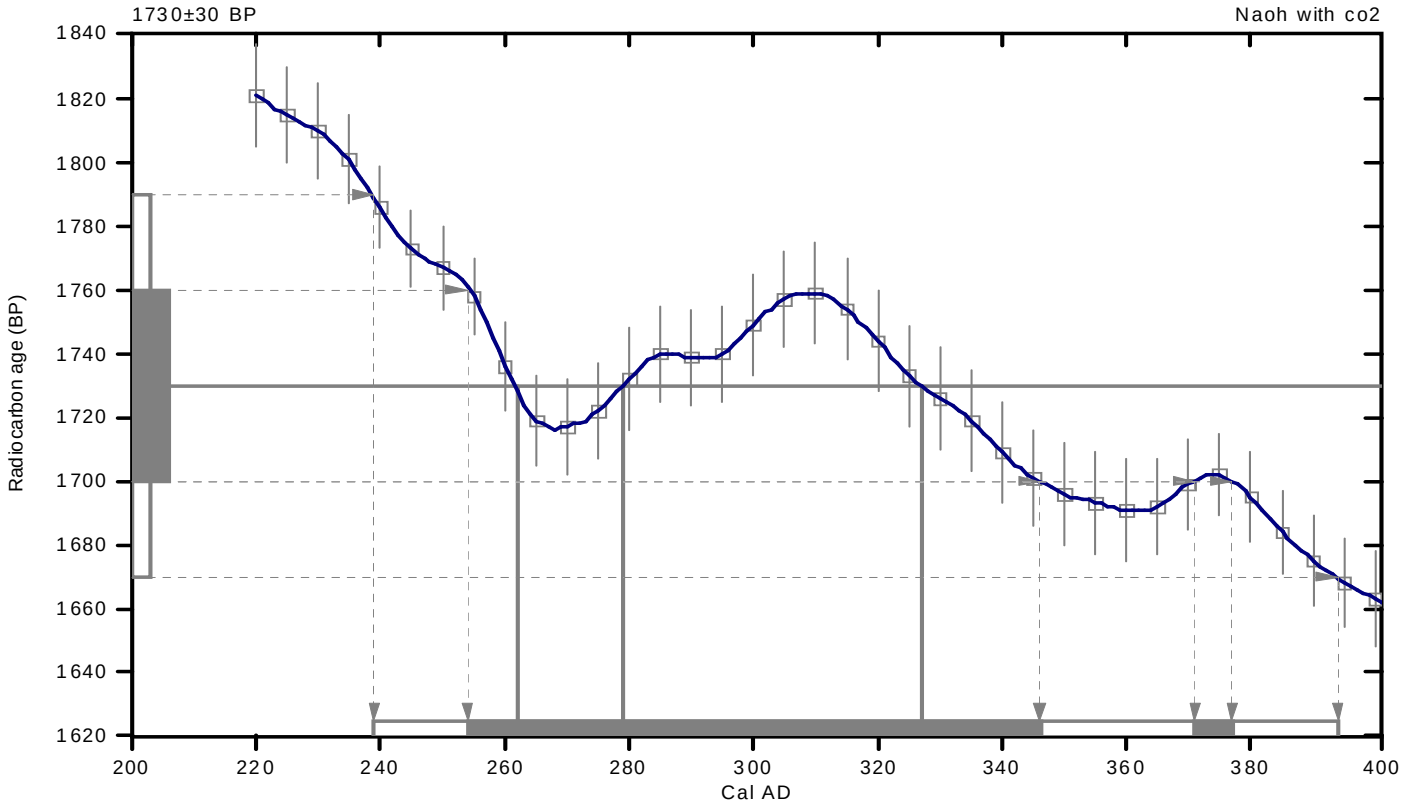
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-21.9:lab. mult=1)

Laboratory number:	**Beta-361725**
Conventional radiocarbon age:	**1730±30 BP**
2 Sigma calibrated result: (95% probability)	**Cal AD 240 to 390 (Cal BP 1710 to 1560)**

Intercept data

Intercepts of radiocarbon age with calibration curve:	Cal AD 260 (Cal BP 1690) and Cal AD 280 (Cal BP 1670) and Cal AD 330 (Cal BP 1620)
1 Sigma calibrated results: (68% probability)	Cal AD 250 to 350 (Cal BP 1700 to 1600) and Cal AD 370 to 380 (Cal BP 1580 to 1570)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

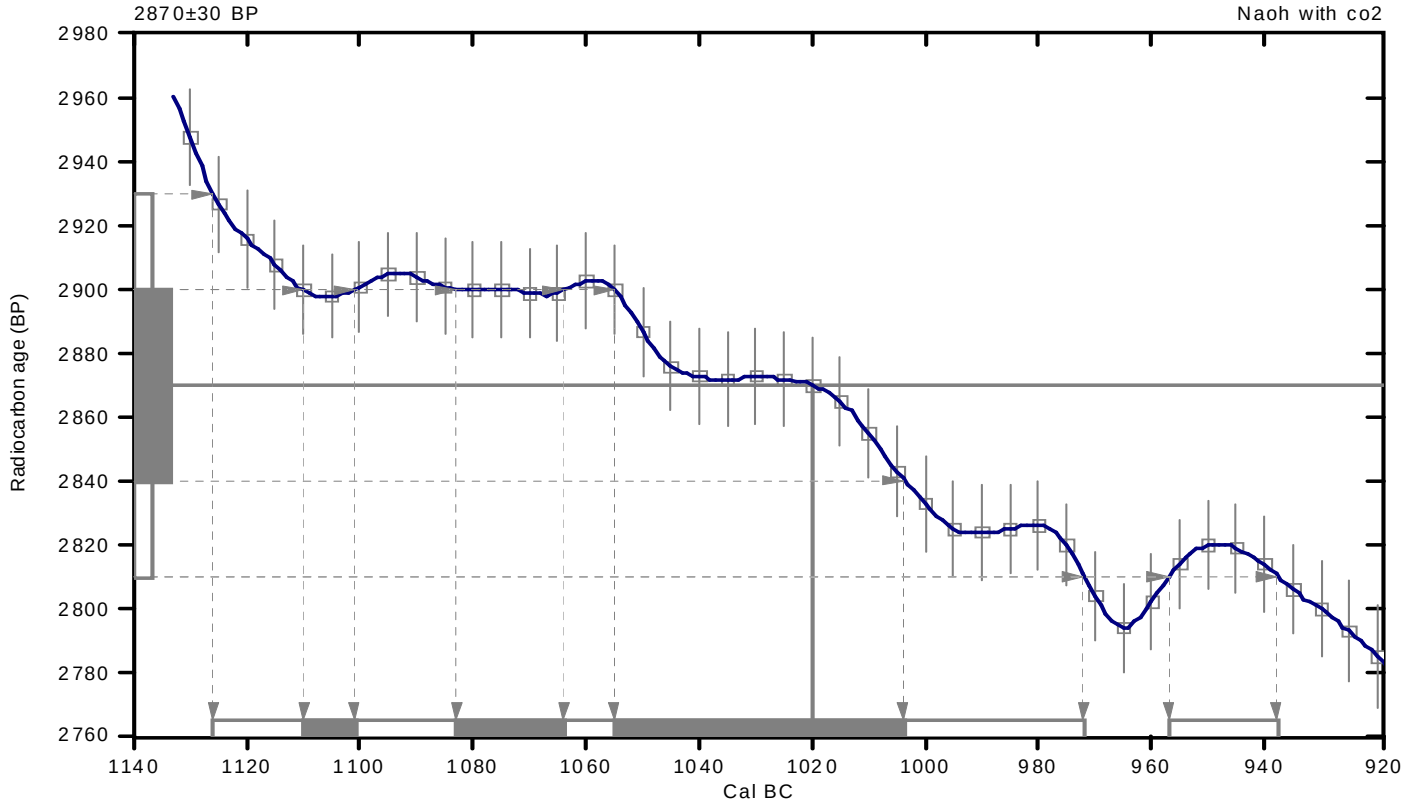
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-23.4:lab. mult=1)

Laboratory number:	**Beta-361726**
Conventional radiocarbon age:	**2870±30 BP**
2 Sigma calibrated results: (95% probability)	**Cal BC 1130 to 970 (Cal BP 3080 to 2920) and Cal BC 960 to 940 (Cal BP 2910 to 2890)**

Intercept data

Intercept of radiocarbon age with calibration curve:	Cal BC 1020 (Cal BP 2970)
1 Sigma calibrated results: (68% probability)	Cal BC 1110 to 1100 (Cal BP 3060 to 3050) and Cal BC 1080 to 1060 (Cal BP 3030 to 3010) and Cal BC 1060 to 1000 (Cal BP 3000 to 2950)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

