MEMORANDUM

Project No.: 070041-004-13A

May 15, 2012

To: Amy Georgeson, Mason County Public Health
Susan Gulick, Sound Resolutions, for WRIA 16 Planning Unit

5/15/12

5-15-12

Erick William Miller
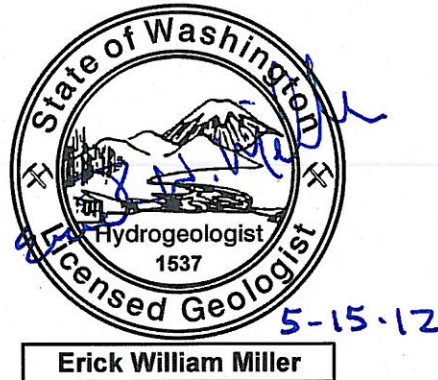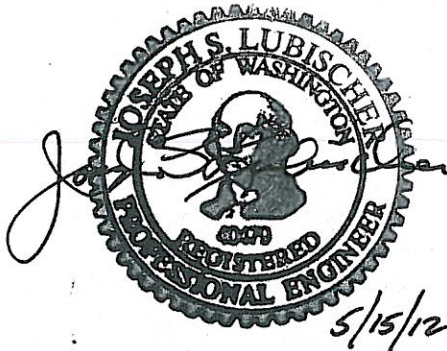
From: Joseph S. Lubischer, PE
Water Resources Engineer

Erick W. Miller, LHG
Senior Associate Hydrogeologist

Re: **Groundwater Age Dating, Webb Hill Biosolids Facility Hydrogeologic Investigation – Phase 2, Mason County, Washington**

Summary

This memorandum presents the results of groundwater age dating for monitoring wells at the Webb Hill Biosolids Facility in Mason County, Washington. Data from both Phase 1 and Phase 2 investigations are included herein. This memorandum is being issued separately and subsequent to the Phase 2 report (Aspect, 2008) due to the length of time required for performance of the analyses.

Aspect Consulting and USGS performed dating analyses of groundwater at the Webb Hill Site. The analytic methods employed and their applicable time ranges were:

- Carbon-14 (^{14}C)   [50,000 to 50 years before present];
- Chlorofluorocarbon (CFC)   [1950s to 1993];
- Tritium-helium ratio (^{3}H/^{3}He$_{tri}$)   [1955 to 2-3 years before present]; and
- Sulfur hexafluoride (SF$_6$)   [1972 to present].

The ^{14}C and CFC methods did not provide date estimates. In the case of ^{14}C, the groundwater was too young for the method to be applicable ($< \sim 50$ years). For the CFC analyses, concentrations in 78% of groundwater samples were at or above historic peak concentrations. The CFC values were unreasonably high and were interpreted to indicate probable bias from CFC compounds in biosolids applied at the site.

The $^3H/^3He_{tri}$ technique estimated apparent ages, or residence times, of *modern*[1] to 4 years for three samples procured during Phase 2 work. The SF_6 results from six samples gave uncorrected ages of 7 to 15 years. In future work, SF_6 ages should be improved by co-analysis of dissolved noble gases, calculation of excess air effect, and investigation to quantify loss of SF_6 (fractionation) in the unsaturated zone. The recharge temperatures used in calculations should be identified and varied to determine the sensitivity of age to recharge temperature for that method. Supplemental sampling for SF_6 within the unsaturated zone may be required for analysis of transport mechanisms (Hinkle et al., 2010).

Because age dating should rely on multiple lines of evidence, and the apparent age determined herein of *modern* to 4 years is based on a single method, we recommend additional age dating be performed to confirm these results (Hinkle et al., 2010; Healy and Scanlon, 2010).

The following sections in this memorandum present the sampling and analyses protocols, results from each of the four dating methods, and a concluding discussion.

Sampling Methods and Analysis

Work at Webb Hill occurred in two phases. During the Phase 1 investigation, dating samples were collected July 9 through 11, 2007, by USGS. Phase 2 samples were obtained from June 10 through 12, 2008, by Aspect Consulting. Phase 1 samples included wells MW-1, MW-2, MW-3, and MW-4, and the Phase 2 work sampled wells MW-5, MW-6, and MW-7.

Phase 1 sampling is reported in Attachment 1 (Barton, 2008). Phase 2 sampling procedures followed recommendations by the USGS Reston Chlorofluorocarbon Laboratory and by the University of Utah Dissolved and Noble Gas Laboratory (§2.2 and §A.3.3 in Aspect, 2008). Dedicated Nylon 6 discharge tubing was used to minimize absorption of CFC and SF_6 gases.

Phase 1 samples were submitted for dating analysis using tritium/helium-3 ($^3H/^3He$) and sulphur hexafluoride (SF_6) methods at Lamont-Doherty Earth Observatory (LDEO) and Reston Chlorofluorocarbon Laboratory (RCL), respectively. Phase 2 analytic methods included ^{14}C, $^3H/^3He$, CFCs, and SF_6. These analyses were performed by the University of Utah Dissolved and Noble Gas Laboratory (DNGL), except that SF_6 was analyzed by the USGS Reston Chlorofluorocarbon Laboratory (RCL).

The dating techniques used in this study must be evaluated with respect to the special conditions at the site. The uppermost portion of groundwater at the study site has two sources of recharge. The infiltrating water is a mixture of precipitation and irrigation, the latter being water in the spray-applied biosolids. The dating analyses used in this study assume that precipitation is the major component of recharge[2]. The isotopic and chemical signatures in precipitation can be estimated, whereas the water sources in the biosolids delivered to the site are of mixed origin and history. Therefore, the equilibrium concentrations of dissolved noble gases and potential tracers used for age dating may be skewed from concentrations expected from precipitation alone.

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[1] *Modern* is 2 to 3 years old (Rigby, 2009).
[2] Irrigation in 2006 was about 4 inches, which is 6% of the average annual precipitation of 65 inches.

Results of dating analyses are presented as *apparent age* in years. This terminology reflects several factors. First, the water itself is not being dated, but rather the period of transit, or *residence time*, since the water was last in equilibrium with the atmosphere. Second, the body of groundwater is typically a mixture of sources due to advection and diffusion processes that occur in the aquifer. Thus, the concept of a single age is not a realistic interpretation. Third, the dating methods rely on physical models to characterize the physical, chemical, and biological processes that affect transport, enrichment, loss, and/or degradation of a tracer in the groundwater. The age result is therefore dependent on the model selected and on the success of the model in duplicating natural processes at a particular site.

In general, multiple lines of evidence are preferred to estimate the most reasonable apparent age or residence time of a groundwater sample. Therefore, the Phase 2 study employed four different dating techniques, which are discussed below.

^{14}C Results

Only Phase 2 samples were analyzed for ^{14}C. The ^{14}C results (Beta Analytic, 2008; Attachment 3) are presented in Table 1 as dissolved inorganic carbon present as dissolved carbon dioxide and carbonate species in the water sample. Groundwater ages were too young for the ^{14}C analysis to resolve. Minimum age for ^{14}C dating is about 50 years and sampled groundwater from Webb Hill therefore has an apparent age less than 50 years.

CFC Results

Chlorofluorocarbon compounds CFC-11, CFC-12, and CFC-113 were analyzed in nine samples, three each from wells MW-5, MW-6, and MW-7. The laboratory worksheet is presented as Table 2, with results presented using recharge temperatures[3] obtained from the noble gas analysis (Table 3). In general, sample concentrations were unrealistically high.

