APPENDIX C

Select Site Investigation Reports
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APPENDIX C.1

Geochemical Evaluation Technical Memorandum (Anchor, 2017)

King County Department of Natural Resources and Parks

Solid Waste Division

Phase 1 – Vashon Island Closed LANDFILL
Contract No. E00102E08
Task No. 310.1.8 – D310.1.8.1

Vashon Island Landfill Geochemical Evaluations

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King County
Department of
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Solid Waste Division

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February 13, 2017

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Technical Memorandum

February 13, 2017

To: John Strunk, Henry Haselton, and Kirsi Longley, Aspect Consulting, LLC

From: Dimitri Vlassopoulos and Jessica Goin, Anchor QEA, LLC

Re: D310.1.8 Vashon Island Closed Landfill Geochemical Evaluation

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This technical memorandum presents the results and findings of the geochemical investigation conducted for the Vashon Island Closed Landfill in King County, Washington.

Overview

The Vashon Island Landfill was capped and lined as part of the final closure process completed in 2001 (B&H 2006). The refuse area has landfill gas (LFG) and leachate recovery systems. Downgradient monitoring wells completed in the Cc2 unit (Cc2) have had persistent low-level detections of volatile organic compounds (VOCs) such as *cis*-1,2-dichloroethene and vinyl chloride, as well as metals. Low concentrations of vinyl chloride and arsenic have also been detected in water samples collected from seeps that emerge from Cc2 where it outcrops in a steep ravine approximately 500 feet to the west of the landfill (King County 2012). The objectives of the geochemical investigation are as follows: 1) to determine the transport pathways for VOCs detected in the Cc2 aquifer (via infiltration of landfill leachate or LFG); and 2) to evaluate metals mobilization and attenuation of VOCs and metals in groundwater downgradient of the landfill.

As part of this investigation, two additional monitoring wells were installed by Aspect Consulting. MW-35 was installed as a replacement for monitoring well MW-5D due to lack of an adequate seal, and sediment accumulation in the latter, and MW-33 was installed to monitor groundwater adjacent to the leachate lagoon located south of the lined refuse area. During drilling of MW-33, refuse was observed from 12 to 28 feet below ground surface.

The geochemical evaluation included collection of groundwater samples from upgradient Cc2 monitoring well MW-20, downgradient Cc2 monitoring wells MW-2, MW-21, MW-33, and MW-35, as well as three hillslope seeps: SW-1, SW-2, and SW-3 (Figure 1). Two rounds of groundwater sampling were conducted, in September 2015 (dry season) and February 2016 (wet season). The geochemical parameters analyzed are summarized in Table 1.

Samples were also collected from the leachate system during each of the sample rounds. Leachate and leachate condensate samples were collected from the leachate conveyance structure identified as the "Leachate Box". Because the sampling location in the Leachate Box is set up in such a way that the flow cascades into a collection basin and can potentially exchange with air, parameters related to concentrations and isotopic compositions of dissolved gases such as methane, helium, CFCs, and sulfur hexafluoride were not collected.

