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Arsenic Mobilization from Silicic Volcanic Rocks in the Southern Willamette Valley

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Arsenic Mobilization from Silicic Volcanic Rocks in the Southern Willamette Valley

by

Gabriela Ribeiro de Sena Ferreira

A thesis submitted in partial fulfillment of the
requirements for the degree of

Master in Science
in
Geology

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Portland State University
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Abstract

Volcanic tuffs and tuffaceous sediments are frequently associated with elevated As groundwater concentrations even though their bulk As contents ($\sim 5 \text{ mg kg}^{-1}$; Savoie, 2013) are only marginally greater than the average crustal abundance of $4.8 \text{ } \mu\text{g g}^{-1}$ (Rudnick & Gao, 2003). Thus, As mobilization must be facilitated by conditions particular to these rocks. Alkaline desorption, anionic competition, reactive glass dissolution, and reductive dissolution of iron oxides are proposed processes of As release from volcanic rocks. Geogenic As contamination of groundwater in the southern Willamette Valley in western Oregon has been well-documented since the early 1960s, and previous studies have identified the Little Butte Volcanics Series and Fisher and Eugene Formations as the source of As contamination.

This study examines 19 samples from 10 units of ash flow tuffs and tuffaceous sediments within the Fisher Formation and Little Butte Volcanics Series, representing a range of weathering and devitrification, to determine conditions of mobilization and mineralogical constraints that control As release into solution. Leachate studies were conducted over a range of pH from 7 to 11, phosphate concentrations from $10 \text{ } \mu\text{M}$ to 100 mM , and in time series from 4 to 196 hours. Results demonstrate that silicic volcanic tuffs are capable of mobilizing As in concentrations above regulatory limits at pH conditions produced naturally by the tuffs (pH 8-9) or with moderate concentrations of P ($10\text{-}100 \text{ } \mu\text{M}$). Alteration products, e.g. zeolites and clays, appear to be the primary host phases for mobile As. Samples that do not contain these alteration products tend to produce concentrations of As well below regulatory limits and often below the instrument detection limits of this study. The type of alteration may influence As mobilization: tuffs containing more clays tend to mobilize As through surficial desorption, and tuffs containing more zeolites tend to mobilize As by dissolution or formation of colloids. Additionally, one volcanoclastic sample demonstrates that extremely elevated concentrations of As, up to $1000 \text{ } \mu\text{g/L}$ are possible as a result of oxidative dissolution of As-bearing sulfide phases.

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Introduction

Arsenic is a widespread toxin that poses significant risks to human health and the environment. Worldwide, as many as 60-100 million people may be at risk of exposure to excessive levels of As in water (Smedley & Kinniburgh, 2002). Naturally elevated groundwater As levels are frequently attributed to volcanic sources, particularly high silica ash-flow tuffs and tuffaceous sediments (Johannesson & Tang, 2009; Mahlkecht, Steinich, & Navarro de Leon, 2004; Smedley & Kinniburgh, 2002; Vinson, McIntosh, Dwyer, & Vengosh, 2011; Welch, Westjohn, Helsel, & Wanty, 2000). However, there is little variability in bulk As content within volcanic rocks (generally $< 8 \mu\text{g g}^{-1}$; Onishi & Sandell, 1955), and their concentrations are equivalent to or only marginally higher than the average concentration in continental crust ($4.8 \mu\text{g g}^{-1}$; Rudnick & Gao, 2003).

The frequent association of As-contaminated groundwater to silicic volcanic aquifers indicates that processes or host phases specific to silicic volcanism must mobilize As from these source rocks despite their modest As contents (Raymahashay & Khare, 2003; Smedley & Kinniburgh, 2002; Welch et al., 2000). A recent study by Savoie (2013) suggests that the specific route of post-depositional alteration may profoundly influence the mobility of As from high silica ash-flow tuffs.

Arsenic contamination in the southern Willamette Basin in western Oregon has been well-documented since the early 1960s. The most recent study concludes that 21.7% (n=158) of groundwater samples exceeded the current USEPA standard of 0.01 mg/L (Hinkle & Polette, 1999). Eugene, located in Lane County, is estimated to be the second largest city in Oregon, and the county overall experienced an 8.9% population growth

from 2000 to 2009 (Population Research Center, 2013). The self-supplied groundwater population is nearly 20% of the total population in Lane County (64,970), which makes Lane County the second-most dependent county on domestic water wells behind Clackamas County (Oregon Water Science Center [OWSC], 2013). The growing population will create further reliance on groundwater supplies as surface water supplies become increasingly depleted, which may in turn increase the risk to human health from As exposure.

All prior studies on As contamination in Lane County indicate the Fisher Formation and Little Butte Volcanics Series as the source of As contamination. The Fisher Formation and Little Butte Volcanics are broadly mapped as non-marine volcanoclastic sedimentary rocks, silicic tuffs, mafic lavas, tuffaceous sandstone, and pebble conglomerates (McClaughry, Wiley, Ferns, & Madin, 2010). Processes of As mobilization into groundwater remain unclear (Goldblatt, Van Denburgh, & Marsland, 1963; Hinkle & Polette, 1999; Whanger, Weswig, & Stoner, 1977).

This study examined ten tuff units of the Fisher Formation and Little Butte Volcanics Series in order to improve understanding of mechanisms governing As mobilization from silicic volcanic rocks. Samples collected from these units were classified in terms of volcanic textures and mineral assemblages, and subjected to a series of aqueous leachate experiments to assess As mobilization under a range of solution conditions. The results were interpreted in terms of potential mechanisms governing As mobilization into solution in an effort to understand how aquifers with near-average bulk As contents result in extensive As contamination.

Background

Arsenic geochemistry

Arsenic is highly mobile in a variety of environments, under both reducing and oxidizing conditions, both acidic and alkaline conditions, and both arid and humid climates (Smedley & Kinniburgh, 2002; Wang & Mulligan, 2008). Arsenic in the environment most commonly occurs in trivalent (As(III) or arsenite) and pentavalent (As(V) or arsenate) forms. As(III) is often considered the more mobile of the two species because As(V) forms more extensive inner-sphere complexes (Kocar & Fendorf, 2009), although under high pH conditions, As(III) may be more strongly sorbed than As(V) (Manning & Goldberg, 1997). In natural waters, As dominantly occurs as various oxyanions depending on redox and pH conditions (Figure 1). However, nonequilibrium behavior of the As(V)/As(III) couple is observed, with As(III) found in oxic waters and As(V) in anoxic, which has been explained by slow kinetics or biological interference (Inskeep, McDermott, & Fendorf, 2002; Smedley & Kinniburgh, 2002).

Arsenic host phases

Sources of As are both anthropogenic (e.g. mining, arsenical pesticides, lumber preservatives, fossil fuel processing) and geogenic. Shales, slate, hydrothermal ore deposits, and volcanic rocks are commonly associated with As-contaminated aquifers (Smedley & Kinniburgh, 2002; Wang & Mulligan, 2006; Welch et al., 2000). Host phases include As-bearing minerals (commonly sulfides), metal oxides, clays, and other surface-charged species. Differences in water conditions may affect the type of host phases as well; for example, As may shift from Fe oxides in oxic waters to sulfides in reducing waters (Hering & Kneebone, 2002).

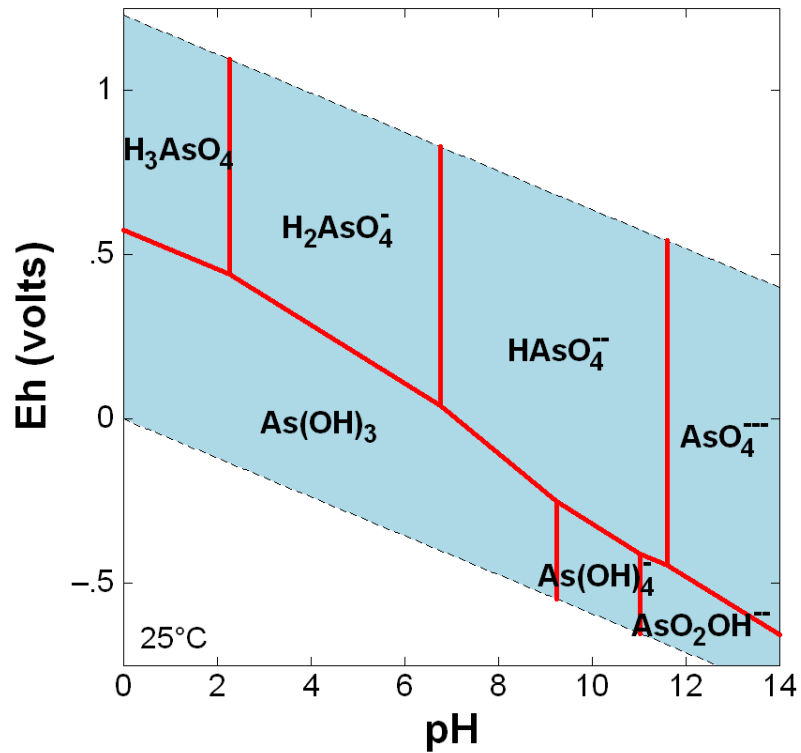


Figure 1: Eh-pH diagram showing dominant species of dissolved arsenic under various environmental conditions (created using Geochemist's Workbench software; SAs = 0.001 m).

As of July 2014, the most recent Mineralogical Society of America publication reported 568 known minerals containing As as a critical component, although many are ore minerals and associated alteration products and are therefore rare in the natural environment (Bowell, Alpers, Jamieson, Nordstrom, & Majzlan, 2014; Smedley & Kinniburgh, 2002). Arsenic frequently substitutes for P(V), Si(IV), Al(III), Fe(III), and Ti(IV) as a trace component within mineral structures. The most common As-bearing minerals are sulfides, in which As occurs as an arsenide or sulfarsenide anion bound to transition metals (e.g. $FeAs_2$; $FeAsS$) (Bowell et al., 2014; Smedley & Kinniburgh, 2002). The most studied As-producing sulfide is pyrite, which occurs in ore bodies and low-temperature sedimentary environments under reducing conditions around buried and

decomposing organic matter or in the presence of sulfate-reducing bacteria (Bowell et al., 2014; Kreidie et al., 2011; Wang & Mulligan, 2008). Arsenic is also found in association with major gold deposits (Bowell et al., 2014). Precipitation of As minerals occurs within magmatic and metamorphic systems, hydrothermal systems, oxidation zones of ore deposits and mineralization, coal basins, mine wastes and tailings, and former industrial sites (Majzlan, Drahota, & Filippi, 2014). However, under oxic and reducing conditions, many common As minerals are too soluble to precipitate or may still have high dissolved equilibrium concentrations of As if precipitated (Hering & Kneebone, 2002).

Unlike mineral precipitation, sorption of As onto minerals is an important control on As concentrations in most natural waters. As(V) has a strong affinity for most metal (hydr)oxides, commonly Al, Mn, and Fe, as well as clay minerals on which it forms surface complexes. In contrast, As(III) more selectively sorbs to Fe (hydr)oxides (Inskeep et al., 2002). This difference in sorption behavior is attributed to the fact that As(III) forms inner sphere complexes while As(V) may form both inner and outer sphere complexes (Pedersen, Postma, & Jakobsen, 2006).

Among different Fe (hydr)oxides, crystalline structure and speciation determine the strength and amount of As sorption and subsequent mobility (Campbell & Nordstrom, 2014; Kreidie et al., 2011; Wang & Mulligan, 2008). Sorption sites on the surface have relatively rapid kinetics, while slow diffusion into the interior of the aggregate may occur given sufficient time (Campbell & Nordstrom, 2014). Despite crystalline and amorphous Fe oxides (e.g. hydrous ferric oxide vs goethite and magnetite) having similar binding strength and intrinsic surface complexation constants, the crystalline phases of iron

oxides typically have lower sorptive capacity for As, owing to a decrease in specific surface area and site density rather than difference in affinity (Dixit & Hering, 2003). As(III) may substitute for Fe(III) on outer layers of sulfides where Fe(II) oxidizes to Fe(III) due to weathering and microbial activity (Kreidie et al., 2011). Goethite has strong sorption of As, such that nearly 80% of goethite must be reductively dissolved before >20% of As is released. Ferrihydrite's sorption is moderate, and lepidocrocite readily releases As into solution (Pedersen et al., 2006). Recrystallization into more stable Fe-oxides results in incorporation of As within the new mineral via occlusion, making it less available to solution (Pedersen et al., 2006). Variations in point of zero charge (ferrihydrite pH = 7.8-7.9; lepidocrocite pH = 6.7-8; goethite pH = 8.9-9.5) and reduction (e.g. ferrihydrite Eh = 1.394 – 0.177 volts; hematite Eh = 1.078 – 0.177 volts) account for variations in As sorption behavior (Pedersen et al., 2006; Raymahashay & Khare, 2003).

Aluminum oxides are structurally similar to Fe oxides because both can have a +3 valency and have similar radii. On Al oxides, As(III) forms weak outer-sphere complexes from pH 3 to 11 whereas As(V) forms inner-sphere complexes which may be stronger than those on Fe oxides and remain sorbed at higher pH (Campbell & Nordstrom, 2014). Manganese oxides are poorly crystalline and may adsorb As, but their catalyzing effect on redox transformations are more important than potential sorbent capacity (Wang & Mulligan, 2008).

Sorption on clay minerals is highly variable but generally, As(III) is stable from pH 4 - 9 and As(V) adsorbs more strongly above pH~7.5 (Lin & Puls, 2000; Manning & Goldberg, 1997). Aluminosilicate clays are distinct among As host phases in their high

surface charge density and diverse behavior of edge hydroxyl groups (Wang & Mulligan, 2008). Lin & Puls (2000) experimentally demonstrated that the structure of clays influences As adsorption to chlorite, which had stronger sorption of As due to its high iron oxide content, while illite/montmorillonite (2:1 layer) had moderate sorption, and kaolin clays (1:1 layer) had low sorption. Aging of clays led to increased adsorption with increased crystallinity reducing available charged edges (Lin & Puls, 2000). In contrast, Manning & Goldberg (1997) found that illite adsorbed significant As(III) due to the difference in point of zero charge at mineral edges that superseded crystalline effects on charged surfaces. Substantial oxidation for kaolinite and illite occurred above pH 9.2 whereas amorphous $\text{Al}(\text{OH})_3$ did not undergo as much oxidation, suggesting reactions with solid phase components on the surface are more significant to oxidation than Al-OH edge sites (Manning & Goldberg, 1997). Several studies have demonstrated the dominating effect of high pH in mobilizing As from a variety of clay minerals (Lin & Puls, 2000; Manning & Goldberg, 1997; Shuichi, Ito, & Hashimoto, 2005).

Due the similar ionic structure of As to P, As may also occur in significant concentrations in phosphate minerals, up to 1000 mg/kg in apatite (Smedley & Kinniburgh, 2002). However, the lower relative abundance of phosphates in most rocks means that these are typically insignificant contributors of As in the environment. Mazziotti-Tagliani et al. (2011) investigated volcanic rocks from the F- and As-contaminated aquifer of Mt. Etna and found that As was exclusively hosted on the rim of apatite crystals and released under reductive dissolution with increased solubility as a result of metasomatism that increased bulk As in the sample. Although As may

preferentially sorb to metal oxides and clays, it also has strong capacity to sorb to different materials as available.

Arsenic mobilization

Dissolved arsenic in natural waters is controlled primarily by dissolution or desorption reactions (Smedley & Kinniburgh, 2002; Wang & Mulligan, 2008; Welch et al., 2000). Common mechanisms of As mobilization include reductive dissolution, sulfide oxidation, interaction with natural organic material, pH desorption, and ionic competition. Precipitation/dissolution reactions are limited by equilibrium with the solid, whereas sorption kinetics allow for greater exchange dependent on sorbent concentration (Hering & Kneebone, 2002).

Reducing conditions mobilize As primarily through dissolution of host phases (commonly Fe(III)-oxyhydroxide on which As is adsorbed). Reduction of As(V) to As(III) may release sorbed As from the surface of Al oxides; however, for Fe-oxyhydroxides, reductive dissolution typically controls mobilization because As(III) may remain sorbed onto Fe oxides (Dixit & Hering, 2003; Inskeep et al., 2002). Amorphous Fe-oxyhydroxides are rapidly dissolved through reduction, with slower reductive kinetics for crystalline phases (Inskeep et al., 2002).

Oxidative dissolution of sulfide minerals is another important source of As (Hering & Kneebone, 2002; Smedley & Kinniburgh, 2002). Pyrite and other iron sulfides are frequent hosts for As, and their instability in aerobic systems results in the formation of Fe oxyhydroxides, the release of dissolved SO_4 and trace elements, including As, and an increased in acidity (Smedley & Kinniburgh, 2002). However, as the system returns to

neutral pH, re-precipitation of hydrous ferric oxides typically readsorb As so this only affects highly acidic waters common to acid mine drainage but atypical for natural waters (Smedley & Kinniburgh, 2002). Abiotic oxidation of As(III) by Mn(IV)-oxides may also occur. The oxidized As(V) may remain sorbed or be released into solution depending on surface site availability and solution conditions (Campbell & Nordstrom, 2014).

The presence of natural organic matter (NOM) has several effects on As mobility. NOM may mobilize As through competitive desorption, particularly from iron oxides, and by affecting redox conditions. NOM can also remove dissolved As from solution through direct complexation on solid organic phases or formation of a ternary surface species between As and the oxide surface (Campbell & Nordstrom, 2014; Smedley & Kinniburgh, 2002). However, formation of stable Fe oxide colloids and particles coated with NOM may ultimately result in increased As mobility due to subsequent changes in solution chemistry that drive As remobilization (Campbell & Nordstrom, 2014; Wilkie & Hering, 1996).

Speciation of As, along with the presence and concentration of other ions, determines the effect of pH on As mobility (Dixit & Hering, 2003). Most common oxy-hydroxides that are effective As sorbents have a point of zero charge around 8-9, above which As would be released into solution. High pH can also affect competitive desorption through direct competition by hydroxyls and increased competition of dissociated species (e.g. Si and P; Xu et al., 2012). With regards to iron oxides, at increasing pH, i.e. $\text{pH} \geq 7$, As(V) desorption is greater than As(III) desorption, which remains stable up to pH 9; at low pH, As(V) is more strongly sorbed than As (III) (Dixit & Hering, 2003; Wilkie & Hering,

1996). Typically cited values of As desorption due to increased pH start at 8.5, although ultimately, As mobility is highly sensitive to Eh/pH conditions (Smedley & Kinniburgh, 2002).

Ionic competition can occur between As oxyanions and phosphate, hydroxyl, sulfate, silicate, inorganic carbon, and other species (Campbell & Nordstrom, 2014). Phosphate is frequently cited as the most effective competitor, owing to its similarities in molecular structure and charge, as well as its potential to form inner-sphere complexes on similar surface sites (Campbell & Nordstrom, 2014). The effectiveness of phosphate competition is also demonstrated experimentally (Dixit & Hering, 2003; Neupane, Donahoe, & Arai, 2014; Xu et al., 2012). Xu et al. (2012) found that phosphate desorbed 2-3 orders of magnitude more As than sulfate, silicate, or bicarbonate. Phosphate most effectively desorbs As(V) at high pH (>10), with limited effects at lower pH and with As(III) (Neupane et al., 2014; Xu et al., 2012).

Other elements may compete with As for sorption sites. Carbonate species, while not effective competitors, are abundant at high pH where carbonate is stable and has greater affinity for surface sites. Sulfate adsorbs to iron oxides but may prefer different surface sites to those preferred by As. Sulfate was observed to competitively desorb As(III) from hydrous ferric oxide within pH 4-7, have decreased competition at higher pH, and have no competitive effect with As(V) (Wilkie & Hering, 1996). Other oxyanion forming metalloids, such as Mo, Se, Cr, and W, may compete with As, but their low concentrations in natural waters makes them poor competitors and unlikely to drive As behavior (Campbell & Nordstrom, 2014). Silica as silicic acid may be an effective

competitor at high pH (>8) when it dissociates to the anionic species, which was experimentally demonstrated by Xu et al. (2012) in As desorption from ferric manganese bearing oxides. Adsorption of divalent cations Ca^{2+} and Mg^{2+} may increase adsorption of As as seen for As(V) on iron oxides perhaps due to the formation of positive surface charges favoring the adsorption of anions. However, the addition of Ca^{2+} decreased As adsorption on kaolinite so effects of cations on As mobility remain unclear (Campbell & Nordstrom, 2014; Wilkie & Hering, 1996).

Volcanic association with arsenic

Volcanic sources of arsenic

Igneous rocks have relatively homogenous As concentrations, slightly increasing with Si content (Onishi, 1955; Smedley & Kinniburgh, 2002; Welch et al., 2000). Concentrations of bulk As in igneous rocks are typically below 5 mg/kg, and volcanic glasses separated from igneous rocks are only marginally enriched (average = 5.9 mg/kg; Figure 2). The frequent association of silicic volcanic rocks with As-contaminated aquifers is commonly attributed to reactive nature of acidic volcanic rocks, particularly fine-grained ash, which tends to produce Na-rich alkaline groundwaters and concentration of As onto weathering products, (e.g. ferric oxyhydroxide; Smedley & Kinniburgh, 2002; Welch, Lico, & Hughes, 1988). Despite relatively low values and variability, many studies attribute As contamination with volcanic rocks, and particularly ash and weathering products (e.g. Smedley & Kinniburgh, 2002; Twarakavi & Kaluarachchi, 2006; Wang & Mulligan, 2006; Welch et al., 1988).

In volcanic processes, $\text{As}(\text{OH})_3$ is the dominant form of As. $\text{As}(\text{OH})_3$ is enriched in the gas phase by two to three orders of magnitude more than magma at temperatures from 400-900°C; below 350°C, As is preferentially enriched in the liquid phase (Pokrovski et al., 2002; Symonds, Reed, & Rose, 1992). In a study of active fumarolic areas in Japan, Mambo and Yoshida (1993) observed elevated As and the narrow range of As concentrations across all fumarolic ejections, regardless of composition, which suggests direct vaporization from magma with little modification, consistent with fumarole temperature correlating with As content (Mambo & Yoshida, 1993).

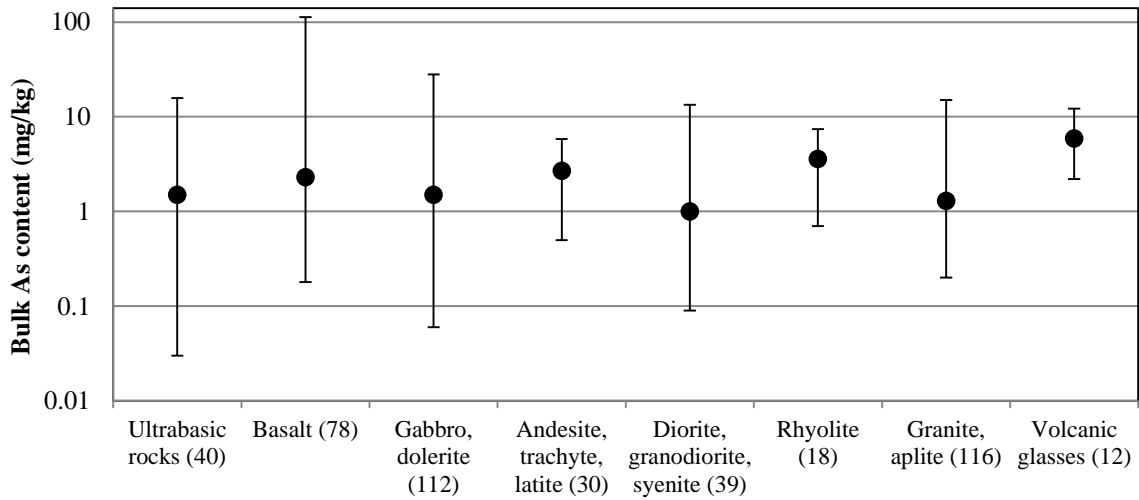


Figure 2: Average bulk As content (mg/kg) in igneous rocks and associated deposits; number in parenthesis indicates number of analyses. Data modified from Smedley & Kinniburgh (2002) and Onishi & Sandell (1955).

Pyroclastic deposits

Ross and Smith (1960) define an ash-flow tuff as “consolidated deposits of volcanic ash resulting from an ash flow.” Ash flow tuffs are distinct from ash fall tuffs in that ash fall tuffs are sorted and may display bedding, whereas ash flow tuffs may preserve flow features due to emplacement processes. Pyroclastic material can then be crystallized

through devitrification, which takes place within glass fragments or masses, or vapor-phase crystallization, wherein vapor phases crystallize within open pores. Devitrification produces radial or needly intergrowths of microcrystalline cristobalite and feldspar (spherulites and axiolites). In contrast, vapor phase crystallization is typically coarser grained and results in a more variable mineral assemblage due to the variation in vapor composition (Breitkreuz, 2013; Ross & Smith, 1960; Vaniman, Chipera, Bish, Carey, & Levy, 2001). Typically, both devitrification and vapor phase crystallization refer to crystallization that occurs during or synchronous with cooling, and any subsequent crystallization is commonly considered secondary, low-grade alteration although it can be difficult to determine the timing of crystallization (Ross & Smith, 1960; Smith, 1980). Welding is the deformation of glass particles that begins immediately after emplacement and continues until the tuff is either completely welded or cooling/crystallization of glass prohibits further welding. Welding and crystallization are interrelated in that the densely welded zone of tuffs has no pore space and only devitrification may occur. Conversely, crystalline porous zones in ash flows are dominated by vapor phase crystallization (Ross & Smith, 1960; Smith, 1980). The type of pyroclastic deposition also determines the form of crystallization: ash fall pyroclastic deposits allow for separation of the gas phase, while pyroclastic flows and surges retain gas in the deposit, allowing for vapor phase crystallization if pore space is retained (De' Gennaro, Inconato, Mastrolorenzo, Adabbo, & Spina, 1999).

Alteration of pyroclastic deposits

Volcanic glass is unstable at surface conditions and will alter to more stable crystalline phases, such as smectite and zeolite, given sufficient time or elevated

temperatures (De' Gennaro et al., 1999; Vaniman et al., 2001). The alteration product depends primarily on eruptive and depositional conditions, and secondarily on composition, grain size, and age. The presence of condensing water vapor is essential to zeolitization and therefore is contingent upon depositional mechanism; ash flow tuffs and surges retain water vapor, whereas there is immediate separation of water vapor in ash fall tuffs (De' Gennaro et al., 1999). Finer grain size allows for more contact between permeating solutions and glass, reducing reaction time (De' Gennaro et al., 1999). In terms of composition, the Si/Al ratio and Na/K ratio are the most important tools in determining which alteration minerals form; for example, zeolites such as phillipsite and chabazite form in K- and Na-rich, Si-poor environments, whereas smectites form in Si-rich, alkaline conditions (De' Gennaro et al., 1999; Fuente, Cuadros, Fiore, & Linares, 2000). Illite and illite-smectite were thought to form from glass with smectite as an intermediary, but direct alteration of glass to illite and illite-smectite was observed on the surface and rims of glass while preserving the original form particle morphology (Fuente et al., 2000). Given the tectonic regimes in which tuffs occur, subsequent hydrothermal alteration or metamorphism is also common (Vaniman et al., 2001).

Extensive chemical modification may also occur at the time of emplacement and subsequent alteration. During initial cooling, devitrification, and hydration, volatiles (potentially including As) may be lost and alkalis locally mobilized. Subsequent leaching of Na, K, and Si, oxidation of metal oxides, enrichment of Ca and Mg, and changes accompanying formation of clay minerals and zeolites may occur (Noble, 1970; Scott, 1971; Vaniman et al., 2001). Aluminum remains relatively immobile during devitrification and zeolitization and alkali to alumina ratios are commonly used as an

indicator of geochemical alterations (Vaniman et al., 2001). While lava flows may be considered a relatively closed system upon emplacement, pyroclastic deposits, particularly tuffs, have significant glass-shard surface area allowing significant fluid migration, constrained by the degree of welding (Scott, 1971). The thickness of the tuff deposit, and in turn its degree of welding and zonation, strongly controls potential for alkali exchange and other modification; thicker units (typically >100 m) display extensive alkali exchange through water-glass interactions in addition to modification made possible by devitrification (Scott, 1971). However, not all studies report geochemical changes accompanying devitrification: Rowe, Ellis, & Lindeberg (2012) in their study of the Tuff of Knob within the Snake River Plain did not observe any difference in bulk geochemical analysis between the vitrophyre and devitrified portion. However, differences in alkali content were observed between the groundmass of each suggesting alteration only affected the tuff on a very local scale.

Considering volcanism's substantial contribution of environmentally hazardous trace elements, alteration of volcanic units which may make these contaminants available to the environment remains remarkably unstudied. Several studies have focused on the potential of fresh, unaltered volcanic glass and ash for sorption, particularly with regard to nuclear waste disposal. Wolfsberg et al. (1979) examined sorption capacity of several tuffs from Jackass Flats, NV, and found that differences in mineralogy indeed effected sorption capacity: the zeolitized and fresh glassy tuffs have high to intermediate sorption while the partially welded, devitrified tuff had low to intermediate sorption and greater total desorption for all elements studied. Glass was particularly associated with high sorption for Sr, Cs, and Ba, while zeolites had high sorption for Sr, Cs, Ba, Eu, and Am.

Anionic or soluble complex-forming elements (I, Sb, Mo, and U) had low or zero sorption under the conditions of the experiment (Wolfsberg et al., 1979).

Stimac et al. (1996) in their study of the Bandelier Tuff observed increased Pb content within and potentially on the surface of fine-grained replacement products (e.g. smectite and hematite), formed during post-emplacment vapor-phase crystallization and devitrification. Most of the Pb distribution within the unit was dependent on original magma chamber distribution, with only local redistribution by vapor transport and devitrification. Elements enriched in high-temperature magmatic vapors are also more abundant in sublimate assemblages (e.g. vapor-phase crystallization), suggesting that they formed directly from magma vapor and continued to form during the earliest stages of cooling. Stimac et al. (1996) suggest that similar to Pb, other metals that partition into the vapor-phase (such as As, Ag, Bi, Cu, Re, and Sb) are incorporated into or deposited onto micron-scale minerals upon eruption and through processes of vapor-phase crystallization and devitrification are more readily available to the environment.

Volcanic aquifers contaminated with arsenic

Volcanic ash and tuffs are responsible for As-contaminated aquifers around the world, e.g. Italy, Mexico, Argentina, and the western United States (Smedley & Kinniburgh, 2002; Welch et al., 2000). Common attributes include Na-HCO₃⁻ type, oxidizing, alkaline ground waters, elevated concentrations of B, Cr, F, Mo, Sb, U, and V (Aiuppa, D'Alessandro, Federico, Palumbo, & Valenza, 2003; Casentini, Pettine, & Millero, 2010; Mahlknecht et al., 2004; H. B. Nicolli, Suriano, Gomez Peral, Ferpozzi, & Baleani, 1989; Rango, Vengosh, Dwyer, & Bianchini, 2013; Tang & Johannesson, 2010;

Vinson et al., 2011). Mobilization of As from silicic volcanic products is commonly attributed to primary glass dissolution followed by secondary sorption onto Fe, Mn, and Al oxyhydroxides and clays, which is subsequently readily mobilized by pH desorption (Aiuppa et al., 2003; Johannesson & Tang, 2009; H. Nicolli, Bundschuh, & García, 2010; Rango et al., 2013; Tabein, Hashimoto, Igarashi, & Yoneda, 2014; Welch et al., 2000). In regions of higher geothermal activity, sulfide oxidation is considered the dominant mechanism mobilizing As (Aiuppa et al., 2003; Mahlkecht et al., 2004).