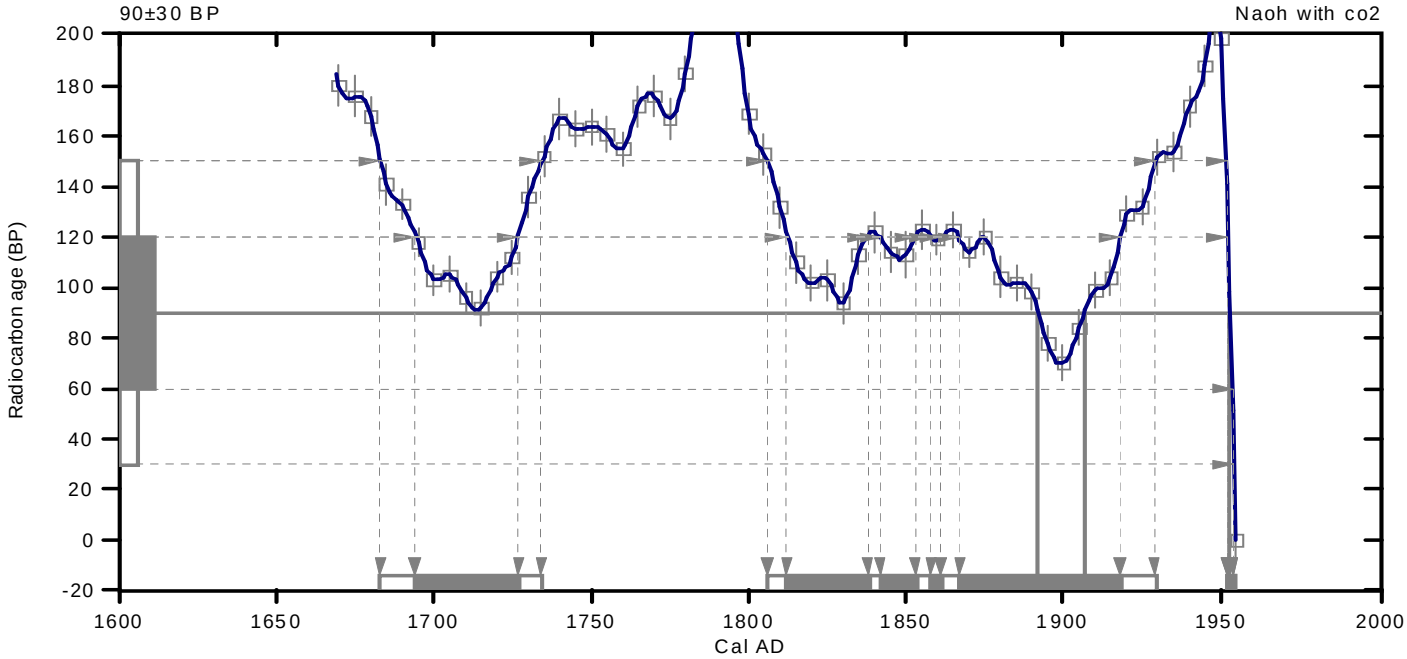
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-27.2:lab. mult=1)

Laboratory number:	**Beta-361727**
Conventional radiocarbon age:	**90±30 BP**
2 Sigma calibrated results: **(95% probability)**	**Cal AD 1680 to 1730 (Cal BP 270 to 220) and** **Cal AD 1810 to 1930 (Cal BP 140 to 20) and** **Cal AD Post 1950**

Intercept data

Intercepts of radiocarbon age with calibration curve:	Cal AD 1890 (Cal BP 60) and Cal AD 1910 (Cal BP 40) and Cal AD Post 1950
1 Sigma calibrated results: (68% probability)	Cal AD 1690 to 1730 (Cal BP 260 to 220) and Cal AD 1810 to 1840 (Cal BP 140 to 110) and Cal AD 1840 to 1850 (Cal BP 110 to 100) and Cal AD 1860 to 1860 (Cal BP 90 to 90) and Cal AD 1870 to 1920 (Cal BP 80 to 30) and Cal AD Post 1950



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

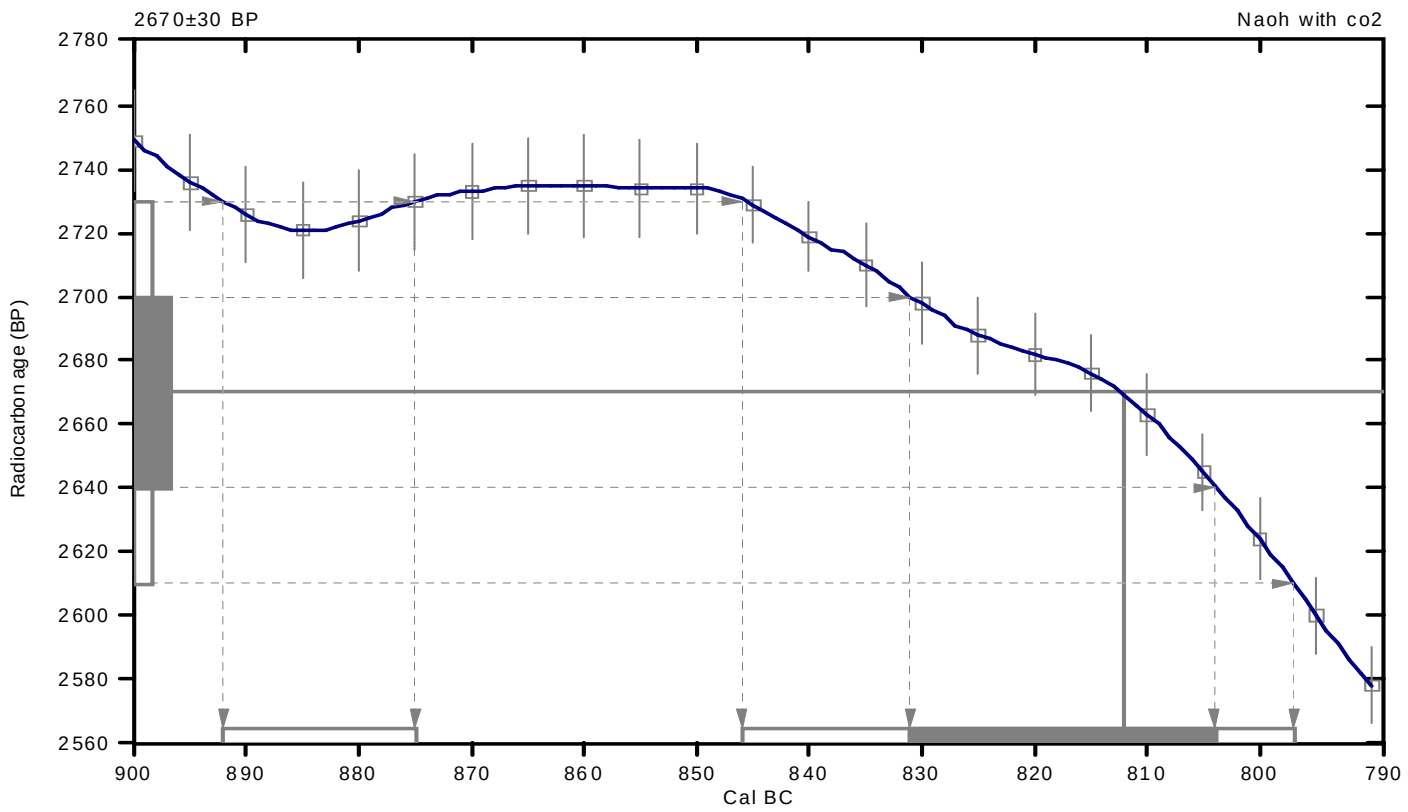
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-34.8:lab. mult=1)

Laboratory number:	**Beta-361728**
Conventional radiocarbon age:	**2670±30 BP**
2 Sigma calibrated results: (95% probability)	**Cal BC 890 to 880 (Cal BP 2840 to 2820) and Cal BC 850 to 800 (Cal BP 2800 to 2750)**

Intercept data

Intercept of radiocarbon age with calibration curve:	Cal BC 810 (Cal BP 2760)
1 Sigma calibrated result: (68% probability)	Cal BC 830 to 800 (Cal BP 2780 to 2750)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