Table 1
Geochemical Parameters

Parameter	Purpose	Pathway	Fate
Conventional water quality parameters	Parameters such as chloride, calcium, alkalinity, and total dissolved solids support evaluation of landfill gas (LFG) and leachate impacts. For example, chloride and alkalinity are both elevated in leachate, while LFG impacts can increase alkalinity in groundwater without significant increase in other ions.	√	√
Arsenic speciation	Arsenic occurs as arsenic (III) under reducing conditions and arsenic (V) when conditions become oxidizing. LFG and leachate impacts can generate reducing conditions, leading to a higher proportion of arsenic (III) which is more soluble and mobile in groundwater. A greater proportion of arsenic (V) can indicate can indicate a return to oxidizing conditions downgradient and when accompanied by reduction in total arsenic concentrations is indicative of attenuation due to arsenic (V) being more strongly adsorbed to the aquifer matrix	√	√
Carbon-14 (^{14}C) content of dissolved inorganic carbon (DIC); dissolved organic carbon (DOC), and methane	^{14}C is a radioactive isotope produced in the atmosphere and is present in DIC of natural surface waters in equilibrium with the atmosphere. Once surface waters enter the subsurface to become groundwater, the ^{14}C content of DIC decreases over time. Carbon species in both LFG and leachate are ^{14}C enriched from the decomposition of recent organic wastes. Increases or elevated ^{14}C content of DIC, DOC or methane in groundwater downgradient of a landfill are therefore indicators of landfill impacts.	√	
Stable carbon ($\delta^{13}C$) isotope ratios of DIC, DOC, and methane	Stable carbon isotope ratios ($^{13}C/^{12}C$) are reported as $\delta^{13}C$ relative to an international reference standard. Stable isotope ratios of carbon are useful tracers of landfill impacts. Biodegradation of organic wastes in landfills produces $\delta^{13}C$ enriched carbon dioxide and DIC and $\delta^{13}C$ depleted methane	√	
Tritium (^{3}H) content of water	Tritium is a radioactive isotope of hydrogen that is produced naturally in the atmosphere. The tritium content of water at the recharge point reflects the atmospheric concentration at the time of recharge, and the ^{3}H content declines as the groundwater ages. Input of precipitation (recharge) along the groundwater flow path can lead to a slight increase in tritium content; however, the tritium content of modern recharge is relatively low. The tritium content of leachate can be elevated to levels thousands of times greater than those seen in groundwater. Anomalously high tritium levels in groundwater downgradient of a landfill are an indication of leachate impacts.	√	
Stable oxygen ($\delta^{18}O$) and hydrogen (δD) isotope ratios of water	The stable isotope signatures of groundwater can distinguish different water sources contributing to groundwater flow.	√	

Parameter	Purpose	Pathway	Fate
Stable sulfur ($\delta^{34}S$) isotope ratio of sulfate	$\delta^{34}S$ is a tracer for sulfur sources in groundwater and a monitor of anaerobic sulfate reduction that can be linked to biodegradation processes.	√	√
Atmospheric Chlorofluorocarbons (CFCs)	The changing concentrations of CFC-11, CFC-12, and CFC-113 in the atmosphere, and in recharge waters, over time have been widely used for age dating young groundwaters (recharged since the 1940s) and estimating groundwater travel times. However, landfills are also potential sources of CFC contamination in groundwater, which may limit the usefulness of CFCs in dating groundwater in some situations.	√	
Sulfur hexafluoride (SF_6) age	Like CFCs, SF_6 is an anthropogenic chemical that is useful tracer for age dating young groundwater. SF_6 concentration in the atmosphere has steadily increased since the 1970s. In contrast to CFCs, SF_6 is less likely to be present in municipal waste landfills.	√	
Tritium-helium age	This method is useful for age dating young groundwater where the dominant source of tritium is precipitation recharge. The initial tritium content of the groundwater is determined from the sum of the tritium measured in the sample and the amount that has decayed to the helium isotope (^3He). The time elapsed since recharge is estimated for the ratio of measured to initial tritium. Interpretation of groundwater ages may be complicated by subsurface tritium sources such as landfill leachate.	√	
Compound-specific stable isotope analysis	biodegradation processes result in a reduction in concentration of an chlorinated organic compounds accompanied by an enrichment of the heavy stable isotopes in the degrading (parent) compounds, while non-destructive processes, such as dilution and dispersion, decrease concentrations of contaminant without affecting their stable isotope ratios.		√
Quantitative polymerase chain reaction (qPCR)	qPCR is used to determine the presence and abundance of specific microorganisms, known to degrade specific contaminants of concern.		√

Results

The results of the geochemical investigation sampling are presented in Attachment A in Tables A-1 through A-3. Table A-1 summarizes field and conventional groundwater quality parameters, metals, and arsenic speciation data. Table A-2 summarizes VOC and dissolved gas concentrations, compound-specific stable isotope analysis (CSIA) data, and quantitative polymerase chain reaction results. Table A-3 summarizes isotopic and age tracer data and calculated groundwater ages.

Discussion

The geochemical investigation was designed to assess potential contaminant sources (leachate versus LFG), groundwater pathways and travel times, mobilization of metals downgradient of the landfill, and attenuation of VOCs and metals.