Arsenic contamination in the Southern Willamette Valley

Arsenic contamination in Lane County, located in western Oregon, has been a well-documented problem since the early 1960s. Goldblatt, Van Denburgh, & Marsland (1963) published the first data on groundwater As, finding 30.5% (n=53) of well samples exceeded 0.02 mg/L. They determined that the As-enriched water was principally dominated by dissolved Na^+ and HCO_3^- with low concentrations of Ca^{2+} and Mg^{2+} , as well as pH greater than 8.0. A second water type with As values mostly less than 0.01 mg/L has high TDS values (>500 mg/L), dominated by dissolved Na, Cl, and Ca, and high B. The third water type reported by Goldblatt et al. (1963) is dilute, with TDS less than 100 mg/L, and negligible values of As. Although well depth did not correlate with As concentration, most water samples in excess of 0.05 mg/L of As came from depths greater than 100 ft. and most samples from depths shallower than 50 ft. contained less than 0.01 mg/L of As. Goldblatt et al. (1963) attribute the elevated As to the Fisher formation, consisting of tuffaceous sediments, conglomerates, vitric and crystalline tuffs, breccias, and andesitic lava flows, with possible influence from the Eugene formation. They note that As is not uniformly distributed within the Fisher formation, but tends to

concentrate in the central and eastern areas of the formation, which typically contain younger units. Goldblatt et al. (1963) hypothesize that As and B were contained within the pyroclastic rocks deposited in the Fisher formation, then percolating surface water chemically altered the groundwater by replacing Ca and Mg with Na (“softening” the water) concurrently releasing As and increasing pH.

Whanger, Weswig, & Stoner (1977) studied As contamination throughout all of Oregon. They reiterate the common characteristics of high As waters in Oregon of low Ca^{2+} and Mg^{2+} relative to Na^+ , high B, high pH, high orthophosphate, with variable TDS, sulfate, and chloride. Their speciation data also showed that the vast majority (>95%) of As is present as As(V), although their specific methodology of As speciation were not reported.

Nadakavukaren, Ingermann, Jeddloh, and Falkowski's (1984) study of fourteen wells in Lane County did not find any correlation with As and pH, although eight of the fourteen wells had lower As concentrations in winter compared to summer. They suggested that deeper wells may have higher As contamination, and rainfall may also play a role although they were unable to make any definitive statements with such a limited study.

Hinkle and Polette (1999) reviewed historical data and conducted additional sample analysis for a combined 728 spatially distinct groundwater samples within the Willamette Valley to further understanding of As sources and mobility within the valley. They reported that 8.0% (n=58) of samples exceeded the EPA As standard at the time of their study (0.05 mg/L), and 21.7% (n=158) exceeded the WHO guideline of 0.01 mg/L,

which is the current EPA standard for As as of 2002 (USEPA, 2014). Similar to Goldblatt et al. (1963), they did not find a correlation of As with depth; they also found that most of the high As groundwater occurred within areas of exposed or thinly-covered bedrock in south-central and eastern Lane and Linn counties. They concluded that elevated As occurs within the Fisher and Eugene Formations, and within undifferentiated tuffaceous sedimentary rocks, tuffs, and basalt. They suggest that volcanic glass – still abundant in the Willamette Basin - is the primary source of As and, further, given that much of the glass in regional volcanic units has been devitrified, As is likely to have become associated with devitrification alteration products (e.g. clays and metal oxides) or to have been released into solution and subsequently precipitated or adsorbed elsewhere or flushed out. However, no direct measurement of As host phases was conducted in their study. Although redox potential was not measured by Hinkle and Polette (1999), field observations frequently noted sulfide odors, which indicate reducing conditions in the groundwater. Previous studies also found low dissolved oxygen, which further supports their hypothesis of reducing conditions. Because their study did not find especially alkaline waters, they believe some combination of reducing conditions, anionic competition, and elevated pH to be the most important factors in As contamination within the Willamette Basin.

These previous studies agree that the source of elevated As in groundwater are the Fisher and Eugene Formations and mostly agree that As-rich groundwater is characterized by low Ca^{2+} and Mg^{2+} relative to Na^+ , high B, high pH, and high phosphate, with variable TDS, sulfate, and chloride. However, precise processes of As liberation into groundwater remain unclear. Goldblatt et al. (1963) argued that the percolation of surface

water promoted weathering of volcanic glasses and minerals and the release of Na^+ which, in conjunction with ion exchange of Ca^{2+} and Mg^{2+} for Na^+ on clay surfaces, increased groundwater pH and mobilized As. Hinkle and Polette (1999) likewise agree that volcanic glass is the primary source of As. However, because their study did not find especially alkaline waters, they conclude that reducing conditions and anionic competition are the most important factors in As contamination within the Willamette Basin.

Although population exposure to As has historically been minimal because alternate water supplies have been used, increasing population and water demands in the future may increase human health risk (Morton, Starr, Pohl, & Stoner, 1976; OWSC, 2013). The self-supplied ground water population is nearly 20% of total population in Lane County (64,970), which makes Lane County the second-most dependent county on domestic water wells behind Clackamas County by both population served and self-supply ground water withdrawals (6.50 Mgal/day). Total water use, including surface and ground water has increased 500% from 1995 to 2005, and 167% from 2000 to 2005. Growing population indicates further reliance on ground water supplies as surface water supplies become increasingly depleted.

Methods

Sample collection and preparation

For this study, 24 samples were collected from 14 distinct outcrops within the Fisher Formation and Little Butte Volcanics Series in the southern Willamette Valley (Figure 3; Table 1). Samples were identified and located using reference maps from McClaughry et al. (2010) and Retallack et al (2004). Every effort was made to collect representative samples of each tuff unit within the formations. However, the region is largely vegetated and exposed outcrops are scarce. Where significant, observable differences were noted at an outcrop, multiple samples were collected. Eight additional samples from a previous study (Savoie, 2013) were included to better represent area tuff units identified by previous workers.

Collected hand samples were first trimmed with a water-cooled rock saw to remove any obviously weathered surfaces. A portion of each sample (~30 g) was then crushed to a fine gravel size with a Braun jaw-crusher and powdered with a tungsten carbide ring mill vibratory pulverizer for 2-3 minutes. The powdered samples were split using a Jones riffle splitter, with a subsample sent to Washington State University (WSU) Geoanalytical Lab, in Pullman, WA for bulk geochemical analysis and the rest retained for mineralogical analyses and leachate studies. Additional portions of the sample were either used for preparation of thin sections or retained for reference.

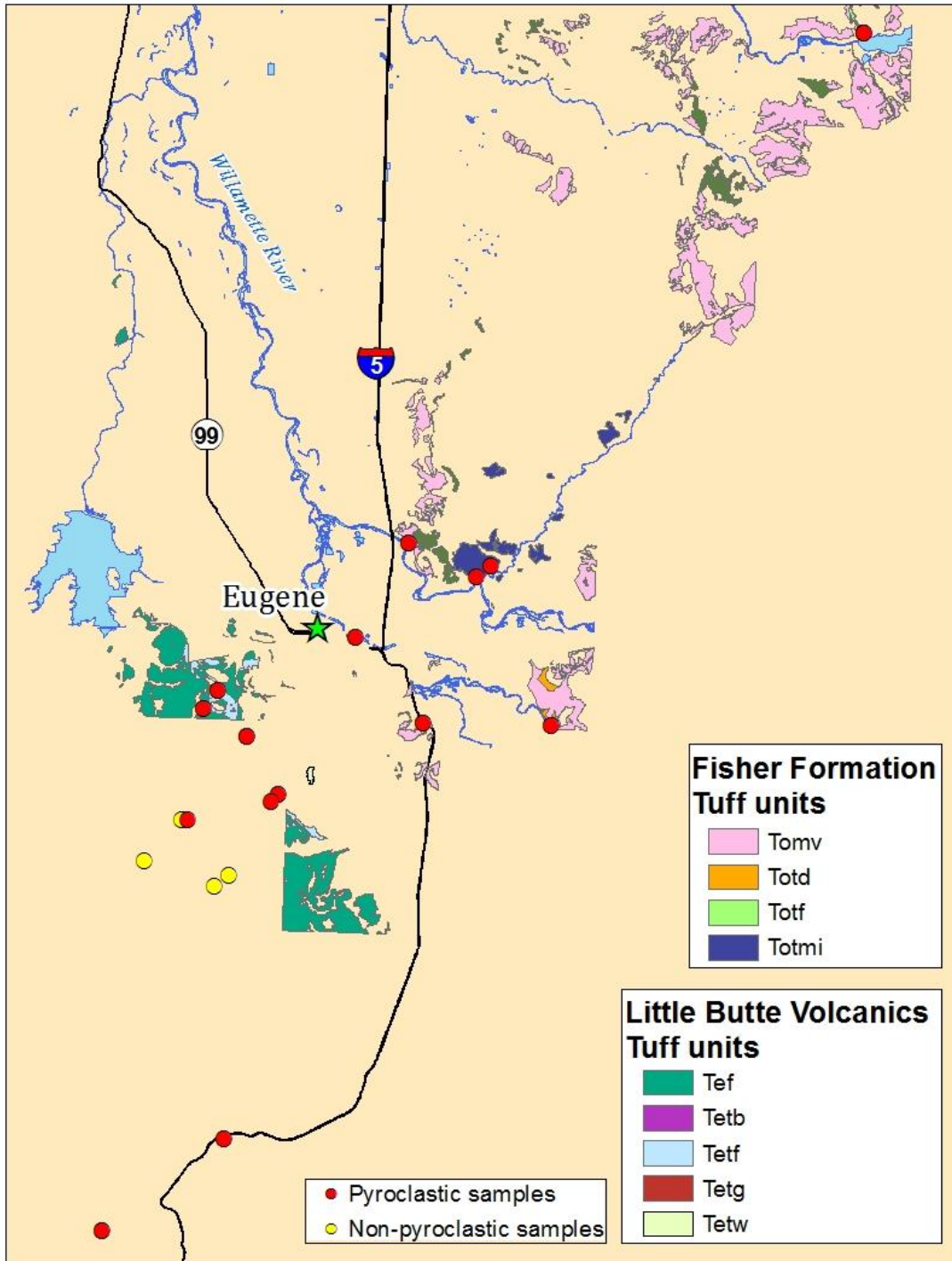


Figure 3: Sample locations referenced in this study

Table 1: Sample locations and units sampled in this study

| Formation | Unit | Age (Ma) | Sample ID | Latitude | Longitude |
|------------------------|--|-------------------|---------------------------|-------------------------------------|---|
| | Tuff of Dexter (Totd) | 25.9 | DX | 44.002109 | -122.908858 |
| | Tuff of Foster Dam (Totf) | 26.3 | FDI-4* | 44.419917 | -122.665317 |
| | Mehama (Tomv) "Tuff above Willamette Flora" | 30.6 ¹ | WF, WFW | 44.001258 | -123.014311 |
| | Tuff of Mohawk, intracaldera facies (Totmi) | 30.9 ² | MK1* MK2* | 44.095583 44.089033 | -122.962883 -122.974017 |
| Little Butte Series | Mehama (Tomv) Tuff of Spores Point | 31.3 ¹ | SP | 44.107890 | -123.031594 |
| | | | FineSS, Upper Cong | 44.002109 | -122.908858 |
| | | | OCshale, Basal SS | 44.001258 | -123.014311 |
| | Mehama (Tomv) | 25.9-34.8 | SporesPtSS WS2* WS3 | 44.107890 43.939033 43.955445 | -123.031594 -123.206820 -123.132974 |
| | Undivided (Tef) | 38 ¹ | LDNTuff | 43.749120 | -123.167949 |
| | Fox Hollow Tuff (Tetf) | 41.0 ¹ | FHr, FHb | 43.989685 | -123.160442 |
| | Tuff of Gimpl Hill (Tetg) | 41.8 ² | GHg GHw | 44.005758 44.016537 | -123.197287 -123.185691 |
| Fisher Formation | | | CongSSWeat | 43.906797 | -123.171772 |
| | | | CongSS, WeatBasalt | 43.899833 | -123.182794 |
| | Undivided (Tef) | 34.8-41.8 | MicaSS PebCong | 43.913169 43.938822 | -123.241703 -123.211908 |
| | | | LDNTuffSS, MicaSS | 43.692377 | -123.266201 |

¹Retallack, 2004; ²McCloughry et al., 2010

*Samples from Savoie, 2013

Bulk chemistry

Samples submitted to WSU were analyzed for major elements and trace elements (As, Ba, Ce, Cr, Cu, Ga, La, Ni, Nb, Nd, Pb, Rb, Sc, Sc, Sr, Th, U, V, Y, Zn, Zr) by x-ray fluorescence (XRF). Additional trace element analysis (Pr, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Cs) was performed by inductively coupled plasma mass spectrometry (ICP-MS).

Five samples were analyzed for bulk As at Portland State University. Acid digests were prepared following US EPA Method 3052 (US EPA, 1996). Powdered samples were weighed to 0.250 ± 0.001 g and added to Teflon containers along with 1.5 mL trace-metal grade HF, 4.5 mL trace-metal grade HNO_3^- , and 1 mL trace-metal grade HCl. Samples were digested in a Milestone Ethos EZ Microwaves digester for 40 minutes, reaching a final temperature of 240°C for 20 minutes. Following digestions, samples were poured into 50 mL plastic centrifuges tubes. The digest solutions were diluted to 50 mL with rinsate from the digest tubes and $18.2 \text{ M}\Omega\text{-cm}$ deionized water. Samples were further diluted ten and fifty times for analysis by Agilent 700 Series ICP-OES.

Optical mineralogy

Cut samples were sent to Spectrum Petrographics in Vancouver, WA, for preparation of covered thin sections which were examined to determine volcanic textures, pyroclastic materials, and primary mineral assembly.

X-Ray diffraction

Sample mineral assemblages were determined via X-ray diffraction (XRD) analyses using a Phillips (now PANalytical) Theta-Theta PW3040 X-ray diffractometer equipped with a standard scintillation counter and copper anode X-ray lamp. For these analyses, powdered samples were further crushed with an agate mortar and pestle until passing a 65- μm sieve and prepared as random powder mounts in a side-pack aluminum sample holder. Diffraction patterns were obtained in continuous mode using a step size of 0.020 degrees two theta ($^{\circ}2\theta$) and scan step times of 1.00 second from 3 to 70 $^{\circ}2\theta$. Sample diffraction patterns were analyzed with the PANalytical X'Pert Highscore Plus software package.

Scanning electron microscopy

Billets that remained after thin section preparation for select samples (FHr, FHb, and BCw) were analyzed by scanning electron microscopy. The billets were polished down to a 1- μm finish by diamond polish and coated with carbon to reduce charging during the SEM examination.

Due to instrument repairs, the FHr and FHb samples were analyzed on an FEI Sirion SEM equipped with Oxford EDS detector at 20 kV. Compositional images were generated by the secondary-electron detector with negative bias turned off to create a pseudo-compositional mode. The BCw sample was analyzed on a Zeiss SIGMA SEM equipped with Oxford WDS/EDS detector at 20 kV. Mineral chemistry was determined using the WDS/EDS detector for in situ point analysis and element abundance maps.

Spectra and mineral phase identification was completed using Oxford AZTEC software package.

Leachate experiments

Powdered samples were evaluated for aqueous As mobility under a variety of pH conditions and P concentrations (Table 2). These experiments utilized 1:20 solid:solution ratios, usually 0.5-1.0 g to 10-20 mL of solution depending on subsequent analyses. All solutions were prepared using 18.2 M Ω -cm deionized water and reagent-grade or trace-metal-grade chemical reagents. Samples were mixed in 50 mL centrifuge bottles at 20 rpm then centrifuged at 3000 rpm for 15 minutes. Except for a set of time-series experiments, samples were mixed for 24 hours. Following centrifugation, 8 mL of supernatant were pipetted from the top of the solution column and acidified with 0.200 mL (2.5%) trace-element-grade HNO₃ for elemental analysis, while the remainder was decanted for pH measurement and anion analysis if applicable.

Time series were conducted by weighing samples to 2.500 g \pm 0.002 g and mixing with 50 mL of solution, either deionized water or 0.1 mM phosphate as P in centrifuge tubes. At five time points (4, 10, 24 or 50, 72, and 194), samples were centrifuged at 3000 rpm for 15 minutes, and 8 mL were pipetted into clean aliquots and acidified with 0.200 mL of trace metal grade nitric acid for analysis. Because a 24 hour analysis had already been performed for water only leachate in prior experiments, samples were additionally separated at 50 h while 0.1 mM phosphate solutions were removed at 24 h.

Elemental analyses were performed using an Agilent 720 axial inductively coupled plasma – optical emission spectrometer (ICP-OES); operating conditions and elemental wavelengths used are included in Appendix A.

Quality assurance

Quality assurance and control procedures were maintained throughout this study to ensure data accuracy and precision. Sample bottles and vials were cleaned by soaking in a 5% (by volume) nitric acid bath for 24+ hours and triple rinsing with 18.2 MΩ-cm deionized water. All leachate experiments were run in duplicate.

For elemental analyses via ICP-OES, a calibration was performed prior to each sample run using a minimum of five external standards prepared from commercial NIST-certified multi-element stock solutions. Most elements were analyzed via multiple wavelengths in case of unexpected spectral interferences and, where interferences were negligible, to provide verification of resulting concentrations.

Table 2: Composition of leachate solutions

| Solution name | Composition | pH of Solution |
|----------------------|---|-----------------------|
| Water | Deionized water (18.2μS/L) | -- |
| MOPS7 | [C ₇ H ₁₅ NO ₄ S] + 0.1 M HCl (10 mM) | 7.0 |
| pH 7 + P | KPO ₄ monobasic + NaPO ₄ dibasic | 7 |
| Tris8, Tris9 | Trizma base [(HOCH ₂) ₃] + Trizma HCl [(HOCH ₂) ₃ CNH ₂ ·HCl] (10 mM) | 8.09, 8.71 |
| pH 9 | Boric acid + NaOH +KCl | 9 |
| CAPS 10 | C ₉ H ₁₉ NO ₃ S + 0.1 M NaOH | 10.0 |
| pH 10 | 0.05 M NaHCO ₃ + 0.1 M NaOH | 10.4 |
| pH 11+P | NaPO ₄ tribasic + NaHCO ₃ | 11 |

| | | |
|------------------------------|-------------------------------|-----------|
| 10 μM P, 0.1 mM P | Diluted from 1 ppm P solution | 6-7 |
| 1 mM P, 100 mM P | K_2HPO_4 | 7.25, 8.8 |

Quality control standards, prepared from different NIST-certified multi-element stock solutions, were run at a minimum after every 20 samples. Instrument detection limits and method reporting limits (IDLs and MRLs) were determined twice during the course of this study by analyses of seven to ten near-blank ($\sim 5 \text{ ug/L}$) standards. The IDLs were calculated to be three times the standard deviation of the resulting measured concentrations for each element and the MRLs ten times the standard deviation. Because results from multiple analyses are combined for comparative purposes, the most conservative limit is used. Since multiple wavelengths are analyzed for each element, wavelength selection was based on the degree of precision (determined by difference from known standards) and detection limits. Quality control/assurance data for elements discussed are included in Appendix C.

Geospatial distribution of groundwater As

Data for groundwater As concentrations were downloaded through the Pacific Northwest Water Quality Data Exchange Network (Department of Environmental Quality, 2015), which provides latitude/longitude of wells sampled and As concentration. The point data were spatially joined to surficial geologic maps in the region created by McClaughry et al. (2010). Geologic units were broadly grouped on the basis of lithologic type. Complete units for each group are provided in Appendix E.

Results

Bulk geochemistry

Bulk chemistry data were examined from analyses of eight tuff and tuffaceous sediment units within the Willamette Valley (BC, DX, FD, FH, MK, SP, WF, and WS; see Table 1 for unit definitions). Interpretation and visualization of bulk chemistry to characterize volcanic rocks and compare samples within units was performed with Geochemical Data Toolkit (Janoušek, Farrow, & Erban, 2006). Complete geochemical results for samples analyzed in this study are included in Appendix B. Additional geochemical data were obtained from McClaughry et al. (2010) and Savoie (2013). A total alkali versus silica plot of tuff samples indicates that most samples plot as rhyolite or dacite (Figure 4).

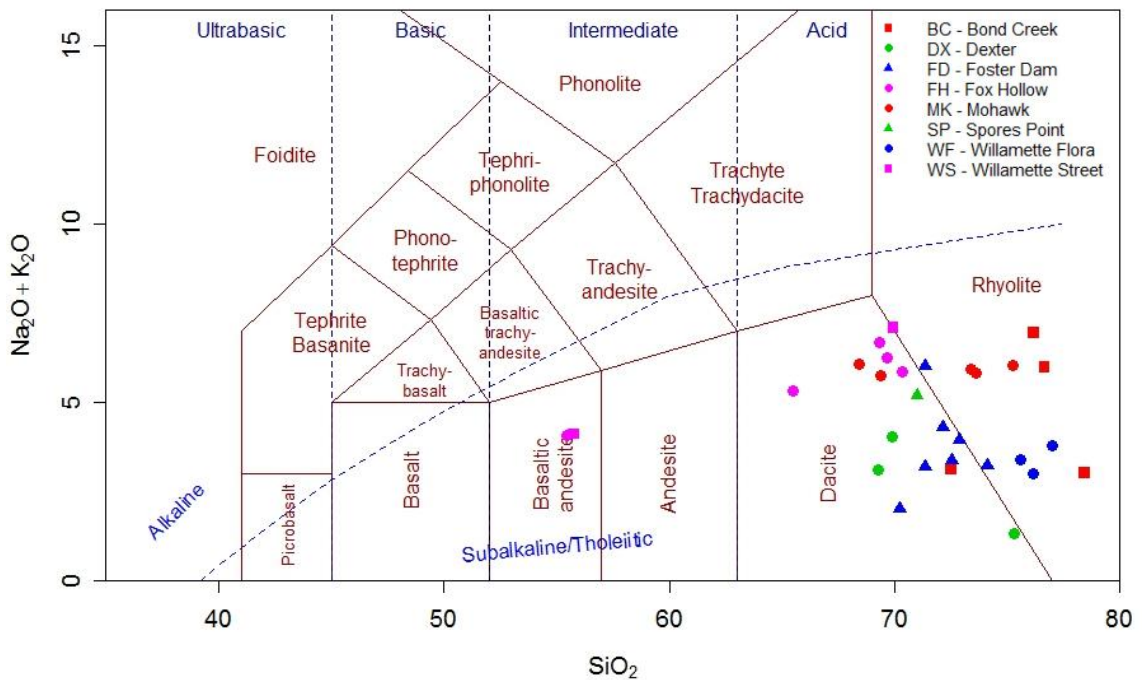


Figure 4: Total alkali silica diagram of samples in the study based on Le Bas et al., 1986.

It is very likely that significant loss of Na₂O and K₂O has occurred in the time since deposition, since samples are 25-42 Ma and any alteration or weathering is likely to result in loss of alkalis (De' Gennaro et al., 1999; Vaniman et al., 2001). Two samples plot as basaltic andesites: a Fox Hollow (FH) sample from DOGAMI's database and sample of Willamette Street (WS) unconsolidated sediment. The Ishikawa alteration index (AI), which quantifies the loss of sodium associated with plagioclase and volcanic glass breakdown, is defined below (Ishikawa, Sawahuchi, Iwaya, & Horiuchi, 1976):

$$AI = \frac{100 (K_2O + MgO)}{(K_2O + MgO + Na_2O + CaO)}$$

The Ishikawa alteration index was originally developed to identify volcanically hosted massive sulfide deposits, but is also applied to glassy volcanic rocks to determine degree of alteration (e.g. Gifkins & Allen, 2001; Large, Gemmell, Paulick, & Huston, 2001).

Ishikawa alteration indices for samples in this study range from 17 to 43 (Table 3).

Values ranging from 20 to 60 are interpreted as weak or diagenetic alteration, and values from 50 to 100 are interpreted as hydrothermal alteration (Gifkins & Allen, 2001; Large et al., 2001).

Table 3: Ishikawa (1976) alteration indices for tuff samples in this study

| | | | | | | | | |
|------------------|------------|------------|------------|------------|------------|------------|------------|------------|
| Sample ID | BCg | BCw | DX | FD1 | FD2 | FD3 | FD4 | |
| Alteration Index | 32.8 | 32.5 | 23.4 | 26.7 | 20.8 | 17.3 | 43.3 | |
| Sample ID | FHb | FHr | MK1 | MK2 | WF | WFw | WS1 | WS2 |
| Alteration Index | 31.0 | 23.9 | 22.6 | 23.7 | 16.2 | 17.3 | 21.2 | 26.5 |

Spider diagrams were constructed for available trace elements to examine differences among samples within the same tuff unit and to confirm that samples collected for this study were associated with the correct unit. Data source for bulk chemistry is indicated by prefix (D: McClaughry et al., 2010; CS: Savoie, 2013; GF: this study). For comparative purposes, samples were normalized to the average composition of three Foster Dam samples analyzed by McClaughry et al. (2010) because they are likely the least altered as evidenced by their glassy groundmass. Trace elements are generally arranged from the left to right by decreasing mobility based on ionic potential, following Pearce (1983).

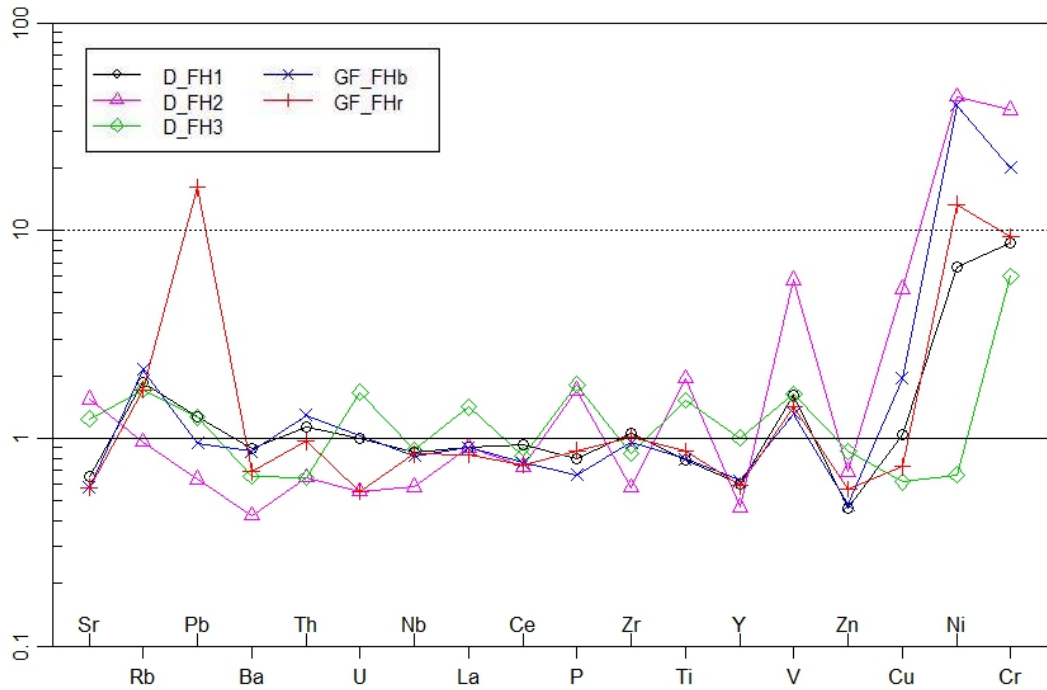


Figure 5: Trace element geochemistry of Fox Hollow tuff samples normalized to average of Foster Dam tuff samples.

D_FH1 corresponds with the location sampled for this study (GF_FHr and GF_FHb) and all three follow similar patterns, with greater deviation occurring for Pb, U, and transition metals Cu and Ni (Figure 5). FHr is enriched in Pb significantly as well as P and depleted in U. FHb has elevated Cu, Ni, Cr, Ba, and Th relative to both D_FH1 and GF_FHr.

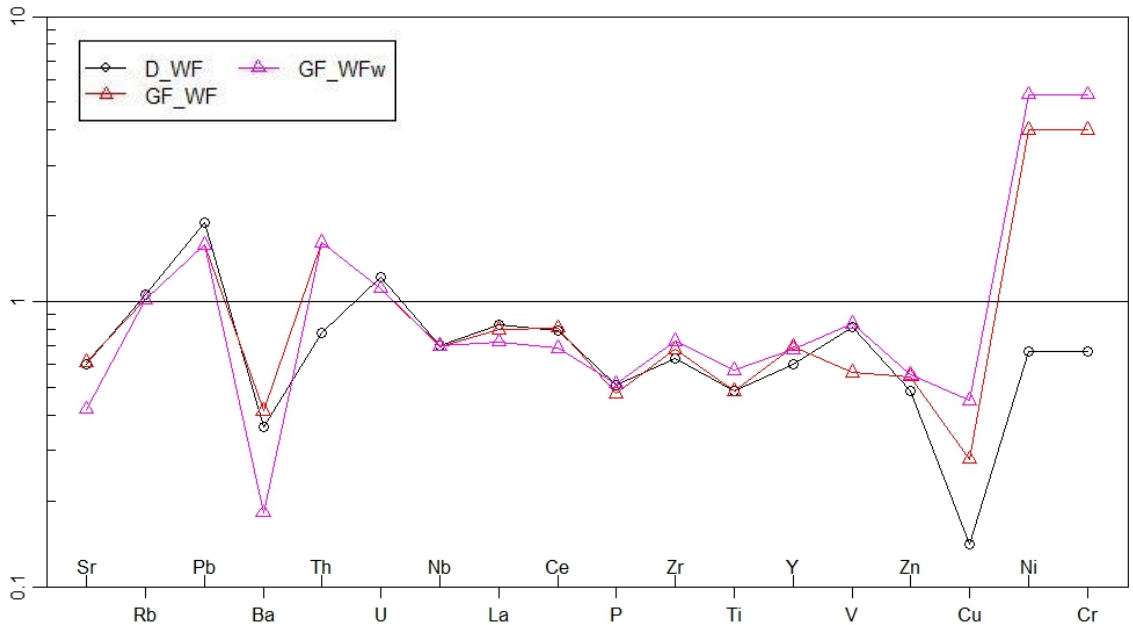


Figure 6: Trace element geochemistry of Tuff above Willamette Flora samples normalized to average of Foster Dam tuff samples.

All three samples of Willamette Flora are from the same outcrop and follow a similar pattern with greater variation occurring for transition metals Cu, Ni, and Cr (Figure 6). GF_WFw is depleted in Sr and Ba, and enriched in Cu, Ni, and Cr relative to GF_WF and D_WF. GF_WF is depleted in V and somewhat enriched in Cu, Ni, and Cr relative to D_WF.

All four samples of Mohawk tuff are from distinct outcrops and display greater variation with the transition metals, Ti, Zn, Cu, Ni, Cr, and V and P (Figure 7). CS_MK1

is enriched in Ni and Cr compared to other MK samples examined. CS_MK2 is depleted in P, Zn, Cu, and Cr relative to other MK samples examined.