Samples concentrations are compared to peak atmospheric concentrations in Table 2. Seven of nine samples had CFC concentrations higher than historic peaks for mid-northern latitudes (NOAA, 2012; USGS, 2006b). CFC-11 and CFC-113 concentrations peaked in the 1993 and 1994, respectively, and CFC-12 peaked in about 2002. The range of CFC-113 concentrations was from 105 to 158 parts per trillion (ppt), significantly above the peak atmospheric concentration of 85 ppt. For samples from well MW-7, concentrations of all three CFC compounds exceeded peak values by 42% to 87%. Only the CFC-11 concentrations at MW-5 and MW-6 gave apparent ages (20 years) that were older than "modern". However, those results were not relied upon given the high concentrations observed in the majority of samples. Due to the high concentrations, ratios of CFC compounds were not calculated and no additional adjustments[4] to the data were performed.

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[3] The recharge temperature was calculated by the University of Utah DNGL for a best fit with dissolved gases yielding the same value of excess air.
[4] Adjustments were made by DNGL for recharge temperature and recharge elevation. No adjustments were performed for excess air or depth of the unsaturated zone.

The CFC dating technique assumes that recharge is from precipitation in equilibrium with atmospheric concentrations of CFCs at the time of recharge. The observed enrichment of groundwater CFC concentrations at the study site to levels above atmospheric equilibrium concentrations is assumed to result from elevated concentrations of CFCs in the biosolids applied to the fields. Sewage effluent has been recognized as a source of CFC contamination (USGS, 2006b citing Schultz et al., 1976 and Busenberg & Plummer, 1992). Because of the potential for CFC contamination from biosolids to affect the analyses of CFC-11, CFC-12, and CFC-113, this method does not appear appropriate for the study site environment. However, future work may investigate use of CFC-13, which is currently used only for very low temperature refrigeration and is unlikely to be found in biosolids (USGS, 2007).

$^3H/^3He_{tri}$ Results

Atmospheric tritium (^3H) concentrations rose dramatically after atomic bomb testing began in the 1950s, but have since declined to near the estimated pre-bomb levels. Peak concentrations in North American precipitation at over 4000 tritium units[5] (TU) occurred in 1963 (DNGL, 2010; Solomon et al., 1992). In comparison, 1990's precipitation at Portland International Airport has been steady at about 4 TU (Hinkle, 2009; also see DNGL, 2010). Groundwater ^3H concentrations below about 0.5 to 1 TU are considered to indicate water recharged prior to bomb testing.

Tritium concentrations in samples from MW-5, MW-6, and MW-7 were low, about 2 TU, suggesting a recent recharge date. However, tritium alone is impractical for dating young groundwaters due to the similarity with pre-bomb values and also the small gradient in the time series since about 1980. Therefore, groundwater ages were calculated from the tritium/tritogenic helium-3 ratio ($^3H/^3He_{tri}$) (Solomon et al., 1992; USGS, 2006c). Tritogenic helium-3 ($^3He_{tri}$) is helium-3 generated by decay of tritium since the water became isolated from the atmosphere and is calculated from a helium isotope mass balance.

Apparent ages of the samples were calculated using two physical models by DGNL (Rigby, 2012). These models are the unfractionated air (UA) model and the partial re-equilibration (PR) model (Cey et al., 2008). The UA model assumes that gases in groundwater are fully dissolved, including from air entrained during recharge, and that no gas fractionation occurs during infiltration. That portion of gas dissolved from entrained air is referred to as *excess air* (EA)[6]. The partial re-equilibration (PR) model also assumes complete dissolution of entrapped air bubbles, but allows for subsequent diffusive degassing. Apparent ages determined from the UA model typically give the youngest dates, whereas the PR model provides the oldest ages (Cey et al., 2008).

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[5] One tritium unit (TU) is equal to one tritium atom per 10^{18} atoms of hydrogen.
[6] Although referred to as "air", "excess air" is elementally fractionated, i.e. heavy gases are enriched more than light gases (Cey, 2008).

Analytic results from the $^3H/^3He_{tri}$ analysis, including dissolved gas concentrations and calculations for recharge temperature and excess air, are presented in Table 3. Apparent age estimates from the UA and PR models are reported as "age using Ne" and "age using EA", respectively. Apparent ages reported by DNGL were *modern* for the UA model and *modern* to 4 years for the PR model, where *modern* indicates less than 2 to 3 years.

The wells at Webb Hill have large unsaturated zone thicknesses (Table 1) and, therefore, significant fractionation may be expected. Nonetheless, the differences in $^3H/^3He_{tri}$ apparent ages between the two physical models are small and the effect of fractionation is not measureable. Therefore, an apparent age of 4 years or less is indicated.

Phase 1 samples were reportedly submitted for $^3H/^3He_{tri}$ analysis (Barton, 2008), but results were not available for inclusion in Table 1.

SF$_6$ Results

Sulphur hexafluoride (SF$_6$) has been used as a tracer for groundwater age dating due to its atmospheric stability and steadily increasing atmospheric concentration. The SF$_6$ analysis is particularly useful for younger groundwater due to the steep increase in atmospheric SF$_6$ since about 1980. SF$_6$ production began in the 1960s and atmospheric concentrations in the northern hemisphere have risen from about 3 ppt in the early 1990s to about 7.7 ppt in 2012 (NOAA, 2012; USGS, 2006a).

Analytic results are summarized in Table 1 for Phase 1 and Phase 2 sampling. Neither the Phase 1 nor Phase 2 analyses included major or noble dissolved gas analysis or reported the groundwater recharge temperatures. No adjustments were made for either excess air or loss of SF$_6$ in the unsaturated zone.

The USGS report (Barton, 2008) for Phase 1 dating of MW-1, MW-2, MW-3, and MW-4 by SF$_6$ methodology is provided in Attachment 1. Uncorrected groundwater residence times, for three of four samples, were estimated to be "equivalent to atmospheric concentrations present in late 1990s to early 2000s". The sample from MW-3 yielded a very high SF$_6$ concentration and age for MW-3, which was interpreted to indicate sample contamination (Barton, 2008). The plotted data (Attachment 1) give uncorrected ages from about 7 to 14 years.

For Phase 2 samples MW-5, MW-6, and MW-7, the SF$_6$ analysis (Cox, 2009; Attachment 2) indicated uncorrected ages from the mid-1990s to 2000. Data give residence times from 8 to 15 years, similar to the range for Phase 1 samples.

Corrections of SF$_6$ ages for excess air and losses in the unsaturated zone are both necessary (Busenberg and Plummer, 2000; USGS, 2006a). The determination of major or noble dissolved gas data are integral to applying these corrections and interpreting the findings. The presence of a deep unsaturated zone, such as at Webb Hill, complicates interpretation of SF$_6$ data and supplemental sampling for SF$_6$ within the unsaturated zone may be required for analysis of transport mechanisms at such sites (Hinkle et al., 2010).

Effects of Corrections to SF_6 Data

Excess air, loss of SF_6 in the unsaturated zone, and natural terrestrial sources of SF_6 are among factors that can bias uncorrected SF_6 ages. Although the Webb Hill SF_6 data were not corrected, some comments can be made regarding the effects of corrections.

The basic physical processes indicate that the presence of excess air will bias an uncorrected age too young, whereas the loss of SF_6 during infiltration through the unsaturated zone will bias age too old (Busenberg and Plummer, 2000). In some areas, concentrations of SF_6 in groundwater have been found to be elevated above atmospheric equilibrium concentrations and were interpreted to be due to enrichment by natural sources[7].

Excess air adjustments were made to SF_6 dates for a set of 23 wells in the Puget Sound region (Hinkle et al., 2010). By comparing data plotted with and without an excess air correction[8] (Figures G25 and G27 in Hinkle et al., 2010), the excess air correction is inferred to be about +3 years. This value may also to be compared to an estimate of +1 to +2.5 years for excess air of 0.001 ccSTP/gr and waters recharged after 1990 (Busenberg and Plummer, 2000).