Leachate versus Landfill Gas Pathway

Potential sources of contaminants detected in the Cc2 aquifer are LFG, landfill leachate, and direct contact with refuse in the hillslope area. There is an LFG control system in place, evaluated by HEC as part of Contract No E00102E08 Task 310.3.1. Landfill leachate from the capped and lined refuse area should be minimal, as the impermeable cover limits infiltration of precipitation. There is potential for infiltration and leachate generation in the unlined hillslope area. Multiple tracers were evaluated to assess contaminant transport pathways to groundwater and seeps downgradient of the landfill.

Conventional Water Quality Indicators

Water quality parameters can be indicative of LFG or leachate impacts to groundwater. LFG impacts can increase alkalinity, generate reducing conditions, and increase specific conductance (SC) and total dissolved solids (TDS) concentrations. Leachate is typically characterized by higher TDS, SC, and alkalinity, as well as elevated concentrations of total organic carbon (TOC), calcium, magnesium, sodium, chloride, sulfate, and ammonia (Lu et al. 1985). Sodium and chloride are considered more reliable indicators of leachate impacts than TDS, calcium, and magnesium, which can be influenced by increased alkalinity. Sulfate and ammonia concentrations can be also affected by microbial processes in the aquifer and thus may not be conservative tracers of leachate impacts. Therefore, reducing conditions and increased TDS and alkalinity in the absence of increased concentration of specific dissolved ions distinguish LFG from leachate impacts in groundwater (leachate impacts can cause reducing conditions as well as elevated TDS and alkalinity, but are also associated with increases in dissolved ions such as sodium and chloride).

Leachate samples are elevated in SC, chloride, nitrate, sulfate, calcium, potassium, sodium, TOC, and TDS (calculated from SC) compared to background groundwater (MW-20). Higher flow was observed at the leachate sampling location during the wet season than the dry season sampling event, and the concentrations were generally lower for the wet season leachate sample, likely due to dilution.

Alkalinity is elevated in all downgradient monitoring wells in Cc2 including new wells MW-33 and MW-35, as well as in the seeps SW-2 and SW-3, as compared to upgradient groundwater in MW-20. A cross-plot of alkalinity and TDS indicates that the increase in alkalinity is not consistent with impacts from leachate (Figure 2). The MW and SW locations define a separate trend from the leachate samples~~ samples~~. Alkalinity at the MW and SW locations is much greater than that associated with leachate for a given TDS. In addition, cross-plots of concentrations of other leachate indicators such as chloride and sulfate with TDS (Figures 3 and 4, respectively), also show different relationships for MW and SW sample locations compared to leachate, suggesting that impacts on groundwater downgradient of the landfill are predominantly from LFG (Figure 3). A cross-plot of chloride with alkalinity (Figure 5) shows that groundwater samples, seep samples, and leachate samples define distinct trends. This appears to confirm no detectable influence from leachate in groundwater monitoring wells, but slightly elevated chloride concentrations relative to groundwater wells in seep samples may suggest a minor contribution from leachate in addition to LFG, particularly at seep SW-2. Similarly, sodium concentrations are also elevated in the leachate samples and seep SW-2 compared to the monitoring wells, also consistent with the observations for chloride. Sulfate is also elevated in leachate relative to upgradient groundwater, but the lack of a relationship between sulfate concentrations and alkalinity in either groundwater or seep samples indicates an absence of leachate sulfate impacts in downgradient groundwater or seeps (Figure 6). In fact, sulfate concentrations in seep samples are consistently slightly lower than in groundwater, potentially indicating either removal of sulfate from groundwater by reactions or dilution of seep concentrations by infiltration of low sulfate recharge downgradient of MW-35.

Isotopic Tracers

Tritium (^{3}H)

Tritium is commonly elevated in both landfill leachate and LFG (Mutch et al. 2007). Tritium is elevated in landfill leachate due to disposal of tritium-based luminescent paints and signs. Elevated tritium levels in the downgradient groundwater samples are indicative of a leachate release, because LFG would introduce a much smaller mass of the tritiated water to the aquifer (Kerfoot et al. 2003).