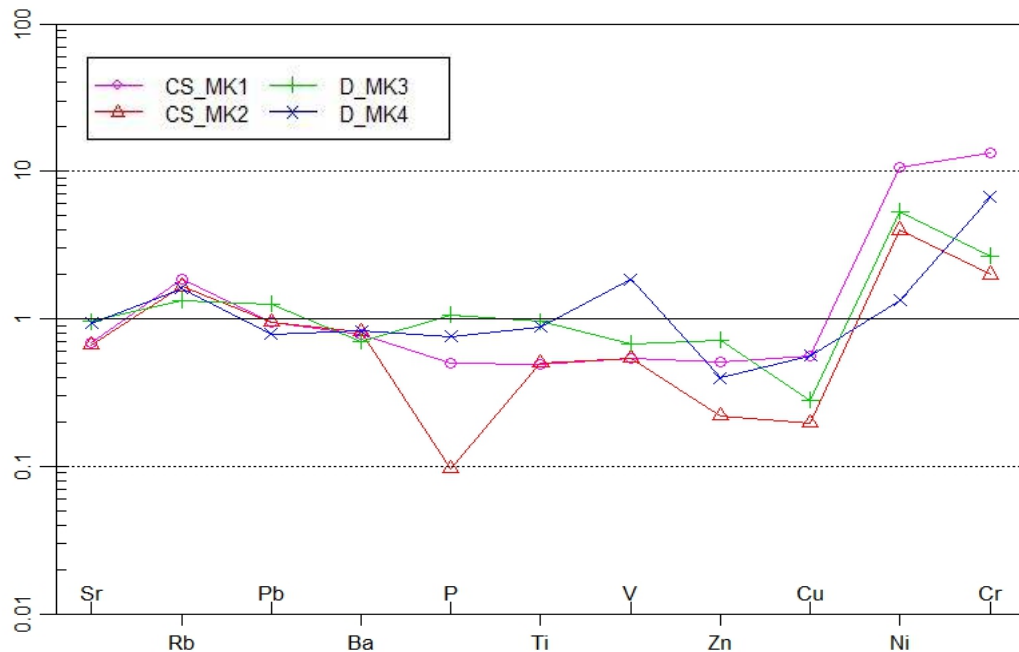


Figure 7: Trace element geochemistry of Mohawk tuff samples normalized to average of Foster Dam tuff samples.

Crystallization and welding classification

Tuffs are classified (Table 4) based on the form of crystallization and welding following Streck (1994) as determined by optical mineralogy. Crystallization is broadly categorized as either glassy or devitrified. Incipiently devitrified tuffs are defined as retaining glass shards with a devitrified fine-grained matrix, often altered to sericite, which occurs post-emplacement (Camp, 2004; Figure 8). Entirely axiolitic shards that retain glass morphology are classified as cryptocrystalline, which Streck (1994) describes as vapor phase crystallization.

Table 4 : Crystallization and welding classification of samples (following Streck, 1994).

| | Unit (Ma) | Sample ID | Crystallization | Welding | Tuff classification |
|--------------------------------------|-------------------------|------------------|--|------------------------------------|--|
| Little Butte Volcanics Series | Totf (26.3) | FD1 | glassy | partially welded | vitric-pumice-lithic ash tuff |
| | | FD2 | glassy | partially welded | vitric-pumice-lithic ash tuff |
| | | FD3 | glassy | partially welded | vitric-pumice-lithic ash tuff |
| | | FD4 | glassy | partially welded | vitric-pumice-lithic ash tuff |
| | Tomv (30.6) | WF | axiolitic rims ¹ | nonwelded | incipiently devitrified ash fall tuff |
| | | WFw | axiolitic rims | nonwelded | incipiently devitrified ash fall tuff |
| | Totmi (30.9) | MK1 | pervasively devitrified (felsitic) | densely welded | devitrified crystal-rich ash flow tuff |
| | | MK2 | pervasively devitrified (felsitic) | densely welded | devitrified crystal-pumice ash flow tuff |
| | Tomv (31.3) | SP | pervasively devitrified (felsitic) | partially welded | devitrified crystal-rich ash flow tuff |
| | Tetb (34.8) | BCg | axiolitic rims, few spherulites | incipiently welded | incipiently devitrified ash flow tuff |
| | | BCw | Volcaniclastic sandstone | | |
| | Fisher Formation | Tetw (35-36) | WS1 | pervasively devitrified (felsitic) | densely welded |
| WS2 | | | pervasively devitrified (felsitic) | densely welded | devitrified crystal-ash tuff |
| WS3 | | | Unconsolidated sediment | | |
| Tef (38) | | LDN | lithophysae | partially welded | crystal-lithic lapilli tuff |
| Tetf (40.8) | | FHr | devitrified (cryptocrystalline) | incipiently welded | devitrified ash-flow tuff |
| | | FHb | devitrified (cryptocrystalline, spherulites) | incipiently welded | devitrified ash-flow tuff |
| Tetg (41.8) | | GHg | lithophysae | partially welded | lapilli-pumice-lithic tuff |
| | | GHw | pervasively devitrified (felsitic) | densely welded | devitrified lithic-tuff |

¹ *Incipiently devitrified* defined by Camp, 2004

Pervasively devitrified with no glass retained is described as felsitic, which Streck (1994) called pervasively devitrified (Figure 8b). Spherulites, radial intergrowths of quartz and plagioclase feldspar, are found in isolation within vugs or completely intergrown forming groundmass (Figure 8c, 8e). Sericite alteration commonly accompanies devitrification products, sometimes entirely replacing spherulites or axiolitic rims. Lithophysae are defined as recrystallization phenomena where a crystallization rind grows outward to form crystal-filled voids, and then may become partially or completely hollow (Figure 8g; Streck, 1994). Lithophysae and spherulites, both considered high temperature crystallization domains, are distinct from vapor phase crystallization and vesicles formed by the exsolution of volatiles (Breitkreuz, 2013).

Nonwelded tuffs completely retain cuspid and Y-junction glass shards. Incipiently welded tuffs indicate preservation of glass shard shape with some adhesion of glass shards. Partially welded with pumice or fiamme (flattened pumice) has deformed or flattened glass shards. Densely welded tuffs are identified on the basis of pervasive devitrification, although most pervasively devitrified tuffs are dominantly felsitic which overprints welding degree. Densely welded obsidian-like black vitrophyre was not found within the sample area as the base of most units within the study are not exposed (McClaghry et al., 2010).

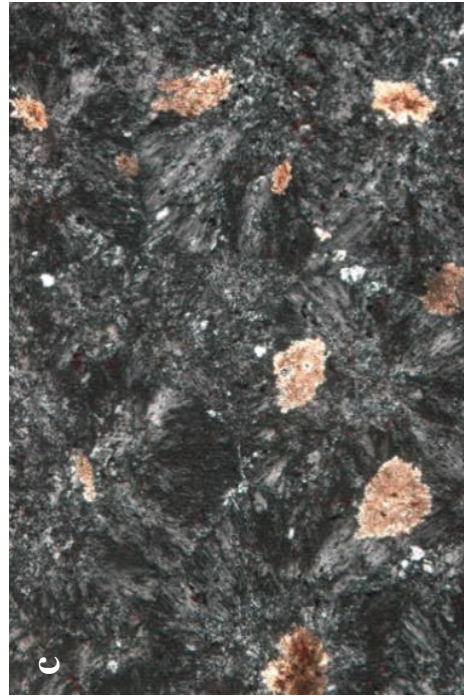
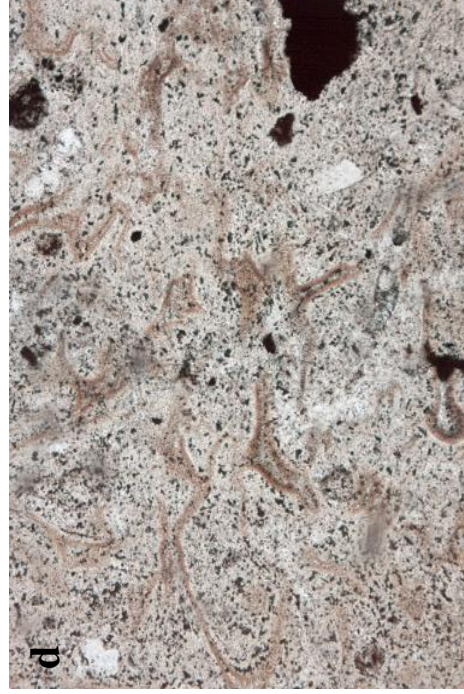
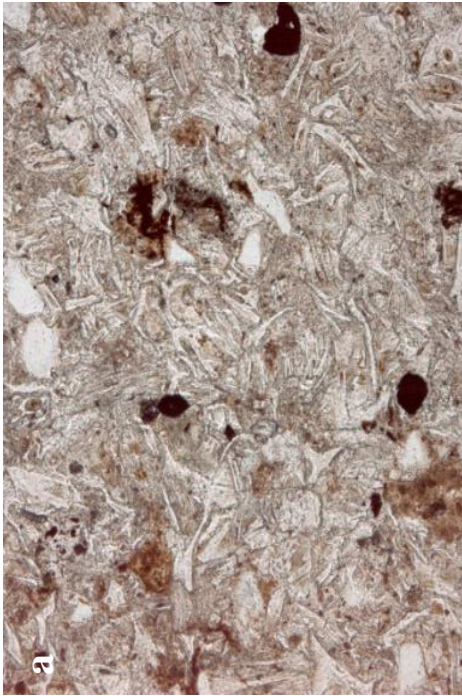
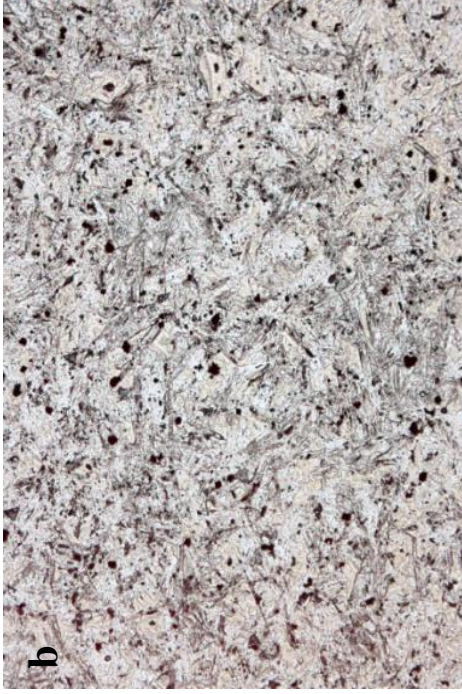


Figure 8a-d: (a) WF: PL incipiently devitrified groundmass with large oxides FOV = 16 μ m; (b) SP: PL felsitic groundmass texture, small oxides, FOV = 16 μ m; (c) FHb: XP, intergrown spherulites and sericite, FOV = 16 μ m; (d) FHr: devit/ox glass gm, FOV = 8 μ m

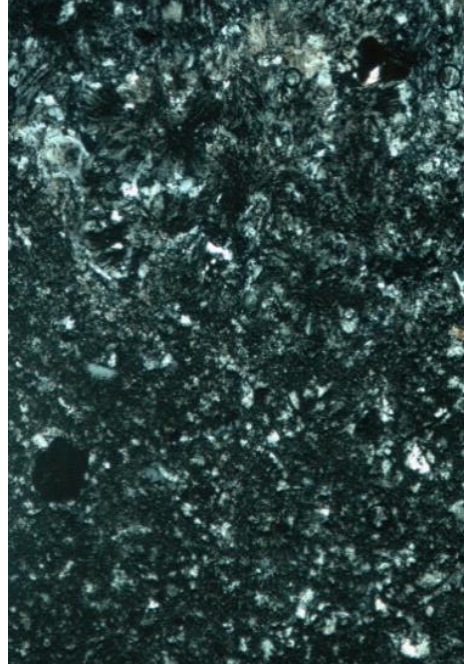
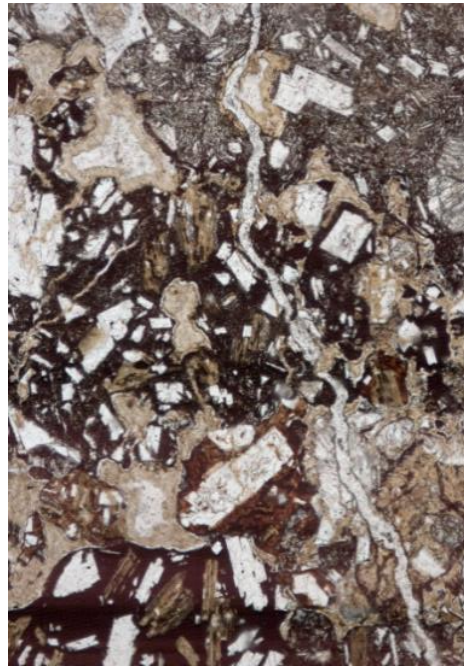
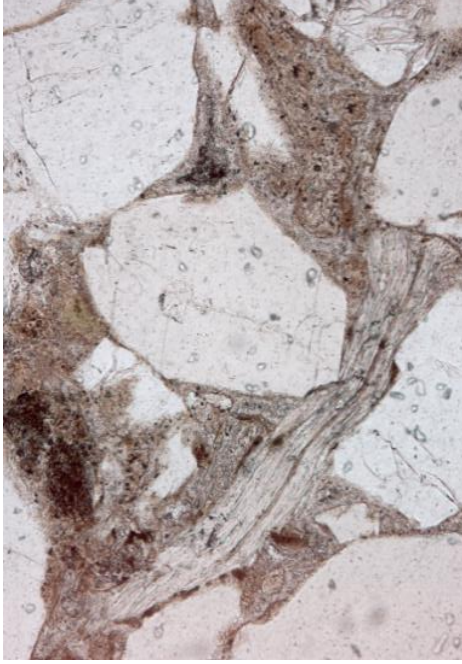
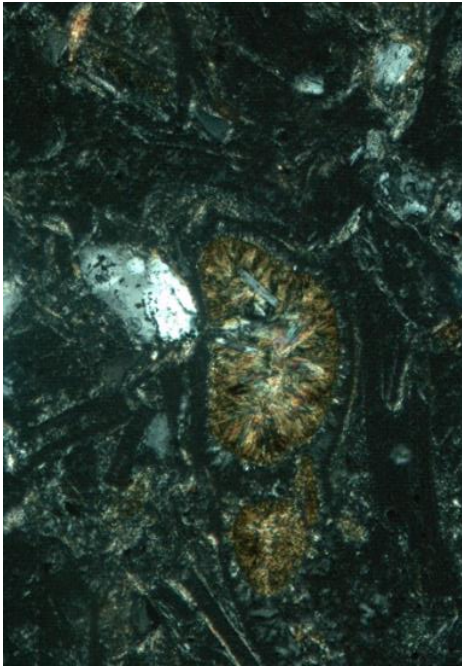


Figure 8e-h: (e) BCg: XP, spherulite altered to sericite, FOV = 8 μ m; (f) BCw: PL, flattened pumice in volcanoclastic ss, FOV = 16 μ m; (g) LD: PL, oxidized gm with lath plagioclase and recrystallized pores, FOV = 64 μ m; (h) GHw: PL, boundary between spherulitic and cryptocrystalline textures, FOV = 32 μ m

Mineral Assemblage

The mineral assemblage was determined by optical microscopy and x-ray diffractometry. Major mineral phases identified in samples are summarized in Table 5. Most common minerals include feldspars, silica phases, clay alteration products, and trace ferromagnesian minerals and oxides. Several feldspar diffraction patterns have similar peaks so the closest pattern match was selected, typically andesine and albite. Alteration products identified by XRD include zeolite minerals, most commonly heulandite, and clay minerals, most commonly montmorillonite and sericite. Ferromagnesian minerals commonly occur as large glomerocrysts, most commonly pyroxenes. Large amorphous oxides, the specific compositions of which were not determined, were identified in several tuffs.

SEM-EDS Compositional Analysis

Mineral phases were identified in BCw through chemical composition element maps and in-situ analyses. Phases were identified by characteristic element spectra to produce mineral phase maps. Mineral phases were identified in FHb and FHr using selected in-situ analyses based on SEM-SE imaging. Individual spectra represent single point data, since phase mapping was not available. Phases identified in FHb and FHr, along with the corresponding count of points, are listed in Table 6.

Table 5: Mineral assemblage and volcanic texture of samples discussed in the study as determined by XRD and optical microscopy. Major mineralogy is >30%, minor is <30% and accessory is <10%.

| | Unit (Ma) | Sample ID | Crystallization | Major | Minor (accessory) |
|--------------------------------------|--------------|-----------|--|--|---|
| Little Butte Volcanics Series | Totd (25.9) | DX | NA | Quartz, andesine, heulandite | (Stellerite) |
| | Totf (26.3) | FD1 | Glassy | Heulandite, glass | Mordenite, quartz, albite (smectite, sericite) |
| | | FD2 | Glassy | Heulandite, glass | Mordenite, quartz, sericite, albite (smectite) |
| | | FD3 | Glassy | Heulandite, glass | Mordenite, quartz, sericite, albite (smectite) |
| | | FD4 | Glassy | Heulandite, glass | Mordenite, quartz, sericite, albite (smectite) |
| | Tomv (30.6) | WF | Axiolitic rims | Mordenite | Quartz, clinoptilolite, albite, am oxides |
| | | WFw | Axiolitic rims | Mordenite | Sanidine, am oxides (qtz, zeolite) |
| | Totmi (30.9) | MK1 | Pervasively devitrified (felsitic) | Albite | Quartz, smectite, clinopyroxene, (oxides) |
| | | MK2 | Pervasively devitrified (felsitic) | Albite, quartz | Oxides (smectite, sericite) |
| | Tomv (31.3) | SP | Pervasively devitrified (felsitic) | Albite | Microcline, tridymite, oxides (sericite, zeolite, ferrobustamite) |
| | Tetb (34.8) | BCg | Axiolitic rims, few spherulites | Clinoptilolite quartz, albite | Orthopyroxene, sericite (zeolite, smectite) |
| | | BCw | Sediment | Quartz, albite, orthoclase, volcanic lithics | Clinoptilolite (augite, pyrite) |
| Fisher Formation | Tetw (35-36) | WS1 | Pervasively devitrified (felsitic) | Albite | Quartz, Cristobalite, illite, smectite |
| | | WS2 | Pervasively devitrified (felsitic) | Heulandite | Albite, stilbite, (illite, chlorite) |
| | | WS3 | Sediment | Quartz | Orthoclase, albite, kaolinite |
| | Tef (38) | LDN | Lithophysae | Anorthite | Orthopyroxene, albite, oxides, qtz (smectite) |
| | Tetf (40.8) | FHr | Devitrified (cryptocrystalline) | Quartz, albite | Anorthite, sanidine, oxides (sericite) |
| | | FHb | Devitrified (cryptocrystalline, spherulites) | Quartz, albite | Sericite, oxides (smectite) |
| | Tetg (41.8) | GHg | Lithophysae | Andesine, heulandite, quartz | Magnetite (smectite) |
| | | GHw | Pervasively devitrified (felsitic) | Quartz, albite, sanidine | Orthopyroxene, orthoclase |

Table 6: Individual spectra count of phases identified in FHb and FHr. Phases are assigned on the basis of chemical composition from SEM-EDS analysis.

| Phase | Total Spectra Counts | |
|------------------|----------------------|--------------|
| | FHb (n = 83) | FHr (n = 35) |
| Glass | 23 | 12 |
| (Fe Ti) oxides | 35 | 14 |
| Aluminosilicates | 10 | 3 |
| Ferrous lime | 4 | 2 |
| Ferrosilicate | 0 | 1 |
| Amphibole | 2 | 0 |
| Apatite | 5 | 0 |
| Lime | 0 | 2 |
| Illite | 1 | 0 |
| Pyrite | 1 | 0 |
| Zircon | 2 | 0 |

BCw was examined using electron dispersal spectroscopy on a total six phase maps. As was identified as a trace component in several phases, most commonly sulfides, although As was also detected in TiO* and three groundmass phases. The sulfide phase contained Fe at a ratio of Fe:S > 2. Although quantification is very approximate, SEM-EDS analysis indicated that As concentration in the sulfide phases was ~0.1-0.4%. The As-bearing sulfide commonly occurs within the groundmass and in mineral grain cracks (Figure 9).

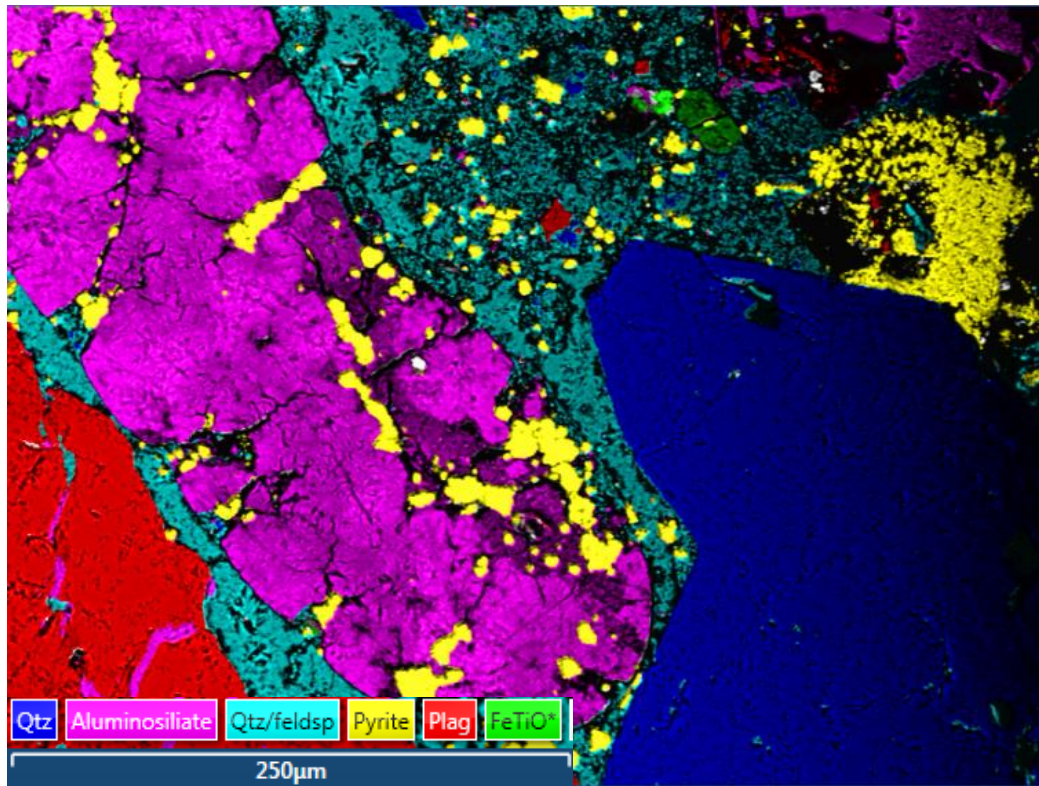


Figure 9: False-colored scanning electron micrograph identifying major phases within BCw. The Sulfide phase and aluminosilicate contain measurable As.

Water leachate

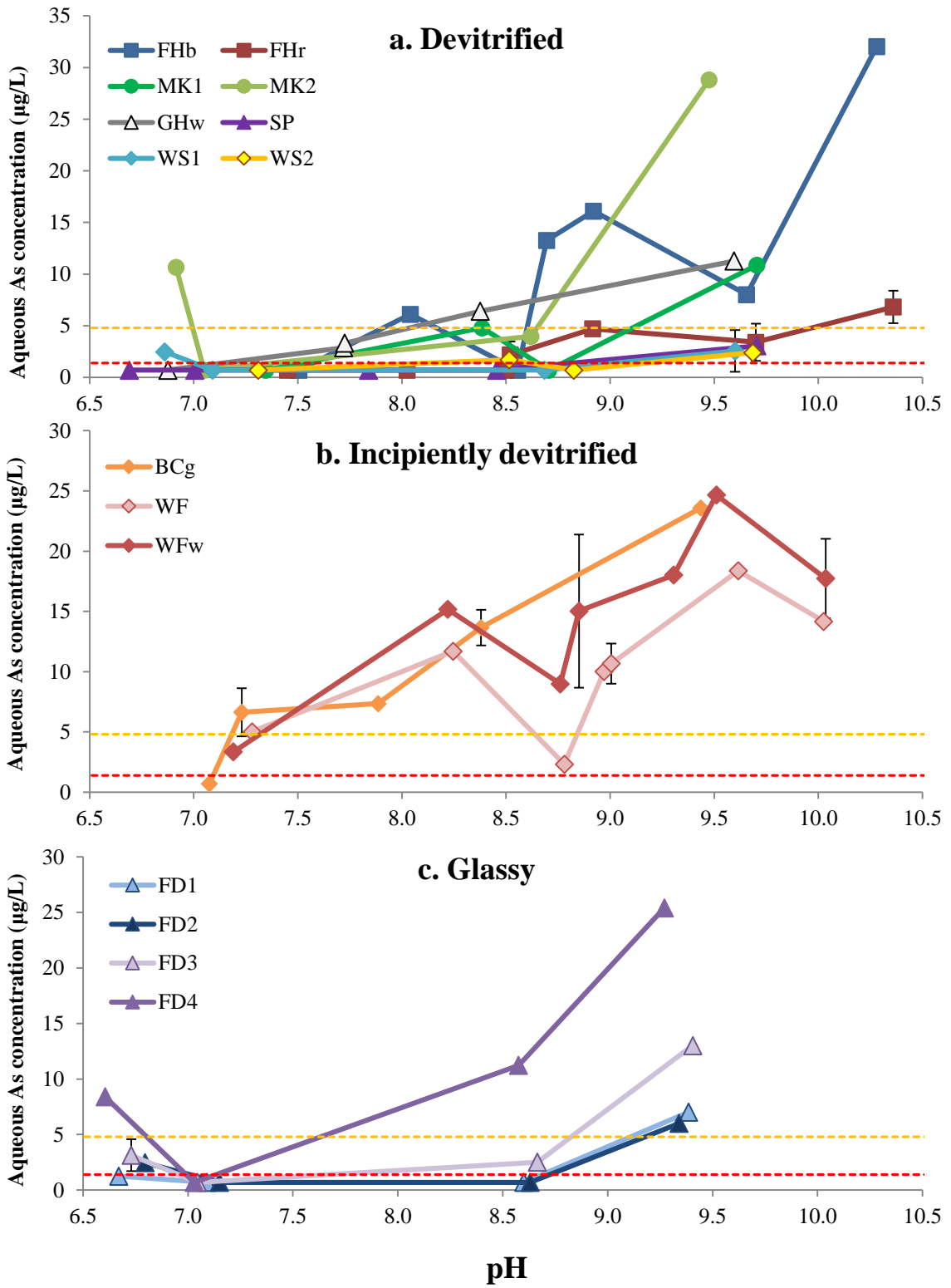
Leachate experiments were performed in order to measure the potential mobility of As from tuff and tuffaceous sediment samples and to try and elucidate modes of occurrence and processes controlling the release of As into solution. Results of quality control standards indicate most elements achieved a 15% recovery; major elements Al, Ca, K, Na, Si exceed 15% recovery in low standards (20-50 $\mu\text{g/L}$) which is acceptable considering these elements tend to occur in solution at higher concentrations. Transition metals, Cu, Fe, and Zn, and metalloid, As, exceed 15% in a few (3-7) check standards but are still within industry-accepted recovery of 20%. Mobility of As was tested under a range of pHs (7 to 11), concentrations of anionic competition (10 μM to 100 mM phosphate as P), and through time (4 to 192 hours). Complete results of leachate

experiments are included in Appendix D. A summary of percent of As mobilized with different solutions is presented in Table 7.

Table 7: Percent of total bulk As mobilized under various pH buffers and phosphate solutions. Darker shaded values percent indicate highest percent mobilized for that sample.

| | | Total As (ppm) | Water | pH 7 | pH 9 | pH 10 | 10 μ M P | 0.1 mM P | 1 mM P | 100 mM P |
|-------------------------|-----|----------------|-------|---------|---------|-------|--------------|----------|--------|----------|
| Devitrified | FHr | 21.0 | 0.2% | <0.004% | 0.2% | 0.3% | 0.1% | 0.2% | 0.3% | 0.8% |
| | FHb | 20.0 | 1.3% | <0.004% | <0.004% | 3.2% | 0.2% | 0.4% | 0.4% | 0.8% |
| | MK1 | 4.7 | 2.1% | >0.02% | >0.02% | 4.6% | 1.9% | | 3.0% | 5.0% |
| | MK2 | 9.2 | 2.3% | 0.3% | 0.9% | 6.3% | 2.6% | 2.9% | 3.3% | 4.1% |
| | SP | 16.8 | 0.7% | 0.2% | 0.6% | 1.3% | | | | |
| | GHg | 11.2 | 2.1% | 0.3% | 2.7% | 4.8% | | | | |
| Incipiently devitrified | WF | 6.5 | 3.3% | 1.5% | 3.1% | 5.6% | 7.8% | | 6.0% | 3.9% |
| | WFw | 8.0 | 4.5% | 0.8% | 3.8% | 6.2% | 6.4% | | 6.9% | 5.5% |
| | BCg | 9.4 | 1.4% | 0.3% | 2.9% | 5.0% | 1.3% | 1.2% | 5.3% | 7.1% |
| Glassy | FD1 | 5.4 | 0.5% | <0.02% | <0.02% | 2.6% | 0.4% | | 2.2% | 5.0% |
| | FD2 | 5.5 | 0.9% | <0.02% | 0.4% | 2.2% | | | | |
| | FD3 | 9.0 | 0.7% | <0.01% | 0.6% | 2.9% | | | | |
| | FD4 | 13.1 | 1.3% | 0.1% | 1.7% | 3.9% | 1.6% | 1.3% | 3.7% | 5.3% |
| Litho-physae | GHw | 4.9 | 1.2% | 0.03% | 1.1% | 2.4% | | | | |
| | LDN | 8.0 | 1.5% | 0.1% | 1.2% | 3.3% | | | | |
| Sed | BCw | 57.2 | 3.7% | 5.7% | 26% | 37% | | | | |

pH experiments



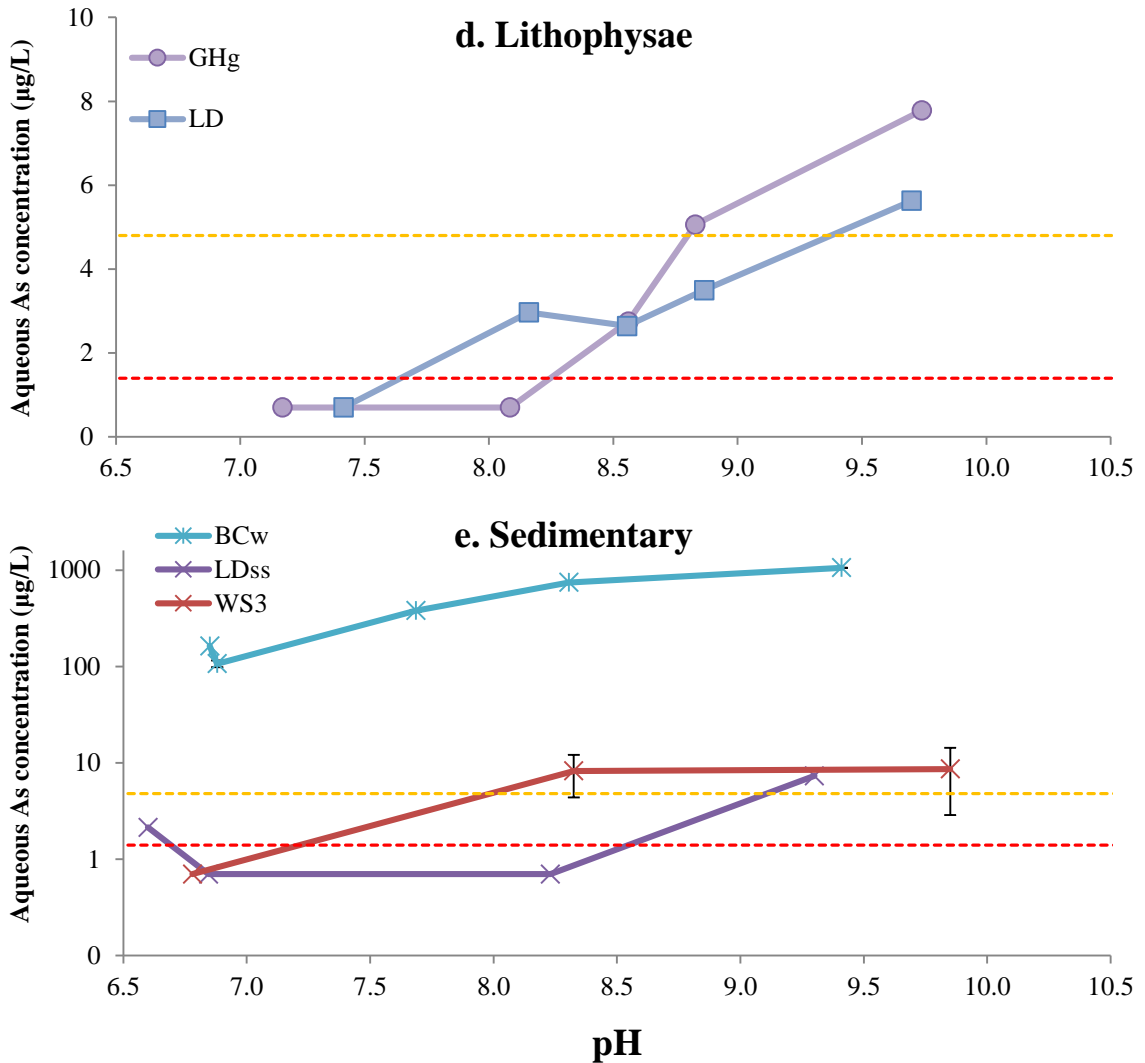


Figure 10a-e: Average aqueous As concentrations resulting from leaching of different classifications of tuffs by various pH buffers. Method detection limit (1.4 µg/L) and method reporting limit (4.8 µg/L) indicated by red and orange dotted lines, respectively. Samples below detection limit are represented by half the detection limit (0.7 µg/L) Difference between duplicates exceeding the method detection level (1.4 ppb) are indicated by error bars.