In the unsaturated zone, dissolved SF_6 is subject to loss via diffusive degassing to interstitial air. The interstitial air is assumed to be older than atmospheric air and would therefore have a lower SF_6 concentration, resulting in loss of SF_6 from infiltrating water to interstitial air. Corrections for loss of SF_6 in unsaturated zone are recommended due to the low solubility of SF_6 in water (USGS, 2006a).

In the Puget Sound study, a comparison of the SF_6 data with $^3H/^3He$ data (Figure G26 in Hinkle et al., 2010) indicated that the SF_6 data was biased about -7 years at the water table, after correction for excess air. That is, SF_6 dates, already increased for excess air (+3 years), would need an additional and opposite adjustment of about 7 years younger (net of -4 years). The authors suggest that the additional -7 years bias is due to loss of SF_6 during recharge (Hinkle et al., 2010).

The unsaturated zone thicknesses of the Puget Sound wells ranged from 6 to 76 feet with a mean of 18 feet. These thicknesses were smaller than those at Webb Hill (87 to 173 feet bgs). Losses of SF_6 to interstitial air are expected to increase with increasing unsaturated zone thickness (Busenberg and Plummer, 2000).

Discussion and Conclusions

The ^{14}C analysis was not applicable for dating the relatively young age of the groundwater samples. The CFC analytic method was not appropriate due to the assumed enrichment of recharging water to above atmospheric equilibrium values by additional CFCs present in biosolids sprayed on the fields. The $^3H/^3He_{tri}$ and SF_6 dating techniques did provide useful information for the Webb Hill study site.

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[7] Elevated SF_6 concentrations in groundwater were observed to be associated with the presence of silica rich igneous rocks in crystalline bedrock and in rhyolitic volcanic rock with high groundwater temperatures (Busenberg and Plummer, 2000).
[8] The excess air correction was determined using the unfractionated air (UA) model (Hinkle et al., 2010).

The ^{3}H/^{3}He$_{tri}$ technique indicated apparent ages, or residence times, of groundwater from *modern* to 4 years. The SF$_6$ methodology indicated uncorrected ages of 7 to 15 years, but adjustments for excess air and unsaturated zone effects were not made. These adjustments appear warranted. The ^{3}H/^{3}He$_{tri}$ data indicate an apparent groundwater age of 4 years or less.

In future work, SF$_6$ ages should be improved by co-analysis of dissolved noble gases, calculation of excess air effect, and investigation to quantify loss of SF$_6$ (fractionation) in the unsaturated zone. The recharge temperatures used in calculations should be identified and varied to determine the sensitivity of age to recharge temperature for that method.

In addition, use of two other tracers applicable for dating modern groundwater should be investigated. These compounds are SF$_5$CF$_3$, which has a dating range of 1975 to present, and CFC-13, which is applicable from 1965 to present. Both tracers have increasing atmospheric inputs, lack terrigenic sources, and are believed stable under reducing groundwater conditions. CFC-13 has been used primarily in very low temperature refrigeration, so is unlikely to be influenced by non-atmospheric sources. (USGS, 2007)

Because age dating should rely on multiple lines of evidence, and the apparent age determined herein of *modern* to 4 years is based on a single method, we recommend additional age dating be performed to confirm these results (Hinkle et al., 2010; Healy and Scanlon, 2010).

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Attachments

Table 1 – Age Dating Summary
Table 2 –CFC Analyses
Table 3 – Tritium/Helium-3 and Dissolved Gas Analyses
Attachment 1 – Barton (2008)
Attachment 2 – Cox (2009)
Attachment 3 – Beta Analytic Inc. (2008)

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Table 1 - Age Dating Summary

Webb Hill Hydrogeologic Investigation - Phase 2
Mason County, Washington

Well ID	Installation Date	Sample Date	Sampler	^{14}C (AMS)			CFC-11, CFC-12, & CFC-113		^{3}H/^{3}He$_{tri}$			SF$_{6}$			Top of Screen Elevation	Bottom of Screen Elevation	Ground Surface Elevation	Approximate Unsaturated Zone Thickness [5]	Screen Interval Depth
				percent modern carbon [1]	apparent age years	laboratory	apparent age years	laboratory	^{3}H TU	apparent age [2] years	laboratory	equivalent air concentration (pptv)	uncorrected age [3] years	laboratory	feet [4]	feet [4]	feet [4]	feet	feet bgs
MW-1	4/26/07	7/9/07	USGS	-	-	-	-	-			LDEO	4.4	8.9	RCL	297.51	278.01	402.51	113	105.0 to 124.5
MW-2	5/3/07	7/11/07	USGS	-	-	-	-	-		Note 7.	LDEO	4.7	7.4	RCL	300.07	275.57	443.97	155	143.9 to 168.4
MW-3	4/24/07	7/11/07	USGS	-	-	-	-	-			LDEO	18.8	Note 8.	RCL	305.34	280.84	465.84	173	160.5 to 185.0
MW-4	4/30/07	7/11/07	USGS	-	-	-	-	-			LDEO	3.1	13.6	RCL	303.09	278.59	375.99	87	72.9 to 97.4
MW-5	12/4/07	6/10/08	Aspect	107.1	< ~50 yrs	Beta Analytic		DNGL	2.40	**modern**	DNGL	3.0	15.3	RCL	270.84	250.84	411.54	145	140.7 to 160.7
MW-6	5/28/08	6/12/08	Aspect	109.7	< ~50 yrs	Beta Analytic	Note 6.	DNGL	2.24	**modern**	DNGL	3.2	14.4	RCL	277.26	252.66	397.46	116	120.2 to 144.8
MW-7	5/30/08	6/11/08	Aspect	112.1	< ~50 yrs	Beta Analytic		DNGL	1.99	**3.9**	DNGL	4.8	7.6	RCL	273.15	248.55	418.55	141	145.4 to 170.0
Applicable Range of Dating Technique				50,000 to 50 yr before present			1950s to 1993		1955 to ~2-3 yrs before present			1972 to present							

Notes

1. Samples contained more carbon than the modern reference standard and are reported as "percent modern carbon" (pmC) with laboratory accuracy of ± 0.5%.
2. Age calculated using excess air and partial re-equilibration (PR) model. Results for UA model were "modern" for all samples (Table 3).
3. The uncorrected ages have not been adjusted for excess air or for loss of SF$_6$ in the vadose zone.
4. Elevations are NAVD88 (1996) using U.S. feet.
5. Vadose zone thicknesses based on average water levels from 5/23/07 through 6/12/08. Only one water level was available for MW-6 and MW-7. The seasonal variation during that period was about 16 feet.
6. Sample concentrations assumed to be elevated by biosolids. See text.
7. Samples were reportedly analyzed (Barton, 2008), but data were not available.
8. Sample interpreted to be contaminated (Barton, 2008).

Abbreviations

AMS = accelerator mass spectrometer
bgs = below ground surface
^{14}C = carbon-14 isotope
DNGL = Dissolved and Noble Gas Laboratory, University of Utah
^{3}He$_{tri}$ = ^{3}He* = tritogenic helium-3
LDEO = Lamont Dougherty Earth Observatory
pmC = percent modern carbon
ppt = parts per trillion
RCL = Reston Chlorofluorocarbon Laboratory, USGS
SF$_6$ = sulphur hexafluoride
TU = tritium unit (1 ^{3}H atom per 10^{18} atoms of H)
btoc = below top of casing
NA = not applicable

Aspect Consulting, LLC
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Table 1
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Table 2 - CFC Analyses [1]