The tritium content of leachate samples is elevated compared to groundwater and seep samples and showed a seasonal difference, being much higher (122 tritium units [TU]) in the dry season sample than the wet season sample (13 TU), similar to the seasonal differences observed for concentrations of other leachate indicators. This is consistent with greater dilution of leachate constituents during the wet season due to higher water flow rates. The tritium content in upgradient well MW-20 was approximately 3 TU, and approximately 2 TU in all downgradient wells sampled and seep SW-1 (Table A-3), without any systematic seasonal differences and indicating no detectable impacts from leachate tritium. The small decrease in tritium content from upgradient to downgradient across the site is consistent with radioactive decay of atmospherically derived tritium during transit along the groundwater flow path (with a half-life of 12.3 years). Tritium is slightly elevated in SW-2 (approximately 5 TU) and SW-3 (approximately 4 TU) compared to the monitoring wells, which may indicate a minor contribution from leachate or enhanced groundwater recharge west of the landfill upgradient of the seeps (e.g., from infiltration of runoff along Westside Highway, Figure 1).

A cross-plot of tritium with chloride (Figure 7) shows that the groundwater samples define a relatively tight cluster with low tritium and chloride. Higher tritium in the seeps correlates with higher chloride. The trend defined by the seep samples appears to extend toward, but does not intersect, the range defined by the two leachate samples. However, the tritium levels in the seep samples are still within the expected range of present-day precipitation (5 to 10 TU). Although the slightly elevated tritium levels in the seep samples could reflect a small contribution from leachate, other lines of evidence presented below, specifically groundwater age dating results, suggest this is due to enhanced groundwater recharge in the area immediately upgradient of the seeps.

Radiocarbon (^{14}C)

Living organisms (plants and animals) assimilate radioactive ^{14}C (radiocarbon) from the atmosphere where it is produced naturally by cosmic radiation. The ^{14}C content is reported in percent of modern carbon (pmc) which is defined as the ^{14}C content of atmospheric carbon dioxide (CO_2) in 1950. During the 1950s, the ^{14}C content of atmospheric CO_2 increased due to nuclear testing, peaking in 1963 at almost twice the natural level (approximately 190 pmc). Following the ban of atmospheric nuclear tests, levels decreased back to natural levels over the ensuing half century. Due to its long half-life (5,730 years), the ^{14}C content of dead organic matter decays slowly (over thousands of years). Bacterial decomposition of recently dead organic matter in landfills therefore produces ^{14}C-enriched dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) in landfill leachate and ^{14}C-enriched CO_2 and methane in LFG. The ^{14}C content of DIC and DOC can be used to distinguish leachate impacts from LFG impacts on groundwater if the background ^{14}C contents of DIC and DOC in groundwater are different from that of the landfill sources, which depends in part on the age of the upgradient groundwater (e.g., Kerfoot et al. 2003).

The ^{14}C content of DIC in leachate is approximately 102.3 pmc (average of two samples) and approximately 94.0 pmc in upgradient well MW-20 (average of two samples). DIC in all the downgradient wells and seeps is ^{14}C-enriched (106.4 to 119.6 pmc) relative to both MW-20 and leachate. The ^{14}C enrichment is indicative of a landfill impact, but the values are higher than those measured in leachate and therefore argue against a leachate source and favor LFG as the main source of the ^{14}C-enriched DIC. A cross-plot of ^{14}C of DIC and chloride shows that leachate has variable chloride but relatively constant ^{14}C content (Figure 8). Downgradient wells and seeps, except for SW-2, show an increase in ^{14}C relative to upgradient well MW-20 without an increase in chloride concentrations, confirming that the ^{14}C enrichment is due to LFG and not leachate impacts. The only exception is seep SW-2, which shows a slight increase in chloride, but the ^{14}C value is higher than that of leachate, and therefore, most of the landfill impact is due to LFG, with at most a minor contribution from leachate. This conclusion is also confirmed by a cross-plot of tritium and ^{14}C of DIC (Figure 9), which shows distinct trends for groundwater samples, seep samples, and leachate. The ^{14}C enrichment of groundwater DIC downgradient of the landfill is not accompanied by an increase in tritium, as would be expected for leachate. Again, the seep sample data are more consistent with LFG impacts, with the exception of a possible minor contribution from leachate at SW-2.