Samples display a variety of As mobilization behavior, between and within crystallization types (Figure 10a-e). There is an overall trend of increasing aqueous As with elevated pH, although in many cases, pH must be well above 9.0 before exceeding regulatory limits (10.0 µg/L). Leachate solutions vary in final pH because the samples

themselves buffer the solutions to varying extents. The largest sample group, devitrified tuffs, contains samples which produce experimental leachate concentrations of As that do not exceed 5 µg/L, even at pH > 9 (SP, WS1, WS2). Leachate solution produced by samples from the same outcrop, FHb and FHR, under the same buffer solution (pH 10) have substantially different maximum As concentrations, 7 µg/L from FHR and 32 µg/L from FHb. Similarly, MK1 and MK2, both from the same unit although different outcrops, produce different maximum As concentrations under the same buffer solution (pH 10), 10 µg/L from MK1 and 29 µg/L from MK2. Incipiently devitrified samples BCg, WF, and WFW produce consistently elevated As concentrations in solution, with relatively steadily increasing As with increasing pH. Lithophysae samples GHg and LD do not produce significant As concentrations in solution, only exceeding the MRL above pH~9. Among sedimentary samples, LDss and WS3 produce at most ~8 µg/L of As in buffer solutions above pH~9, while BCw produces the highest aqueous As concentrations of any sample in the study, ranging from 110 µg/L to >1000 µg/L at pH 9.4.

Kendall tau rank statistics were applied to samples for which there were sufficient treatments ($n \geq 5$) to determine which elements behaved similarly to As in solution (Table 8). Kendall tau was selected due to the small number of sample treatments and nonparametric distribution. The Mann-Whitney test was performed to determine statistical significance for $\alpha=0.05$.

Table 8: Correlation of As with other elements in pH experiment conditions. Degree of correlation is calculated by Kendall correlation coefficient. Number of buffer solutions included in correlation test indicated in parentheses. Negative sign indicates the correlation is negative. Italicized values are not significant at $\alpha=0.05$.

| | Devitrified | | Incipiently devitrified | | |
|--|-----------------------------------|------------------------------------|--|------------------------------------|---|
| | FHr (7) | FHb (7) | BCg (5) | WF (7) | WFw (7) |
| No correlation ($\tau < 0.3$) | Si, Fe, K, Ni <i>Zn</i> | <i>Zn</i> , Fe, | Si, Al, <i>Cu</i> , <i>Cr</i> , Ni, Pb, <i>Zn</i> , Fe, -K | Ca, Sr, K | Sr, Ca, K |
| Weak correlation ($0.3 \leq \tau < 0.5$) | Al, -Mg, <i>Cr</i> , <i>Cu</i> | Si, Al, K, Ni, -Mg, -Mn, -Cu | -Sr, | Al, Mg, Cu | Cu |
| Moderate correlation ($0.5 \leq \tau < 0.7$) | -Mn, -Ca, V, <i>-Pb</i> , -Sr | -Ca, Cr, -Sr, V | -Ca | Si, Fe, Mn, <i>Cr</i> , Ni, Pb, | <i>Ni</i> , <i>Cr</i> , <i>Zn</i> , Si, Al, Pb, V |
| Strong correlation ($\tau \geq 0.7$) | | -Pb | -Mn, -Mg, V | V, Zn | Mg, Mn, Fe |

For most leachate solutions, As concentration in solution correlates with V. Leachate solutions produced by FHr, FHb, and BCg show no correlation for As with Si nor Al. Concentrations of As in solutions produced by WF and WFw correlate with Si and Al, along with several transition metals (Mn, Fe, Ni, Cr).

Phosphate experiments

Samples exhibiting a variety of devitrification textures which produced solutions with elevated As were tested for mobilization by anionic competition through introduction of phosphate at increasing concentrations, from 10 μM to 100 mM as P (Figure 11).

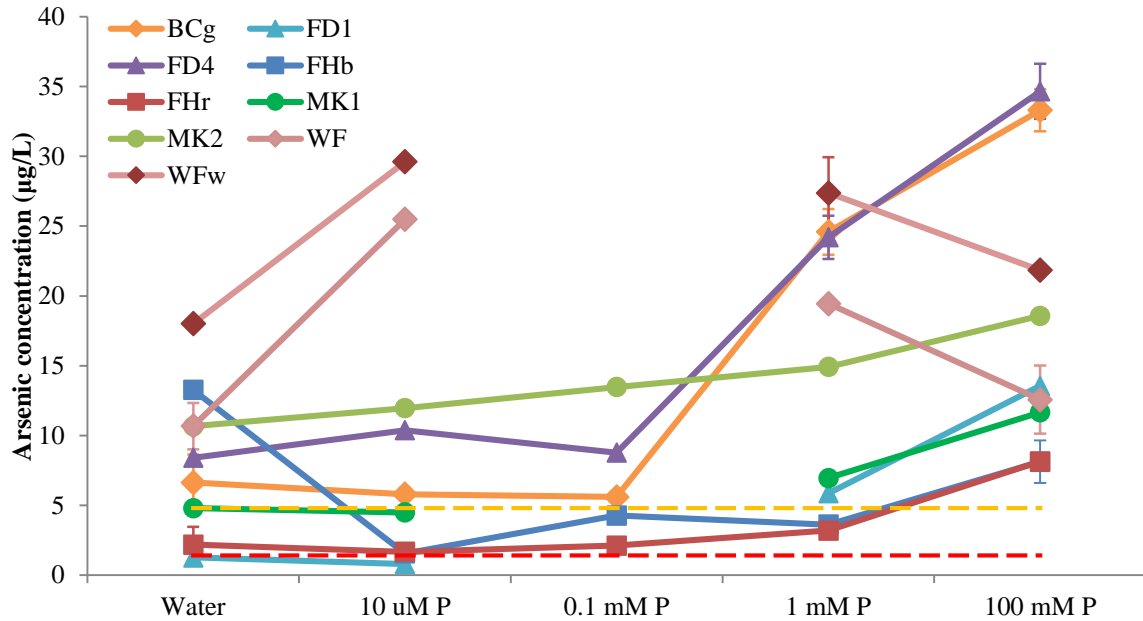


Figure 11: Concentration of arsenic in solution with varying concentrations of phosphate. Method detection limit (1.4 µg/L) and method reporting limit (4.8 µg/L) indicated by red and orange dotted lines, respectively. Samples below detection limit are represented by half the detection limit (0.7 µg/L) Difference between duplicates exceeding the method detection level (1.4 ppb) are indicated by error bars.

Leachate solutions produced by BCg and FD4 exhibit rapidly increased As concentrations above 1 mM P. Concentrations of As in leachate solutions produced by WF and WFw increase slightly with 10 uM P, but then experience a decrease with additional phosphate, suggesting secondary precipitation. Leachate solutions produced by MK1, MK2, FD1, and FHR experience slight but relatively insignificant increases in As and only with very high concentrations of P (100 mM). Aqueous concentrations of As in solutions produced by FHb decreases markedly with the introduction of phosphate, from 13.3 ug/L with water to less than 5 ug/L for all phosphate concentrations examined.

Aqueous leachate concentrations of As were compared with other elements by Kendall tau rank statistical test for individual samples (Table 9). Higher values of τ

indicate greater correlation. The Kendall tau rank statistical test was applied to samples for which there were sufficient treatments ($n \geq 5$). Kendall tau was selected due to the small number of samples and nonparametric distribution. The Mann-Whitney test was performed to determine statistical significance for $\alpha=0.05$.

Table 9: Kendall tau rank correlation of As to other elements in solution with varying concentrations of phosphate. N=5 for all samples included. Negative sign indicates the correlation is negative. Italicized values are not significant at $\alpha=0.05$.

| | Devitrified | | | Incipiently Devitrified | Glassy |
|--|---|--------------------------------|-----------------------------------|--|-------------------------------|
| | FHr | FHb | MK2 | BCg | FD4 |
| No correlation ($\tau < 0.3$) | <i>Cr</i> | Si, Al, Fe, Mn, Mg, Ca, Cr, Pb | Si, Al, Fe, Mn, Cu, Mn, V, Zn, Ni | Ca, Cr, Mg, Pb, Sr, V | Si, Cu |
| Weak correlation ($0.3 \leq \tau < 0.5$) | -Ni, -V, Pb -Ca, -Sr, Mg, <i>Na</i> | -V, Cu, Na | -Cu, Ni | | Ni, Pb, -Al, -Fe, -Mn, -Zn |
| Moderate correlation ($0.5 \leq \tau < 0.7$) | -Zn, -Mn | -Ni, -Zn | <i>Sr</i> | -Cu | Ca, <i>Na</i> |
| Strong correlation ($\tau \geq 0.7$) | -Fe, -Al, -Si, -Cu | | Na, Ca, Mg, Pb, Cr | <i>Na</i> , -Al, -Fe, -Mn, -Ni, -Si, -Zn | Mg, Sr, V, Cr |

Leachate solutions produced by FHb, MK2, and FD4 display no or weak correlation for As in solution with Si and Al. Solutions produced by FHr and BCg display negative correlation for As in solution with Si and Al. Solutions produced by MK2 and FD4 have positive moderate to strong correlations for As with Sr, Na, Ca, and Mg. As in solutions produced by FHr and BCg correlates negatively with Fe, Al, Si, and other metals.

Time series

Time series experiments were performed on five tuff samples with varied alteration and secondary mineralogy and which produced leachate solutions with As concentrations above the regulatory limit (10 µg/L).

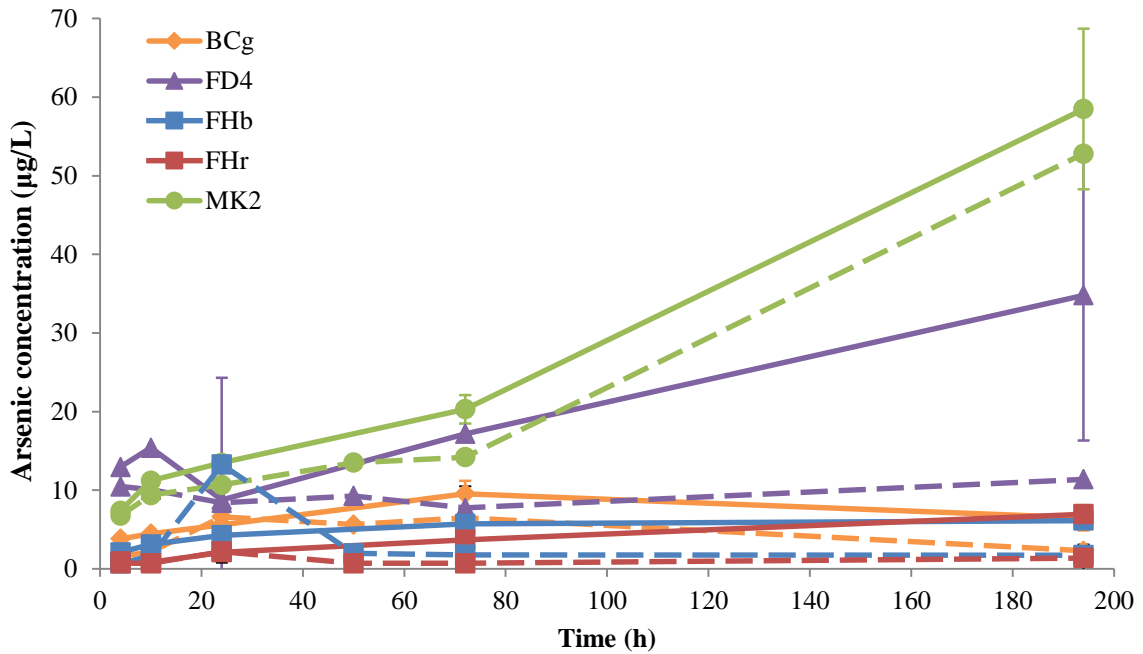


Figure 12: Aqueous arsenic concentrations in leachates over time for select samples. Solid lines indicate 0.1 mM phosphate and dotted lines indicate water solution, including 24h analysis from previous experiment. Samples below detection limit are represented by half the detection limit (0.7 µg/L) Difference between duplicates exceeding the method detection level (1.4 ppb) are indicated by error bars.

Examination of As in leachate over time indicates that As either increases continually (FD4 and MK2) or does not increase significantly (BCg, FHb, FHR; Figures 12-13).

Cumulative percent is calculated based on a liquid:solid ratio of 1:20 and dividing by bulk As concentration. Concentrations of As in leachate produced by FD4 and MK2 continue increasing during the time series, reaching 14% and 24% respectively of total As mobilized by 0.1 mM P and 7% and 21% with water only solutions. Leachate solutions produced by BCg increase slightly in As, but flatline at 72h. Concentrations of

As in leachate produced by FHR and FHB remain relatively low, under 1% and 2% of total As, respectively.

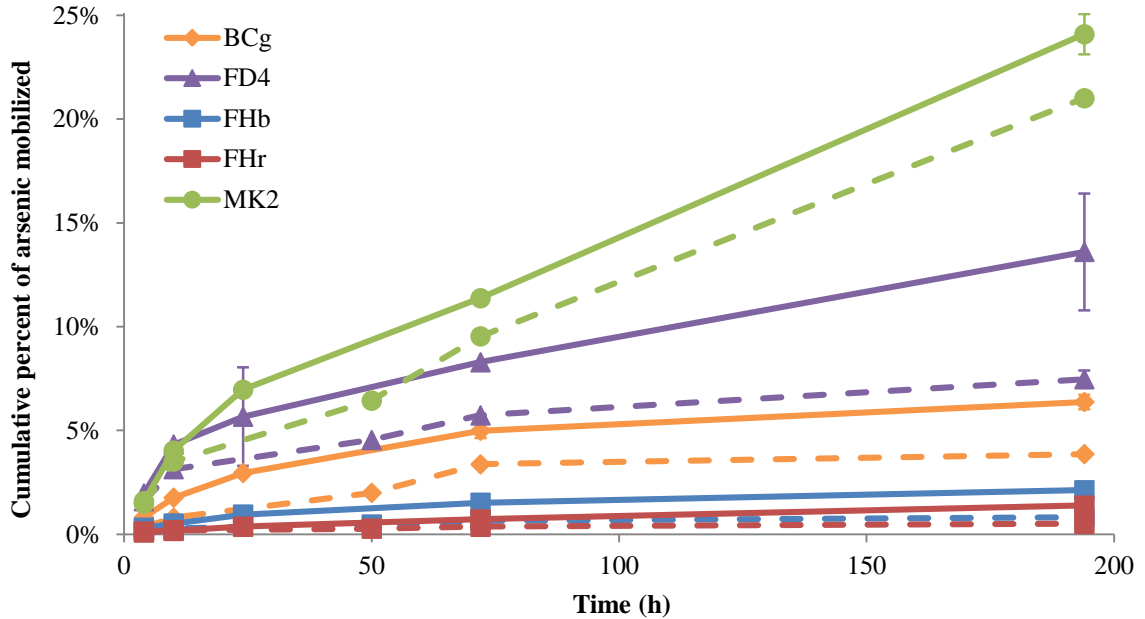


Figure 13: Cumulative percent of total arsenic mobilized during time series. Dotted line indicates water solution, solid line indicates presence of 0.1 mM phosphate. Samples below detection limit are represented by half the detection limit (0.7 $\mu\text{g/L}$) Difference between duplicates exceeding the method detection level (1.4 ppb) are indicated by error bars.

Aqueous leachate concentrations of As were compared with other elements by Kendall tau rank statistical test for individual samples (Table 10). Higher values of τ indicate greater correlation. The Kendall tau rank statistical test was applied to samples which had sufficient experimental conditions ($n > 5$). Kendall tau was selected due to the small number of samples and nonparametric distribution.

Leachate solutions produced by MK2 and BCg display high correlation between As and most elements, which increase substantially in concentration with time along with As. Leachate solutions produced by FD4 also display increased As concentrations over

time but As does not correlate with other elements. FHb and FHr produce leachate solutions with low release of As through the time series; there is no correlation between As concentrations and most other elements.

Table 10: Kendall tau rank correlation of As to other elements in time series for both water and 0.1 mM P solutions. N=10 for all samples included. Negative sign indicates the correlation is negative. Italicized values are not significant at $\alpha=0.05$.

| | Devitrified | | | Incipiently devitrified | Glassy |
|--|---------------------------------|---|--|--|---|
| | FHb | FHr | MK2 | BCg | FD4 |
| No correlation ($\tau < 0.3$) | Ca, Cu, Mn, Na, Ni, V, Zn | Cr, Fe, K, Mg, Mn, Ni, <i>Pb</i> , Si, Al, V, Zn, Cu | | | Ca, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Si, Al, <i>Sr</i> , Zn |
| Weak correlation ($0.3 \leq \tau < 0.5$) | -Cr, -Fe, Mg, -Al, -Si | Na, K | | K, Si | K, Na, V |
| Moderate correlation ($0.5 \leq \tau < 0.7$) | K | Ca | | Cr, Na, V, Al | |
| Strong correlation ($\tau \geq 0.7$) | -Pb | | Ca, Cr, Cu, Fe, K, Mg, <i>Mn</i> , Na, Ni, Pb, Si, Al, V, Zn | Ca, <i>Cu</i> , Fe, Mg, Mn, <i>Ni</i> , Pb, Zn | |

Geospatial distribution of groundwater As in relation to mapped surface lithologies

Arsenic concentrations in groundwater reported by the USGS and ODEQ were obtained through the Pacific Northwest Water Quality Exchange (2015). The geospatial distribution of As concentrations in the study area was then analyzed with respect to surface lithologies as mapped by McClaughry et al. (2010). Of 1,481 distinct data points included in the resulting As distribution map (Figure 14), 101 (7%) exceeded the EPA MCL. The locations of these 101 wells define localized “hotspots” of elevated As concentration.

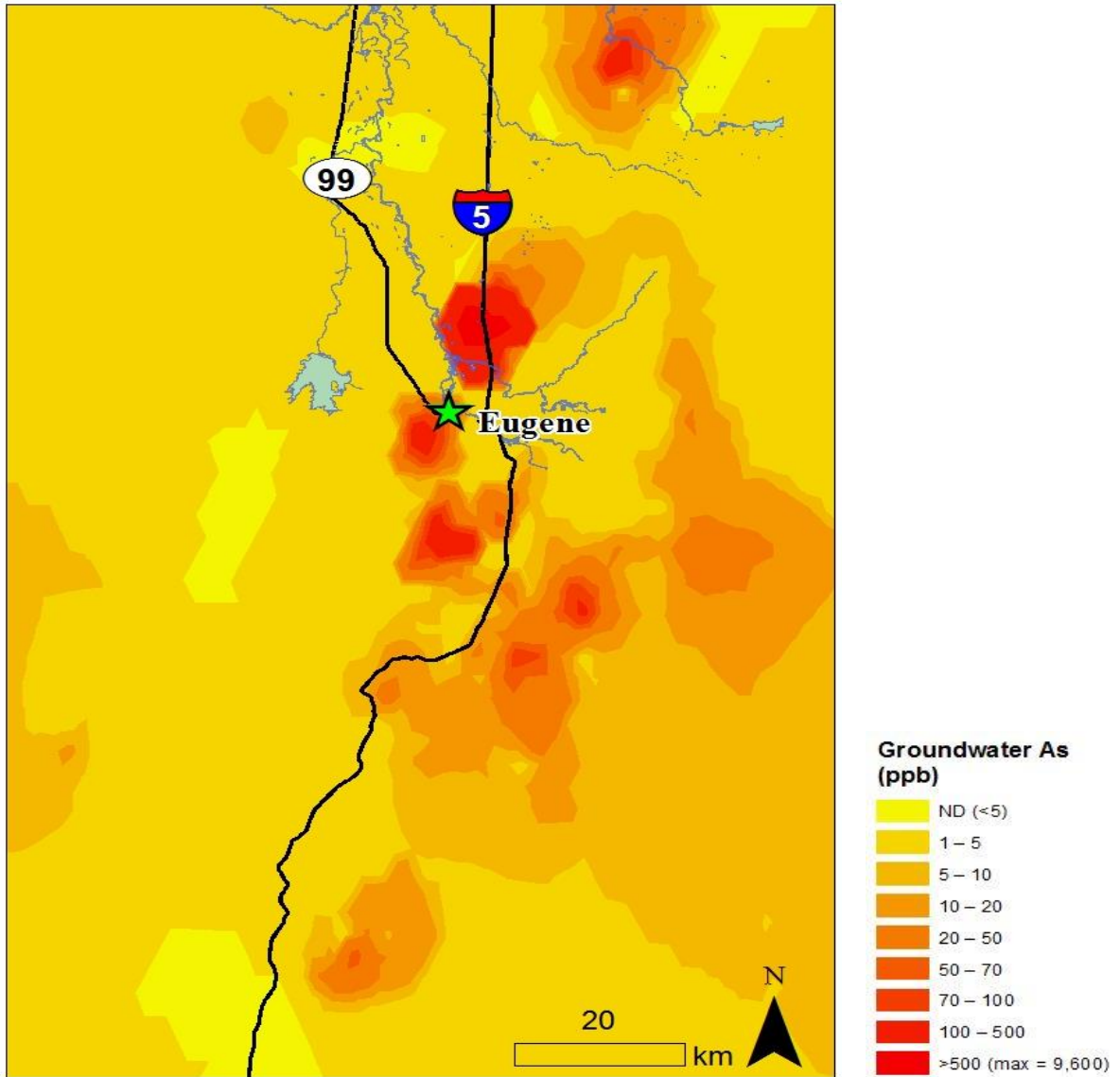


Figure 14: Inverse distance weighted distribution of groundwater As concentrations (in parts per billion) from USGS and ODEQ water databases, available through Pacific Northwest Exchange (2015).

Point data of As measurements in groundwater were spatially joined to lithologies to determine which, if any, units are associated with high As. This was done with the realization that the surficial units may not correspond with geologic units at the depths that wells are screened. Geologic units mapped by McClaughry et al. (2010) were grouped according to major lithologies present in the Willamette Valley. Fisher and Little

Butte Volcanics, undifferentiated, were named as their own group to determine if they presented distinct As distributions. Three potential outliers at the 1% significance level were identified by Rosner’s outlier test, and were consequentially removed from the dataset.

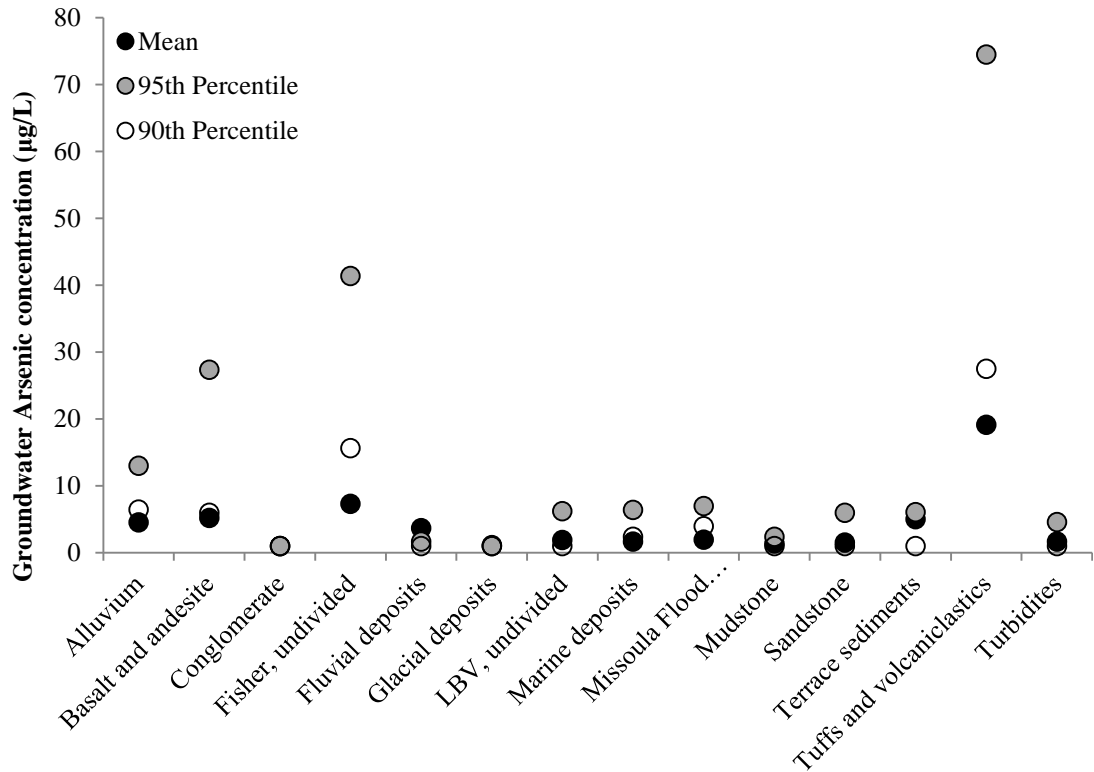


Figure 15: Groundwater arsenic concentration associated with major lithologies combined from geologic units mapped in the Willamette Valley. Data modified from Department of Environmental Quality, 2015; McClaughry et al., 2010.

Measurements of As in groundwater overlain by surficial units of tuffs and volcaniclastic lithology average 19 ppb, which is far greater than the other lithologies, which all average less than 10 ppb (Figure 15). Discrete points included in the tuff lithology group total 5% (n = 62) of examined data. The distribution of As groundwater

concentrations associated with surficial tuff lithologies are the highest included in the dataset, followed by Fisher, undivided lithologies.

Discussion

This study demonstrates that silicic volcanic tuffs are capable of producing leachate solutions with concentrations of arsenic above regulatory limits, at alkaline pH conditions produced naturally by the tuffs (pH 8-9) and with typical concentrations of P (10-100 μM P). Different alteration products, e.g. zeolites and clays, are potential host phases for As, which form as a result of devitrification and diagenetic alteration. Dissolution and/or desorption of As from these host phases results in concentrations of As significantly above the regulatory limit, which has significant implications for human health. Additionally, one volcanoclastic sample (BCw) demonstrates how weathering of pyroclastic deposits to sediment and subsequent sulfide alteration produces leachate solutions with highly toxic concentrations of As, up to 1000 $\mu\text{g/L}$.

Alteration Products

Tuffs display a variety of alteration products developed in the time since deposition. Glass is unstable at the surface and will devitrify during or post-emplacement (De' Gennaro et al., 1999; Vaniman et al., 2001). Devitrification textures identified include spherulites, axiolitic textures, and entirely felsitic groundmass (Table 4; Figure 8). Many of the devitrification textures were mostly or entirely replaced by sericite, which also occurs in veins and groundmass.

Alteration products identified by XRD analysis are primarily zeolites and clays. Formation of zeolites within these tuffs likely results from the hydrolysis of glass, which produces elevated pH, and/or the dissolution of glasses, as is the case for tuff units in the John Day formation, which correlate temporally with the Fisher Formation tuffs (Cotton, 2008; Retallack et al., 2004; Sheppard & Hay, 2001). Formation of clays may occur directly on glass surfaces and coat glass particles syn- or post-depositionally (De' Gennaro et al., 1999; Fuente et al., 2000; Gifkins & Allen, 2001). Location within a flow has been observed to influence alteration, such that lower portions of the flow tend to completely alter due to percolation of water (Sheppard & Hay, 2001). However, tuff units examined in this study do not typically have exposed contacts. Groundwater composition and primary tephra characteristics, i.e. crystallinity, zonation, original porosity and permeability, exert first-order controls on which zeolite or clay forms (Gifkins & Allen, 2001; Sheppard & Hay, 2001). Significant variation can occur in the composition of alteration products as a result of cation to hydrogen ion ration and high ionic activity (Sheppard & Hay, 2001).

Alteration products were identified in devitrified and glassy samples (Foster Dam). Some tuffs, despite being >30 Ma and containing substantial alteration products, retain preserved glassy components (e.g. Bond Creek and Willamette Flora tuffs). Given the extensive alteration of samples examined in this study and lack of multiple exposed outcrops within the same ash flow a unit, conclusions regarding the specific factors controlling composition of alteration product formation are beyond the scope of this study. The range of alteration indices (Table 3) indicates observed alteration is weak and regionally extensive, which suggests it is diagenetic in origin. Based on the observed

proximity of alteration products to glass shards, the partial or complete dissolution of glass is likely a precursor to formation of alteration products, and the constituents of the alteration products are likely entirely derived from original glass composition, as observed in other studies (e.g. de la Fuente, Cuadros, & Linares, 2002; Hawkins, 1981).