Webb Hill Hydrogeologic Investigation - Phase 2
Mason County, Washington

SAMPLE ID	CFC-11 (pmoles/kg)	CFC-12 (pmoles/kg)	CFC-113 (pmoles/kg)	Salinity (‰)	Recharge Elev. (m)	Recharge Temp (C) [2]	Pwater	Elev. correction	KRT_11	KRT_12	KRT_113	eq. air conc_11 (ppt)	eq. air conc_12 (ppt)	eq. air conc_113 (ppt)	CFC-11 Recharge Year	CFC-12 Recharge Year	CFC-113 Recharge Year	Comparison with Historic Peak Concentration		
Calculation using calculated recharge temperature.																				
MW-5-1	4.12479707	2.44793067	0.52676669	0	125.47	14.1	0.01586	0.969351	0.01703	0.00452	0.00515	249.8054	558.1008	105.5367	1987.5	Modern	Modern	91%	102%	124%
MW-5-2	4.33423151	2.68913056	0.62621788	0	125.47	14.1	0.01586	0.969351	0.01703	0.00452	0.00515	262.4891	613.0917	125.4615	1989	Modern	Modern	96%	112%	148%
MW-5-3	4.27822445	2.60194174	0.64185915	0	125.47	14.1	0.01586	0.969351	0.01703	0.00452	0.00515	259.0972	593.2136	128.5952	1988.5	Modern	Modern	95%	109%	151%
MW-6-1	4.67148919	2.71466044	0.61558266	0	121.17	12.3	0.01410	0.971614	0.01868	0.00491	0.00570	257.3419	568.5945	111.1229	1988.5	Modern	Modern	94%	104%	131%
MW-6-2	4.72777952	2.75540577	0.62614802	0	121.17	12.3	0.01410	0.971614	0.01868	0.00491	0.00570	260.4428	577.1287	113.0302	1989	Modern	Modern	95%	106%	133%
MW-6-3	4.66685017	2.60118084	0.58609494	0	121.17	12.3	0.01410	0.971614	0.01868	0.00491	0.00570	257.0864	544.8258	105.7999	1988.5	2007.5	Modern	94%	100%	124%
MW-7-1	6.07144442	3.57451764	0.62850368	0	127.61	15.6	0.01747	0.967489	0.01581	0.00423	0.00474	396.866	872.5691	136.9811	Modern	Modern	Modern	145%	160%	161%
MW-7-2	5.94384451	3.40218700	0.72870099	0	127.61	15.6	0.01747	0.967489	0.01581	0.00423	0.00474	388.5253	830.5018	158.8189	Modern	Modern	Modern	142%	152%	187%
MW-7-3	5.99817279	3.26726265	0.52335597	0	127.61	15.6	0.01747	0.967489	0.01581	0.00423	0.00474	392.0765	797.5657	114.0644	Modern	Modern	Modern	143%	146%	134%

Approximate historic peak value	*274*	*545*	*85*
Approximate year	*1993*	*2002*	*1994*
Source	*NOAA, 2012 & USGS, 2006b*		

CFC-11 CFC-12 CFC-113

Notes
1. Laboratory analysis provided by University of Utah Dissolved Noble Gas Laboratory, except for comparison with historic peak concentrations.
2. Recharge temperatures (noble gas temperature, NGT) determined from noble gas analyses by DNGL (Table 3).

Aspect Consulting, LLC
5/15/2012
W:\070041 WRIA 16 - Webb Hill\Deliverables\Memo GW Age Dating\Aspect CFC Results.xls

Table 2
Page 1 of 1

Table 3 - Tritium/Helium-3 and Dissolved Gas Analyses [1]

Webb Hill Hydrogeologic Investigation - Phase 2
Mason County, Washington

Sample ID	RunID	N2 (ccSTP/g)	Ar40 (ccSTP/g)	Kr84 (ccSTP/g)	Xe129 (ccSTP/g)	Ne20 (ccSTP/g)	He4 (ccSTP/g)	R/R$_a$	Tritium (TU)	Age [2] using Ne (yr)	Age [3] using EA (yr)	Recharge Temp [4] (C)	Excess Air (ccSTP/g)	ΔNe [5] (%)	Recharge Elev (m)	Well Temp (C)	Tot Dis Gas (atm)	Assumed R$_{terr}$
MW-5	07010804	1.59E-02	4.28E-04	5.12E-08	3.39E-09	2.19E-07	5.47E-08	0.99	2.40	Modern	**Modern**	14.1	0.115	14%	125.47	10.20	1.107	2.8E-08
MW-6	07010805	1.97E-02	4.69E-04	5.34E-08	3.56E-09	2.91E-07	7.46E-08	1.00	2.24	Modern	**Modern**	12.3	0.024	49%	121.17	9.80	1.311	2.8E-08
MW-7	07010806	1.35E-02	4.93E-04	5.87E-08	4.04E-09	2.80E-07	7.51E-08	0.99	1.99	Modern	**3.9**	15.6	0.108	48%	127.61	10.10	0.920	2.8E-08

Notes

1. Data provided by University of Utah Dissolved and Noble Gas Laboratory, except for excess air calculated as % ΔNe.
2. Uses unfractionated air (UA) model.
3. Uses partial re-equilibration model (PR) model.
4. Recharge temperature calculated from excess air.
5. Excess air calculated using the partial re-equilibration model.
6. Excess air reported as ΔNe (%). Equilibrium Ne concentrations in water calculated following Healy (2012).

Abbreviations

atm = atmosphere
C = degrees Centigrade
ccSTP/g = cubic centimeters at standard temperature and pressure per gram water
EA = excess air
m = meters
R = ^{3}He/^{4}He ratio
R$_a$ = R$_{atm}$ = atmospheric standard for ^{3}He/^{4}He ratio
R$_{terr}$ = radiogenic ^{3}He/^{4}He ratio
yr = year

Aspect Consulting, LLC
4/12/2010
W:\070041 WRIA 16 - Webb Hill\Deliverables\Memo GW Age Dating\Aspect Summary (10-13-08) Noble Gases.xls

Table 3
Page 1 of 1

Attachment 1

Barton (2008)

United States Department of the Interior

U.S. Geological Survey

USGS Washington Water Science Center
934 Broadway, Suite 300
Tacoma, Washington 98402
(253) 552-1600 . FAX (253) 552-1581
http://wa.water.usgs.gov/

June 26, 2008

Ms. Pam Bennett-Cumming
Mason County Department of Community Development
Senior Planner - Water Resource Planning
411 North 5th
P.O. Box 279
Shelton, Washington 98584

Dear Ms. Bennett-Cumming:

Attached are results of the laboratory analyses of archived water-quality samples collected by the U.S. Geological Survey (USGS) from four Webb Hill monitoring wells (MW-1, MW-2, MW-3 and MW-4) in July 2007. The USGS unique site identification numbers for these wells are 4718281223063501, 471831123070001, 471845123063701, and 471815123061801, respectively. Sample results are stored in and can be retrieved from our National Water Quality Database (http://waterdata.usgs.gov/nwis) using these site identification numbers. For future reference, please refer to these numbers.

The samples were analyzed for selected constituents that have been identified by the USGS National Research Program as useful tracers of recently recharged ground water. These types of data, in particular the sulfur hexafluoride data, may provide information useful to Mason County in its ongoing hydrologic investigation of the Webb Hill Biosolids disposal facility and nutrient issues in Hood Canal. General discussions of the use of environmental tracers for dating recently recharged ground water are summarized by Plummer and others, 1993.

Samples were collected to analyze for three suites of environmental tracers, including sulfur-hexafluoride, tritium-helium, and waste-water treatment compounds. Sulfur-hexafluoride (SF_6) is present in the atmosphere primarily as a result of anthropogenic origin. The atmospheric concentration of SF_6 has increased from a steady-state value of about 0.05 parts per trillion to more than 4 parts per trillion during the past 40 years. The date of ground-water recharge can be estimated from SF_6 concentrations if it is in equilibrium with atmospheric SF_6 at the time of recharge. Methods describing the sulfur hexafluoride technique and its limitations can be found in E. Busenberg and L.N. Plummer, 2000.