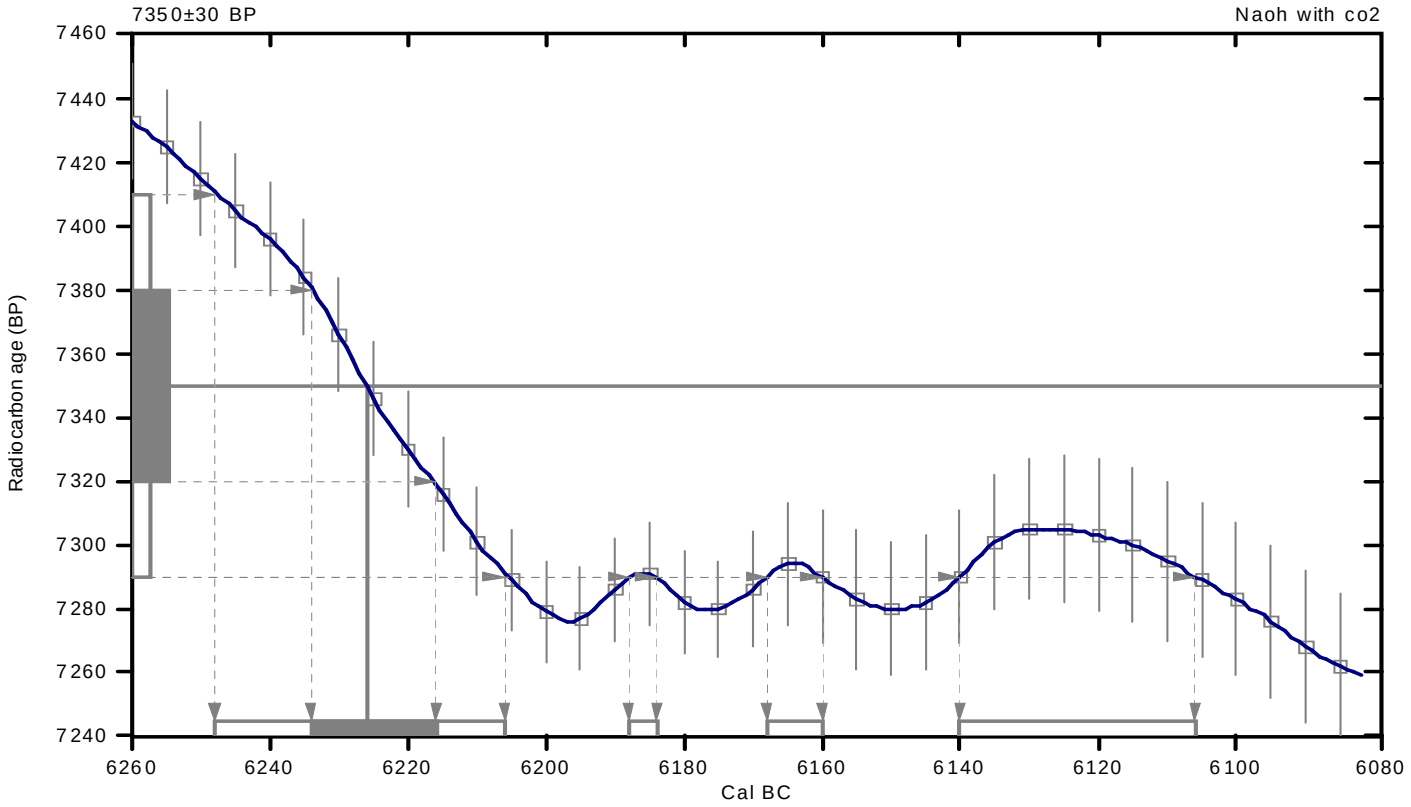
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-20.3:lab. mult=1)

Laboratory number:	**Beta-361729**
Conventional radiocarbon age:	**7350±30 BP**
2 Sigma calibrated results: (95% probability)	**Cal BC 6250 to 6210 (Cal BP 8200 to 8160) and Cal BC 6190 to 6180 (Cal BP 8140 to 8130) and Cal BC 6170 to 6160 (Cal BP 8120 to 8110) and Cal BC 6140 to 6110 (Cal BP 8090 to 8060)**

Intercept data

Intercept of radiocarbon age with calibration curve:	Cal BC 6230 (Cal BP 8180)
1 Sigma calibrated result: (68% probability)	Cal BC 6230 to 6220 (Cal BP 8180 to 8170)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

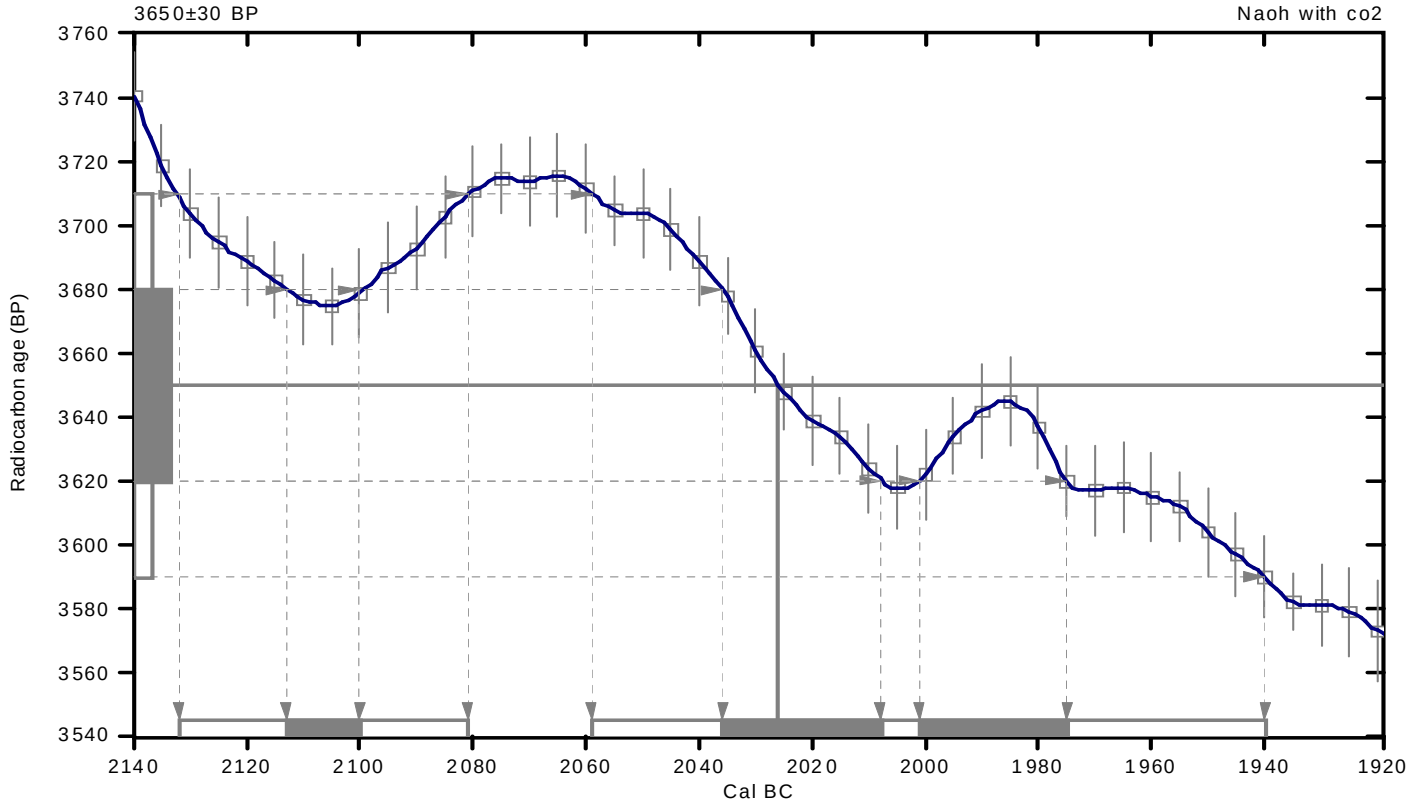
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-29.8:lab. mult=1)

Laboratory number:	**Beta-361730**
Conventional radiocarbon age:	**3650±30 BP**
2 Sigma calibrated results: **(95% probability)**	**Cal BC 2130 to 2080 (Cal BP 4080 to 4030) and** **Cal BC 2060 to 1940 (Cal BP 4010 to 3890)**

Intercept data

Intercept of radiocarbon age with calibration curve:	Cal BC 2030 (Cal BP 3980)
1 Sigma calibrated results: (68% probability)	Cal BC 2110 to 2100 (Cal BP 4060 to 4050) and Cal BC 2040 to 2010 (Cal BP 3990 to 3960) and Cal BC 2000 to 1980 (Cal BP 3950 to 3920)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