Solution chemistry and mobilization

Tuff samples examined in this study produce leachate solutions in response to increased pH and phosphate concentrations according to a variety of mobilization behaviors. Individual tuff units and their specific mobilization processes are discussed in more detail below.

Fox Hollow Tuff

Fox Hollow tuff samples examined in this study (FHB₁, FHB₂, and FHR) are devitrified, displaying a cryptocrystalline texture, although glass morphology is still apparent. FHB contains frequent spherulites replaced by sericite. Both samples contain sericite and FHB contains smectite.

FHB₁ produces solutions which increase in As along with other oxyanion forming elements, e.g. Cr and V, with increasing pH (Figure 10a)

Solutions produced by FHR and FHB₁ under pH leachate conditions do not demonstrate correlation between As with Si nor Al, which indicates As is not released by dissolution of aluminosilicates (Table 8). FHB₁ releases up to six times more As than FHR under the same buffer conditions, possibly as a result of FHB₁ containing increased spherulites altered to sericite. During the phosphate mobilization and time series experiments, FHB₂ and FHR produce As in solutions at concentrations typically below 5

ppb. Release of other elements is not significantly elevated in those experiments, suggesting stability of host phases under the conditions tested.

The results of the pH experiments suggest Fhb₁ releases As through desorption from a charged surface as a result of increased pH. Locally, the Fox Hollow outcrop sampled in this study displays significant differences among examined samples. Though both Fhb₁ and Fhr are devitrified, Fhb₁ has more spherulites which are altered to sericite, quantified by a higher alteration index (Table 3). The spherulites may provide a nucleus for alteration of feldspar and quartz to sericite. Sericite, a fine-grained clay alteration product, may host As on positively charged corners and broken edges in contrast to negatively charged clay surfaces, primarily due to isomorphous substitution (Lin & Puls, 2000; Manning & Goldberg, 1997). These positively charged corners then subsequently release As with increasing pH due to deprotonation of charged surfaces or increased hydroxyl competition.

Tuff of Mohawk, Intracaldera Facies

The Mohawk tuffs (MK1, MK2) are pervasively devitrified, demonstrating a felsitic texture. In MK1, smectite and clinopyroxene occur as primary minerals, with amorphous oxides as a trace component. MK2 contains oxides as a secondary mineral with smectite and sericite as a trace mineral (Table 5).

Under increasing pH conditions, MK1 and MK2 produce solutions with increased As above pH 9 (Figure 10a). Although there are not sufficient data points for correlation, As in solutions produced by MK2 follow a pattern similar to that of Fe, Si, Al, Mn, V, and Zn with increasing pH. The values of these elements are substantially elevated and

increase more than fivefold fold with increased pH, which may indicate dissolution of aluminosilicates phases, e.g. sericite and smectite, and/or Fe oxhydroxides. Greatest increases occur for Fe and Al, which increase 14 and 12 times respectively. MK1 contains less than half the bulk As compared to MK2 and typically mobilizes less As by percent although it also mobilizes increased As into solution with increased pH. MK2 appears to release As as a result of colloidal transport, and MK1 does not release significant concentrations of As into solution. The higher alteration index of MK2 (Table 3) suggests more alteration products are present, which may host As on surficial species, making As more available to solution.

Both MK1 and MK2 release increased concentrations of As with increased addition of phosphate. MK1 increases from 4.8 ppb to 11.7 ppb, and MK2 increases from 10.7 ppb to 18.6 ppb. Correlation statistics demonstrate significant increases of Mg and Ca along with As in solutions produced by MK2 with increased P concentrations. Solutions produced by MK2 present positive correlation between concentrations of As with Na, Ca, Mg, and Pb.

MK2 was further examined in the time series, during which concentrations of As increased from 7 ppb to 52 and 58 ppb in the water only leachate and 0.1 mM phosphate. Other elements, most significantly Si, Al, Cr, Cu, Fe, Mg, Mn, Ni, Sr, V, and Zn, also increased by 20 to 30 times over the 196 hour experiment. The substantial increase and magnitude of these concentrations suggests colloids are formed as secondary precipitates in leachate solutions produced by MK2 over time, both in the presence of phosphate and in deionized water. MK2 has substantial oxide particles and alteration products sericite

and smectite, which may dissolve to form colloidal particles which release As into solution.

Tuff above Willamette Flora

The tuff above Willamette Flora unit, WF and WFw, is a small ash fall tuff exposed within a marine sedimentary sequence. The tuffs are incipiently devitrified, with axiolitic rims on glass particles still retained and visible in thin section. Both tuffs contain mordenite as a major component. The Willamette Flora tuffs are substantially oxidized, with large amorphous oxides and fine-grained oxides occurring in veins and groundmass. WFw is more oxidized and weathered, with more frequent and larger oxides.

During the pH experiments, both tuffs mobilize steadily increasing amounts of As into solution (Figure 10b). Leachate produced by the Willamette Flora tuffs appear clouded in the solution column even after centrifugation, and concentrations of As in solution correlate with several elements, including Si, Al, Fe, Mn, Mg, Pb, V, Zn, and Cr, which are measured in solution at exceptionally elevated concentrations (Appendix D). WFw produces solutions with greater concentrations of As compared with WF. The elevated concentrations of aluminosilicate-forming elements, which increase concurrent with As, suggests that the Willamette Flora tuffs mobilize As through the formation of colloids, potentially dissolved from mordenite, which was identified by XRD.

In the phosphate experiments, WF and WFw release increasing concentrations of As into solutions with the addition of 10 μM P and 1 mM P. At the highest concentration of phosphate examined, 100 mM P, As concentrations in solution decreases (Figure 11). Although the small number of experiments limits interpretation of correlation statistics,

several other elements experience a significant decrease in concentration along with As, including Cu, Fe, Al, Mg, Pb, V, Zn, and Si, in the 100 mM P experiment. This suggests that the Willamette Flora Tuff hosts As associated with colloidal particles, and extremely elevated concentrations of P produce secondary precipitates. WFW is more altered, as evidenced by the alteration index (Table 3) and may produce more colloids, which would result in the observed higher concentrations of As and associated elements.

Tuff of Foster Dam

The Foster Dam tuffs retain the greatest glass content, and contain significant amounts of heulandite, as well as minor amounts of mordenite and sericite. Generally, FD1 has less sericite observed in thin sections with increasing sericite content from FD1 to FD4. Differences in mineralogy were not quantifiable with XRD. FD4 has an increased alteration index compared to FD1-FD3, which may relate to its greater concentration of bulk As and increased concentrations of As mobilized into solution.

During the pH experiments, FD1, FD2, and FD3 release concentrations of As above the MRL only when buffered near pH 10. FD4 produces 8.4 µg/L of As when mixed with deionized water, and increases to 25.4 µg/L under pH 9 and pH 10 buffers, respectively (

c). Most other elements in leachate solution produced by FD4 do not increase in concentration with increased pH, except for V which forms similar oxyanions. This suggests FD4 mobilizes As into solution as pH increases due to surficial desorption from a host phase, which also releases V as an oxyanion.

Both Foster Dam tuffs examined in the phosphate experiments mobilize more As into solution with moderate to extreme concentrations of phosphate (1 mM and 100 mM P; Figure 7). The concentrations of most other elements do not increase in solution with addition of phosphate, except those of Sr, Mg, and Na which increase ~20 times with increasing phosphate. Concentrations of other elements, e.g. Al, Si, Mn, and Fe, either do not change significantly or decrease; in the case of Fe, concentrations in solution decrease from 2200 µg/L and 1200 µg/L in the water leachate experiment to 23 µg/L and 32 µg/L in the 100 mM P experiment for FD1 and FD4 respectively. This suggests these elements may form secondary precipitates due to increased ionic strength resulting from the addition of phosphate. The predominance of heulandite, which is an aluminosilicate series with Ca, Sr, and Ba as possible end member cations, is a potential source of the elevated concentrations observed for Sr, Mg, Na, and As. Breakdown of heulandite may result from cationic displacement caused by the K_2HPO_4 salt used to create the phosphate solutions. pH increases with the addition of phosphate as well, from pH = 6.6-6.7 when the Foster Dam samples are mixed with deionized water to 7.9-8.1 when mixed with 100 mM P solution, which may also induce dissolution (Cotton, 2008).

Mobilization of As from FD4 was further examined through the time series experiment, performed with deionized water and moderate concentrations of phosphate (0.1 mM as P; Figure 11). Concentrations of As mobilized to solution increase through the time series, particularly in the presence of phosphate: during the 0.1 mM P time series, As increased from 13.0 µg/L after 4 hours to 34.8 µg/L at 194 hours. The concentrations of nearly every other element increase 2-5 times steadily through the time

series in 194 hours, except Sr which increases in concentration in the first 50-72 hours followed by a decrease to nondetect. This suggests that dissolution of zeolites is controlling the mobility of these elements which are released into solution over time. The addition of phosphate increases ionic strength, which may contribute to dissolution over time.

Bond Creek

The Bond Creek tuffs include one volcanoclastic sample and one incipiently devitrified sample. BCg is incipiently devitrified, containing glass particles which retain a glassy interior and are rimmed with axiolitic intergrown fine-grained minerals, along with few spherulites altered to sericite. Clinoptilolite is a primary mineral, with zeolite and smectite identified as trace minerals. BCw is a volcanoclastic sandstone, with rounded grains of quartz and plagioclase, along with few spherulites and pumice fragments indicating proximal diagenesis and minimal alteration of the sediment. Sericite and sulfide phases are common in the groundmass and mineral cracks.

When mixed with buffers of increasing pH, BCg releases gradually increasing concentrations of As, which correlate positively with V and negatively with Mn, Mg, and Ca. The correlation with another oxyanion forming element, V as HVO_4^- or H_2VO_4^- , and lack of correlation with other elements suggests desorption from a charged surface as increased pH deprotonates the surface. Concentrations of As released from BCw increase drastically with increased pH, from 107 $\mu\text{g/L}$ in deionized water, to 1100 $\mu\text{g/L}$ when buffered with pH 10 solution. The concentrations of nearly every other element increases in solution along with As, most notably Cr and V, which increased tenfold.

Concentrations of Fe in solution increase from 6 mg/L to 30 mg/L. A sulfide was the most common As-bearing phase in SEM analysis and at pH 10, 30% of total As was released. Sulfide oxidation is a common mobilization method for As, and becomes unstable in oxidized environments (Smedley & Kinniburgh, 2002; Wang & Mulligan, 2008). The rate of dissolution of pyrite, the most commonly studied As-bearing sulfide, is described by the following equation (Williamson & Rimstidt, 1994):

$$R_{\text{Pyrite}} = 10^{-10.19}(\text{O}_{2(aq)})^{0.5}(\text{H}^+)^{-0.11}$$

Decreasing proton concentration would increase the rate of sulfide dissolution, and therefore increase As mobilized into solution, which follows experimental observations. The oxidation of ferrous iron is also implicated in increasing the rate of dissolution, although specific mechanisms remain unclear (Wang & Mulligan, 2008; Williamson & Rimstidt, 1994). The disparate increases in Fe compared to As, where As increases more significantly than Fe, indicates that As is preferentially hosted on surface species which are first to dissolve or release As and/or that some Fe reprecipitates, potentially as an iron oxyhydroxide species but does not remove As from solution (Williamson & Rimstidt, 1994). BCw demonstrates the potential for weakly altered volcanic sediments to produce readily mobilized As associated with sulfides.

Under increasing concentrations of phosphate, As released into solution produced by BCg increases substantially to 33 µg/L. Leachate experiments with increased concentrations of phosphate produce solutions with decreased concentrations of Fe, Si, and Al, and increased concentrations of Mg, Na, and Sr four to five times greater than in deionized water. This suggests P precipitates with other elements, and As mobilization

may be related to dissolution of clinoptilolite. Clinoptilolite is similar to heulandite, although clinoptilolite is observed to dissolve at higher pH compared with heulandite (Cotton, 2008). The correlation with Sr, Mg, and Na released into solution supports the role of dissolution of clinoptilolite. The decrease of Si and Al may be due to secondary precipitation of these elements due to increased ionic strength with the addition of phosphate or incongruent dissolution of clinoptilolite. Since clinoptilolite appears to dissolve at higher pH, As released during the pH experiments does not demonstrate the same pattern of increased element concentration.

During the time series, BCg mobilizes low amounts of As, ranging from 1.6 $\mu\text{g/L}$ to a maximum value of 9.6 $\mu\text{g/L}$ with 0.1 mM P after 72 hours. No other elements are released or increase in substantial amounts (i.e., greater than a twofold increase or decrease) except for Zn, which increases from 25 $\mu\text{g/L}$ to 490 $\mu\text{g/L}$ after 194 hours with 0.1 mM P, and Pb which increases from 4.72 to 15.92 after 72 hours with 0.1 mM P then decreases to 12.5 mM P in the subsequent analysis at 194 hours. Concentrations of Zn are typically controlled by adsorption onto clay minerals, Fe, Mn, or Al hydroxides, and organic matter (Smedley & Kinniburgh, 2002). This indicates that circumstances required to dissolve clinoptilolite or surficially desorb As were not achieved during the time series.

Low-As tuffs

Some tuffs did not mobilize significant amounts of As under any conditions presented in the study. These include both lithophysae samples, GHw and LDN, and two devitrified samples, SP and GHg. All four samples have bulk As concentrations similar to other tuffs, which mobilize As into solution (Table 5). SP and LDN contain trace

amounts of alteration products, smectite, sericite, and zeolite. GHg contains primary amounts of heulandite and no alteration products were identified in GHw. It initially appears that the lack of these alteration products may be related to the low mobilization of As. However, GHg does not release significant amounts of As, despite evidence of significant amounts of heulandite. Solutions produced by GHg which were buffered at elevated pH released 142 µg/L of V in the water leachate experiment and increased to 220 µg/L of V when buffered with pH 10 solution. It may be that vanadate anions occupy sites that are occupied by As in other tuffs. Minor differences in zeolite composition have been observed to result in significant changes in sorption behavior (Sheppard & Hay, 2001).

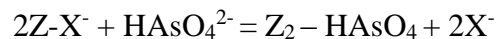
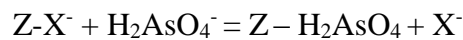
In summary, samples which exhibit surficial desorptive control on As mobility are FHB₁ and BCg under more extreme leachate conditions. Samples which exhibit dissolution control on As mobility include MK2, FD4, BCw, WF, and WFw. Of these, WF and WFw produce colloids under all leachate conditions examined, and MK2 appeared to produce colloids during the time series experiment.

Mineral control on As mobility

Alteration products, e.g. zeolites and clays, may serve as host phases for As. At increased pH or phosphate concentrations, these alteration products may dissolve or desorb As, producing concentrations which pose human health risks. Results of this study suggest that desorption tends to control As mobility in samples with primarily clay alteration products, and dissolution tends to control As mobility in samples with primarily zeolite alteration products.

Sorption activities to/from a charged surface are potentially operating in FHB₁, BCg, MK1, and MK2 under certain leachate conditions. Although specific sorption phases could not be identified, the most probable sorption sites are aluminosilicates or Fe and Mn oxyhydroxides (Dixit & Hering, 2003; Wilkie & Hering, 1996). Increased pH will desorb As through deprotonation and subsequent surface charge reversal, which is shown on a modeled desorption of As from hydrous ferric oxide surface as pH increases from 6-11 (Figure 16). The presence of 10 mM phosphate decreases the initial amount of sorbed As. Depending on the water chemistry conditions, host phases in BCg, MK1, and MK2 dissolve to produce elevated As in solution. WF and WFw produced As-bearing colloids under most experimental conditions examined, possibly dissolved from mordenite.

Arsenic anions are capable of sorbing to clay and zeolite surfaces which are altered by surface complexation, as demonstrated in the following equations, following Li, Beachner, McManama, & Hanlie (2007):



Where X represents a surficially bound anion, and Z represents a host phase, e.g. clay or zeolite. Natural zeolites have been experimentally determined to sorb As at circumneutral pH, owing to protonation of the surface creating positively charged sites onto which anionic As species can sorb (Šiljeg, Foglar, & Gudelj, 2012). Increased pH has varying effects on As mobilization due to minor differences in zeolite composition and surface complexes. Experimental sorption studies demonstrate that As desorbed from some clinoptilolites at increased pH, while others did not release As, which was

attributed to oxidation and subsequent resorption onto the zeolite surface (Elizalde-González, Mattusch, Einicke, & Wennrich, 2001).

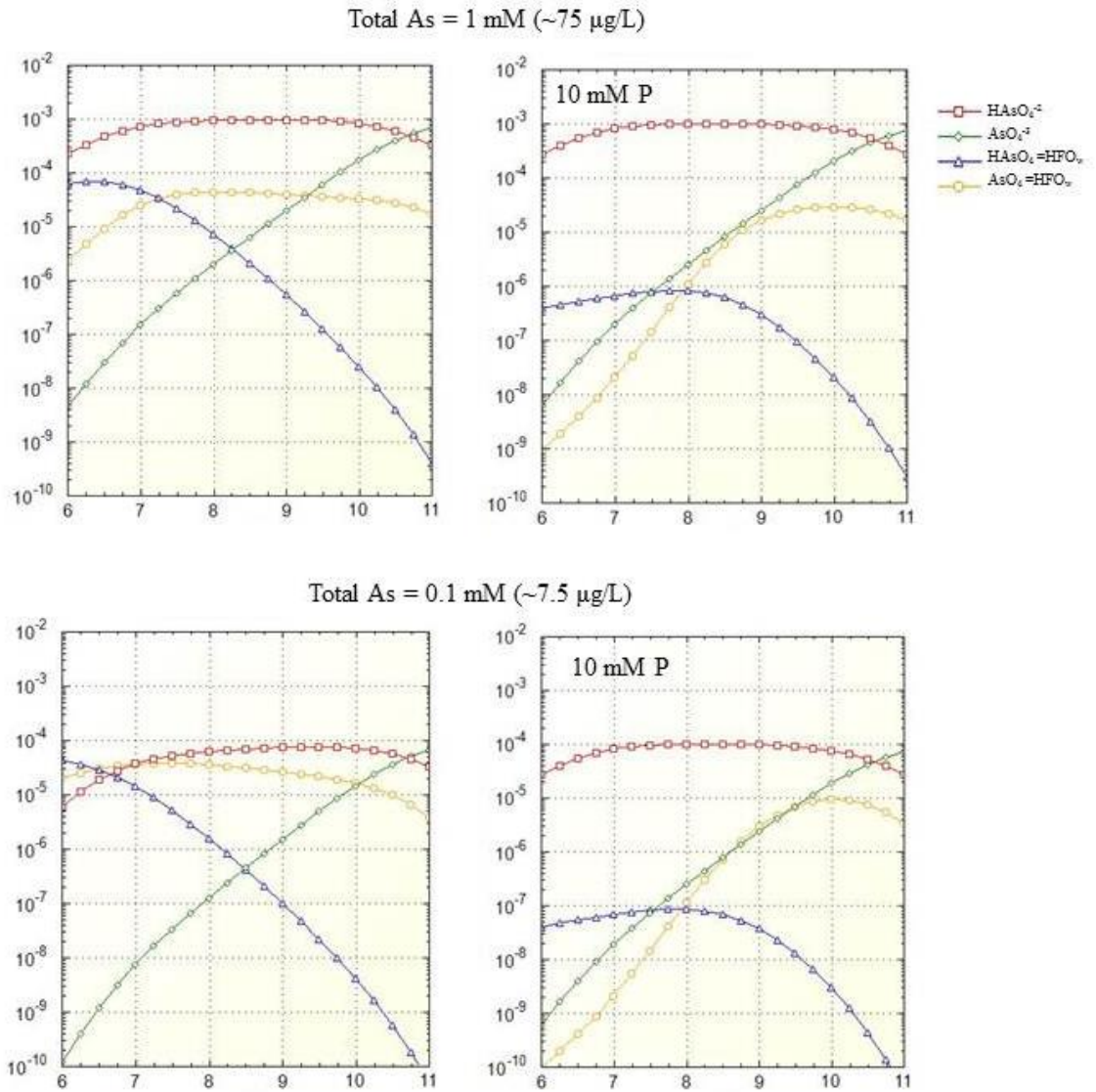


Figure 16: Concentrations of 1 mM and 0.1 mM As from hydrous ferric oxide under increasing pH and in the presence of 10 mM P modeled with PHREEQCi (Parkhurst & Appelo, 1999).

Colloidal behavior was observed in WF, WFw, and MK2. Many studies demonstrate the importance of colloids in transporting contaminants (de Jonge, Kjaergaard, & Moldrup, 2004; McCarthy & Zachara, 1989; Ryan & Elimelech, 1996; Schemel, Kimball, & Bencala, 2000) and potential for colloidal-transport of As anions (Puls & Powell, 1992). Colloid mobilization may occur as a result of increased pH, particularly when pH is raised above the point of zero charge of a surface, such that surface forces repel any colloidal particles attached (Ryan & Elimelech, 1996). The pH range examined in this study (7-10) coincides with the PZC of common oxyhydroxides and silicate minerals (Kosmulski, 2009). A combination of both the increased oxidation of As(V) above pH = 7-8 (Figure 1) and change in surface charges may release colloids capable of transporting surficially bound or incorporated As. Colloids may also form secondarily, following dissolution of alteration host phase of As.

A spike in As after 72 hours is observed in FD4 and MK2 which may be a result of diffusion controlled release of arsenic and increased ionic strength necessary to catalyze zeolite release or dissolution (Elizalde-González et al., 2001).

The production of zeolites and clays can occur during diagenetic or hydrothermal alteration. It is evident that if any hydrothermal alteration has occurred within these units, it is limited in extent given that glass morphology and volcanic particles are relatively preserved (De' Gennaro et al., 1999; Gifkins & Allen, 2001). The alteration indices calculated for samples in this study also suggest weak alteration, ranging from 17-43; alteration indices from 50-100 are indicative of hydrothermal alteration (Large et al., 2001). Sericite alteration, observed in several tuffs in this study, is interpreted to

represent early alteration of volcanic glass synchronous with regional burial and compaction (e.g. Gifkins & Allen, 2001). The alteration represented is characterized by locally complex distribution of alteration on a small scale (millimeters to centimeters) which may have significant implications for As mobilization, as demonstrated by FHB₁, FHB₂, and FHR. Between pairs of samples within units, the sample which mobilizes greater As concentrations in solutions is consistently the more altered sample, evidenced by mineralogy and alteration indices (Table 3; Table 5). Alteration type may also control As mobilization behavior: samples which displayed surficial desorption behavior (FHB, BCg) were composed of clay alteration products, and samples which displayed dissolution and/or formation of colloids (WF, WFw, FD4) were more likely composed of zeolite alteration products. MK2 and BCw are exceptions: MK2 contains significant oxide particles, which may host As and dissolve under elevated pH and P conditions, rather than the clay alteration products present. BCw contains detectable As in sulfide phases (Figure 9), which preferentially host As, released upon oxidative dissolution. Samples with no or trace alteration products, e.g. SP, LDN, and GHw do not release significant As, even at elevated pH values (pH > 10). These mechanisms are summarized in Figure 17. The geospatial analysis suggests that tuffs are influential in developing high As groundwater in the Willamette Valley. The average As concentration for data points located within surficial tuffs was 19 ppb, nearly double the regulatory limit, despite comprising a small percentage of values examined (Figure 15). The overall distribution of groundwater As values occurring within surficially mapped tuff lithologies was also substantially greater than observed for other lithologies.

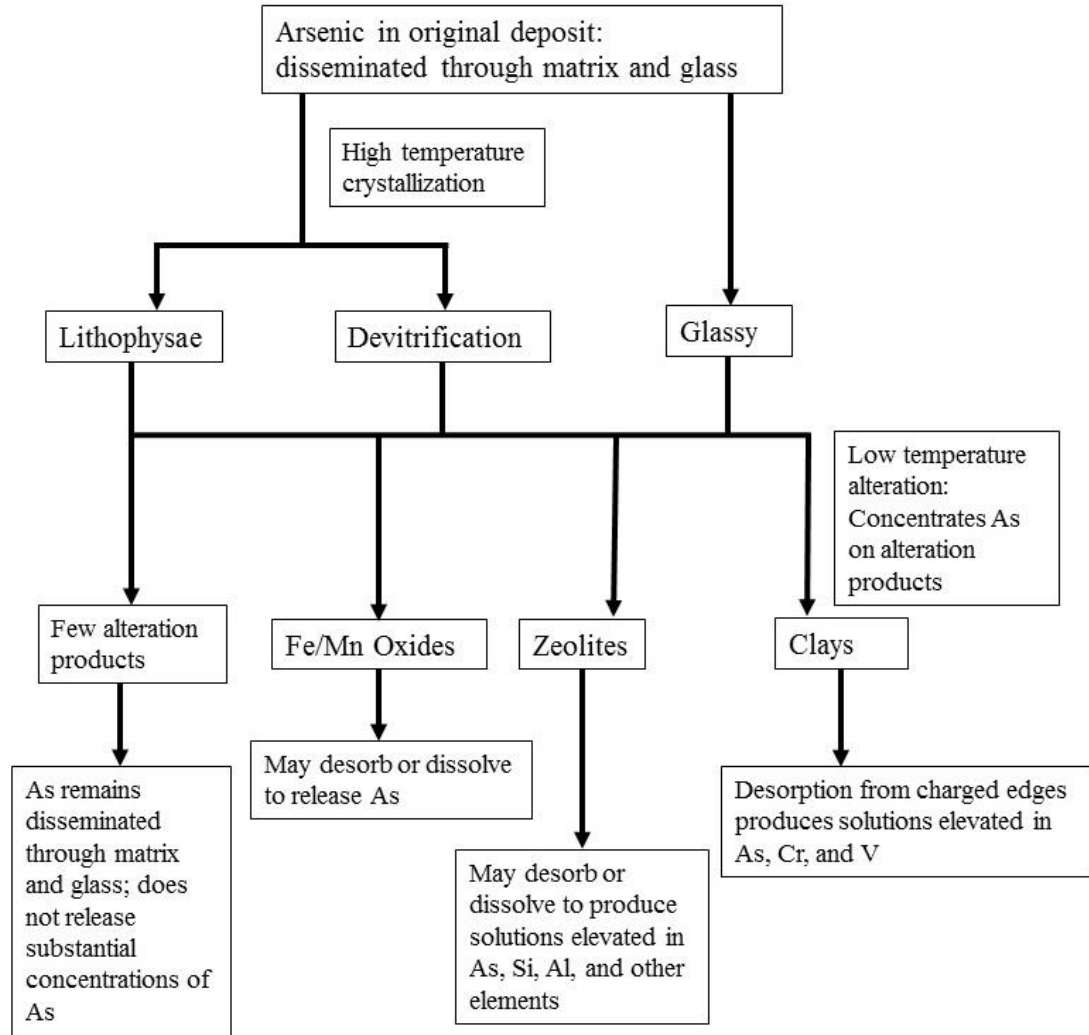


Figure 17: Summary diagram illustrating primary processes controlling As

Future Work

Collection of additional tuff samples, primarily from locations that displayed high variability, would allow for better definition of factors controlling As mobility. Future leachate studies should consider the possibility of colloids and filter leachate columns at different sizes to determine the size and mobility of colloids generate, and potentially analyze filtrate using WDS/EDS if resolution permits. Although groundwater analysis of

arsenic and distribution exists in the region, complete groundwater chemistry could be analyzed and modeled to determine how experimental leachate may serve as an example of groundwater conditions. The addition of a leachate experiment controlling redox state may also shed light on oxidative conditions which control As mobility.

Conclusions

This study demonstrates that silicic volcanic tuffs are capable of mobilizing As at concentrations above regulatory limits at pH conditions produced naturally by the tuffs (pH 8-9) and with moderate concentrations of P (10-100 μM). Alteration products, e.g. zeolites and clays, are interpreted to influence mobilization of As with significant implications for human health. Samples which do not contain these alteration products tend to produce concentrations of As below detection limit. Within a natural pH range produced by tuffs (pH 8-9), incipiently devitrified and devitrified tuffs are more likely to produce concentrations of As in leachate solutions above the regulatory limit. The process of devitrification allows for subsequent alteration to host phases, e.g. clays, zeolites, and amorphous oxides, which are susceptible to mobilization of As through dissolution and desorption processes. The type of alteration may influence As mobilization, in that tuffs containing more clays tend to mobilize As through surficial desorption, and tuffs containing more zeolites tend to mobilize As by dissolution or colloids. Additionally, one volcanoclastic sample (BCw) demonstrates how minor alteration to sediment and subsequent formation of As-bearing sulfide phases is capable of producing extremely elevated concentrations of As, up to 1000 $\mu\text{g/L}$, as a result of oxidative dissolution of the sulfides.

Geospatial analysis suggests the connection of mapped tuff units and elevated As in groundwater in the Willamette Valley. The results of this study suggest that this may relate to the capacity for tuffs to alter to host phases which mobilize As by alkaline pH and introduction of phosphate. Therefore, diagenetically altered tuffs within volcanic aquifers contain moderate concentrations of As likely associated with alteration products, clays and zeolites which are available to solution through surficial desorption, dissolution, and formation of colloids.