The ^{14}C content of DOC was also measured in select wells and leachate during the wet season sampling event. The ^{14}C content of DOC in leachate with 5.9 milligrams per liter (mg/L) TOC was approximately 97.5 pmc. The ^{14}C content of DOC in MW-20 was not measured because TOC was below detection limits (<1 mg/L). The ^{14}C content of DOC was measured in MW-33 and MW-35 was 78.4 and 86.8 pmc, respectively. These values correspond to apparent ages of the organic matter of 210, 1,200, and 2,000 years for leachate, MW-33, and MW-35, respectively. The apparent age of the leachate DOC likely reflects a mixture of very recent and older organic materials. The much older apparent age of the DOC in the well samples precludes it being derived from leachate, and indicates it is of natural origin.

The ^{14}C content of dissolved methane in MW-33 and MW-35 is approximately 119 pmc, with a ^{14}C enrichment comparable to that of the DIC sampled in these wells, which further supports an LFG source.

Stable Carbon Isotopes

Bacterial fermentation of organic matter in landfill refuse produces methane that is depleted in carbon-13 ($\delta^{13}C$) and CO_2 (and DIC) that is enriched in $\delta^{13}C$ (Hackley et al. 1996). Groundwater DIC that is enriched in both $\delta^{13}C$ and ^{14}C content can be used as an indicator of landfill impacts from either leachate or LFG (Kerfoot et al. 2003).

Figure 10 is a cross-plot of $\delta^{13}C$ and ^{14}C content of DIC. Groundwater, seep, and leachate samples all define separate, non-overlapping clusters in Figure 10. If groundwater downgradient of the landfill was impacted by leachate, groundwater samples would be expected to plot along a mixing line between upgradient groundwater in MW-20 and leachate. The fact that the downgradient wells and seeps do not define such a trend rules out leachate and again implicates LFG as the source of the elevated DIC in downgradient wells and seeps.

Stable carbon isotope ratios of methane and DOC in groundwater and leachate were also assessed to determine whether groundwater impacts are associated with leachate or LFG. Only MW-33 and MW-35 had sufficient methane concentrations for isotopic analysis. The $\delta^{13}C$ of methane in both MW-33 and MW-35 is isotopically depleted (approximately-58 per mil) compared to both DOC (approximately-27 per mil) and DIC (-12 to -14 per mil), as is characteristic of methane produced by microbial fermentation of organic matter. The $\delta^{13}C$ of DOC in leachate is extremely depleted (-45 per mil), indicating that DOC is produced by methanotrophic processes (direct fixation of carbon from landfill methane) as described by Mohammadzadeh and Clark (2011). The $\delta^{13}C$ of DOC in MW-33 and MW-35 is well within the range of natural organic matter and distinct from leachate. The absence of a depleted isotopic signature for DOC in the downgradient wells is also consistent with an LFG pathway.

Stable Isotopes of Water

Oxygen and hydrogen isotope ratios ($\delta^{18}O$ and δD, respectively) in precipitation around the world generally follow a consistent linear relationship characteristic of latitude and climatic conditions called the Global Meteoric Water Line (GMWL). The conservative nature of $\delta^{18}O$ and δD allows these isotopes to be used as tracers of groundwater recharge and leakage or mixing between water reservoirs that are isotopically distinct (Hackley et al. 1996).

All the samples plot along the GMWL, within a restricted range of $\delta^{18}O$ and δD (Figure 11). The landfill leachate and LFG condensate samples plot on the isotopically heavy or enriched end of the range (i.e., more positive $\delta^{18}O$ and δD values) with little overlap with groundwater. The most δD-enriched sample is the dry season leachate sample, which is shifted above the GMWL, reflecting isotopic fractionation associated with methanogenesis, which occurs within the landfill (Hackley et al. 1996). None of the groundwater and seep samples show any δD enrichment, consistent with the overall absence of evidence of leachate impacts on groundwater.