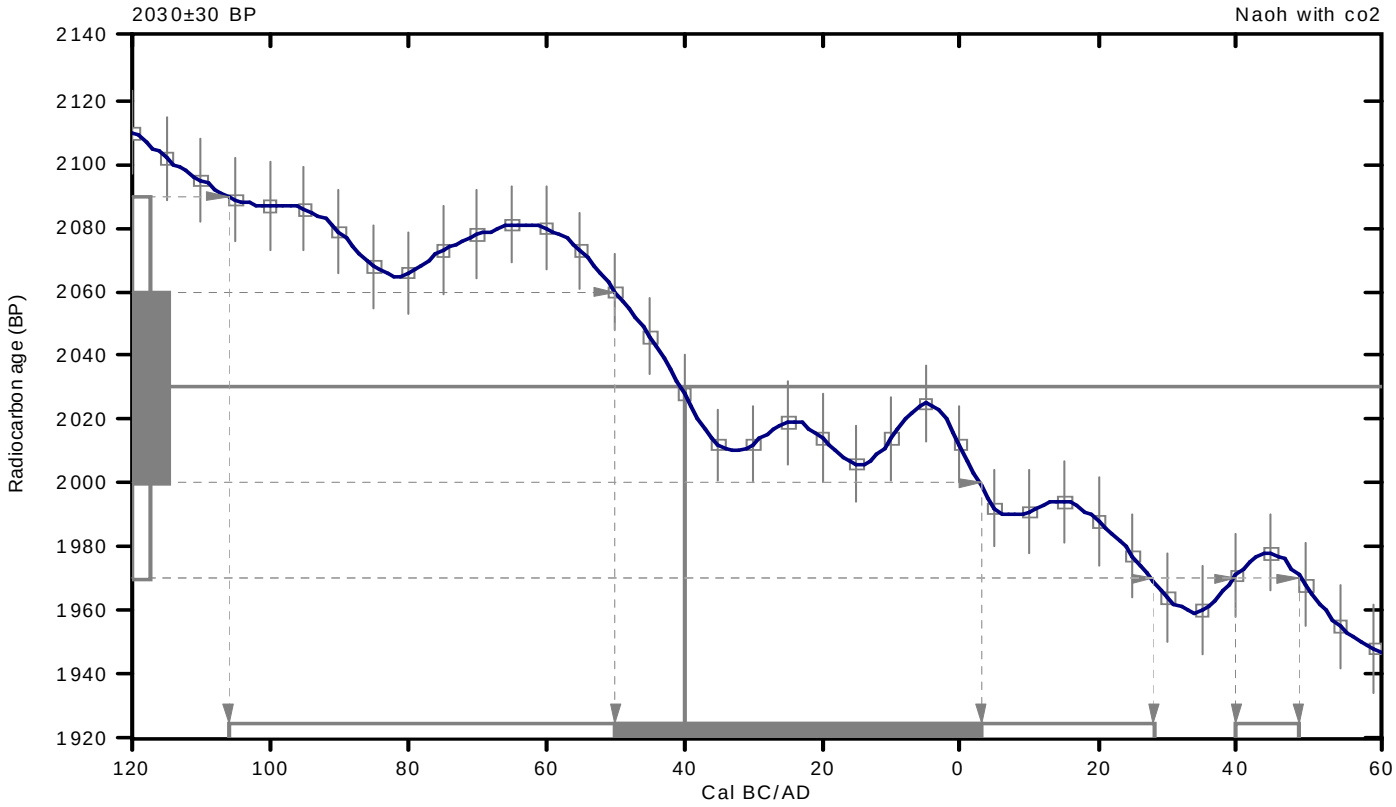
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-26.6:lab. mult=1)

Laboratory number:	**Beta-361731**
Conventional radiocarbon age:	**2030±30 BP**
2 Sigma calibrated results: (95% probability)	**Cal BC 110 Cal AD 30 (Cal BP 2060 to 1920) and Cal AD 40 to 50 (Cal BP 1910 to 1900)**

Intercept data

Intercept of radiocarbon age with calibration curve:	Cal BC 40 (Cal BP 1990)
1 Sigma calibrated result: (68% probability)	Cal BC 50 Cal AD 0 (Cal BP 2000 to 1950)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

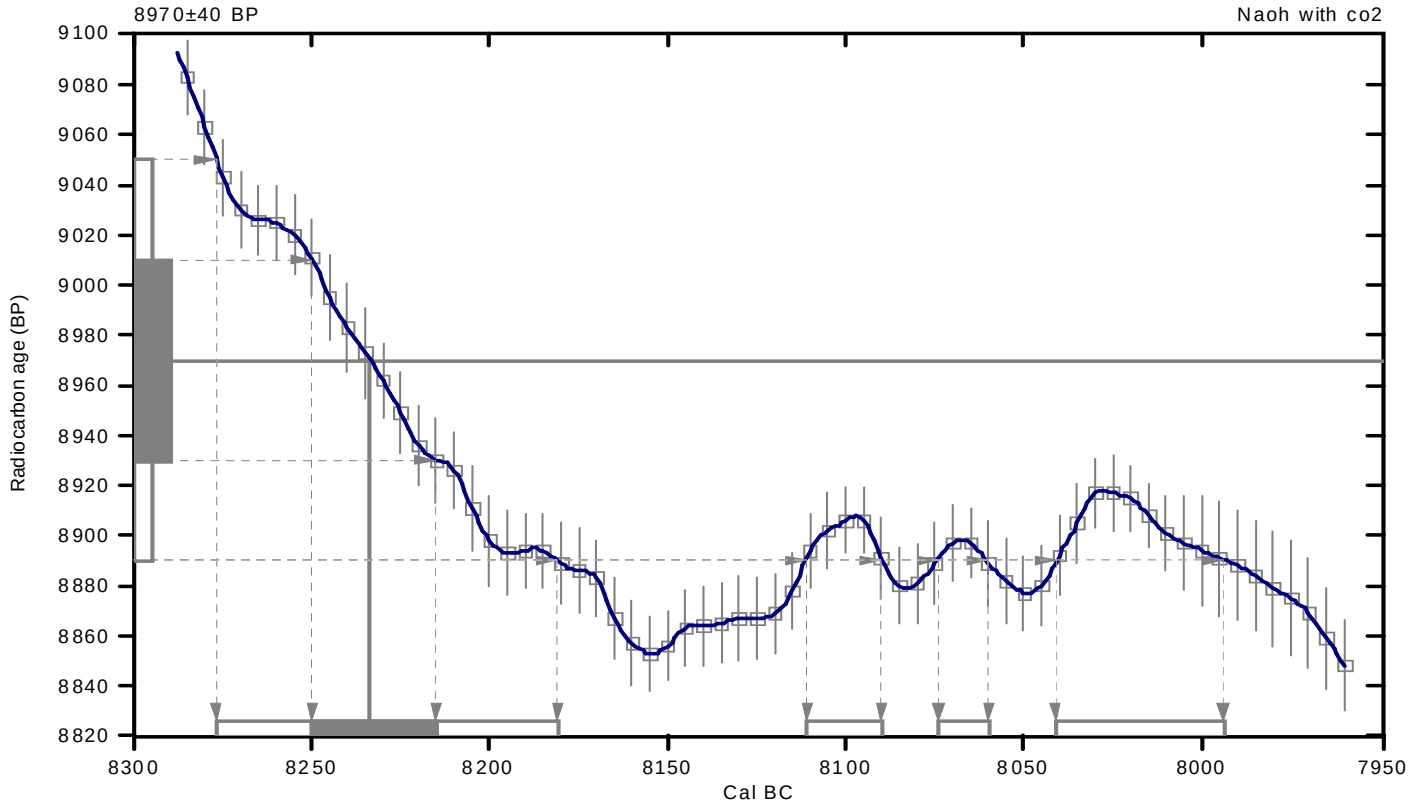
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-20.5:lab. mult=1)

Laboratory number:	**Beta-361732**
Conventional radiocarbon age:	**8970±40 BP**
2 Sigma calibrated results: **(95% probability)**	**Cal BC 8280 to 8180 (Cal BP 10230 to 10130) and** **Cal BC 8110 to 8090 (Cal BP 10060 to 10040) and** **Cal BC 8070 to 8060 (Cal BP 10020 to 10010) and** **Cal BC 8040 to 7990 (Cal BP 9990 to 9940)**

Intercept data

Intercept of radiocarbon age with calibration curve:	Cal BC 8230 (Cal BP 10180)
1 Sigma calibrated result: (68% probability)	Cal BC 8250 to 8220 (Cal BP 10200 to 10160)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