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Appendix A: ICP Operating conditions

| Operating Condition | Date of Analysis | | | | | | | | | | |
|--------------------------------|------------------|-----------|------|-----|-----------|-----------|-----------|----------|-----------|----------|-----------|
| | 11/24/2014 | 9/24/2014 | 1.3 | 1.3 | 8/11/2015 | 7/23/2014 | 7/18/2014 | 6/5/2015 | 4/23/2015 | 7/9/2015 | 6/19/2015 |
| Power (kW) | 1.3 | 1.3 | 1.35 | 1.3 | 1.25 | 1.25 | 1.25 | 1.25 | 1.3 | 1.35 | 1.35 |
| Replicate read time | 45 | 45 | 45 | 40 | 45 | 45 | 45 | 45 | 40 | 45 | 45 |
| Instrument stabilization delay | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| Sample uptake delay | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 | 25 |
| Max rinse | 60 | 60 | 60 | 60 | 60 | 60 | 60 | 60 | 60 | 60 | 60 |
| Number of replicates | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| PolyBoost | On | On | On | On | On | On | On | On | On | On | On |
| Plasma | 15 L/min | | | | | | | | | | |
| Auxillary | 1.5 L/min | | | | | | | | | | |
| Nebulizer | 0.75 L/min | | | | | | | | | | |

Appendix C: Quality control/quality assurance data

Date of analysis: 5/30/2014

| | IDL1 | IDL2 | IDL3 | IDL4 | IDL5 | IDL6 | IDL7 | Standard Deviation | IDL | MRL |
|------------|------|------|------|------|------|------|------|--------------------|-----|------|
| Al 236.705 | 6.0 | 5.5 | 8.4 | 4.1 | 5.5 | 7.1 | 6.2 | 1.4 | 4.1 | 13.7 |
| Al 237.312 | 7.2 | 6.8 | 7.2 | 6.2 | 6.6 | 7.3 | 6.5 | 0.4 | 1.3 | 4.2 |
| As 188.980 | 7.3 | 7.5 | 9.3 | 7.9 | 7.1 | 7.2 | 8.4 | 0.8 | 2.4 | 8.1 |
| As 193.696 | 8.2 | 7.2 | 7.1 | 7.1 | 7.8 | 7.6 | 6.9 | 0.5 | 1.4 | 4.8 |
| Ba 233.527 | 6.3 | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 | 6.1 | 0.1 | 0.2 | 0.6 |
| Ba 455.403 | 7.3 | 7.0 | 7.0 | 7.1 | 7.1 | 7.0 | 7.1 | 0.1 | 0.3 | 0.9 |
| Be 249.473 | 7.3 | 8.0 | 7.5 | 7.2 | 7.2 | 7.1 | 7.1 | 0.3 | 1.0 | 3.3 |
| Be 313.042 | 7.1 | 7.0 | 6.9 | 7.0 | 7.1 | 7.0 | 7.0 | 0.1 | 0.2 | 0.5 |
| Ca 317.933 | 6.0 | 9.6 | 5.4 | 5.2 | 5.2 | 5.3 | 5.1 | 1.6 | 4.9 | 16 |
| Ca 396.847 | 2.3 | 6.2 | 1.5 | 1.4 | 1.3 | 1.5 | 1.2 | 1.8 | 5.4 | 18 |
| Co 228.615 | 6.6 | 6.5 | 6.4 | 6.5 | 6.5 | 6.5 | 6.4 | 0.1 | 0.3 | 0.9 |
| Cr 267.716 | 6.9 | 6.9 | 6.8 | 6.7 | 6.8 | 6.7 | 6.7 | 0.1 | 0.3 | 1.0 |
| Cu 327.395 | 6.8 | 6.6 | 6.7 | 6.7 | 6.8 | 6.8 | 6.7 | 0.1 | 0.2 | 0.6 |
| Fe 238.204 | 5.4 | 6.0 | 5.4 | 5.6 | 5.4 | 5.5 | 5.0 | 0.3 | 1.0 | 3.2 |
| Fe 258.588 | 6.5 | 7.1 | 6.2 | 6.0 | 6.3 | 6.2 | 5.6 | 0.5 | 1.4 | 4.5 |
| Fe 259.940 | 6.1 | 6.3 | 6.2 | 6.1 | 6.2 | 6.2 | 5.7 | 0.2 | 0.6 | 2.0 |
| K 766.491 | 44 | 44 | 42 | 42 | 45 | 41 | 41 | 1.5 | 4.4 | 15 |
| Mg 279.078 | 5.8 | 5.9 | 5.7 | 5.0 | 6.4 | 5.2 | 5.4 | 0.5 | 1.4 | 4.5 |
| Mn 260.568 | 6.5 | 6.4 | 6.3 | 6.4 | 6.5 | 6.4 | 6.4 | 0.1 | 0.2 | 0.7 |
| Ni 231.604 | 6.4 | 6.5 | 6.2 | 6.4 | 6.2 | 6.1 | 6.4 | 0.2 | 0.5 | 1.6 |
| P 177.434 | 53 | 52 | 52 | 52 | 52 | 52 | 51 | 0.6 | 1.9 | 6.4 |
| Pb 220.353 | 5.9 | 6.0 | 5.7 | 6.3 | 5.8 | 5.3 | 5.6 | 0.3 | 0.9 | 3.0 |
| Si 185.005 | 36 | 41 | 38 | 37 | 72 | 42 | 40 | 13 | 38 | 125 |
| Si 250.690 | 41 | 43 | 41 | 41 | 72 | 43 | 38 | 12 | 35 | 117 |
| Sr 407.771 | 7.3 | 7.1 | 7.0 | 7.1 | 7.2 | 7.1 | 7.1 | 0.1 | 0.2 | 0.7 |
| V 311.837 | 6.2 | 6.2 | 6.1 | 6.1 | 6.1 | 6.1 | 6.0 | 0.1 | 0.2 | 0.7 |
| Zn 202.548 | 4.9 | 4.5 | 4.2 | 4.2 | 4.2 | 4.1 | 4.0 | 0.3 | 0.9 | 3.1 |
| Zn 206.200 | 4.1 | 3.7 | 3.5 | 3.7 | 3.4 | 3.4 | 3.3 | 0.3 | 0.9 | 2.8 |

Date of analysis: 6/6/2015

| | IDL1 | IDL2 | IDL3 | IDL4 | IDL5 | IDL6 | IDL7 | IDL8 | IDL9 | IDL10 | Standard Deviation | IDL | MRL |
|------------|------|------|------|------|------|------|------|------|------|-------|--------------------|-----|-----|
| Al 236.705 | 15 | 14 | 13 | 14 | 11 | 14 | 13 | 15 | 13 | 13 | 1.1 | 3.4 | 11 |
| Al 237.312 | 4.8 | 7.5 | 5.4 | 6.5 | 8.3 | 7.4 | 6.8 | 7.8 | 6.1 | 6.4 | 0.8 | 2.4 | 8.1 |
| As 188.980 | 6.4 | 5.8 | 5.9 | 6.6 | 6.7 | 6.5 | 6.2 | 7.4 | 6.2 | 7.0 | 0.5 | 1.5 | 4.9 |
| As 193.696 | 8.0 | 7.6 | 7.8 | 8.2 | 8.4 | 8.6 | 7.6 | 8.1 | 8.2 | 8.4 | 0.4 | 1.1 | 3.5 |
| Ba 233.527 | 7.1 | 7.1 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 0.0 | 0.1 | 0.3 |
| Ba 455.403 | 7.3 | 7.3 | 7.3 | 7.3 | 7.3 | 7.3 | 7.3 | 7.3 | 7.3 | 7.3 | 0.0 | 0.1 | 0.2 |
| Be 249.473 | 7.0 | 6.8 | 7.0 | 6.7 | 6.9 | 7.1 | 7.2 | 6.7 | 6.7 | 6.9 | 0.2 | 0.6 | 1.8 |
| Be 313.042 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 7.0 | 0.0 | 0.1 | 0.2 |
| Ca 317.933 | 7.9 | 7.7 | 7.8 | 7.7 | 8.5 | 8.0 | 11 | 8.6 | 8.4 | 7.7 | 0.9 | 2.7 | 9.0 |
| Co 228.615 | 7.0 | 7.0 | 7.0 | 6.9 | 7.0 | 6.9 | 6.9 | 7.0 | 7.0 | 7.0 | 0.0 | 0.1 | 0.4 |
| Co 237.863 | 6.9 | 7.0 | 7.0 | 6.9 | 6.9 | 7.2 | 6.9 | 6.9 | 7.2 | 7.1 | 0.1 | 0.4 | 1.3 |
| Cr 267.716 | 7.2 | 7.2 | 7.3 | 7.1 | 7.3 | 7.2 | 7.2 | 7.2 | 7.3 | 7.3 | 0.1 | 0.2 | 0.5 |
| Cu 327.395 | 7.2 | 7.2 | 7.4 | 7.2 | 7.3 | 7.1 | 7.2 | 7.4 | 7.3 | 7.2 | 0.1 | 0.3 | 0.9 |
| Fe 238.204 | 8.8 | 8.7 | 8.7 | 8.8 | 9.6 | 9.1 | 8.8 | 9.0 | 9.4 | 9.1 | 0.3 | 0.9 | 3.2 |
| Fe 258.588 | 9.5 | 9.5 | 9.6 | 9.5 | 11 | 9.8 | 9.6 | 10.0 | 9.9 | 9.7 | 0.3 | 0.9 | 3.1 |
| Fe 259.940 | 7.5 | 7.4 | 7.4 | 7.5 | 8.5 | 7.8 | 7.4 | 7.7 | 7.8 | 7.7 | 0.3 | 1.0 | 3.4 |
| Mg 279.078 | 32 | 32 | 32 | 32 | 32 | 32 | 33 | 33 | 33 | 32 | 0.4 | 1.3 | 4.4 |
| Mg 383.829 | 5.3 | 6.0 | 6.3 | 6.0 | 6.8 | 6.1 | 6.2 | 6.0 | 5.4 | 6.7 | 0.5 | 1.4 | 4.7 |
| Mn 260.568 | 6.8 | 6.7 | 6.8 | 6.8 | 6.8 | 6.7 | 6.8 | 6.8 | 6.8 | 6.7 | 0.0 | 0.1 | 0.3 |
| Mn 261.020 | 9.9 | 10 | 10 | 8.9 | 9.7 | 9.5 | 9.9 | 9.6 | 10 | 11 | 0.6 | 1.9 | 6.4 |
| Na 588.995 | 21 | 21 | 20 | 22 | 22 | 20 | 21 | 21 | 22 | 21 | 0.6 | 1.7 | 5.5 |
| Na 589.592 | 17 | 17 | 17 | 17 | 17 | 17 | 17 | 17 | 17 | 17 | 0.2 | 0.5 | 1.6 |
| Ni 231.604 | 6.9 | 6.9 | 6.9 | 7.1 | 6.9 | 7.0 | 7.0 | 7.0 | 6.8 | 7.1 | 0.1 | 0.2 | 0.7 |
| Pb 220.353 | 7.6 | 7.4 | 6.9 | 7.4 | 7.5 | 7.5 | 7.1 | 7.4 | 7.3 | 7.4 | 0.2 | 0.6 | 2.1 |
| Si 185.005 | 7.0 | 7.3 | 7.8 | 7.8 | 6.9 | 7.6 | 7.2 | 7.8 | 7.6 | 7.5 | 0.3 | 1.0 | 3.4 |
| Si 250.690 | 37 | 36 | 35 | 32 | 36 | 33 | 31 | 34 | 50 | 34 | 5.2 | 16 | 52 |
| Sr 407.771 | 7.5 | 7.3 | 7.3 | 7.2 | 7.6 | 7.8 | 7.3 | 7.0 | 7.3 | 7.2 | 0.2 | 0.7 | 2.4 |
| Sr 460.733 | 6.7 | 6.6 | 6.7 | 6.8 | 6.6 | 6.7 | 6.6 | 6.6 | 6.7 | 6.7 | 0.1 | 0.2 | 0.6 |
| V 311.837 | 7.4 | 7.9 | 7.1 | 7.3 | 7.1 | 7.7 | 7.7 | 7.4 | 7.5 | 7.2 | 0.3 | 0.8 | 2.8 |
| Zn 202.548 | 6.8 | 6.7 | 6.8 | 6.8 | 7.0 | 6.8 | 6.7 | 6.8 | 6.7 | 6.7 | 0.1 | 0.3 | 1.0 |
| Zn 206.200 | 6.6 | 6.7 | 6.7 | 6.6 | 7.0 | 6.8 | 6.6 | 6.8 | 6.6 | 6.6 | 0.1 | 0.4 | 1.3 |

| Date of analysis | Al | As | Ca | Cr | Cu | Fe | K | Mg | Mn | Na | Ni | Pb | Si | Sr | V | Zn |
|------------------|--|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| | 237.312 | 193.696 | 317.933 | 267.716 | 327.395 | 238.204 | 766.491 | 279.078 | 260.568 | 589.592 | 231.604 | 220.353 | 185.005 | 407.771 | 311.837 | 202.548 |
| QC blank | 1.5 | 0.7 | 2.6 | 0.3 | ND | 0.2 | 2.0 | ND | ND | -- | 0.1 | ND | 7.5 | 0.0 | ND | ND |
| QC1a | 38.5 | 39.9 | 42.5 | 40.5 | 40.5 | 39.0 | 162.8 | 38.6 | 39.9 | -- | 40.0 | 39.6 | 203.7 | 41.0 | 39.4 | 38.2 |
| QC2a | 205.0 | 208.5 | 202.8 | 205.9 | 209.3 | 205.7 | 911.9 | 203.7 | 204.8 | -- | 204.9 | 206.0 | 1041.3 | 206.2 | 207.0 | 212.2 |
| QC1b | 42.5 | 44.7 | 44.4 | 42.5 | 44.2 | 41.3 | 180.3 | 41.0 | 42.0 | -- | 41.9 | 42.3 | 223.4 | 44.2 | 42.4 | 39.6 |
| QC2b | 216.6 | 222.7 | 204.3 | 205.8 | 219.3 | 207.5 | 954.8 | 203.9 | 207.4 | -- | 206.9 | 209.4 | 1108.8 | 214.2 | 212.3 | 204.5 |
| QC1c | 46.7 | 48.6 | 42.4 | 43.8 | 47.0 | 42.2 | 224.0 | 42.1 | 42.6 | -- | 43.2 | 42.3 | 243.3 | 46.8 | 44.0 | 41.9 |
| QC2c | 229.2 | 238.5 | 212.8 | 215.5 | 235.9 | 215.8 | 1017.7 | 211.2 | 212.7 | -- | 213.1 | 217.5 | 1196.1 | 228.8 | 223.8 | 212.1 |
| | QC1 = 40 µg/L (K, Si = 200 µg/L); QC2 = 200 µg/L (K, Si = 1000 µg/L) | | | | | | | | | | | | | | | |
| QC blank | 1.0 | ND | ND | 0.0 | 0.6 | 0.2 | 10.9 | ND | 0.2 | 17.6 | 0.0 | ND | 71.8 | 0.0 | 2.3 | 1.3 |
| QC1a | 19.4 | 18.1 | 19.7 | 18.9 | 19.2 | 18.8 | 93.9 | 13.1 | 18.7 | 33.4 | 18.9 | 19.4 | 145.7 | 17.9 | 19.6 | 19.4 |
| QC2a | 203.1 | 199.5 | 202.8 | 198.1 | 201.5 | 203.1 | 1025.1 | 203.1 | 197.5 | 188.5 | 206.6 | 201.6 | 987.8 | 188.6 | 199.1 | 202.1 |
| QC2b | 204.4 | 203.7 | 207.0 | 202.9 | 208.7 | 205.1 | 1054.7 | 205.1 | 198.8 | 194.3 | 206.5 | 203.9 | 998.7 | 194.4 | 203.8 | 202.6 |
| | QC1 = 20 µg/L (K, Si = 100 µg/L); QC2 = 200 µg/L (K, Si = 1000 µg/L) | | | | | | | | | | | | | | | |
| QC blank | ND | ND | ND | 0.4 | ND | ND | 43.4 | ND | ND | 4.3 | 0.0 | 1.0 | ND | ND | 0.0 | 0.6 |
| QC1a | -- | 15.7 | 13.8 | 18.6 | 20.0 | -- | 115.0 | 6.8 | 18.5 | 21.3 | 19.7 | 19.0 | 38.4 | 18.7 | 17.1 | 18.3 |
| QC2a | 193.9 | 200.9 | 202.7 | 201.5 | 220.4 | 207.8 | 1004.9 | 210.6 | 207.4 | 200.0 | 223.2 | 199.3 | 1044.1 | 203.9 | 194.4 | 202.5 |
| QC1b | -- | 16.1 | 15.0 | 18.7 | 19.6 | -- | 116.9 | 8.3 | 18.2 | 20.2 | 19.6 | 19.0 | 74.1 | 18.6 | 17.1 | 18.3 |
| QC2b | 200.0 | 201.4 | 205.5 | 204.6 | 219.6 | 212.4 | 996.6 | 214.0 | 206.4 | 199.3 | 223.2 | 200.7 | 1109.9 | 201.6 | 194.3 | 205.7 |
| QC1c | -- | 15.7 | 14.2 | 18.8 | 20.1 | -- | 119.6 | 8.1 | 18.5 | 20.5 | 19.8 | 19.0 | 47.5 | 18.8 | 17.1 | 18.5 |
| QC2c | 196.7 | 203.1 | 206.0 | 203.0 | 221.1 | 211.5 | 1002.6 | 212.3 | 204.9 | 196.0 | 221.9 | 198.7 | 1090.4 | 202.8 | 194.0 | 204.0 |
| | QC1 = 20 µg/L (K, Si = 100 µg/L); QC2 = 200 µg/L (K, Si = 1000 µg/L) | | | | | | | | | | | | | | | |

| Date of analysis | Al | As | Ca | Cr | Cu | Fe | K | Mg | Mn | Na | Ni | Pb | Si | Sr | V | Zn |
|------------------|--|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| | 237.312 | 193.696 | 317.933 | 267.716 | 327.395 | 238.204 | 766.491 | 279.078 | 260.568 | 589.592 | 231.604 | 220.353 | 185.005 | 407.771 | 311.837 | 202.548 |
| QC blank | ND | 0.1 | ND | ND | 0.0 | ND | 30.1 | ND | ND | 196.6 | ND | ND | 8.2 | 0.0 | ND | ND |
| QC1a | 20.2 | 17.7 | -- | 19.4 | 19.4 | 19.0 | 106.3 | 23.0 | 19.1 | 231.8 | 19.0 | 18.9 | 102.4 | 20.4 | 18.3 | 22.3 |
| QC2a | 427.0 | 360.9 | -- | 382.0 | 384.5 | 377.2 | 1694.9 | 439.1 | 373.9 | 924.5 | 376.0 | 367.7 | 1880.1 | 389.6 | 378.2 | 380.4 |
| QC1b | 19.3 | 17.4 | -- | 19.3 | 19.9 | 19.1 | 109.1 | 21.6 | 19.1 | 232.6 | 19.0 | 19.2 | 96.0 | 20.6 | 18.1 | 22.5 |
| QC2b | 421.7 | 358.0 | -- | 379.7 | 384.4 | 374.4 | 1700.5 | 437.9 | 370.5 | 916.4 | 373.4 | 366.9 | 1832.7 | 389.4 | 378.3 | 376.0 |
| QC1c | 19.6 | 16.9 | -- | 18.9 | 19.7 | 18.5 | 127.3 | 21.6 | 18.7 | 250.5 | 18.5 | 18.5 | 96.5 | 20.6 | 17.8 | 21.4 |
| QC2c | 423.1 | 358.6 | -- | 376.1 | 390.0 | 371.8 | 1704.5 | 432.3 | 366.8 | 916.2 | 367.9 | 361.3 | 1839.1 | 393.3 | 378.6 | 366.6 |
| | QC1 = 20 µg/L (K, Si = 100 µg/L); QC2 = 400 µg/L (K, Si = 2000 µg/L) | | | | | | | | | | | | | | | |
| QC1a | 32.5 | 36.0 | 28.5 | 36.5 | 40.5 | 36.6 | 43.8 | 38.5 | 37.1 | -- | -- | 37.4 | 33.4 | 35.8 | 36.5 | 35.6 |
| QC2a | 410.2 | 394.6 | 394.0 | 395.3 | 428.2 | 410.7 | 1802.3 | 418.7 | 405.0 | -- | -- | 404.7 | 412.9 | 406.3 | 398.2 | 388.3 |
| QC3a | 50.0 | 48.8 | 42.9 | 50.1 | 54.5 | 51.3 | 57.5 | 54.0 | 50.9 | -- | -- | 50.8 | 47.4 | 48.6 | 49.6 | 49.1 |
| QC1b | 34.7 | 35.9 | 29.2 | 37.1 | 41.3 | 41.4 | 45.5 | 38.5 | 37.4 | -- | -- | 37.9 | 33.9 | 36.3 | 37.3 | 38.6 |
| QC1c | 33.4 | 37.4 | 30.4 | 36.5 | 40.8 | 36.4 | 50.3 | 37.8 | 36.8 | -- | -- | 37.0 | 31.9 | 35.4 | 36.9 | 35.6 |
| QC2c | 413.7 | 404.7 | 398.3 | 393.6 | 430.0 | 408.4 | 1829.3 | 417.5 | 401.1 | -- | -- | 401.6 | 421.4 | 405.0 | 401.2 | 393.4 |
| QC1d | 31.0 | 35.1 | 27.9 | 34.8 | 38.8 | 35.0 | 46.4 | 37.0 | 36.8 | -- | -- | 36.9 | 29.3 | 34.3 | 35.4 | 35.2 |
| QC2d | 418.3 | 404.4 | 390.5 | 391.4 | 420.5 | 406.9 | 1809.1 | 414.9 | 412.3 | -- | -- | 412.6 | 420.6 | 400.0 | 394.0 | 399.3 |
| QC1e | 38.5 | 35.6 | 74.4 | 101.8 | 44.7 | 363.5 | 158.6 | 39.0 | 58.2 | -- | -- | 155.4 | 37.0 | 35.7 | 37.2 | -- |
| QC2e | 418.9 | 432.4 | 396.4 | 395.3 | 449.1 | 405.6 | 379.2 | 414.4 | 417.2 | -- | -- | 412.2 | 395.6 | 402.3 | 416.8 | 695.2 |
| QC1f | 39.3 | 34.4 | 29.2 | 34.6 | 40.4 | 46.8 | 50.0 | 36.1 | 36.3 | -- | -- | 36.2 | 30.4 | 34.3 | 36.0 | 33.9 |
| QC2f | 422.2 | 419.3 | 388.7 | 391.2 | 450.7 | 404.5 | 382.3 | 405.6 | 411.5 | -- | -- | 403.5 | 389.9 | 398.1 | 416.4 | 661.2 |
| | QC1 = 35 µg/L; QC2 = 400 µg/L; QC3 = 50 µg/L | | | | | | | | | | | | | | | |
| QC blank | 2.1 | 1.8 | 1.6 | 0.1 | ND | 2.0 | ND | 0.4 | ND | 10.5 | ND | 0.7 | 23.6 | 0.0 | 0.0 | 0.1 |
| QC1a | 18.5 | 20.2 | 20.8 | 20.1 | 20.4 | 20.7 | 16.5 | 20.2 | 19.5 | 28.0 | 19.6 | 21.0 | -- | 20.4 | 19.1 | 19.5 |
| QC2a | 98.7 | 102.7 | 102.8 | 104.7 | 104.8 | 100.5 | 110.4 | 102.8 | 102.5 | 104.4 | 102.7 | 106.6 | -- | 105.0 | 104.4 | 102.6 |
| QC1b | 20.1 | 21.5 | 26.4 | 20.6 | 21.1 | 22.4 | 17.7 | 20.3 | 19.9 | 38.0 | 19.9 | 20.6 | -- | 21.3 | 20.0 | 20.1 |
| QC2b | 104.7 | 107.2 | 107.4 | 108.8 | 110.9 | 105.0 | 114.8 | 105.8 | 106.0 | 110.5 | 106.4 | 110.1 | -- | 110.6 | 110.0 | 104.3 |
| | QC1 = 20 µg/L; QC2 = 200 µg/L | | | | | | | | | | | | | | | |

| Date of analysis | Al | As | Ca | Cr | Cu | Fe | K | Mg | Mn | Na | Ni | Pb | Si | Sr | V | Zn |
|------------------|----------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| | 237.312 | 193.696 | 317.933 | 267.716 | 327.395 | 238.204 | 766.491 | 279.078 | 260.568 | 589.592 | 231.604 | 220.353 | 185.005 | 407.771 | 311.837 | 202.548 |
| 6/6/2015 | QC blank | 2.1 | 1.8 | 1.6 | 0.1 | 0.0 | 2.0 | 0.0 | 0.4 | 0.0 | 10.5 | 0.0 | 0.7 | 23.6 | 0.0 | 0.1 |
| | QC1a | 18.7 | 20.2 | 20.8 | 20.1 | 20.4 | 16.5 | 20.2 | 19.5 | 28.0 | 19.6 | 21.0 | -- | 20.4 | 19.1 | 19.6 |
| | QC2a | 99.2 | 102.7 | 102.8 | 104.7 | 104.8 | 110.4 | 102.8 | 102.5 | 104.4 | 102.7 | 106.6 | -- | 105.0 | 104.4 | 102.6 |
| | QC1b | 20.2 | 21.5 | 26.4 | 20.6 | 21.1 | 22.4 | 17.8 | 20.3 | 19.9 | 38.0 | 19.9 | 20.6 | -- | 21.3 | 20.0 |
| | QC2b | 105.0 | 107.2 | 107.4 | 108.8 | 110.9 | 105.0 | 114.8 | 105.8 | 106.0 | 110.5 | 106.4 | 110.1 | -- | 110.6 | 110.0 |
| | | | | | | | | | | | | | | | | |
| 6/19/2015 | QC blank | 2.6 | 1.1 | 4.7 | 0.2 | ND | 1.6 | 169.5 | ND | 0.0 | 3.9 | 0.0 | 0.6 | 37.5 | 0.0 | 0.1 |
| | QC1a | 20.7 | 20.5 | 25.6 | 20.3 | 20.2 | 25.5 | -- | 18.6 | 20.6 | 22.4 | 20.1 | 21.3 | -- | 20.8 | 20.6 |
| | QC2a | 102.8 | 102.2 | 109.2 | 101.8 | 101.7 | 106.5 | -- | 103.7 | 104.9 | 101.8 | 102.4 | 106.2 | -- | 104.2 | 106.2 |
| | QC1b | 22.5 | 20.0 | 25.0 | 19.5 | 19.3 | 24.3 | -- | 18.0 | 19.6 | 22.2 | 19.1 | 19.8 | -- | 20.2 | 19.7 |
| | QC2b | 101.7 | 100.6 | 106.3 | 99.2 | 100.1 | 103.6 | -- | 99.5 | 101.8 | 99.9 | 99.3 | 102.9 | -- | 102.8 | 102.5 |
| | QC1c | 18.9 | 19.3 | 23.0 | 18.8 | 19.2 | 20.1 | -- | 16.8 | 18.6 | 27.3 | 18.3 | 18.0 | -- | 19.8 | 19.4 |
| 7/9/2015 | QC blank | 1.3 | ND | 1.3 | 0.2 | 0.1 | 0.5 | -- | ND | ND | ND | 0.1 | 0.6 | 0.0 | 0.1 | ND |
| | QC1a | 20.6 | 20.5 | 21.5 | 20.9 | 20.7 | 20.7 | -- | 20.2 | 20.9 | 19.9 | 20.3 | 20.8 | -- | 21.2 | 20.3 |
| | QC2a | 19.8 | 19.1 | 21.0 | 19.8 | 19.5 | 19.8 | -- | 19.6 | 19.8 | 18.7 | 19.3 | 19.8 | -- | 20.1 | 19.2 |
| | QC1b | 105.6 | 103.0 | 107.6 | 104.8 | 104.8 | 104.5 | -- | 104.5 | 106.1 | 105.5 | 103.4 | 106.9 | -- | 106.0 | 105.6 |
| | QC2b | 24.6 | 20.2 | 22.7 | 21.1 | 21.3 | 23.8 | -- | 21.0 | 20.9 | 20.3 | 20.2 | 21.1 | -- | 21.8 | 20.8 |
| | QC1c | 22.5 | 18.8 | 21.1 | 19.5 | 19.8 | 21.1 | -- | 18.8 | 19.3 | 19.0 | 18.8 | 19.8 | -- | 20.1 | 18.7 |
| QC2c | 107.0 | 104.1 | 107.1 | 103.8 | 105.6 | 104.0 | -- | 103.2 | 104.4 | 107.0 | 101.4 | 104.2 | -- | 107.1 | 106.1 | |
| | | | | | | | | | | | | | | | | |

QC1 = 20 µg/L; QC2 = 100 µg/L

QC1 = 20 µg/L; QC2 = 200 µg/L

QC1 = 20 µg/L (K, Si = 100 µg/L); QC2 = 200 µg/L (K, Si = 1000 µg/L)

| Date of analysis | Al | As | Ca | Cr | Cu | Fe | K | Mg | Mn | Na | Ni | Pb | Si | Sr | V | Zn |
|---|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| | 237.312 | 193.696 | 317.933 | 267.716 | 327.395 | 238.204 | 766.491 | 279.078 | 260.568 | 589.592 | 231.604 | 220.353 | 185.005 | 407.771 | 311.837 | 202.548 |
| QC blank | 3.9 | 0.0 | 0.5 | 0.0 | 0.3 | 0.6 | 212.1 | ND | 0.0 | 0.1 | 0.0 | 1.9 | 81.8 | 0.0 | 0.1 | 0.6 |
| QC1a | 20.0 | 18.8 | 16.3 | 19.3 | 19.4 | 18.9 | -- | 17.8 | 19.5 | 18.4 | 19.0 | 20.0 | -- | 19.9 | 18.6 | 17.5 |
| QC2a | 103.1 | 102.2 | 100.8 | 100.6 | 100.1 | 103.9 | -- | 101.2 | 102.4 | 99.1 | 100.5 | 101.7 | -- | 102.5 | 101.0 | 99.7 |
| QC3a | 206.0 | 202.4 | 202.6 | 199.9 | 199.0 | 209.4 | -- | 201.8 | 202.2 | 199.8 | 200.7 | 197.7 | -- | 201.7 | 202.3 | 197.9 |
| QC1b | 22.2 | 20.6 | 16.4 | 20.5 | 20.5 | 21.5 | -- | 18.3 | 20.4 | 19.3 | 19.9 | 20.3 | -- | 21.5 | 20.1 | 17.1 |
| QC2b | 107.6 | 105.9 | 102.8 | 102.9 | 103.6 | 106.2 | -- | 103.6 | 103.3 | 100.5 | 101.3 | 101.2 | -- | 107.6 | 105.5 | 97.8 |
| QC1c | 22.7 | 21.4 | 19.1 | 21.5 | 21.6 | 22.5 | -- | 18.9 | 21.1 | 20.2 | 20.6 | 21.2 | -- | 22.7 | 21.2 | 17.8 |
| QC2c | 111.3 | 108.6 | 114.0 | 106.3 | 106.5 | 110.1 | -- | 107.9 | 105.5 | 102.8 | 103.7 | 103.3 | -- | 111.4 | 108.7 | 100.4 |
| QC1d | 22.8 | 21.1 | 17.0 | 20.4 | 20.9 | 22.7 | -- | 17.3 | 19.9 | 19.4 | 19.4 | 19.5 | -- | 21.9 | 20.4 | 16.3 |
| QC2d | 108.9 | 107.0 | 104.9 | 103.2 | 105.1 | 107.4 | -- | 101.4 | 101.6 | 101.8 | 99.5 | 99.9 | -- | 109.7 | 106.0 | 95.4 |
| QC1e | 26.2 | 21.3 | 17.4 | 20.9 | 21.2 | 23.5 | -- | 17.7 | 20.3 | 19.8 | 19.7 | 20.4 | -- | 22.4 | 20.8 | 16.7 |
| QC2e | 109.4 | 106.1 | 104.8 | 103.9 | 104.8 | 106.7 | -- | 102.2 | 101.8 | 100.9 | 99.4 | 100.3 | -- | 109.9 | 106.2 | 97.9 |
| QC1f | 27.8 | 21.1 | 20.1 | 21.5 | 21.7 | 30.2 | -- | 20.0 | 20.7 | 20.7 | 20.2 | 20.7 | -- | 22.8 | 21.3 | 17.5 |
| QC2f | 113.0 | 106.2 | 107.3 | 105.0 | 104.9 | 109.5 | -- | 104.0 | 102.1 | 133.6 | 100.4 | 101.7 | -- | 110.9 | 107.8 | 97.1 |
| QC3f | 247.2 | 215.7 | 215.6 | 213.7 | 215.0 | 225.6 | -- | 212.2 | 206.6 | 209.0 | 205.5 | 205.4 | -- | 223.6 | 220.4 | 199.2 |
| QC1 = 20 µg/L; QC2 = 100 µg/L; QC3 = 200 µg/L | | | | | | | | | | | | | | | | |

8/11/2015

Appendix D: Leachate Data

Table notes: All values in µg/L except where otherwise noted. Values less than the method detection limit (MDL) are represented by ND. Values exceeding the detection limit but less than the method reporting limit (MRL) are italicized to indicate quantitation is estimated.