Stable Sulfur Isotopes

Sulfate concentrations are elevated (approximately 50 to 470 mg/L), and sulfate is isotopically enriched ($\delta^{34}S$ of +16 to +18 per mil) in leachate relative to upgradient groundwater (approximately 17 mg/L and +0.6 per mil), as is typical of landfills (Fritz et al. 1994). Sulfate concentrations in downgradient monitoring wells are similar to upgradient groundwater (15 to 20 mg/L) but show a wide range of $\delta^{34}S$ (0 to +21 per mil). Sulfate concentrations are somewhat lower (8 to 14 mg/L) and also show a wide range of $\delta^{34}S$ (+7 to +22 per mil). An isotope mixing diagram was used to test whether the isotopic enrichment observed in sulfate in the downgradient wells could be due to leachate (Figure 12). The mixing diagram plots $\delta^{34}S$ against the inverse sulfate concentration. On this plot, samples that are related by mixing of two end-members (i.e., leachate and upgradient groundwater) fall along a linear trend between the end-members. It is evident that none of the downgradient well or seep samples plot along a mixing line between MW-20 and leachate, which rules out leachate as a source of sulfate in downgradient wells and seeps. The observed isotopic enrichment without increasing sulfate concentrations can be explained by microbial sulfate reduction, which is accompanied by a strong isotopic fractionation.

Groundwater Age Tracers

Atmospheric tracers that can be used for groundwater age dating include the following: 1) anthropogenic chemicals whose atmospheric concentration history is known, such as chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6); and 2) radioactive isotopes with a known decay rate and whose initial concentration in water at the time of recharge can be estimated, such as tritium. Groundwater ages calculated from tracer concentrations are model ages, meaning they are based on an assumed model for groundwater flow that relates the tracer concentration to the time elapsed since the water recharged to the subsurface. For this study, model ages were calculated using the piston-flow model (PFM) (Kazemi et al. 2006). In interpreting the atmospheric tracer data, it is important to note that during both sampling events, the water table was within the screen interval in wells MW-21 and MW-35. This condition can result in partial re-equilibration of dissolved atmospheric gases with unsaturated zone air, which complicates the age interpretation.

Chlorofluorocarbons (CFC-11, CFC-12, CFC-113)

Atmospheric CFCs have been widely used to evaluate groundwater ages and travel times of young groundwater recharged since the 1940s (Kazemi et al. 2006; Plummer et al. 2001). The use of CFCs for groundwater age dating at landfill sites can be limited by the presence of CFCs in LFG, which can overwhelm the atmospheric CFC signature that allows for the determination of groundwater age.

Wells MW-20, MW-33, and MW-35 and seeps SW-2 and SW-3 were sampled for CFCs (CFC-11, CFC-12, and CFC-113) during the first sampling event in September 2015. The CFC-12 results were much higher than would be expected from atmospheric levels, indicating contamination. In some cases, CFC-11 and CFC-113 results were also affected by contamination. It was possible to calculate groundwater ages at three locations. Groundwater ages were calculated using the Piston-Flow Model, which assumes all the water in the sample has a single age (by definition equal to the mean age or residence time in the aquifer). Results are summarized in Table 2.

Table 2
CFC Model Ages

Age Tracer	MW-20	MW-35	SW-2
CFC-11	C	54.2*	28.0
CFC-113	34.0	27.7	26.7

Notes:
* Detection of methane in this sample indicates CFC-11 concentration may be affected by degradation, and the age is likely overestimated.
C: contaminated, age could not be calculated.

The CFC-113 model ages decrease from upgradient well MW-20 to downgradient well MW-35, contrary to what would be expected along a groundwater flow path. This could be due to recharge of a younger water component between MW-20 and MW-35, or partial re-equilibration of CFCs with soil air at MW-35 to make the water appear younger. The latter explanation is less likely because, if it were the case, the CFC-11 concentration in MW-35 would also be affected and would yield a younger age. Therefore, these results support enhanced recharge downgradient of the landfill, consistent with the tritium data. The similarity in CFC-113 model ages at MW-35 and SW-2 suggests rapid groundwater travel times of less than 1 year between these locations.

Due to the limited usefulness of CFCs for groundwater age dating at the site, as a result of the occurrence of non-atmospheric CFCs at the site, CFC samples were not collected during the second event.

Sulfur Hexafluoride (SF_6)

SF_6 is predominantly an industrial chemical, which is not typically present in municipal landfills, and a potentially useful atmospheric tracer of groundwater age at landfill sites. Samples for SF_6 dating were collected during both the dry and wet season sampling events, and PFM ages are summarized in Table 3 below.