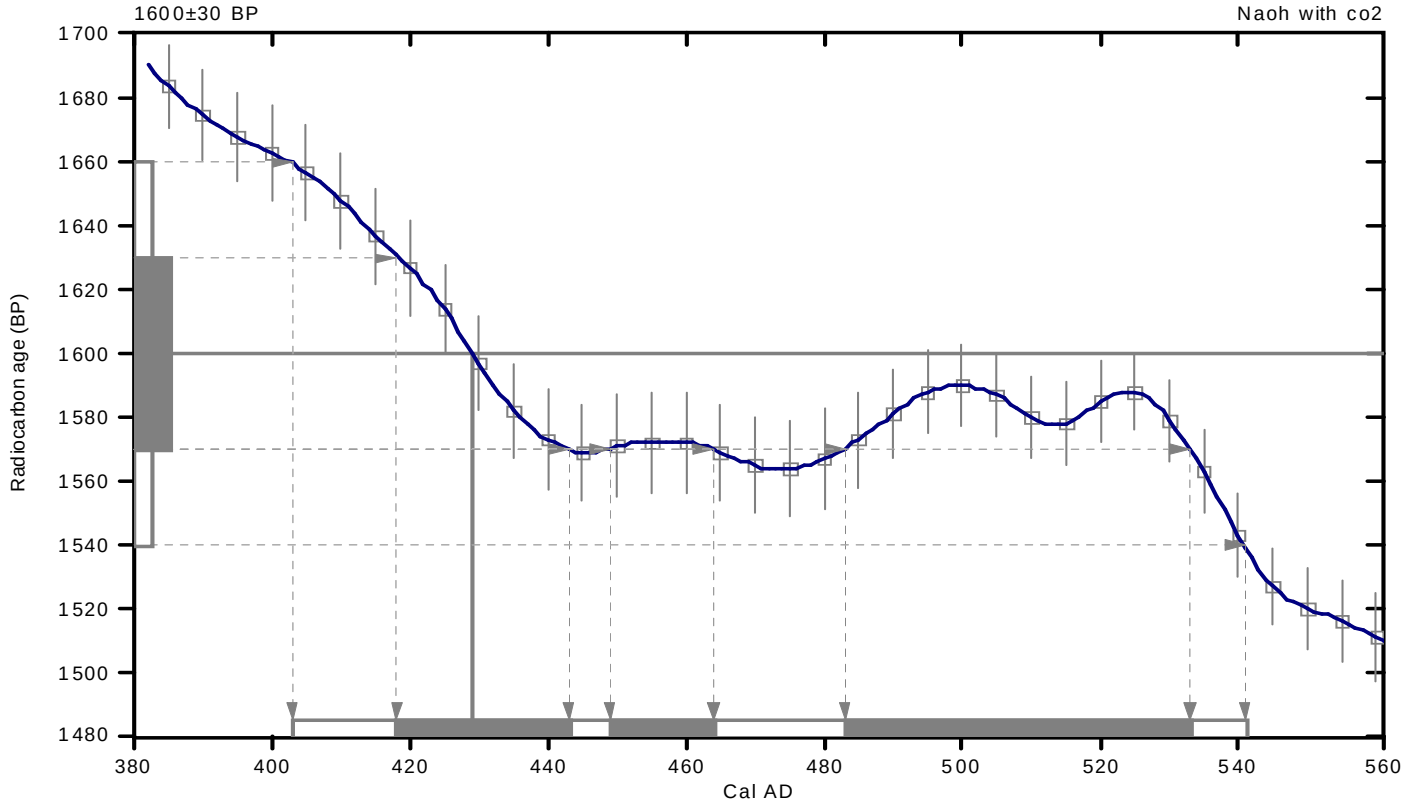
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-21.8:lab. mult=1)

Laboratory number:	**Beta-361733**
Conventional radiocarbon age:	**1600±30 BP**
2 Sigma calibrated result: (95% probability)	**Cal AD 400 to 540 (Cal BP 1550 to 1410)**

Intercept data

Intercept of radiocarbon age with calibration curve:	Cal AD 430 (Cal BP 1520)
1 Sigma calibrated results: (68% probability)	Cal AD 420 to 440 (Cal BP 1530 to 1510) and Cal AD 450 to 460 (Cal BP 1500 to 1490) and Cal AD 480 to 530 (Cal BP 1470 to 1420)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

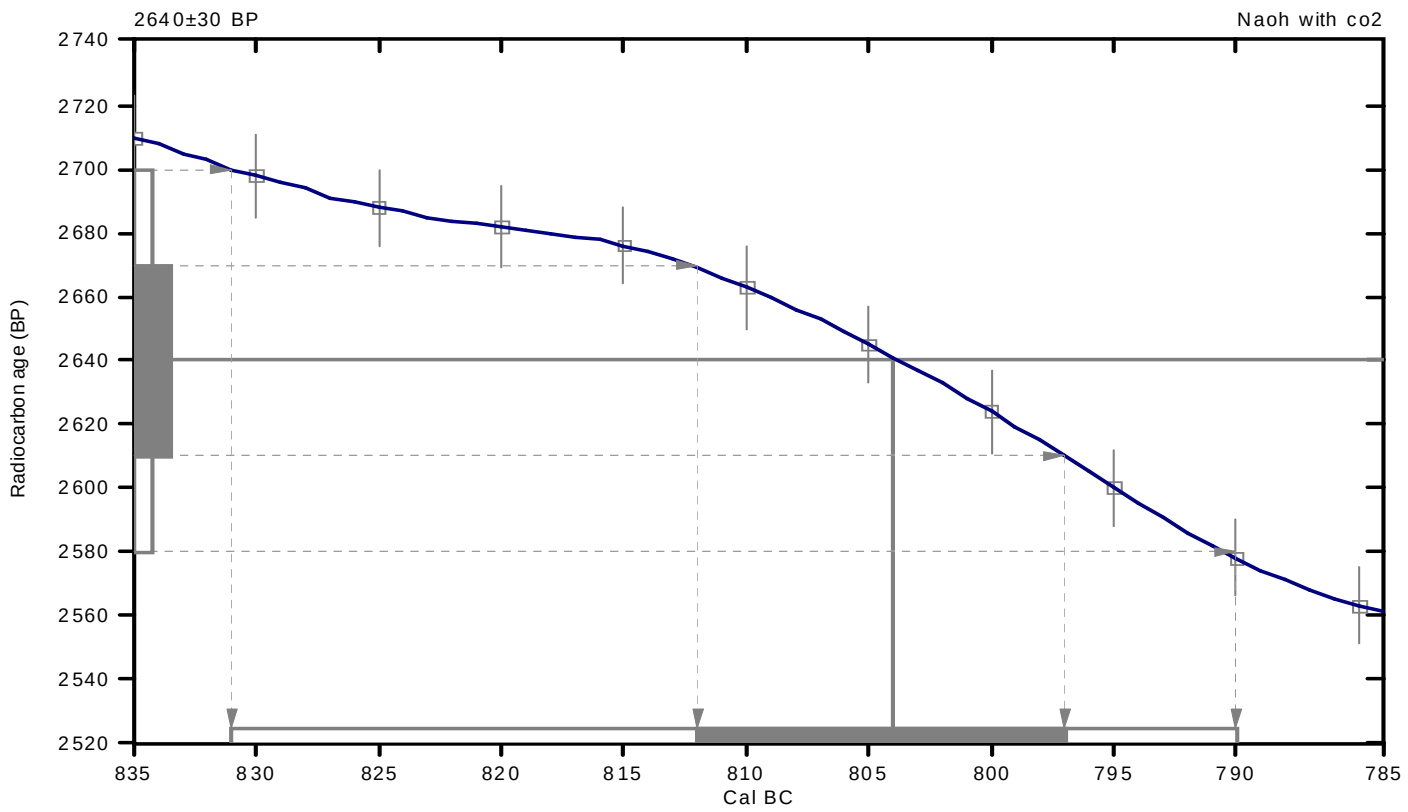
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-26.7:lab. mult=1)

Laboratory number:	**Beta-361734**
Conventional radiocarbon age:	**2640±30 BP**
2 Sigma calibrated result: (95% probability)	**Cal BC 830 to 790 (Cal BP 2780 to 2740)**

Intercept data

Intercept of radiocarbon age with calibration curve:	Cal BC 800 (Cal BP 2750)
1 Sigma calibrated result: (68% probability)	Cal BC 810 to 800 (Cal BP 2760 to 2750)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