| Leachate condition | pH | Al (µg/L) | As | Ca (mg/L) | Co | Cr | Cu | Fe (mg/L) | K (mg/L) | Mg (mg/L) | Mn | Na (mg/L) | Ni | P | Pb | Si (mg/L) | V | Zn |
|--------------------|------|-----------|-------|-----------|------|-------|-------|-----------|----------|-----------|------|-----------|-------|---------|------|-----------|------|------|
| MDL (µg/L) | | 2.42 | 1.43 | 4.93 | 0.26 | 0.31 | 0.27 | 0.96 | 4.42 | 1.35 | 0.20 | 0.47 | 0.47 | 1.92 | 0.90 | 34.98 | 0.35 | 0.30 |
| MRL (µg/L) | 8 | 4.77 | 16.43 | 0.87 | 1.04 | 0.89 | 1.47 | 3.19 | 14.75 | 4.49 | 0.68 | 1.58 | 1.55 | 6.39 | 2.98 | 116.61 | 1.16 | 1.00 |
| DX | 7.4 | 13 | ND | 5.47 | 13.2 | 4.99 | 20.4 | 26.5 | 0.775 | 6.9 | 257 | 4.13 | 1.93 | 690 | 4.49 | 79.5 | 106 | 31.9 |
| Fine SS | 19.4 | 3.7 | 7.45 | 9.33 | 3.16 | 20.7 | 22.6 | 1.61 | 6.02 | 3.24 | 324 | 18.5 | 1.47 | 187 | 6.96 | 105 | 327 | 42.8 |
| WF | 9.0 | 210 | 10.7 | 30 | 101 | 9.39 | 49.9 | 14.3 | 49.7 | 1330 | 20.4 | 13.6 | 51.3 | 62.3 | 1210 | 233 | 608 | 608 |
| WFw | 9.3 | 261 | 18 | 41.3 | 85.3 | 15.2 | 76.4 | 18.4 | 4.34 | 56.4 | 1600 | 29.3 | 21.4 | 438 | 55.3 | 1380 | 365 | 452 |
| OC Shale | 9.4 | 5.71 | 12.8 | 3.01 | 7.09 | 5.43 | 24.5 | 9.02 | 0.799 | 2.61 | 94.3 | 16.5 | 3.25 | 225 | 1.62 | 45 | 572 | 21.1 |
| OC Shale 2 | 7.5 | 0.533 | 1.9 | 18.6 | 0.76 | 0.531 | 5.57 | 1.09 | 0.574 | 2.07 | 54.4 | 22.4 | ND | 138 | 1.02 | 12.9 | 16.3 | 1.56 |
| Basal SS | 6.34 | 5.76 | 5.19 | 7.74 | 2.19 | 12.1 | 12.8 | 1.49 | 3.97 | 132 | 16.2 | 16.2 | 1.99 | 753 | 1.51 | 50.9 | 250 | 9.78 |
| Cong SS | 7.4 | 5.96 | ND | 5.93 | 7.56 | 3.2 | 56.3 | 10.1 | 2 | 3.53 | 73.6 | 8.52 | 3.31 | 211 | 1.11 | 40.9 | 25.3 | 9.86 |
| Mica SS | 7.9 | 13.4 | ND | 1.21 | 35.6 | 15.8 | 5.81 | 22.3 | 0.919 | 2.13 | 541 | 1.19 | 28.8 | 548 | 3.03 | 42.7 | 51.8 | 14.6 |
| Peb Cong | 7.5 | 2.85 | ND | 6.84 | 3.55 | 0.946 | 9.71 | 6.1 | 0.225 | 2.71 | 108 | 3.77 | 0.576 | 143 | ND | 20.4 | 23.8 | 5.83 |
| FHr | 8.5 | 4.72 | 2.18 | 6.06 | 5.56 | 1.17 | 2.04 | 1.66 | 2.2 | 0.748 | 27.1 | 3.04 | ND | 29.7 | 1.25 | 27.9 | 8.17 | 15.4 |
| FHb | 8.7 | 4.87 | 13.3 | 4.82 | 18.2 | 1.55 | 21.2 | 1.02 | 3.42 | 2.53 | 20 | 3.02 | ND | 31.3 | ND | 27.9 | 8.57 | 4.22 |
| LDNss | 6.4 | 17.8 | 2.13 | 2.55 | 9.62 | 22.2 | 17.7 | 18.8 | 1.55 | 3.84 | 70.3 | 2.22 | 20.6 | 401 | 3.77 | 64.7 | 27.8 | 45.7 |
| Mica SS | 7.0 | 3.12 | ND | 8.14 | 3.01 | 10.4 | 0.619 | 4.72 | 0.957 | 5.74 | 48.7 | 0.594 | 2.64 | 21 | 1.53 | 17.1 | 20.8 | 8.16 |
| LDN | 8.9 | 12 | 3.5 | 10.7 | 20.7 | 16.5 | 26.7 | 25 | 0.883 | 20.6 | 203 | 2.87 | 36.2 | 376 | 1.63 | 94.7 | 374 | 15.2 |
| WS3 | 7.3 | 5.28 | 2.43 | 0.0143 | 4.63 | 2.58 | 1.44 | 1.21 | 1.03 | 0.104 | 2.45 | 0.195 | 1.98 | 16 | 1.68 | 18.6 | 4.12 | 8.17 |
| GHg | 8.8 | 6.08 | 5.06 | 8.62 | 12.1 | 3.15 | 61.2 | 12.5 | 0.316 | 5.13 | 180 | 2.58 | 2.07 | 392 | 1.24 | 44.5 | 142 | 8.91 |
| GHw | 7.7 | 16 | 2.88 | 1.17 | 11.7 | 2.06 | 11 | 2.73 | 3.46 | 0.675 | 7.77 | 1.29 | 0.851 | 58.9 | 1.86 | 67.7 | 13.4 | 12.5 |
| BCg | 7.2 | 8.72 | 6.64 | 13 | 4.39 | 8.03 | 2.33 | 6.79 | 4.42 | 1.37 | 10.9 | 3.75 | 3.75 | 67.6 | 3.56 | 67 | 17 | 19.7 |
| BCw | 6.9 | 7.25 | 107 | 1.61 | 30.7 | 23.5 | 4.19 | 6.54 | 2.67 | 1.14 | 16.8 | 1.04 | 1.11 | 110 | 2.48 | 59.8 | 35.4 | 11.1 |
| SP | 6.7 | 12.2 | 1.73 | 2.78 | 23 | 1.64 | 52.5 | 18.4 | 1.2 | 4.43 | 167 | 0.825 | 2.41 | 330 | 2.12 | 84.5 | 35.2 | 47 |
| FD1 | 6.7 | 2 | ND | 1.64 | 1.61 | ND | 1.4 | 2.17 | 0.286 | ND | 21.3 | 2.74 | ND | 1.29 | 22.1 | 3.92 | 9.53 | |
| FD2 | 6.8 | 1.47 | 2.46 | 0.891 | 2.78 | ND | 0.939 | 1.38 | 0.471 | 0.113 | 18.3 | 3.5 | ND | 1.15 | 22 | 4.57 | 8.09 | |
| FD3 | 6.7 | 1.78 | 3.14 | 1.17 | 1.79 | 38.7 | 2.87 | 1.6 | 0.378 | 0.151 | 38.6 | 2.9 | 59.4 | 1.41 | 23.6 | 1.7 | 491 | |
| FD4 | 6.6 | 1.48 | 8.4 | 1.33 | 1.68 | ND | 1.89 | 1.2 | 1.23 | 0.465 | 12.1 | 2.42 | ND | ND | 24.1 | 4.73 | 5.77 | |
| MK1 | 8.4 | 0.834 | 4.8 | 3.16 | 6.89 | ND | 1.32 | 0.994 | 2.78 | 1.44 | 21.5 | 7.09 | ND | ND | 18.9 | 7.25 | 1.91 | |
| MK2 | 6.9 | 2.25 | 10.7 | 0.775 | 35.3 | 0.433 | 1.67 | 1.94 | 0.901 | 3.56 | 3.44 | 3.44 | 1.26 | ND | 26.3 | 12.6 | 6.57 | |
| TW1 | 6.9 | 2.66 | 2.48 | 1.17 | 14.9 | 1.42 | 2.64 | 1.59 | 2.36 | 0.401 | 139 | 3.66 | 1.18 | ND | 23.4 | 12.3 | 7.49 | |
| TW2 | 8.5 | 1.01 | 1.71 | 1.59 | 2.05 | ND | 8.94 | 1.76 | 0.15 | 0.473 | 17.8 | 12.9 | 0.251 | ND | 13.3 | 43.4 | 1.52 | |
| WF | 6.9 | 130 | 10.7 | 22.1 | 72.7 | 57.2 | 37.7 | 85.5 | 499 | 33.2 | 788 | 1760 | 8.23 | 1040000 | 33.5 | 1080 | 175 | 379 |
| WFw | 7.0 | 120 | 19.2 | 18.1 | 47.4 | 57.9 | 45.6 | 79.7 | 574 | 27.1 | 560 | 1760 | 8.95 | 1040000 | 15.5 | 949 | 214 | 175 |
| OC Shale | | | 0.573 | 33.8 | 11.5 | 11.3 | 56.1 | 74.6 | 0.793 | 7.78 | 67.8 | 1790 | 4.29 | 1060000 | ND | 60.1 | 595 | 1.74 |
| Mica SS | | 3.37 | 2.82 | 7.42 | 49.7 | 68.1 | 15.3 | 3.77 | 1470 | 10.7 | 300 | 1720 | 9.54 | 1070000 | ND | 27.3 | 69.1 | 2.35 |
| FHr | 7.1 | 6.1 | 13.9 | 12.4 | 71 | 62.2 | 14.2 | 1.38 | 1960 | 4.06 | 111 | 1710 | 1.72 | 1070000 | ND | 75.5 | 22 | |
| FHb | 7.1 | 6.88 | 60.6 | 13 | 124 | 63.6 | 99.8 | 1.06 | 1970 | 10.5 | 114 | 1720 | 3.1 | 1060000 | ND | 60.3 | 18.2 | 1.48 |
| LDN ss | 7.0 | 0.339 | 17.9 | 7.22 | 33.3 | 60.7 | 22.9 | 0.306 | 473 | 21.4 | 119 | 83.2 | 12.1 | 1340000 | ND | 18.9 | 18.2 | 3.68 |
| LDN | 7.1 | 0.354 | 12 | 11 | 6.21 | 56.9 | 59.9 | 0.427 | 473 | 22.7 | 68.8 | 86 | 3.06 | 1370000 | ND | 52.7 | 332 | 1.94 |
| WS3 | 7.1 | 0.382 | 14.4 | ND | 58.6 | 63 | 7.32 | 0.047 | 497 | 0.174 | 3.05 | 83.1 | 1.32 | 1350000 | ND | 8.23 | 5.16 | 8.86 |
| GHg | 7.1 | 0.186 | 17.5 | 10.6 | 5.04 | 57.6 | 67.8 | 0.18 | 464 | 13.8 | 79.1 | 83.4 | 1.17 | 1360000 | ND | 44.1 | 211 | 61.6 |
| LDN | 7.1 | 0.923 | 10.1 | 10 | 62 | 61.4 | 12.2 | 0.161 | 497 | 7.79 | 24 | 84.4 | 2.49 | 1350000 | ND | 30 | 21.7 | 3.75 |
| BCg | 6.9 | 3.82 | 47 | 18.1 | 24.7 | 54.5 | 11.4 | 3.28 | 389 | 38.8 | 303 | 84.2 | 10.4 | 1360000 | 1.39 | 59.6 | 30.8 | 14.2 |
| BCw | 7.1 | 0.475 | 904 | 13.2 | 104 | 62.8 | 8.19 | 0.239 | 495 | 5.49 | 29.1 | 83.3 | 2.81 | 1350000 | ND | 29.1 | 18 | 4.61 |
| SP | 7.1 | 1.77 | ND | 11.8 | 50.9 | 62.3 | 20.3 | 2.35 | 497 | 11.6 | 148 | 83.2 | 3.36 | 1340000 | ND | 23.9 | 3.83 | 14.7 |

| Leachate condition | Sample ID | pH | Al (mg/L) | As | Ca (mg/L) | Co | Cr | Cu | Fe (mg/L) | K (mg/L) | Mg (mg/L) | Mn | Na (mg/L) | Ni | P | Pb | Si (mg/L) | V | Zn |
|--------------------|--------------|-------|-----------|--------|-----------|-------|-------|--------|-----------|----------|-----------|-------|-----------|-------|-------|------|-----------|-------|-------|
| MOP7 | Buffer blank | 7.0 | ND | ND | 0.00766 | ND | ND | 0.761 | ND | 0.183 | ND | ND | 77.1 | ND | ND | ND | ND | ND | ND |
| | BCg | 7.1 | 0.162 | ND | 41.9 | ND | ND | 1.73 | 0.095 | 3.98 | 7.19 | 188 | 74.4 | 0.488 | ND | ND | 12.1 | 1.06 | 1.7 |
| | BCw | 6.9 | 3.71 | 163 | 5.33 | 43.2 | 13.7 | 6.13 | 4.19 | 7.06 | 1.74 | 19.9 | 75.3 | 1.56 | ND | 3.84 | 36 | 22.6 | 14.6 |
| | DX | 7.1 | 2.39 | ND | 9.11 | 2.7 | 0.732 | 4.97 | 4.85 | 1.02 | 2 | 64.3 | 76.6 | 0.477 | ND | ND | 24.2 | 17.9 | 6.09 |
| | FD1 | 7.1 | 0.0196 | ND | 39.8 | ND | ND | 1.31 | 0.0111 | 0.974 | 4.02 | 21.7 | 71.9 | ND | ND | ND | 16 | ND | 0.67 |
| | FD2 | 7.2 | 0.0336 | ND | 40.8 | 1.1 | ND | 1.16 | 0.0114 | 1.61 | 1.33 | 21.4 | 72.5 | ND | ND | ND | 16.5 | ND | ND |
| | FD3 | 7.0 | 0.0776 | ND | 41.8 | ND | ND | 1.36 | 0.0203 | 1.65 | 2.54 | 45.4 | 71.9 | ND | ND | ND | 16.9 | ND | 0.852 |
| | FD4 | 7.0 | 0.0958 | ND | 34.4 | 1.2 | ND | 1.9 | 0.0306 | 1.1 | 7.65 | 27.7 | 71 | ND | ND | ND | 16.9 | 0.388 | 0.597 |
| | FHB | 7.5 | 0.178 | ND | 38.4 | 1.29 | ND | 4.18 | 0.165 | 7.03 | 16.7 | 168 | 167 | 76.1 | ND | 1.66 | 7.5 | 0.458 | 1.38 |
| | FHR | 7.5 | 0.136 | ND | 48.2 | 0.542 | ND | 2.06 | 0.0621 | 7.14 | 2.86 | 167 | 167 | 76 | ND | 7.23 | 9.15 | 0.408 | 3.47 |
| | GHg | 7.2 | 0.0842 | ND | 67.6 | ND | ND | 3.44 | 0.108 | 3.8 | 9.12 | 237 | 237 | 76.2 | ND | ND | 9.89 | 8.07 | 0.933 |
| | GHw | 6.9 | 0.303 | ND | 3.37 | 4.74 | 0.36 | 1.47 | 0.0679 | 9.44 | 1.4 | 9.63 | 9.84 | 76.1 | 0.814 | ND | 11 | 1.23 | 0.444 |
| | LDN | 7.4 | 0.146 | ND | 50.6 | ND | ND | 2.57 | 0.172 | 5.39 | 6.34 | 9.84 | 9.84 | 76.1 | 0.814 | ND | 7.4 | 10.4 | 83.8 |
| | LDNss | 6.8 | 0.0759 | ND | 8.94 | ND | ND | 1.87 | 0.082 | 1.61 | 3.36 | 38.7 | 38.7 | 74.8 | 0.9 | ND | 5.33 | ND | 1.14 |
| | MK1 | 7.3 | 0.0153 | ND | 21.5 | 12 | ND | 1.53 | 0.0137 | 7.78 | 7.62 | 193 | 193 | 76.5 | 0.801 | ND | 9.5 | ND | ND |
| | MK2 | 7.1 | 0.0978 | ND | 7.17 | 12 | ND | 1.1 | 0.0842 | 8.01 | 2.25 | 0.477 | 0.477 | 74.9 | 0.799 | ND | 15.6 | 1.67 | 0.982 |
| | SP | 7.0 | 0.356 | ND | 6.27 | 2.68 | ND | 2.36 | 0.403 | 4.99 | 2.37 | 37.4 | 37.4 | 75.2 | ND | ND | 8.53 | ND | 1.83 |
| | WS1 | 7.1 | 0.856 | ND | 5.74 | 4.06 | 0.338 | 1.63 | 0.505 | 14 | 1.38 | 43.8 | 43.8 | 75.6 | 0.516 | ND | 16.4 | 1.99 | 1.38 |
| | WS2 | 7.3 | 0.0282 | ND | 24 | ND | ND | 2.08 | 0.0248 | 0.771 | 2.06 | 3.5 | 3.5 | 76.8 | ND | ND | 8.87 | 1.59 | 0.52 |
| | WF | 7.3 | 47.2 | 5.01 | 16.7 | 25.5 | 2.56 | 13.4 | 35.7 | 2.79 | 11.3 | 324 | 324 | 138 | 3.04 | 12.9 | 452 | 77.2 | 175 |
| WFw | 7.2 | 98.6 | 3.35 | 19.7 | 16 | 2.07 | 17.6 | 37.8 | 2.87 | 11.4 | 334 | 334 | 121 | 3.51 | 13 | 450 | 73 | 133 | |
| WS3 | 6.8 | 0.251 | ND | 0.0289 | ND | ND | 1.23 | 0.0711 | 3.3 | 0.0358 | 0.6 | 0.6 | 75 | ND | ND | 2.4 | 1.14 | 0.71 | |
| Buffer blank | WF | 8.2 | 228 | ND | 24.5 | 106 | 10 | 59.3 | 153 | 3.5 | 53.4 | 1410 | 43.4 | 14 | 469 | 56.3 | 1270 | 247 | 649 |
| T188 | WFw | 8.2 | 175 | 15.2 | 24.8 | 52.2 | 9.21 | 46.9 | 121 | 3.07 | 36.4 | 969 | 45.1 | 12.1 | 308 | 30.8 | 1010 | 233 | 279 |
| | FHR | 8.0 | 0.409 | 1.51 | 31 | 0.462 | 0.327 | 4.16 | 0.0587 | 3.16 | 2.45 | 54.4 | 3.7 | ND | 9.63 | ND | 12.1 | 1.12 | 0.304 |
| | FHB | 8.0 | 0.193 | 6.1 | 27.7 | 2.1 | 0.591 | 147 | 0.0986 | 4.5 | 7.88 | 54.7 | 54.7 | 3.6 | ND | 23.1 | 1.28 | 8.66 | 1.16 |
| | LDN | 8.2 | 0.672 | 2.97 | 35.7 | 0.617 | 1.85 | 50.3 | 0.827 | 0.654 | 5.88 | 10.5 | 10.5 | 4.03 | ND | 9.14 | ND | 15.1 | 140 |
| | GHg | 8.1 | 0.335 | 1.87 | 31.7 | ND | 0.338 | 22.2 | 0.154 | 0.334 | 3.73 | 14.7 | 14.7 | 4.05 | ND | 15.6 | ND | 10.4 | 20.3 |
| | GHw | 7.7 | 2.44 | 3.32 | 2.43 | 2.63 | 0.663 | 2.68 | 0.488 | 4.42 | 1.11 | 4.15 | 4.15 | 1.62 | ND | 27.6 | ND | 21.7 | 6.89 |
| | BCg | 7.9 | 2.93 | 7.35 | 16.9 | 1.34 | 2.94 | 2.28 | 1.89 | 1.08 | 4.37 | 76.7 | 76.7 | 11.1 | 0.954 | 22.3 | 1.36 | 33.3 | 7.54 |
| | BCw | 7.7 | 7.74 | 379 | 2.36 | 52.8 | 28.7 | 8.92 | 8.76 | 2.45 | 1.62 | 23.2 | 23.2 | 0.905 | 2.09 | 293 | 2.46 | 59.1 | 45.8 |
| | SP | 7.8 | 2.98 | 1.48 | 5.81 | 6.35 | 0.579 | 12.8 | 3.71 | 1.91 | 3.01 | 56.7 | 56.7 | 1.12 | ND | 141 | 1.17 | 25.8 | 1.4 |
| | Buffer blank | BCg | 8.4 | 7.59 | 13.7 | 7.69 | 3.92 | 7.51 | 5.21 | 6.05 | 1.44 | 3.04 | 113 | 15.9 | 3.59 | ND | 2.48 | 64.8 | 24.7 |
| | BCw | 8.3 | 37.5 | 737 | 2.15 | 75.8 | 217 | 16.6 | 16.6 | 25 | 6.78 | 5.51 | 54 | 2.94 | 4.72 | ND | 256 | 287 | 156 |
| | DX | 8.8 | 10.1 | ND | 5.03 | 12.2 | 4.21 | 22.9 | 23.4 | 0.762 | 6.41 | 261 | 261 | 20.2 | 2.26 | ND | 4.61 | 69.8 | 97.2 |
| FD2 | 8.6 | 4.2 | ND | 2.11 | ND | ND | 1350 | 3.5 | 0.638 | 0.217 | 43.4 | 43.4 | 6.9 | ND | 3.36 | 38.8 | 9.16 | 39.7 | |
| FD3 | 8.7 | 6.16 | 2.52 | 2.93 | 0.871 | 0.366 | 6.05 | 6.5 | 0.759 | 0.611 | 89.3 | 89.3 | 5.09 | 0.851 | 3.51 | 46.4 | 5.46 | 35.8 | |
| FD4 | 8.6 | 4.15 | 11.2 | 2.1 | 0.476 | ND | 11.3 | 4.19 | 1.38 | 0.806 | 31.8 | 31.8 | 1.67 | 0.562 | 3.19 | 35 | 7.5 | 22.8 | |
| FHB | 8.6 | 1.63 | ND | 5.71 | 1.5 | 0.553 | 134 | 0.377 | 2.23 | 5.79 | 9.67 | 9.67 | 4.77 | ND | 4.61 | 16.6 | 3.67 | 4.72 | |
| FHR | 8.5 | 10.1 | 7.8 | 7.75 | 10.1 | 2.6 | 7.23 | 4.43 | 2.44 | 1.13 | 62.1 | 62.1 | 5.67 | 1.01 | 1.94 | 46.1 | 13.7 | 27.8 | |
| GHg | 8.6 | 2.79 | 2.75 | 7.98 | 5.64 | 0.934 | 78.3 | 5.95 | 0.474 | 3.03 | 92.8 | 92.8 | 6.57 | 1.03 | 3.37 | 24.8 | 95.1 | 5.03 | |
| GHw | 8.4 | 32.6 | 6.4 | 1.93 | 24.5 | 5.89 | 26.3 | 9.22 | 4.23 | 1.72 | 12.2 | 12.2 | 2.23 | 2.69 | 0.946 | 129 | 62.4 | 43.1 | |
| LDN | 8.6 | 6.2 | 2.64 | 9.89 | 9.49 | 7.75 | 132 | 10.8 | 1.08 | 9.99 | 107 | 107 | 7.02 | 16.5 | 1.77 | 56.7 | 313 | 12.3 | |
| LDNss | 8.2 | 11.6 | ND | 2.39 | 9.2 | 16.4 | 16.3 | 12.4 | 0.988 | 3.1 | 64.3 | 64.3 | 16.2 | ND | 1.86 | 42.3 | 22.8 | 42.5 | |
| MK1 | 8.7 | 1.78 | ND | 4.48 | ND | ND | 87.2 | 1.67 | 1.99 | 2.3 | 43.6 | 43.6 | 9.44 | 3.3 | 1.81 | 19 | 4.59 | 6.51 | |
| MK2 | 8.6 | 17.1 | 3.96 | 2.8 | 2.04 | 0.47 | 15.3 | 15.8 | 1.41 | 2.16 | 19.9 | 19.9 | 2.4 | 0.997 | ND | 100 | 23.9 | 33.8 | |
| SP | 8.5 | 4.62 | ND | 2.23 | 17.3 | 1.02 | 36.1 | 8.7 | 1.44 | 2.74 | 103 | 103 | 0.826 | 1.38 | ND | 45.2 | 2.71 | 34 | |
| WS1 | 8.7 | 3.64 | ND | 1.59 | 0.538 | 1.35 | 4.66 | 2.64 | 2.57 | 0.625 | 130 | 130 | 6.98 | 0.895 | 1.39 | 30.1 | 13.5 | 12 | |
| WS2 | 8.8 | 2.09 | ND | 3.96 | 2.18 | 0.357 | 6510 | 4.53 | 0.241 | 1.13 | 42.4 | 42.4 | 18.3 | 1.23 | 3.81 | 17.3 | 30.8 | 80.7 | |
| WF | 9.0 | 216 | 10 | 33.4 | 122 | 12.2 | 67.7 | 158 | 3.32 | 55.7 | 1640 | 1640 | 60.8 | 15.5 | 73.5 | 1450 | 329 | 946 | |
| WFw | 8.9 | 224 | 15 | 37.1 | 79.7 | 12.7 | 77.9 | 167 | 3.88 | 51.4 | 1590 | 1590 | 59.4 | 18.5 | 53.4 | 1470 | 382 | 618 | |
| WS3 | 8.3 | 14.4 | 8.23 | 0.0427 | 11.2 | 7.21 | 5.81 | 3.85 | 0.816 | 6.82 | 6.82 | 6.82 | 1.62 | 1.62 | 1.88 | 40 | 16.6 | 18.8 | |