Table 3
Sulfur Hexafluoride Model Ages

Location	September 2015	February 2016
MW-20	34.7	38.9
MW-2	NS	36.2
MW-21	NS	26.9
MW-33	23.2	29.2
MW-35	25.5	26.9
SW-2	4.7*	25.7*
SW-3	7.7*	5.2*

Notes:
* Seep samples may be partially re-equilibrated with air prior to sampling.
NS: not sampled

The SF_6 model ages are younger in the downgradient wells than in the upgradient monitoring well MW-20, similar to the trend observed for the CFC ages. This could be due to potential contribution of this compound from the landfill, or higher recharge downgradient of the landfill. The striking similarity between CFC-113 and SF_6 model ages for samples where both are available rules out the landfill as a source of SF_6 and supports enhanced recharge as a viable explanation.

Additionally, SF_6 is elevated in the seep samples SW-2 and SW-3, resulting in very young model ages. This could be due to enhanced recharge along Westside Highway and the steep slope of the ravine, re-equilibration of SF_6 in seepage water with soil air in the hillslope prior to emerging, or contact of water samples with air during sampling. To minimize the potential for artifacts, additional steps were taken during the second sampling event to minimize air contact during sample collection by manually driving a steel pipe into the soil immediately above the seep to form a water stream, and collecting the sample using a peristaltic pump and tubing inserted to the end of the pipe. This resulted in an older model age of 25.7 years for seep SW-2, which is in keeping with the model ages in wells MW-21 and MW-35 (26.9 years). As for CFCs, the SF_6 ages indicate a very short groundwater travel time between these wells and the seeps.

Tritium-Helium (^3H-^3He)

Three wells were sampled for age dating by the tritium-helium method during the second sampling event. In addition to tritium, samples are analyzed for helium isotopes to determine the tritiogenic helium (^3He derived from the radioactive decay of tritium) in order to estimate the initial tritium concentration at the time of recharge. The ratio of measured tritium to initial tritium is used to calculate the time elapsed since recharge. Tritium-helium ages require a correction for excess air, which affects the helium concentration. Model ages were calculated using either nitrogen/argon concentrations (excess air) or neon to correct for excess air, and results from both methods were in excellent agreement. The results are summarized in Table 4.

Table 4
Tritium-Helium Model Ages

Model Age	MW-20	MW-2	MW-21
Neon	27.3	18.2	3.0*
Excess Air	27.1	17.4	3.7*

Note:
* Likely underestimated due to helium loss

Similar to the other age tracers, tritium-helium ages become younger downgradient, indicating significant recharge along the groundwater flow path. The south ponds are located between MW-20 and MW-2 (Figure 1) and are unlined. This and the other age dates are consistent with the ponds as a recharge source. The very young age calculated for MW-21 is likely underestimated because, as mentioned earlier, the water table was within the well screen interval during sampling. Helium loss to soil air would result in a lower initial tritium estimate, making the apparent age of the water younger.

Seasonality

No notable seasonal differences between wet and dry season sampling events were noted in groundwater or seep concentrations. As discussed earlier, the leachate sampling location had much greater flow in the wet season sampling event, and the wet season leachate sample had lower concentrations of chloride, alkalinity, and sulfate.

Arsenic and Metals

Origin

The microbial decomposition of organic matter in landfills (or other organic-rich environments) results in consumption of terminal electron acceptors in sequence as follows (from the most to least energetically favorable): oxygen, nitrate, manganese (IV) oxides, iron (III) oxides, and sulfate, and ultimately leading to methanogenic fermentation. Increased arsenic concentrations also commonly occur under reducing conditions, as arsenic can be released by the dissolution of naturally occurring arsenic-bearing iron oxyhydroxides in the aquifer matrix (O'Day et al. 2004). For example, Whitlock and Kelly (2010) attributed arsenic mobilization in an aquifer to impacts from LFG (methane), which resulted in development of reducing conditions.