Results from three of the four sulfur hexafluoride (SF_6) samples provided good estimates of the year of ground-water recharge. The SF_6 measurements results are reported using a NOAA scale as mass concentrations (FMoles/kg) but have been converted to equivalent concentrations as partial volume (pptv) for comparison to regularly monitored atmospheric SF_6 concentrations. On the attached figure, the results of the analysis of MW1, MW2, and MW4 are plotted on the curve of SF_6 concentrations in air. Their location on the curve indicates that these samples contained SF_6 concentrations equivalent to atmospheric concentrations present in late 1990's to early 2000's. Refinements to the estimates of recharge date could be made if additional information was available on the temperature of ground water at the point of recharge and measurements to determine if excess air was incorporated during the recharge process. The very large concentrations of SF_6 in the sample from MW-3 indicate that the sample was contaminated, which will result in inaccurate estimates of the recharge.

Large tritium (^{3}H) inputs to ground water occurred in a series of spikes resulting from atmospheric testing of nuclear devices occurring from 1952 to 1963. Concentrations of ^{3}H in precipitation have decreased since the mid-1960's bomb peak and provide limited information on recharge related to the period of nuclear testing. Measurements of tritium (^{3}H) and its decay product, tritiogenic helium (^{3}He), provide a ^{3}H/^{3}He ratio which can be used to calculate the ^{3}H/^{3}He apparent age of ground water from a single water sample (Schlosser and others, 1988, 1989; Poreda and others, 1988; Solomon and others, 1992, 1993).

The process for the analysis of ^{3}H/^{3}He ratios is lengthy, because the accumulation of daughter products requires several months to generate measureable quantities when the initial concentrations of ^{3}H are small. The analytical laboratory at Lamont-Doherty Earth Observatory has been experiencing difficulties with the specialized mass-spectrophotometer that is used for this analysis and thus has delayed the analysis of the ^{3}H/^{3}He data. Once these data are released from the laboratory, they will be provided to you.

The analysis of waste-water compounds in samples from three wells (MW1, MW3, and MW4) resulted in few detections and thus did not provide substantial useful data when applied to ground-water samples from this site. The waste-water analytical suite focuses on compounds typically found in domestic and industrial wastewater. The suite analyzes for 61 compounds that include the alkylphenol ethoxylate nonionic surfactants and their degradates, food additives, fragrances, antioxidants, flame retardants, plasticizers, industrial solvents, disinfectants, fecal sterols, polycyclicaromatic hydrocarbons, and high-use domestic pesticides. Data from these samples are in the attached table.

If you have any questions, please don't hesitate to call Steve Cox of this office at 253-552-1623.

<div style="text-align:center">

Sincerely yours,

//s//

Cynthia Barton, Ph.D., L.G., L.H.G.
Director

</div>

References

E. Busenberg and L. N. Plummer. Dating young ground water with sulfur hexafluoride: Natural and anthropogenic sources of sulfur hexafluoride. Water Resources Research, v. 36, p. 3011-3030, October, 2000.

Plummer, L.N., Michel, R.L., Thurman, E.M., and Glynn, P.D., 1993, Environmental tracers for age-dating young ground water: in Alley, W.M., ed., Regional Ground-water Quality, Chap. 11, Van Nostrand Reinhold, New York, p. 255-294.

Poreda, R.J., Cerling, T.E., and Solomon, D.K., 1988, Tritium and helium isotopes as hydrologic tracers in a shallow unconfined aquifer: Journal of Hydrology, v. 103, p. 1-9.

Schlosser P., Stute, M., Dorr, H., Sonntag, C., and Munnich, K.O., 1988, Tritium/^{3}He dating of shallow groundwater: Earth and Planetary Science Letters, v. 89, p. 353-362.

Schlosser P., Stute, M., Sonntag, C., and Munnich, K.O., 1989, Tritiogenic ^{3}He in shallow groundwater: Earth and Planetary Science Letters, v. 94, p. 245-256.

Solomon, D.K., Poreda, R.J., Schiff, S.L., and Cherry, J.A., 1992, Tritium and Helium 3 as groundwater age tracers in the Borden Aquifer: Water Resources Research, v. 28, no. 3, p. 741-755.

Solomon, D.K., and Sudicky, E.A., 1992, Correction to "Tritium and helium 3 isotope ratios for direct estimation of spatial variations in groundwater recharge": Water Resources Research, v. 28, no. 4, p. 1197.

Results of SF6 analyses in ground-water samples from monitoring wells collected by the USGS in July 2007, at Webb Hill Biosolids Facility, Mason County, WA

Sample Name	Sampling Date (Mo/day/year)	Time	NOAA Scale fMol/L	Calculated SF6 (pptv)
MW-1	07/09/07	1410	1.8040	4.4779
MW-1	07/09/07	1410	1.7104	4.2456
MW-2	07/11/07	1200	1.5844	3.9388
MW-2	07/11/07	1200	2.2187	5.5156
MW-3	07/11/07	1300	10.4911	26.1021
MW-3	07/11/07	1300	4.6028	11.4518
MW-4	07/11/07	930	1.2576	3.1185
MW-4	07/11/07	930	1.2270	3.0427
Tap water	01/28/08		4.7782	15.0989
Tap water	01/28/08		4.7652	15.0579

Sulfur hexafluoride in ground water samples from Webb Hill monitoring wells
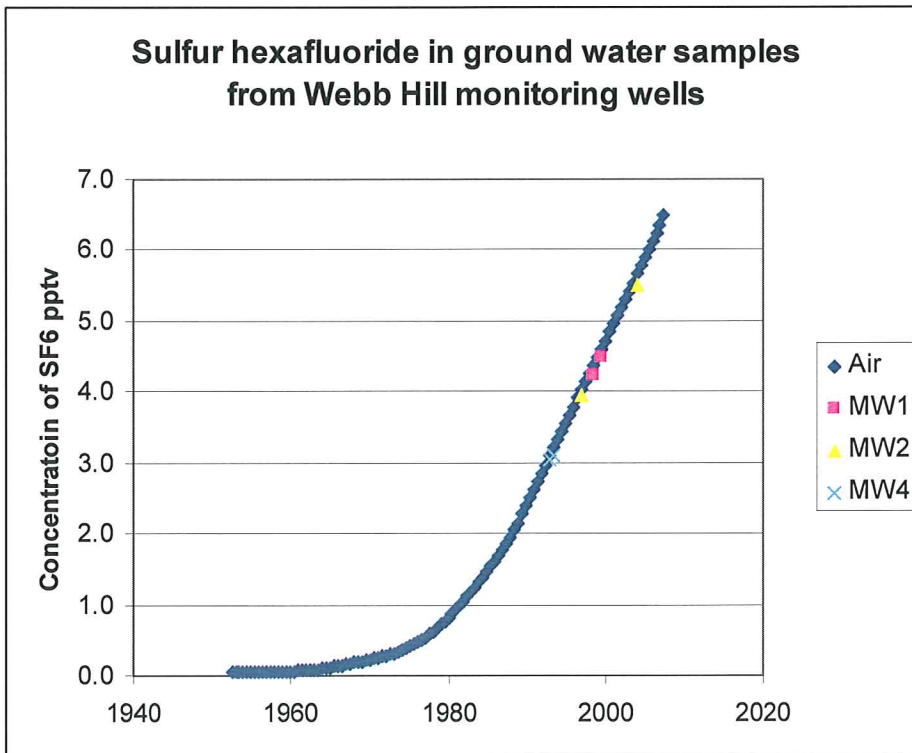
Concentrations of waste water treatment compounds in ground-water samples from monitoring wells collected by the USGS in July 2007, at Webb Hill Biosolids Facility, Mason County, WA

[Abbreviations: ug/L, micrograms per liter; E, estimated value, concentration is less than the detection limit; M, presence verified but not quanitifed; <, actual value is less than value shown]