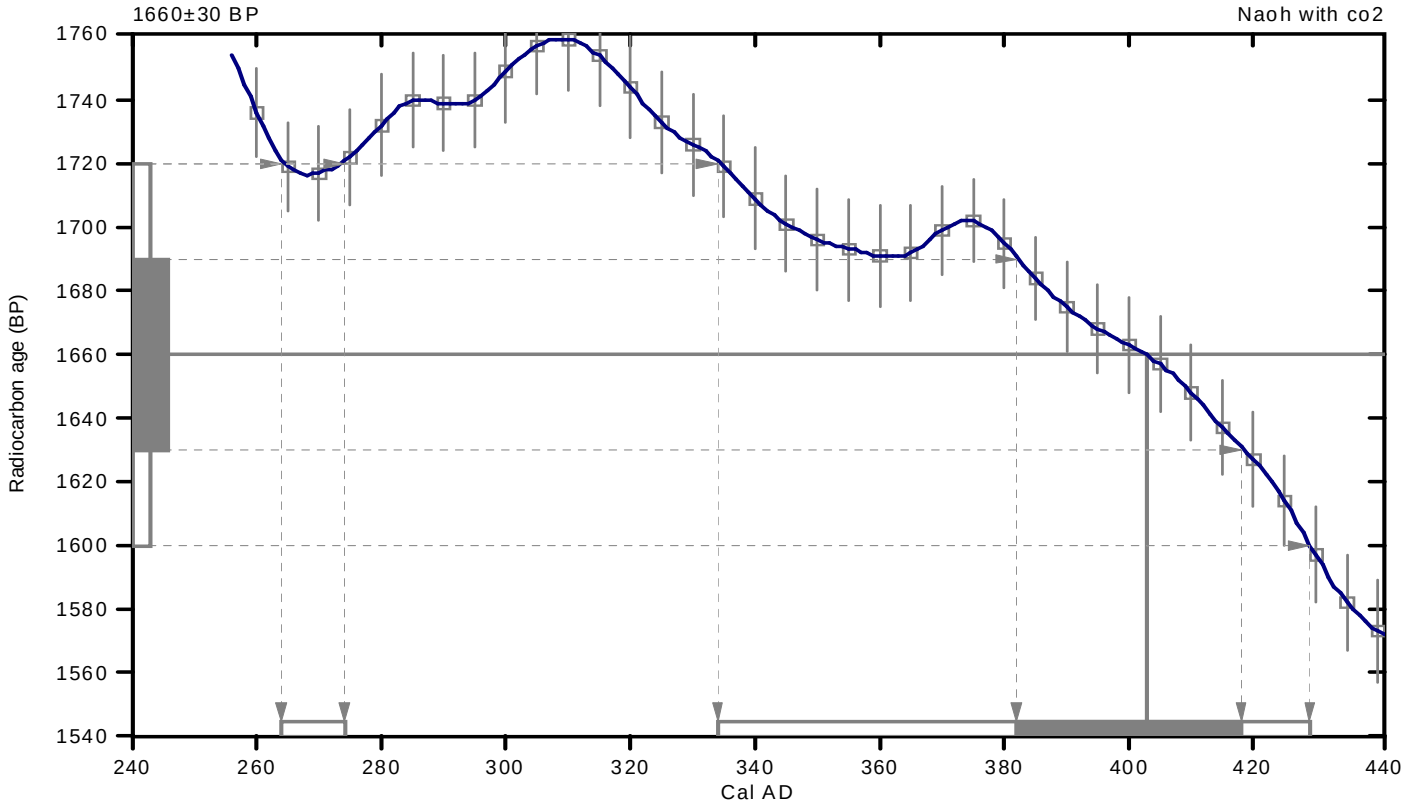
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-25.6:lab. mult=1)

Laboratory number:	**Beta-361736**
Conventional radiocarbon age:	**1660±30 BP**
2 Sigma calibrated results: (95% probability)	**Cal AD 260 to 270 (Cal BP 1690 to 1680) and Cal AD 330 to 430 (Cal BP 1620 to 1520)**

Intercept data

Intercept of radiocarbon age with calibration curve:	Cal AD 400 (Cal BP 1550)
1 Sigma calibrated result: (68% probability)	Cal AD 380 to 420 (Cal BP 1570 to 1530)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates

Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

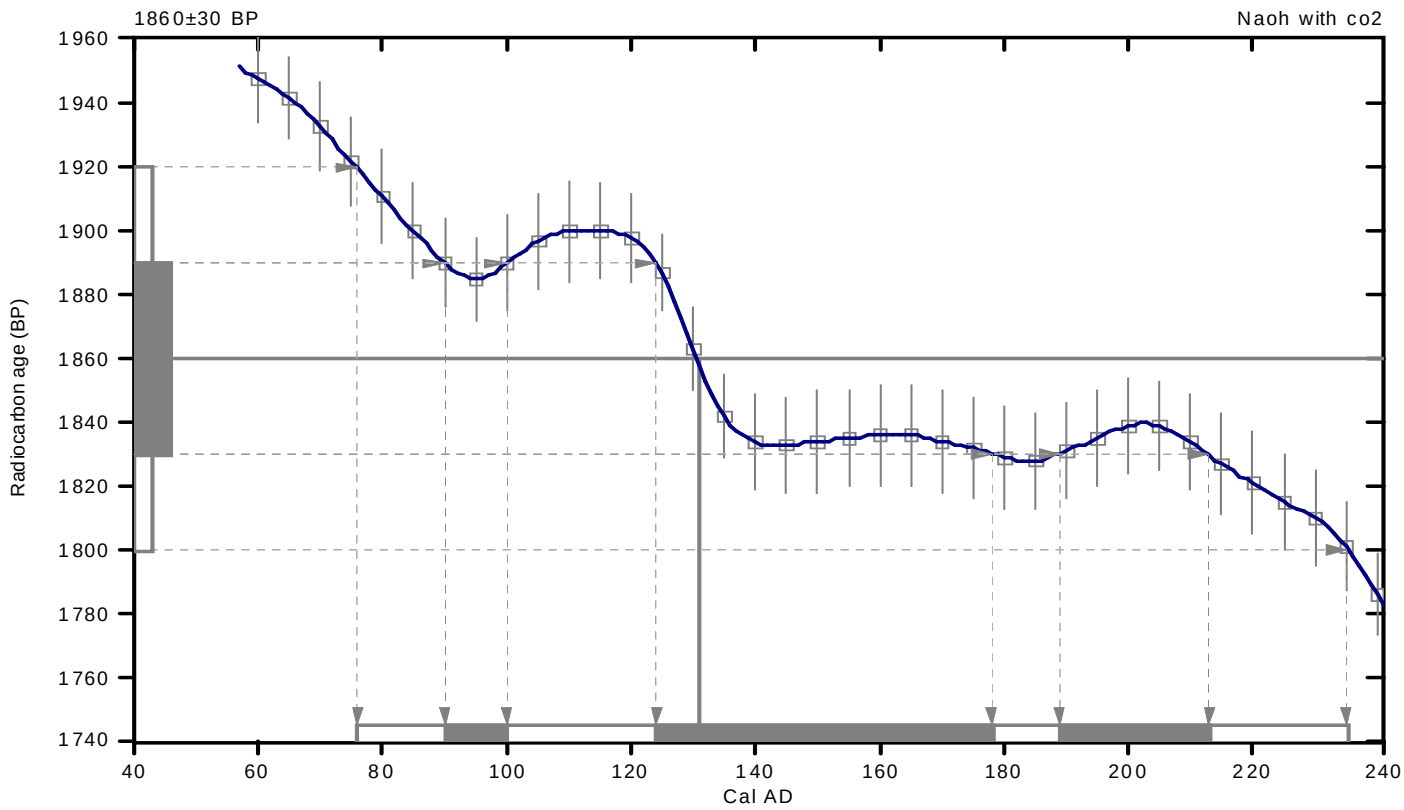
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-26:lab. mult=1)

Laboratory number:	**Beta-361737**
Conventional radiocarbon age:	**1860±30 BP**
2 Sigma calibrated result: (95% probability)	**Cal AD 80 to 240 (Cal BP 1870 to 1720)**

Intercept data

Intercept of radiocarbon age with calibration curve:	Cal AD 130 (Cal BP 1820)
1 Sigma calibrated results: (68% probability)	Cal AD 90 to 100 (Cal BP 1860 to 1850) and Cal AD 120 to 180 (Cal BP 1830 to 1770) and Cal AD 190 to 210 (Cal BP 1760 to 1740)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