The low dissolved oxygen (0.2 to 0.6 mg/L), absence of detectable nitrate, and elevated manganese (1 to 2 mg/L) and dissolved iron (7 to 12 mg/L) in wells MW-33 and MW-35 are consistent with the existence of iron-reducing conditions downgradient of the landfill, likely due to localized LFG impacts. The elevated dissolved arsenic concentrations detected at MW-33, MW-35, and the wet season sample from seep SW-2 are associated with elevated dissolved iron concentrations (Figure 13). Dissolved iron and arsenic were not detected in leachate samples, indicating that arsenic and iron are mobilized in the aquifer. Arsenic speciation data show that the higher arsenic concentrations predominantly reflect an increase in the reduced arsenic(III) species (Figure 14), which is characteristic of reducing conditions and more mobile than arsenic(V).

Attenuation

Dissolved oxygen concentrations increase downgradient of wells MW-33 and MW-35 to levels similar to background (1 to 2 mg/L) and even higher (7 to 11 mg/L) in the seeps, indicating a return to aerobic conditions. Under these conditions, iron is oxidized and typically precipitates as iron oxide coatings on the aquifer matrix grains. The iron oxides strongly adsorb dissolved arsenic from groundwater, resulting in its attenuation. As a result, all the seep samples have very low dissolved arsenic (<0.005 mg/L) and iron (<1 mg/L) concentrations with one exception: the wet season sample for SW-2. The partial attenuation of arsenic (0.016 mg/L) and iron (approximately 9 mg/L) observed during this period compared to the dry season sample from the same location (0.0016 mg/L arsenic and approximately 0.02 mg/L iron) may be due to higher flow rates and shorter residence time of groundwater downgradient of the landfill.

Volatile Organic Compounds

Attenuation

The concentrations of VOCs in the Cc2 wells and the seeps have been consistently decreasing over time. Microorganisms capable of degrading chlorinated VOCs (e.g., *Dehalococcoides* spp.) and aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes) were identified in MW-33, MW-35, MW-2, MW-21, SW-2, and SW-3 (Table A-2). The reported abundances of these microbes were highest in the wells with higher detected VOC concentrations (MW-33 and MW-35).

Dissolved methane, ethane, and ethene were sampled and analyzed during the wet season sampling event. Methane, an indicator of strongly reducing conditions, as well as ethane and ethene, which are products of microbial reductive dechlorination of chlorinated ethenes and ethanes, were detected in all the wells and seeps sampled, with highest concentrations detected at MW-33, MW-35, and SW-2. No chlorinated VOCs were detected in SW-2, and only sporadic trace detections of vinyl chloride (approximately 0.05 micrograms per liter) were reported in SW-1 and SW-3, indicating essentially complete biodegradation of chlorinated VOCs upgradient of the seeps.

CSIA of VOCs was limited due to the low concentrations. Only *cis*-1,2-dichloroethene, vinyl chloride, and methane were present at concentrations high enough for CSIA, and only in MW-33 and MW-35 (Table A-2). The limited CSIA data set for VOC compounds did not permit a detailed evaluation of biodegradation processes, although the $\delta^{13}C$ values of methane clearly indicate a microbial origin.

Summary

Using a multiple lines-of-evidence approach, the following are key findings of the geochemical investigation of contaminant sources, pathways, and fate downgradient of the Vashon Island Closed Landfill:

Source Evaluation

- Groundwater quality at monitoring wells MW-33 and MW-35 appears to be impacted by LFG.
- Low-level vinyl chloride detections in seep SW-2 appear to be predominantly related to LFG, potentially with a minor contribution from leachate.
- Elevated arsenic concentrations detected in monitoring wells MW-33 and MW-35 and seep SW-2 are of natural origin, and mobilized under locally iron-reducing conditions in the aquifer resulting from the LFG impacts.

Attenuation of Chlorinated Volatile Organic Compounds

- Declining concentrations of chlorinated VOCs over time in the Cc2 monitoring wells and seeps, and the presence of chlorinated VOC degrading bacteria, indicate that attenuation is occurring due to both physical (dispersion, dilution) and biological (reductive dechlorination) processes at the site.

Arsenic Attenuation

- Mobilization of arsenic is associated with iron-reducing conditions. Arsenic and iron are attenuated downgradient of the landfill due to infiltration of oxygenated water, which oxidizes iron to form iron oxides in the subsurface which are effective sorbents for dissolved arsenic.

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