	USGS Site ID, Well number, and date sampled		
	471828123063501	471845123063701	471815123061801
	MW-1	MW-3	MW-4
	7/10/07 2:10 PM	7/11/07 1:00 PM	7/11/07 9:30 AM
Analyte	(ug/L)	(ug/L)	(ug/L)
1,4-Dichlorobenzene	<.1	<.5	<.1
1-Methylnaphthalene	<.1	<.6	<.1
2,6-Dimethylnaphthalene	<.2	<1.2	<.2
2-Methylnaphthalene	<.1	<.5	<.1
3-beta-Coprostanol	<2	<10	<2
3-Methyl-1H-indole	<.08	<.48	<.08
3-tert-Butyl-4-hydroxyanisole	<.6	<4	<.6
4-Cumylphenol	<.14	<.84	<.14
4-Nonylphenol	<2	<11	<2
4-Octylphenol	<.16	<.96	<.16
4-tert-Octylphenol	<.10	<.6	<.10
5-Methyl-1H-benzotriazole	<2	<11	<2
9,10-Anthraquinone	<.2	<1.0	<.2
Acetophenone	<.1	<.6	<.1
Acetyl hexamethyl tetrahydro naphthalene	<.5	<3.0	<.5
Anthracene	<.1	<.5	<.1
Benzo[a]pyrene	<.1	<.7	<.1
Benzophenone	<.2	<1.1	<.2
beta-Sitosterol	<2	<12	<2
beta-Stigmastanol	<2	<12	<2
Bromacil	<.4	<2.4	<.4
Caffeine	<.2	<1.2	<.2
Camphor	<.1	<.6	<.1
Carbaryl	<1	<6	<1
Carbazole	<.1	<.5	<.1
Chlorpyrifos	<.2	<1.2	<.2
Cholesterol	<1	<8	<1
Cotinine	<.400	<2.40	<.400
p-Cresol	<.18	M	<.18
DEET	M	<1.2	<.2
Diazinon	<.2	<1.0	<.2
Diethoxynonylphenol	<5	<30	<5
Diethoxyoctylphenol	<1	<6	<1
D-Limonener	<.1	<.8	<.1
Fluoranthene	<.1	<.5	<.1
Hexahydrohexamethyl cyclopentabenzopyran	<.5	<3.0	<.5

Indole	<.1	<.8	<.1
Isoborneol	<.1	<.4	<.1
Isophorone	<.1	<.8	<.1
Isopropylbenzene	<.1	<.6	<.1
Isoquinoline	<.4	<2.4	<.4
Menthol	<.2	<1.2	<.2
Metalaxyl	<.2	<1.2	<.2
Methyl salicylate	<.2	<1.1	<.2
Metolachlor	<.2	<1.0	<.2
Monoethoxyoctylphenol	<1	<6	<1
Naphthalene	<.1	<.6	<.1
Phenanthrene	<.1	<.5	<.1
Phenol	<.4	**E.3**	**7.2**
Prometon	<.4	<2.4	<.4
Pyrene	<.1	<.5	<.1
Tetrachloroethene	<.2	<1.1	<.2
Tribromomethane	<.1	<.5	<.1
Tributyl phosphate	<.2	<1.2	**E1.8**
Triclosan	<.2	<1	<.2
Triethyl citrate	<.4	<2.4	<.4
Triphenyl phosphate	<.2	<1.0	**0.4**
Tris(2-butoxyethyl) phosphate	<.5	<3.0	<.5
Tris(2-chloroethyl) phosphate	**M**	<1.1	<.2
Tris(dichloroisopropyl) phosphate	<.2	<1.1	<.2

Attachment 2

Cox (2009)

Joseph Lubischer

From:	Stephen E Cox [secox@usgs.gov]
Sent:	Monday, June 29, 2009 4:38 PM
To:	Joseph Lubischer; Pam Bennett-Cumming
Cc:	Gary L Turney
Subject:	SF6 results MW5, MW6, & MW7

Joe and Pam,
Unpublished results from the analysis of sulfur hexafluoride (SF_6) samples from three wells (MW5, MW6, & MW7) located near Webbb Hill that were sampled by Aspect Consulting in June 2008 are similar to results of the samples from similar wells collected by USGS during the previous summer. As before, SF_6 measurements results are reported as mass concentrations (FemtoMoles/kg) and have been converted to the equivalent concentration as partial volume (pptv) for comparison to regularly monitored atmospheric SF_6 concentrations. On the attached plot, the results of the analysis of MW5, MW6, and MW7 have been plotted on the curve of SF_6 concentrations in air indicating that these samples contained SF_6 concentrations equivalent to equilibrium with atmospheric concentration occurring in the mid 1990s to 2000 with corresponding groundwater residence times of 7 to 15 years. These results are similar in range to the results reported for MW1, MW2, and MW4 that were sampled in 2007.

7/30/2009
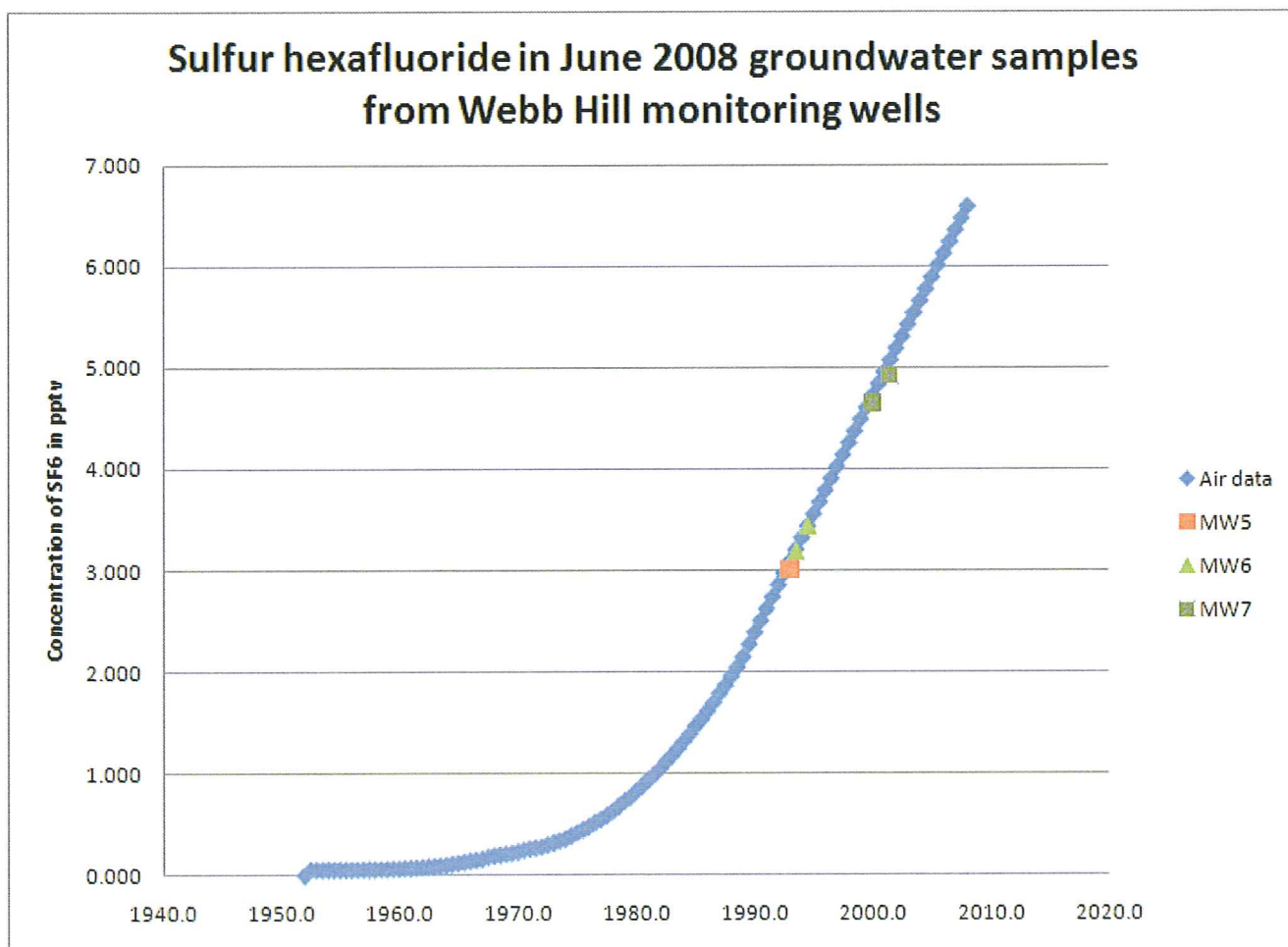
Attachment 3

Beta Analytic Inc. (2008)