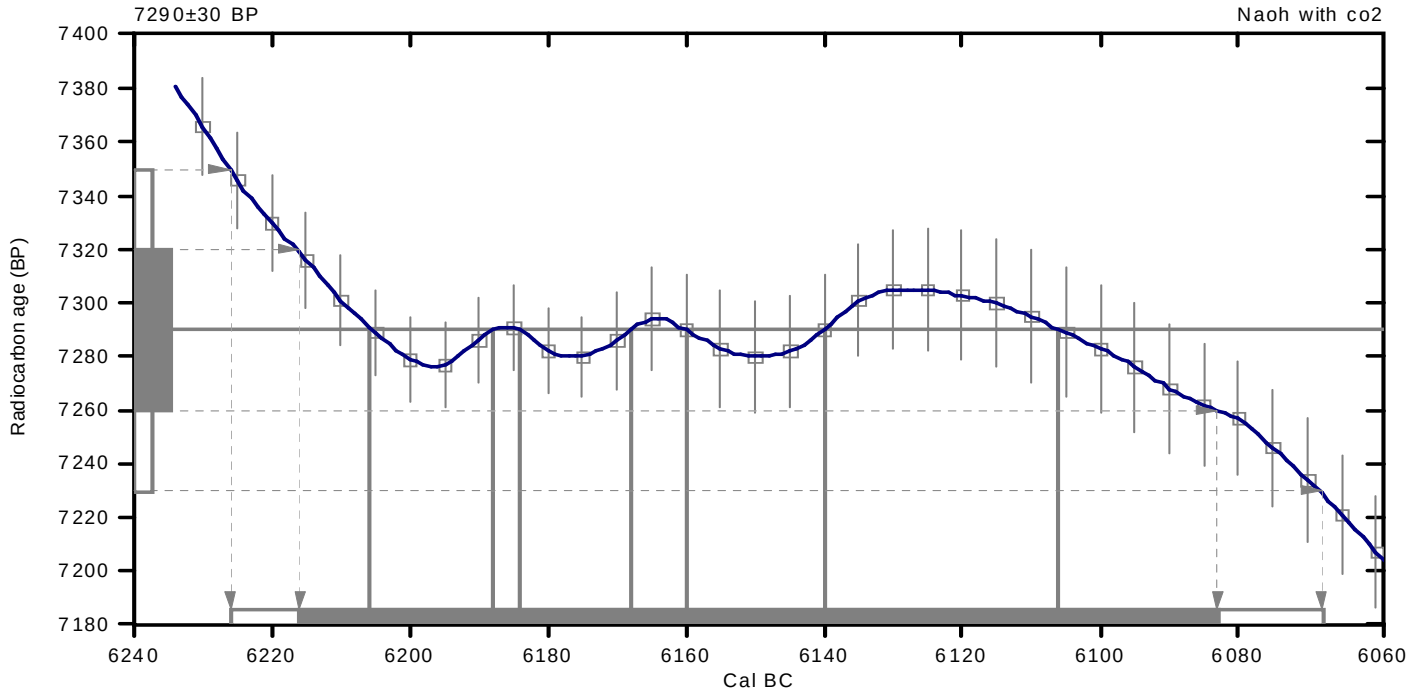
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-13.7:lab. mult=1)

Laboratory number:	**Beta-361739**
Conventional radiocarbon age:	**7290±30 BP**
2 Sigma calibrated result: (95% probability)	**Cal BC 6230 to 6070 (Cal BP 8180 to 8020)**

Intercept data

Intercepts of radiocarbon age with calibration curve:	Cal BC 6210 (Cal BP 8160) and Cal BC 6190 (Cal BP 8140) and Cal BC 6180 (Cal BP 8130) and Cal BC 6170 (Cal BP 8120) and Cal BC 6160 (Cal BP 8110) and Cal BC 6140 (Cal BP 8090) and Cal BC 6110 (Cal BP 8060)
1 Sigma calibrated result: (68% probability)	Cal BC 6220 to 6080 (Cal BP 8170 to 8030)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

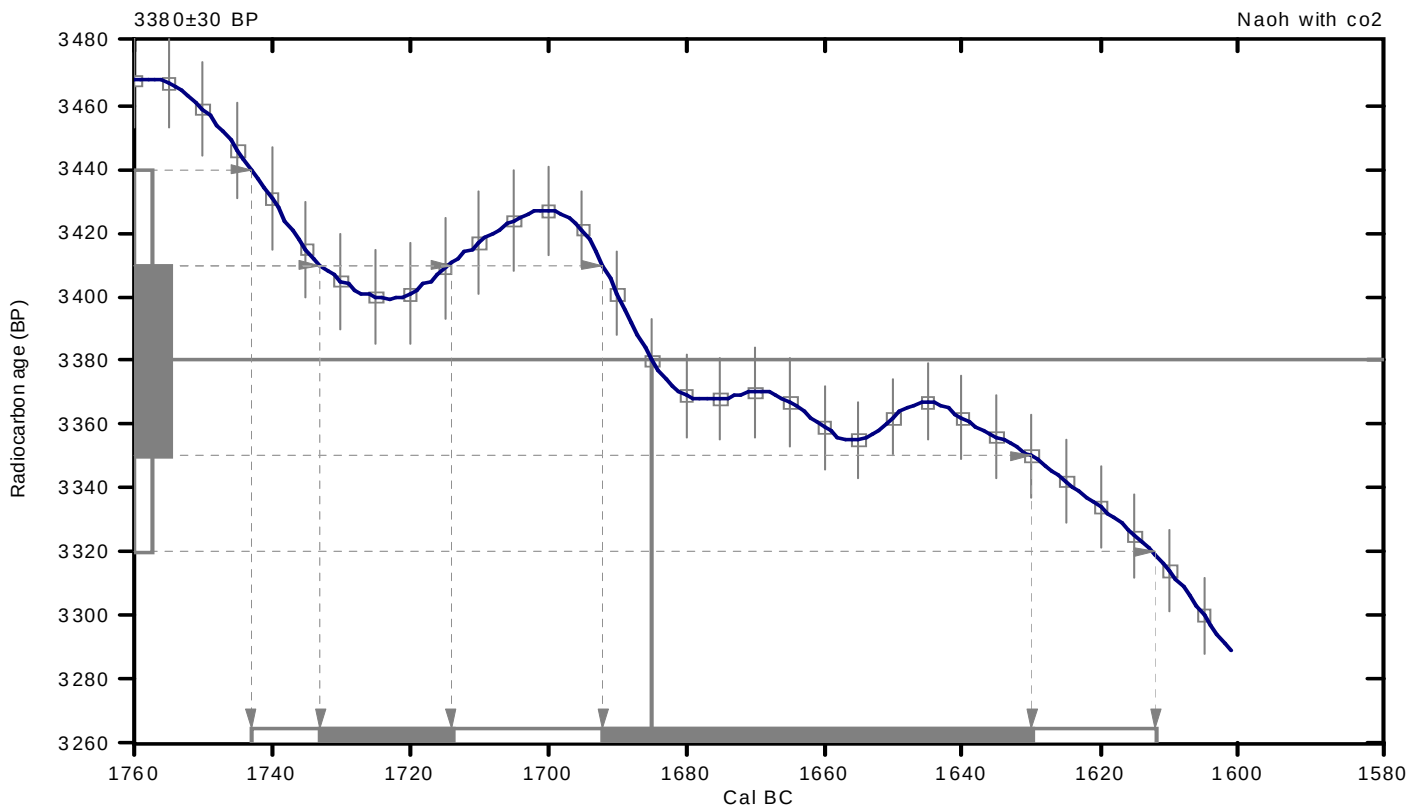
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-33.5:lab. mult=1)

Laboratory number:	**Beta-361740**
Conventional radiocarbon age:	**3380±30 BP**
2 Sigma calibrated result: (95% probability)	**Cal BC 1740 to 1610 (Cal BP 3690 to 3560)**

Intercept data

Intercept of radiocarbon age with calibration curve:	Cal BC 1680 (Cal BP 3640)
1 Sigma calibrated results: (68% probability)	Cal BC 1730 to 1710 (Cal BP 3680 to 3660) and Cal BC 1690 to 1630 (Cal BP 3640 to 3580)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