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4985 SW 74 Court
Miami, Florida 33155 USA
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Fax: 305 663 0964
beta@radiocarbon.com
www.radiocarbon.com

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BY:
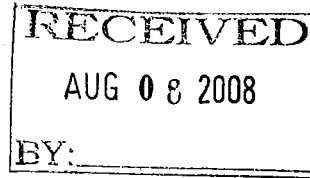
MR. DARDEN HOOD
Director

Mr. Ronald Hatfield
Mr. Christopher Patrick
Deputy Directors

July 17, 2008

Mr. Joe Lubischer
Aspect Consulting
179 Madrone Lane N.
Bainbridge Island, WA 98110
USA

RE: Radiocarbon Dating Results For Samples MW5 WebbHill, MW6 WebbHill, MW7 WebbHill

Dear Mr. Lubischer:

Enclosed are the radiocarbon dating results for three samples recently sent to us. They each provided plenty of carbon for accurate measurements and all the analyses went normally. The analyses was performed on the DIC within the submitted waters. Results are reported both as fraction of modern (Fmdn) and as the Apparent Radiocarbon Age. The report sheet also includes the method used, material type, and applied pretreatments.

The reported Apparent Radiocarbon Ages have not been corrected for any effects. They do not necessarily represent the residence time of the water within the aquifer. That would have to be derived by incorporating the radiocarbon dating result into models which take hydrologic conditions into account. The Apparent Radiocarbon Age is used as a relational tool, of understandable units to the layman, to interpret hydrologic differences between wells and to monitor temporal changes. For example, if semi-annual measurements on the same well provided consecutively decreasing apparent ages, it may indicate over-pumping or eminent surface water uptake.

We analyzed these samples on a sole priority basis. No students or intern researchers who would necessarily be distracted with other obligations and priorities were used in the analysis. We analyzed them with the combined attention of our entire professional staff.

Information pages are also enclosed with the mailed copy of this report. If you have any specific questions about the analysis, please do not hesitate to contact us. Someone is always available to answer your questions.

Thank you for prepaying the analyses. As always, if you have any questions or would like to discuss the results, don't hesitate to contact me.

Sincerely,

Darden Hood

REPORT OF RADIOCARBON DATING ANALYSES

Mr. Joe Lubischer

Report Date: 7/17/2008

Aspect Consulting

Material Received: 6/18/2008

Sample Data	Apparent C14 Age (fraction modern)	C13/C12 Ratio
Beta - 245608	107.1 +/- 0.5 pMC (Fmdn 1.0710 +/- 0.0050)	-20.0 o/oo

SAMPLE : MW5 WebbHill
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (water DIC): carbonate precipitation

Beta - 245609	109.7 +/- 0.5 pMC (Fmdn 1.0970 +/- 0.0050)	-20.4 o/oo

SAMPLE : MW6 WebbHill
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (water DIC): carbonate precipitation

Beta - 245610	112.1 +/- 0.5 pMC (Fmdn 1.1210 +/- 0.0050)	-21.0 o/oo

SAMPLE : MW7 WebbHill
ANALYSIS : AMS-Standard delivery
MATERIAL/PRETREATMENT : (water DIC): carbonate precipitation

PRETREATMENT GLOSSARY
Standard Pretreatment Protocols at Beta Analytic

Unless otherwise requested by a submitter or discussed in a final date report, the following procedures apply to pretreatment of samples submitted for analysis. This glossary defines the pretreatment methods applied to each result listed on the date report form (e.g. you will see the designation "acid/alkali/acid" listed along with the result for a charcoal sample receiving such pretreatment).

Pretreatment of submitted materials is required to eliminate secondary carbon components. These components, if not eliminated, could result in a radiocarbon date, which is too young or too old. Pretreatment does not ensure that the radiocarbon date will represent the time event of interest. This is determined by the sample integrity. Effects such as the old wood effect, burned intrusive roots, bioturbation, secondary deposition, secondary biogenic activity incorporating recent carbon (bacteria) and the analysis of multiple components of differing age are just some examples of potential problems. The pretreatment philosophy is to reduce the sample to a single component, where possible, to minimize the added subjectivity associated with these types of problems. If you suspect your sample requires special pretreatment considerations be sure to tell the laboratory prior to analysis.

"acid/alkali/acid"

The sample was first gently crushed/dispersed in deionized water. It was then given hot HCI acid washes to eliminate carbonates and alkali washes (NaOH) to remove secondary organic acids. The alkali washes were followed by a final acid rinse to neutralize the solution prior to drying. Chemical concentrations, temperatures, exposure times, and number of repetitions, were applied accordingly with the uniqueness of the sample. Each chemical solution was neutralized prior to application of the next. During these serial rinses, mechanical contaminants such as associated sediments and rootlets were eliminated. This type of pretreatment is considered a "full pretreatment". On occasion the report will list the pretreatment as "acid/alkali/acid - insolubles" to specify which fraction of the sample was analyzed. This is done on occasion with sediments (See "acid/alkali/acid - solubles"

Typically applied to: charcoal, wood, some peats, some sediments, and textiles "acid/alkali/acid - solubles"

On occasion the alkali soluble fraction will be analyzed. This is a special case where soil conditions imply
That the soluble fraction will provide a more accurate date. It is also used on some occasions to verify the present/absence or degree of contamination present from secondary organic acids. The sample was first pretreated with acid to remove any carbonates and to weaken organic bonds. After the alkali washes (as discussed above) are used, the solution containing the alkali soluble fraction is isolated/filtered and combined with acid. The soluble fraction, which precipitates, is rinsed and dried prior to combustion.

"acid/alkali/acid/cellulose extraction"

Following full acid/alkali/acid pretreatments, the sample is bathed in (sodium chlorite) $NaCIO_2$ under very controlled conditions (Ph = 3, temperature = 70 degrees C). This eliminates all components except wood cellulose. It is useful for woods that are either very old or highly contaminated.

Applied to: wood

"acid washes"

Surface area was increased as much a possible. Solid chunks were crushed, fibrous materials were shredded, and sediments were dispersed. Acid (HCI) was applied repeatedly to ensure the absence of carbonates. Chemical concentrations, temperatures, exposure times, and number of repetitions, were applied accordingly with the uniqueness of each sample. The sample was not be subjected to alkali washes to ensure the absence of secondary organic acids for intentional reasons. The most common reason is that the primary carbon is soluble in the alkali. Dating results reflect the total organic content of the analyzed material. Their accuracy depends on the researcher's ability to subjectively eliminate potential contaminants based on contextual facts.

Typically applied to: organic sediments, some peats, small wood or charcoal, special cases

PRETREATMENT GLOSSARY
Standard Pretreatment Protocols at Beta Analytic
(Continued)

"collagen extraction: with alkali or collagen extraction: without alkali

The material was first tested for friability ("softness"). Very soft bone material is an indication of the
potential absence of the collagen fraction (basal bone protein acting as a "reinforcing agent" within the crystalline apatite structure). It was then washed in de-ionized water, the surface scraped free of the outer most layers and then gently crushed. Dilute, cold HCI acid was repeatedly applied and replenished until the mineral fraction (bone apatite) was eliminated. The collagen was then dissected and inspected for rootlets. Any rootlets present were also removed when replenishing the acid solutions. "With alkali" refers to additional pretreatment with sodium hydroxide (NaOH) to ensure the absence of secondary organic acids. "Without alkali" refers to the NaOH step being skipped due to poor preservation conditions, which could result in removal of all available organics if performed.

Typically applied to: bones

"acid etch"

The calcareous material was first washed in de-ionized water, removing associated organic sediments and debris (where present). The material was then crushed/dispersed and repeatedly subjected to HCI etches to eliminate secondary carbonate components. In the case of thick shells, the surfaces were physically abraded prior to etching down to a hard, primary core remained. In the case of porous carbonate nodules and caliches, very long exposure times were applied to allow infiltration of the acid. Acid exposure times, concentrations, and number of repetitions, were applied accordingly with the uniqueness of the sample.

Typically applied to: shells, caliches, and calcareous nodules

"neutralized"

Carbonates precipitated from ground water are usually submitted in an alkaline condition (ammonium
Hydroxide or sodium hydroxide solution). Typically this solution is neutralized in the original sample container, using deionized water. If larger volume dilution was required, the precipitate and solution were transferred to a sealed separatory flask and rinsed to neutrality. Exposure to atmosphere was minimal.

Typically applied to: Strontium carbonate, Barium carbonate
(i.e. precipitated ground water samples)

"carbonate precipitation"

Dissolved carbon dioxide and carbonate species are precipitated from submitted water by complexing them as ammonium carbonate. Strontium chloride is added to the ammonium carbonate solution and strontium carbonate is precipitated for the analysis. The result is representative of the dissolved inorganic carbon within the water. Results are reported as "water DIC".

Applied to: water

"solvent extraction"

The sample was subjected to a series of solvent baths typically consisting of benzene, toluene, hexane, pentane, and/or acetone. This is usually performed prior to acid/alkali/acid pretreatments.

Applied to: textiles, prevalent or suspected cases of pitch/tar contamination, conserved materials.

"none"

No laboratory pretreatments were applied. Special requests and pre-laboratory pretreatment usually accounts for this.

Consistent Accuracy ...
Delivered On Time.

Final Report

The final report package includes the final date report, a statement outlining our analytical procedures, a glossary of pretreatment terms, calendar calibration information, billing documents (containing balance/credit information and the number of samples submitted within the yearly discount period), and peripheral items to use with future submittals. The final report includes the individual analysis method, the delivery basis, the material type and the individual pretreatments applied. The final report has been sent by mail and e-mail (where available).

Pretreatment

Pretreatment methods are reported along with each result. All necessary chemical and mechanical pretreatments of the submitted material were applied at the laboratory to isolate the carbon which may best represent the time event of interest. When interpreting the results, it is important to consider the pretreatments. Some samples cannot be fully pretreated, making their ^{14}C ages more subjective than samples which can be fully pretreated. Some materials receive no pretreatments. Please look at the pretreatment indicated for each sample and read the pretreatment glossary to understand the implications.

Analysis

Materials measured by the radiometric technique were analyzed by synthesizing sample carbon to benzene (92% C), measuring for ^{14}C content in one of 53 scintillation spectrometers, and then calculating for radiocarbon age. If the Extended Counting Service was used, the ^{14}C content was measured for a greatly extended period of time. AMS results were derived from reduction of sample carbon to graphite (100% C), along with standards and backgrounds. The graphite was then detected for ^{14}C content in one of 9 accelerator-mass-spectrometers (AMS) .

The Radiocarbon Age and Calendar Calibration

The "Conventional ^{14}C Age (*)" is the result after applying $^{13}C/^{12}C$ corrections to the measured age and is the most appropriate radiocarbon age. If an "*" is attached to this date, it means the $^{13}C/^{12}C$ was estimated rather than measured (The ratio is an option for radiometric analysis, but included on all AMS analyses.) Ages are reported with the units "BP" (Before Present). "Present" is defined as AD 1950 for the purposes of radiocarbon dating.

Results for samples containing more ^{14}C than the modern reference standard are reported as "percent modern carbon" (pMC). These results indicate the material was respiring carbon after the advent of thermo-nuclear weapons testing (and is less than ~ 50 years old).

Applicable calendar calibrations are included for materials between about 100 and 19,000 BP. If calibrations are not included with a report, those results were either too young, too old, or inappropriate for calibration. Please read the enclosed page discussing calibration.

Beta Analytic Inc.
4985 SW 74 Court
Miami, Florida 33155 USA
Tel: 305 667 5167
Fax: 305 663 0/97
Beta@radiocarbon.com
Www.radiocarbon.com

Mr. Darden Hood
Director

Mr. Ronald Hatfield
Mr. Christopher Patrick
Deputy Directors

BETA

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Calendar Calibration at Beta Analytic

Calibrations of radiocarbon age determinations are applied to convert BP results to calendar years. The short-term difference between the two is caused by fluctuations in the heliomagnetic modulation of the galactic cosmic radiation and, recently, large scale burning of fossil fuels and nuclear devices testing. Geomagnetic variations are the probable cause of longer-term differences.

The parameters used for the corrections have been obtained through precise analyses of hundreds of samples taken from known-age tree rings of oak, sequoia, and fir up to about 10,000 BP. Calibration using tree-rings to about 12,000 BP is still being researched and provides somewhat less precise correlation. Beyond that, up to about 20,000 BP, correlation using a modeled curve determined from U/Th measurements on corals is used. This data is still highly subjective. Calibrations are provided up to about 19,000 years BP using the most recent calibration data available.

The Pretoria Calibration Procedure (Radiocarbon, Vol 35, No.1, 1993, pg 317) program has been chosen for these calendar calibrations. It uses splines through the tree-ring data as calibration curves, which eliminates a large part of the statistical scatter of the actual data points. The spline calibration allows adjustment of the average curve by a quantified closeness-of-fit parameter to the measured data points. A single spline is used for the precise correlation data available back to 9900 BP for terrestrial samples and about 6900 BP for marine samples. Beyond that, splines are taken on the error limits of the correlation curve to account for the lack of precision in the data points.

In describing our calibration curves, the solid bars represent one sigma statistics (68% probability) and the hollow bars represent two sigma statistics (95% probability). Marine carbonate samples that have been corrected for $^{13}C/^{12}C$, have also been corrected for both global and local geographic reservoir effects (as published in Radiocarbon, Volume 35, Number 1, 1993) prior to the calibration. Marine carbonates that have not been corrected for $^{13}C/^{12}C$ are adjusted by an assumed value of 0 %0 in addition to the reservoir corrections. Reservoir corrections for fresh water carbonates are usually unknown and are generally not accounted for in those calibrations. In the absence of measured $^{13}C/^{12}C$ ratios, a typical value of -5 %0 is assumed for freshwater carbonates.

(Caveat: the correlation curve for organic materials assume that the material dated was living for exactly ten years (e.g. a collection of 10 individual tree rings taken from the outer portion of a tree that was cut down to produce the sample in the feature dated). For other materials, the maximum and minimum calibrated age ranges given by the computer program are uncertain. The possibility of an "old wood effect" must also be considered, as well as the potential inclusion of younger or older material in matrix samples. Since these factors are indeterminant error in most cases, these calendar calibration results should be used only for illustrative purposes. In the case of carbonates, reservoir correction is theoretical and the local variations are real, highly variable and dependent on provenience. Since imprecision in the correlation data beyond 10,000 years is high, calibrations in this range are likely to change in the future with refinement in the correlation curve. The age ranges and especially the intercept ages generated by the program must be considered as approximations.)