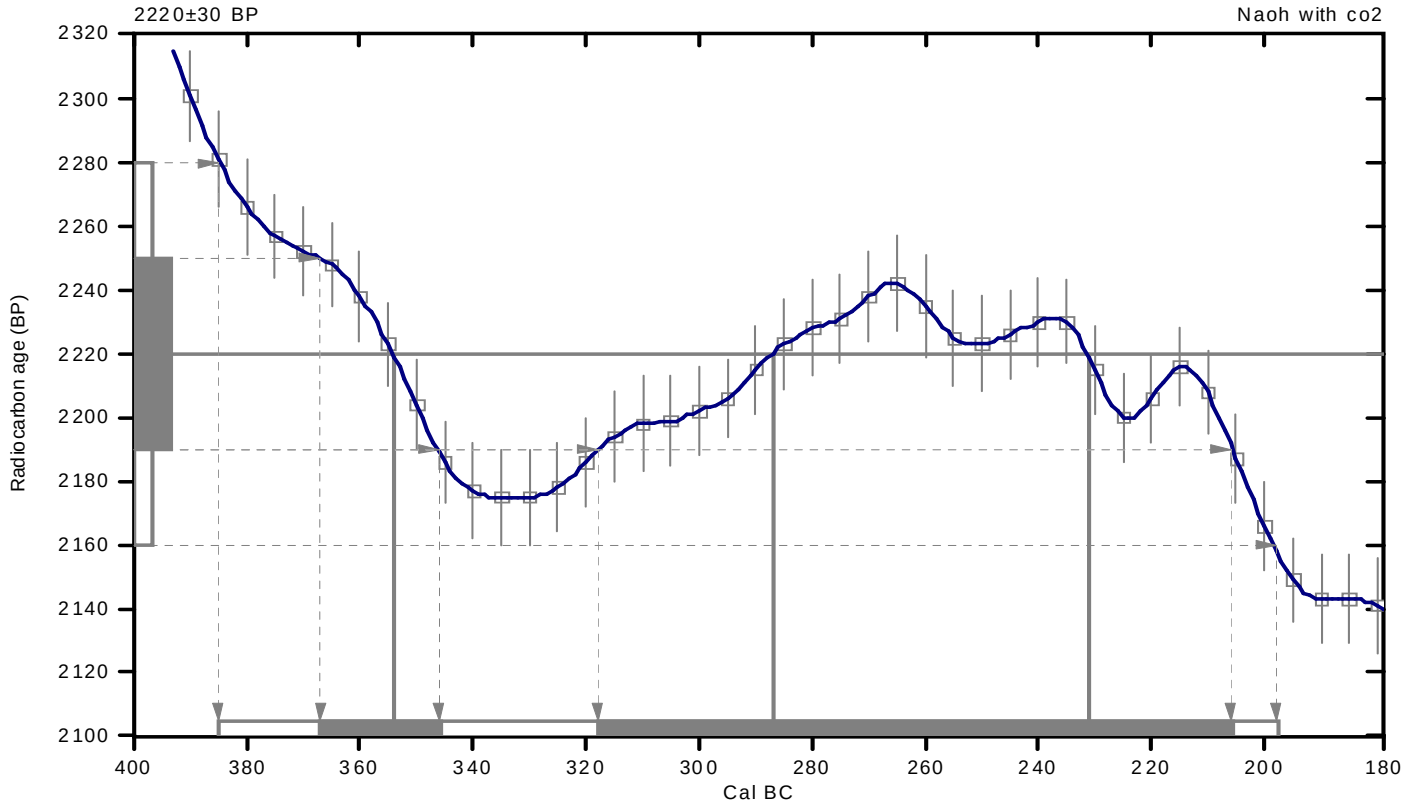
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-23.5:lab. mult=1)

Laboratory number:	**Beta-361741**
Conventional radiocarbon age:	**2220±30 BP**
2 Sigma calibrated result: (95% probability)	**Cal BC 380 to 200 (Cal BP 2340 to 2150)**

Intercept data

Intercepts of radiocarbon age with calibration curve:	Cal BC 350 (Cal BP 2300) and Cal BC 290 (Cal BP 2240) and Cal BC 230 (Cal BP 2180)
1 Sigma calibrated results: (68% probability)	Cal BC 370 to 350 (Cal BP 2320 to 2300) and Cal BC 320 to 210 (Cal BP 2270 to 2160)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com

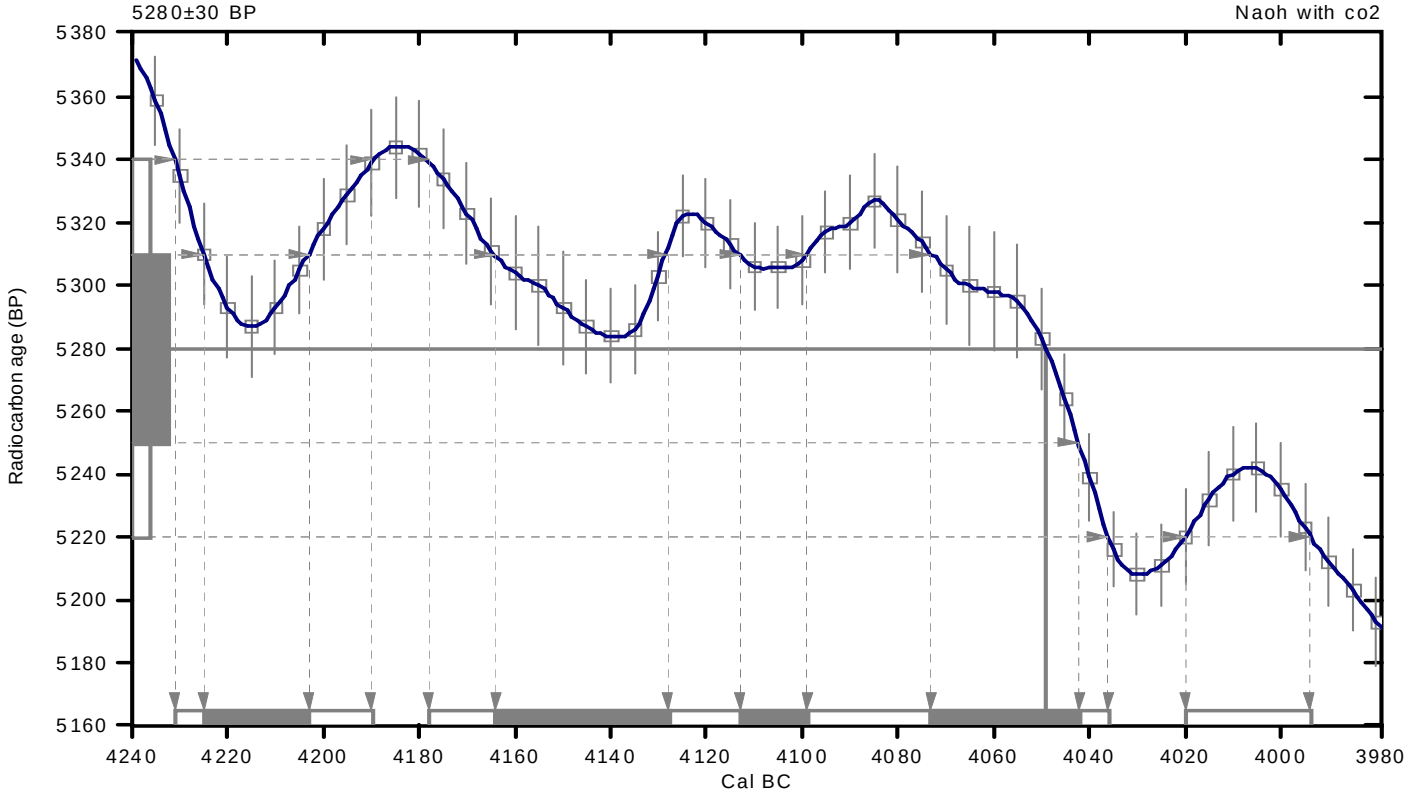
CALIBRATION OF RADIOCARBON AGE TO CALENDAR YEARS

(Variables: C13/C12=-32.4:lab. mult=1)

Laboratory number:	**Beta-361742**
Conventional radiocarbon age:	**5280±30 BP**
2 Sigma calibrated results: (95% probability)	**Cal BC 4230 to 4190 (Cal BP 6180 to 6140) and Cal BC 4180 to 4040 (Cal BP 6130 to 5990) and Cal BC 4020 to 3990 (Cal BP 5970 to 5940)**

Intercept data

Intercept of radiocarbon age with calibration curve:	Cal BC 4050 (Cal BP 6000)
1 Sigma calibrated results: (68% probability)	Cal BC 4220 to 4200 (Cal BP 6180 to 6150) and Cal BC 4160 to 4130 (Cal BP 6110 to 6080) and Cal BC 4110 to 4100 (Cal BP 6060 to 6050) and Cal BC 4070 to 4040 (Cal BP 6020 to 5990)



References:

Database used

INTCAL09

References to INTCAL09 database

Heaton,et.al.,2009, Radiocarbon 51(4):1151-1164, Reimer,et.al, 2009, Radiocarbon 51(4):1111-1150, Stuiver,et.al,1993, Radiocarbon 35(1):137-189, Oeschger,et.al.,1975,Tellus 27:168-192

Mathematics used for calibration scenario

A Simplified Approach to Calibrating C14 Dates
Talma, A. S., Vogel, J. C., 1993, Radiocarbon 35(2):317-322

Beta Analytic Radiocarbon Dating Laboratory

4985 S.W. 74th Court, Miami, Florida 33155 • Tel: (305)667-5167 • Fax: (305)663-0964 • E-Mail: beta@radiocarbon.com