| Leachate condition | Sample ID | pH | Al (mg/L) | As | Ca (mg/L) | Co | Cr | Cu | Fe (mg/L) | K (mg/L) | Mg (mg/L) | Mn | Na (mg/L) | Ni | P | Pb | Si (mg/L) | V | Zn |
|--------------------|-------------------|--------|-----------|------|-----------|-------|-------|--------|-----------|----------|-----------|---------|-----------|--------|--------|------|-----------|------|-------|
| PH 9 | WF | 8.8 | 0.364 | 2.32 | 229 | ND | 1.32 | 9.96 | 0.0723 | 528 | 2.07 | 3.7 | 611 | ND | 67.8 | ND | 29.5 | 20.4 | ND |
| | WFw | 8.8 | 0.326 | 8.99 | 214 | ND | 1.01 | 10.1 | 0.112 | 590 | 1.92 | 4.75 | 582 | ND | 62.1 | ND | 31.2 | 53.8 | ND |
| | OC Shale | 0.0708 | 7.92 | 214 | 3.14 | ND | 1.09 | 9.62 | 0.0404 | 765 | 6.23 | 9.4 | 488 | ND | 26.6 | ND | 12.3 | 204 | 8.1 |
| | FHr | 8.9 | 0.616 | 4.71 | 3.13 | 0.946 | 1.33 | 9.05 | 2010 | 3.1 | 7.21 | 308 | ND | 182 | ND | 10.6 | 6.04 | ND | ND |
| | FHB | 8.9 | 1.54 | 16.1 | 4.35 | 1.94 | 16.8 | 16.8 | 0.096 | 2000 | 9.16 | 47.7 | 310 | ND | 165 | ND | 14.4 | 6.78 | ND |
| | TF477B | 0.249 | 2.42 | 3.64 | 181 | 2.42 | 49.2 | 0.0983 | 1930 | 0.268 | 14.4 | 1350 | 72.2 | 15 | 665 | 67.7 | 1120 | 274 | 666 |
| | WF | 10.0 | 189 | 14.2 | 4.47 | 108 | 11.4 | 46.8 | 135 | 9.78 | 50.4 | 1630 | 71.2 | 22.3 | 937 | 69 | 1110 | 388 | 522 |
| | WFw | 10.0 | 204 | 17.7 | 5.26 | 89.8 | 17.6 | 67.8 | 160 | 11.7 | 52.2 | 1630 | 71.2 | 22.3 | 937 | 69 | 1110 | 388 | 522 |
| | OC Shale | 2.91 | 20.1 | 4.53 | 3.88 | 17.6 | 5.98 | 3.77 | 2.06 | 52.3 | 70 | 2.17 | 133 | ND | 27.7 | 61.2 | 18.2 | 18.2 | 18.2 |
| | Mica SS (5) | 1.16 | 1.74 | 1.05 | 2.36 | 2.27 | 3.56 | 1.42 | 3.97 | 0.889 | 24.8 | 63.9 | 1.44 | 1600 | ND | 13.7 | 53.6 | 6.28 | 6.28 |
| PH 10 | FHr | 10.4 | 3.64 | 6.82 | 0.887 | 3.61 | 1.18 | 4.74 | 1.02 | 12.9 | 0.672 | 10.9 | 62.3 | 0.523 | 74.9 | ND | 24.9 | 18.1 | 6.35 |
| | FHB | 10.3 | 2.32 | 32 | 1.32 | 6.91 | 0.973 | 16.4 | 0.518 | 19 | 7.35 | 12.8 | 62.5 | 0.713 | 90.6 | ND | 24.5 | 15.1 | 4.9 |
| | Buffer blank (BP) | 10.0 | ND | 2.42 | ND | ND | 0.81 | ND | 0.0886 | ND | ND | ND | 74.1 | ND | ND | ND | ND | ND | ND |
| | Buffer blank (CF) | 10.0 | ND | 4.54 | ND | ND | 0.575 | ND | 0.03 | ND | ND | ND | 70.7 | ND | ND | ND | ND | ND | 0.547 |
| | BCg | 9.4 | 1.23 | 23.6 | 9.9 | 0.348 | 0.603 | 2.18 | 0.895 | 1.99 | 0.994 | 16.7 | 62.2 | 0.648 | ND | 23.2 | 36.6 | 36.6 | 2.79 |
| | BCw | 9.4 | 47.2 | 1060 | 3.96 | 114 | 27.3 | 26.8 | 29.7 | 12.2 | 6.89 | 69.7 | 287 | 5.68 | ND | 379 | 373 | 61 | 61 |
| | DX | 9.6 | 8.87 | 1.46 | 7.52 | 1.16 | 3.45 | 19 | 20.8 | 1.16 | 6.14 | 238 | 65.9 | 1.95 | 2.61 | 54.2 | 106 | 24.8 | 24.8 |
| | FD1 | 9.4 | 0.947 | 7.02 | 1.18 | 0.574 | ND | 1.45 | 0.741 | 0.546 | 0.572 | 5.35 | 57.5 | ND | 386 | ND | 40.1 | 17.4 | 2.26 |
| | FD2 | 9.3 | 1 | 6.01 | 13 | 0.847 | ND | 1.64 | 0.667 | 1.03 | 0.213 | 6.48 | 59.6 | ND | ND | ND | 45.3 | 12.5 | 3.65 |
| | FD3 | 9.4 | 0.509 | 13 | 13.9 | ND | ND | 1.31 | 0.32 | 0.853 | 0.36 | 3.67 | 58.6 | ND | 321 | ND | 44 | 62.1 | 2.98 |
| CAPS10 | FD4 | 9.3 | 0.729 | 25.4 | 9.33 | 0.285 | ND | 3.13 | 0.323 | 4.77 | 1.14 | 2.83 | 56 | ND | ND | ND | 29.7 | 17.5 | 1.52 |
| | FHB | 9.7 | 12.9 | 8.02 | 1.92 | 10.2 | 4.92 | 19 | 3.52 | 4.21 | 2.3 | 29 | 101 | 1.95 | 86 | ND | 78.7 | 25.7 | 19.6 |
| | FHr | 9.7 | 14.4 | 3.4 | 3.38 | 16.1 | 18.1 | 6.32 | 6.35 | 4.25 | 0.97 | 64 | 98.1 | 26.9 | 1.77 | 68.9 | 23 | 4150 | |
| | GHg | 9.7 | 1.49 | 7.78 | 4.36 | 1.8 | ND | 19.8 | 2.82 | 1.27 | 1.19 | 37.4 | 63.9 | ND | 18 | 3.37 | 18 | 221 | 4.94 |
| | GHw | 9.6 | 4.12 | 11.3 | 1.72 | 15 | 0.581 | 7.88 | 0.651 | 5.56 | 7.25 | 7.25 | 65.2 | 0.629 | ND | 28.5 | 33.3 | 9.99 | 9.99 |
| | LDN | 9.7 | 6.67 | 5.63 | 6.34 | 13.9 | 12.4 | 19.3 | 15.3 | 2.1 | 12.2 | 133 | 64.5 | 23.3 | ND | 58.8 | 451 | 12.2 | 12.2 |
| | LDN ss | 9.3 | 13.4 | 7.32 | 3.4 | 11.2 | 21.2 | 16.7 | 12.8 | 1.59 | 3.39 | 75.5 | 62.9 | 15.9 | 2.42 | 71.1 | 37.9 | 54.4 | 54.4 |
| | MK1 | 9.7 | 1.92 | 10.9 | 1.69 | 8.09 | ND | 1.75 | 1.98 | 3.5 | 0.81 | 29.7 | 68.7 | ND | 103 | ND | 32.6 | 12.1 | 1.28 |
| | MK2 | 9.5 | 27.5 | 28.8 | 3.88 | 101 | 2.3 | 8.92 | 27.2 | 4.32 | 3.49 | 36.2 | 92 | 5.18 | 542 | ND | 205 | 59.3 | 44.1 |
| | SP | 9.7 | 2.28 | 3.06 | 3.22 | 15.9 | 0.474 | 13.9 | 2.54 | 2.95 | 1.46 | 65.4 | 66.4 | 1.03 | ND | 25.2 | 4.43 | 25.1 | 25.1 |
| PH 11 + P | WS1 | 9.6 | 16.8 | 2.55 | 4.85 | 59.8 | 8.88 | 10.9 | 9.92 | 9.78 | 2.81 | 417 | 91.7 | 5.92 | ND | 151 | 74.9 | 39.8 | 39.8 |
| | WS2 | 9.7 | 0.644 | 2.4 | 3.51 | ND | ND | 5.03 | 0.405 | 0.293 | 0.17 | 3.67 | 66 | ND | 18.3 | 61 | 5.52 | 5.52 | |
| | WF | 9.6 | 208 | 18.4 | 40.1 | 113 | 12.2 | 57.5 | 161 | 4.68 | 50.8 | 1530 | 126 | 15 | 571 | 80.2 | 1580 | 361 | 1360 |
| | WFw | 9.5 | 247 | 24.7 | 45.6 | 79.2 | 13.2 | 74.8 | 193 | 6.31 | 53 | 1690 | 122 | 18.6 | 844 | 60.7 | 1740 | 420 | 633 |
| | WS3 | 9.9 | 1.6 | 8.61 | 10.3 | 0.516 | 0.689 | 13.3 | 0.74 | 3.69 | 0.386 | 5.51 | 198 | ND | ND | 54.1 | 183 | 1.62 | 1.62 |
| | WF | 10.4 | 1.25 | 11 | 1.87 | 0.625 | 17.5 | 6.2 | 0.813 | 12.7 | 0.28 | 10 | 1790 | ND | 731000 | ND | 71.3 | 38 | 3.45 |
| | WFw | 10.4 | 1.43 | 13.3 | 1.9 | 0.343 | 16.4 | 9.15 | 0.956 | 12.7 | 0.284 | 13.9 | 1720 | 0.549 | 688000 | ND | 68 | 97 | 2.37 |
| | OC Shale | 0.962 | 25.3 | 1.79 | 0.438 | 19 | 8.21 | 0.755 | 9.57 | 0.317 | 8.22 | 8.22 | 1910 | 0.489 | 765000 | ND | 30.2 | 666 | ND |
| | Mica SS | 4.52 | 4.99 | 1.53 | 4.16 | 28.6 | 7.17 | 4 | 9.37 | 2.09 | 52.4 | 2120 | 3.64 | 804000 | ND | 33.1 | 82.1 | 1.41 | 1.41 |
| | FHr | 10.9 | 10.3 | 14.3 | 1.71 | 3.84 | 22.8 | 9.53 | 1.71 | 18.7 | 0.7 | 14.8 | 2040 | 0.543 | 783000 | ND | 61.4 | 34.1 | 2.03 |
| 10 uM P | FHB | 10.9 | 8.14 | 43.7 | 1.29 | 16.2 | 24.5 | 32.7 | 1.41 | 24.5 | 3.1 | 13.4 | 2160 | ND | 795000 | ND | 57.9 | 20.5 | 3.03 |
| | 10 uM P Blank | 1.2 | ND | ND | 0.274 | ND | ND | 0.189 | 0.0633 | 0.229 | 2 | 0.00112 | ND | 358 | ND | 9.18 | 1.22 | 1.06 | 1.06 |
| | FD1 | 7.21 | 4.42 | ND | 2.18 | 3.72 | 0.76 | 3.37 | 4.91 | 0.468 | 0.502 | 42.4 | 1.98 | 0.476 | 278 | 2.29 | 37.7 | 7.79 | 21.2 |
| | FD4 | 7.07 | 3.58 | 10.4 | 1.56 | 2.74 | 0.626 | 2.89 | 3.21 | 1.66 | 0.656 | 27.3 | 1.89 | 0.61 | 277 | 1.55 | 43.3 | 7.6 | 15.1 |
| | MK1 | 8.9 | 1.22 | 4.49 | 3.01 | 6.2 | 0.383 | 1.66 | 1.34 | 2.11 | 1.33 | 29.5 | 5.65 | 0.474 | 291 | 1.48 | 23.2 | 9.18 | 4.49 |
| | MK2 | 7.8 | 4.12 | 12 | 0.953 | 36.3 | 0.825 | 2.36 | 3.78 | 0.801 | 0.647 | 7.03 | 2.66 | 1.69 | 375 | ND | 42.5 | 17 | 10.4 |
| | BCg | 7.16 | 6.33 | 5.79 | 8.27 | 4.42 | 7.09 | 2.07 | 5.55 | 1.21 | 2.97 | 124 | 9.84 | 3.21 | 105 | 2.43 | 45.8 | 17 | 15.1 |
| | FHB | 8.75 | 3.92 | 1.56 | 3.93 | 3.61 | 1.47 | 8.56 | 1 | 2.27 | 4.06 | 13.7 | 2.48 | 0.621 | 166 | ND | 25.5 | 8.58 | 6.71 |
| | FHr | 8.45 | 5.95 | 1.67 | 6.59 | 10.7 | 1.81 | 3.27 | 2.39 | 2.51 | 0.846 | 47 | 3.52 | 0.562 | 349 | ND | 35.3 | 11.4 | 11.5 |
| | WF | 9.08 | 188 | 25.5 | 31.2 | 103 | 11.1 | 51.1 | 102 | 2.74 | 47.1 | 1320 | 24 | 12.9 | 591 | 62.3 | 1450 | 329 | 750 |
| WFw | 8.64 | 195 | 29.6 | 30.7 | 60.3 | 10.2 | 58.1 | 107 | 3.91 | 43.4 | 1250 | 19.6 | 13.4 | 772 | 42.4 | 1460 | 338 | 493 | |

| Leachate condition | Sample ID | pH | Al (mg/L) | As | Ca (mg/L) | Co | Cr | Cu | Fe (mg/L) | K (mg/L) | Mg (mg/L) | Mn | Na (mg/L) | Ni | P | Pb | Si (mg/L) | V | Zn | |
|--------------------|-----------|--------|-----------|-------|-----------|--------|-------|-------|-----------|----------|-----------|---------|-----------|-------|--------|--------|-----------|-------|------|------|
| 1 mM P | Blank | | 2.04 | ND | 0.0127 | ND | 0.689 | ND | 1.28 | 60.2 | 0.368 | 4.82 | 0.025 | ND | 33200 | ND | 17.9 | 2.32 | ND | |
| | FD1 | 7.5 | 1.47 | 5.86 | 9.98 | 0.927 | 0.507 | 0.797 | 1.07 | 0.91 | 1.23 | 16.6 | 11 | ND | 22800 | ND | 28.9 | 8.95 | 5.49 | |
| | FD4 | 7.3 | 2.09 | 24.2 | 9.56 | 2.01 | 0.638 | 1.49 | 1.8 | 3.91 | 2.65 | 26.9 | 9.32 | ND | 22700 | ND | 36 | 10.4 | 6.79 | |
| | MK1 | 8.3 | 0.882 | 6.95 | 4.15 | 6.81 | 0.536 | 0.57 | 0.924 | 30.5 | 2.42 | 22.9 | 8.12 | ND | 27000 | ND | 17.8 | 9.71 | 2.76 | |
| | MK2 | 7.5 | 2.77 | 14.9 | 2.81 | 39.7 | 1.24 | 1.99 | 2.55 | 24.9 | 1.07 | 6.96 | 8.7 | 1.9 | 24200 | ND | 34.2 | 16.6 | 4.41 | |
| | BCg | 7.4 | 2.76 | 24.6 | 11 | 1.04 | 3.31 | 1.04 | 1.93 | 1.96 | 2.67 | 7.6 | 18.8 | 1.19 | 22200 | ND | 30.4 | 22.7 | 6.15 | |
| | FHb | 8.5 | 2.44 | 3.61 | 3.31 | 5.34 | 1.86 | 9.51 | 0.723 | 39 | 4.81 | 17.3 | 3.74 | 1.11 | 26400 | ND | 16.5 | 10 | 280 | |
| | FHr | 8.1 | 3.72 | 3.19 | 6.75 | 11.4 | 1.6 | 1.56 | 1.5 | 38.7 | 0.982 | 35.7 | 5.12 | 0.473 | 27600 | ND | 22.3 | 10.9 | 7.49 | |
| | WF | 8.9 | 1.79 | 19.4 | 31.4 | 76.4 | 10.7 | 45.6 | 107 | 3.8 | 43.5 | 1200 | 41.1 | 11.6 | 28600 | 52.9 | 1070 | 324 | 702 | |
| | WFw | 8.3 | 187 | 27.4 | 30.7 | 37.2 | 9.77 | 52.7 | 113 | 5.21 | 40.9 | 1130 | 36.8 | 12.3 | 28200 | 38.7 | 1060 | 333 | 460 | |
| | 100 mM P | Blank | | 0.022 | 3.95 | 0.0384 | ND | 69.2 | 1.62 | 0.0271 | 500 | 0.00498 | 2.8 | 1.67 | 1.37 | 223000 | ND | 0.377 | ND | 0.32 |
| | FD1 | 7.9 | 0.0304 | 13.6 | 7.35 | ND | ND | 52.9 | 1.12 | 0.023 | 527 | 7.62 | 4.84 | 50 | ND | 374000 | ND | 33.3 | 13.8 | 1.25 |
| | FD4 | 8.1 | 0.0371 | 34.7 | 7.85 | 0.775 | 54.2 | 61.7 | 1.93 | 0.0321 | 470 | 11.7 | 7.62 | 46.3 | 0.476 | 372000 | ND | 27.5 | 9.68 | 1.68 |
| | MK1 | 8.6 | 0.0616 | 11.7 | 4.12 | 11 | 11 | 61.7 | 0.969 | 0.0766 | 456 | 9.68 | 11.4 | 11.4 | 1.54 | 374000 | ND | 14 | 9.39 | 9.87 |
| MK2 | 8.6 | 0.0302 | 18.6 | 5.5 | 18.5 | 18.5 | 60.1 | 0.388 | 0.0205 | 471 | 6.89 | 4.56 | 12.7 | 1.48 | 377000 | ND | 20.6 | 15.2 | 1.42 | |
| BCg | 8.1 | 0.0666 | 33.3 | 8.78 | ND | ND | 51.5 | 1.52 | 0.0659 | 520 | 19 | 31.9 | 51.6 | 1.13 | 373000 | ND | 19.8 | 18.9 | 1.26 | |
| FHb | 8.8 | 0.0942 | 8.13 | 3.23 | 1.31 | 60.9 | 60.9 | 4.69 | 0.0681 | 496 | 12.4 | 11.1 | 5.75 | 0.518 | 376000 | ND | 8.65 | 8.77 | 2.56 | |
| FHr | 8.7 | 0.0607 | 8.14 | 3.8 | 1.48 | 60.4 | 60.4 | 0.964 | 0.0256 | 486 | 1.94 | 6.41 | 6.71 | ND | 383000 | ND | 9.93 | 8.73 | 2.6 | |
| WF | 7.9 | 0.107 | 12.6 | 3.94 | ND | ND | 59.8 | 1.43 | 0.0736 | 523 | 1.26 | 2.47 | 51.2 | ND | 314000 | ND | 31.2 | 27.5 | 2.98 | |
| WFw | 7.9 | 0.234 | 21.8 | 4.67 | ND | ND | 53.4 | 2.26 | 0.17 | 525 | 1.22 | 3.17 | 53.2 | ND | 308000 | ND | 35.7 | 43.4 | 2.34 | |
| Water 4h | BCg | 7.3 | 11.4 | 7.6 | 6.76 | 3.46 | 9.85 | 2.13 | 7.38 | 1.84 | 3.21 | 126 | 6.32 | 2.74 | 53.2 | 3.78 | 72.3 | 17.9 | 17.7 | |
| | FD4 | 6.5 | 12.1 | 10.5 | 3.39 | 5.33 | 0.921 | 5.46 | 9.19 | 4.53 | 1.45 | 79.8 | 1.26 | 0.796 | 224 | 3 | 82.3 | 10.9 | 28.9 | |
| | FHb | 8.8 | 7.81 | ND | 3.6 | 7.36 | 2.19 | 12.4 | 1.69 | 2.81 | 3.57 | 22.5 | 2.31 | 0.835 | 20.6 | 0.9 | 40.4 | 9.99 | 6.34 | |
| | FHr | 8.6 | 14.3 | ND | 5.11 | 14.9 | 3.14 | 4.69 | 4.79 | 2.54 | 0.957 | 69.9 | 2.87 | 0.907 | 39 | 0.932 | 59.8 | 15.3 | 13.1 | |
| | MK2 | 6.5 | 5.98 | 6.77 | 1.41 | 29.3 | 0.655 | 3.07 | 4.77 | 0.847 | 7.88 | 1.21 | 7.88 | 1.21 | 1.38 | 164 | ND | 39.5 | 12 | 10.2 |
| | BCg | 12.1 | 2.16 | 8.56 | 5.13 | 9.31 | 2.85 | 9.31 | 1.72 | 3.75 | 1.72 | 168 | 6.74 | 3.95 | 83.4 | 6.65 | 54 | 17.7 | 29.4 | |
| Water 10h | FD4 | 11.9 | 10.1 | 4.8 | 6.7 | 0.74 | 0.74 | 6.58 | 7.2 | 3.49 | 1.45 | 65.7 | 1.54 | 0.778 | 256 | 4.23 | 57.8 | 10.1 | 27.3 | |
| | FHb | 5.49 | 1.62 | 4.38 | 10.4 | 2.76 | 19 | 1.48 | 2.78 | 3.95 | 30.3 | 30.3 | 2.61 | 1.94 | 42.3 | 8.13 | 30.5 | 8.44 | 21.4 | |
| | FHr | 7.85 | ND | 5.83 | 18.6 | 1.81 | 3.23 | 2.29 | 2.49 | 0.975 | 63.5 | 2.81 | 0.678 | 38.9 | 1.96 | 38.2 | 11 | 11.8 | | |
| | MK2 | 8.94 | 9.37 | 3.75 | 86.3 | 0.857 | 6.15 | 6.81 | 1.3 | 1.52 | 15.4 | 15.4 | 1.66 | 4.32 | 219 | ND | 54.3 | 14.9 | 20.2 | |
| | BCg | 20.7 | 5.64 | 14.4 | 11.1 | 20.3 | 6.25 | 20.9 | 2.27 | 7.17 | 7.17 | 353 | 7.56 | 9.8 | 185 | 12.3 | 85 | 38.5 | 75.9 | |
| | FD4 | 11.4 | 9.26 | 5.86 | 9.05 | 0.824 | 8.29 | 0.824 | 8.29 | 7.69 | 3.27 | 1.74 | 71.3 | 1.94 | 1.09 | 278 | 5.15 | 59 | 10.9 | |
| Water 50h | FHb | 8.2 | 3.95 | 1.97 | 5.29 | 12 | 1.2 | 20.1 | 1.27 | 2.72 | 4.65 | 32.7 | 2.47 | 0.726 | 31.1 | ND | 25.1 | 8.26 | 16.6 | |
| | FHr | 8.4 | 9.93 | ND | 8.09 | 36.2 | 2.42 | 4.27 | 2.6 | 3.13 | 1.49 | 116 | 3.27 | 1.03 | 57.1 | 2.75 | 47.1 | 14.8 | 68 | |
| | MK2 | 7.2 | 12.4 | 13.5 | 6.52 | 145 | 1.26 | 1.26 | 10.5 | 10.6 | 1.64 | 2.49 | 23.3 | 2.22 | 7.22 | 268 | 1.22 | 77.1 | 20.7 | |
| | BCg | 31.2 | 6.48 | 21.1 | 17.5 | 28 | 28 | 28 | 9.14 | 31 | 2.87 | 10.6 | 541 | 8.46 | 14.7 | 275 | 19.2 | 101 | 54.5 | |
| | FD4 | 16.3 | 7.74 | 9.04 | 14.1 | 0.936 | 11.2 | 0.936 | 11.2 | 9.84 | 4.28 | 2.59 | 98.8 | 2.57 | 1.47 | 319 | 7.76 | 68 | 13.5 | |
| | FHb | 3.48 | 1.77 | 5.82 | 10.5 | 1.11 | 17.3 | 1.13 | 2.68 | 5.02 | 28.5 | 2.49 | 0.68 | 33.7 | 1.14 | 23.2 | 7.79 | 7.71 | 20.1 | |
| Water 72h | FHr | 11.2 | ND | 9.21 | 42.8 | 2.88 | 4.75 | 3.16 | 3.34 | 1.69 | 138 | 3.4 | 1.21 | 43.1 | 2.93 | 51.1 | 16.6 | 20.1 | | |
| | MK2 | 16.6 | 14.2 | 8.2 | 187 | 1.86 | 1.86 | 13.2 | 23.8 | 1.98 | 3.55 | 33.1 | 2.82 | 9.39 | 244 | 1.58 | 165 | 27.8 | 58.4 | |
| | BCg | 7.25 | 2.29 | 13 | 4.94 | 6.16 | 3.48 | 7.56 | 1.22 | 4.09 | 192 | 9.29 | 4.13 | 123 | 6.04 | 39.8 | 11.8 | 33.7 | | |
| | FD4 | 17 | 11.4 | 13.9 | 20.2 | 0.855 | 11.6 | 8.02 | 4.65 | 3.74 | 112 | 3.33 | 1.87 | 427 | 10.8 | 60.3 | 15.6 | 55.7 | | |
| | FHb | 2.75 | 1.74 | 10.2 | 16.3 | 3.49 | 0.699 | 2.8 | 4.99 | 3.12 | ND | 53.4 | 3.12 | ND | 31.6 | 1.86 | 21.1 | 8.05 | 4.08 | |
| | FHr | 2.98 | ND | 9.88 | 16.3 | 1.14 | 3.96 | 0.765 | 2.8 | 4.73 | 52.4 | 3.12 | ND | 38 | 1.3 | 21.7 | 8.63 | 4.8 | | |
| Water 194h | MK2 | 187 | 52.8 | 18.5 | 461 | 13.5 | 59.3 | 132 | 6.12 | 20.8 | 225 | 5.68 | 28.6 | 7.41 | 1110 | 226 | 226 | 350 | | |

| Leachate condition | Sample ID | pH | Al (mg/L) | As | Ca (mg/L) | Co | Cr | Cu | Fe (mg/L) | K (mg/L) | Mg (mg/L) | Mn | Na (mg/L) | Ni | P | Pb | Si (mg/L) | V | Zn |
|--------------------|-----------|------|-----------|------|-----------|-------|-------|-------|-----------|----------|-----------|------|-----------|-------|------|-------|-----------|------|------|
| 0.1 mM P 4h | BCg | 7.2 | 10.9 | 3.82 | 7.42 | 4.45 | 8.71 | 2.75 | 8.22 | 1.67 | 3.32 | 144 | 6.66 | 3.42 | 488 | 4.72 | 53.2 | 17.6 | 25.4 |
| | FD4 | 6.5 | 9.18 | 12.9 | 3.52 | 3.78 | 0.692 | 4.75 | 6.29 | 3.41 | 1.24 | 56.1 | 1.83 | 0.543 | 2060 | 2.77 | 54.7 | 9.05 | 21.7 |
| | FHb | 8.8 | 6.79 | 2.08 | 3.66 | 9.66 | 1.93 | 16.1 | 1.55 | 3 | 3.78 | 25.9 | 2.36 | 1.01 | 2190 | 0.929 | 33 | 9.33 | 9.17 |
| | FHr | 8.6 | 8.11 | ND | 5.93 | 16.2 | 1.8 | 3.07 | 2.45 | 2.64 | 0.993 | 60.2 | 2.78 | 0.529 | 2650 | ND | 36.2 | 10.2 | 9.36 |
| | MK2 | 6.5 | 4.76 | 7.38 | 1.33 | 26.2 | 0.548 | 2.84 | 3.69 | 1.22 | 0.631 | 6.58 | 2.05 | 1.23 | 2220 | ND | 33 | 10.5 | 18.4 |
| | BCg | 14.1 | 4.47 | 9.49 | 6.31 | 11.8 | 11.8 | 3.55 | 11.9 | 1.88 | 4.44 | 203 | 6.98 | 5.06 | 482 | 7.14 | 61.7 | 23.6 | 35.5 |
| 0.1 mM P 10h | FD4 | 9.11 | 15.4 | 15.4 | 4.15 | 4.76 | 0.644 | 5.57 | 5.74 | 2.96 | 1.27 | 52.5 | 1.86 | 0.703 | 1910 | 3.57 | 47.9 | 9.57 | 23.6 |
| | FHb | 4.29 | 3.72 | 3.93 | 10.1 | 1.27 | 16.5 | 1.17 | 2.83 | 3.93 | 26.4 | 2.28 | 0.625 | 2070 | ND | 23.8 | 7.94 | 4.94 | |
| | FHr | 9.24 | ND | 7.31 | 26.3 | 2.18 | 3.61 | 2.54 | 3.13 | 1.31 | 1.31 | 90.4 | 3.1 | 0.814 | 2610 | 1.09 | 42.5 | 12 | 16.5 |
| | MK2 | 8.79 | 11.2 | 3.73 | 85.2 | 0.959 | 6.26 | 6.76 | 1.7 | 1.5 | 1.5 | 15.7 | 2.49 | 4.17 | 2190 | 1.09 | 54.4 | 15.1 | 21.4 |
| | BCg | 7 | 16.9 | 5.6 | 11.7 | 8.19 | 15 | 4.86 | 15.2 | 2.05 | 5.52 | 260 | 7.33 | 6.98 | 479 | 11.2 | 72.1 | 29.3 | 52.7 |
| | FD4 | 6.8 | 6.98 | 8.78 | 3.34 | 4.24 | 0.619 | 4.96 | 4.56 | 2.12 | 1.02 | 42.7 | 1.1 | ND | 1670 | 3.17 | 30.6 | 6.85 | 28.6 |
| 0.1 mM P 24h | FHb | 8.6 | 4.46 | 4.27 | 4.6 | 12.3 | 1.35 | 20.5 | 1.36 | 2.98 | 4.44 | 33.4 | 2.49 | 0.913 | 1930 | ND | 25.8 | 9.38 | 6.65 |
| | FHr | 7.7 | 9.2 | 2.12 | 8.16 | 30.7 | 2.29 | 3.96 | 2.63 | 3.24 | 1.44 | 104 | 3.23 | 0.916 | 2520 | 1.84 | 43.9 | 13.9 | 16.3 |
| | MK2 | 6.5 | 10.2 | 13.5 | 4.84 | 109 | 1.05 | 8.06 | 8.25 | 1.78 | 1.94 | 18.8 | 2.67 | 5.37 | 2120 | 2.37 | 65.6 | 17.8 | 30.4 |
| | BCg | 25.6 | 9.56 | 17.7 | 13.6 | 13.6 | 23.9 | 8.03 | 25.1 | 2.62 | 8.63 | 431 | 8.16 | 12 | 612 | 15.9 | 96 | 46.9 | 88.8 |
| | FD4 | 13.3 | 17.2 | 7.68 | 9.51 | 0.967 | 10.5 | 9.61 | 3.79 | 2.35 | 82 | 2.53 | 1.31 | 1.31 | 1240 | 6.92 | 69 | 14.5 | 46.2 |
| | FHb | 3.3 | 5.71 | 5.33 | 11.4 | 1.1 | 18.1 | 1.05 | 2.9 | 4.95 | 26.3 | 2.61 | 0.934 | 1570 | ND | 22.4 | 10.1 | 6.12 | |
| 0.1 mM P 72h | FHr | 10.8 | 3.7 | 10 | 41.2 | 2.91 | 2.91 | 5.17 | 3.24 | 3.6 | 1.76 | 138 | 3.52 | 1.18 | 2290 | 3.42 | 50.1 | 18.1 | 26.2 |
| | MK2 | 23.3 | 20.3 | 20.3 | 8.68 | 194 | 2.67 | 14.1 | 31.2 | 2.58 | 4.22 | 40.1 | 3.73 | 10.2 | 1740 | 2.3 | 240 | 38.5 | 77.6 |
| | BCg | 14.4 | 6.49 | 16.6 | 9.88 | 12.1 | 6.14 | 14.8 | 1.7 | 5.97 | 298 | 9.54 | 7.94 | 42.3 | 12.5 | 53 | 23.6 | 48.7 | |
| | FD4 | 52.5 | 34.8 | 15.3 | 19.9 | 3.11 | 14.8 | 39.6 | 9.86 | 5.33 | 175 | 3.62 | 3.67 | 1320 | 14 | 327 | 34.2 | 206 | |
| | FHb | 2.2 | 6.13 | 7.94 | 4.98 | 0.694 | 5.17 | 0.494 | 3.46 | 7.02 | 11.4 | 3.52 | ND | 932 | ND | 21.9 | 9.5 | 6.5 | |
| | FHr | 2.87 | 6.95 | 10.2 | 20.5 | 1.24 | 2.21 | 0.732 | 2.87 | 1.66 | 59.7 | 59.7 | 3.37 | ND | 1810 | ND | 23.1 | 14.1 | 31.5 |
| 0.1 mM P 194h | MK2 | 198 | 58.5 | 19.2 | 480 | 13.8 | 61.6 | 138 | 6.67 | 21.7 | 234 | 5.85 | 29.5 | 1900 | 8.26 | 1190 | 240 | 320 | |

Appendix E: Lithologic Groups

| Lithologic group | Unit | Lithologic description |
|---------------------|---------------------|--|
| Alluvium | Qg1 | Sand and gravel that postdates Missoula Floods |
| | Qls | Landslide deposits |
| | Qa | Fine grained alluvium |
| | Qal | Alluvium |
| | Qau | Alluvium, undifferentiated |
| | Qt | Alluvium on terraces |
| | Qns | Nonmarine sedimentary deposits |
| | Qoa | Older alluvium |
| | Qfd | Fan-delta Alluvium |
| | Qal | Meander-belt Alluvium |
| | Qc | Colluvium |
| | Qls | Landslide debris |
| | Qda | Debris avalanche deposits |
| | Qg2 | Sand and gravel that predates Missoula Floods |
| | Qbf | Fine-grained alluvium |
| | QTal | Older alluvium |
| | Qoam | Older alluvium |
| | Qf | Braided-fan alluvium |
| | Qoal | Older alluvium |
| | Qa | Recent alluvium |
| | Qf | Alluvial fan |
| | Qal | Alluvium and beach deposits |
| | Qls | Landslide |
| | Qpal | Older alluvium |
| | Qyal | Recent alluvium |
| | Qral | Recent alluvium |
| | Qms | Youngest till deposits |
| Qys | Young sand and silt | |
| Basalt and andesite | Tb | Basalt and basaltic andesite |
| | Tb | Basalt flows and volcaniclastic sedimentary rocks |
| | Ta | Andesite, basalt, gabbro, and norite; plugs and dikes |
| | Tlb | Little Butte Volcanic Series; basaltic andesite and olivine basalt flows |
| | Tb | Basalt flows |
| | Tbf | Basalt flows |
| | Ttb | Basaltic andesite flows |
| | Ti | Intrusive basalt |
| | Ti | Intrusive rocks |
| | Tsr | Siletz River volcanic series |
| | Tsr | Submarine basalt flows |
| | Jrs | Serpentinized ultramafic rock |
| | Taf | Andesite flows |
| | Tla | ` |
| | Tbm | Basalt of Mohawk |
| | Tib | Basaltic intrusive rocks |
| | Tlbb | Little Butte Volcanics, basalt and basaltic andesite |
| | Tpb | Pyroxene Basalt |
| | Tl | Tholeiitic lavas |
| | Tub | Umpqua Formation, basalt member |
| | Tiba | Basaltic andesite intrusive rocks |
| | Tgr | Granitic intrusions |
| | KJi | Intrusive rocks |
| | Tub | Basalt and basaltic andesite flows and flow breccias |
| | Ts | Calc-alkaline lavas |
| | Ti2 | Intrusive rocks, undivided |
| | Jri | Mafic intrusive unit |
| | Tsr | Siletz River Volcanics |
| | Tbah | Basalt and andesite of Coburg Hills |
| | Tf | Basalt flows |

| Lithologic group | Unit | Lithologic description |
|---------------------------|-----------|---|
| Conglomerate | KJr | Riddle Formation |
| | KJrc | Riddle Formation, conglomerate |
| | Tbr | Bushnell Rock Formation, conglomerate |
| Fisher | Tf | Fisher Formation |
| Fluvial | Qf | Fluvial deposits |
| | Qalc | Floodplain deposits of the Willamette River and major tributaries |
| | Qft | Fluvial terrace deposits |
| | Qws | Willamette Silt |
| Glacial and glaciofluvial | Qgf1 | Glacial and glaciofluvial deposits |
| LBV | Tlb | Little Butte Volcanics, undivided |
| Marine | Tte | Tyee Formation; Elkton Siltstone member |
| | Te | Eugene Formation |
| | Tms1 | Marine sedimentary rocks |
| | TI | Lorane Shale |
| | Tev | Umpqua Group, Camas Valley Formation |
| Missoula Flood deposits | Qff2 | Main body of fine-grained Missoula Flood deposits |
| Mudstone | Tmm | Tenmile Formation, Basin plain mudstone |
| | Tus | Umpqua Formation, siltstone member |
| | KJdm | Dothan Formation, mudstone matrix melange |
| | Twrn | White Tail Ridge Formation, mudstone |
| Sandstone | Ts | Spencer Formation |
| | Ts | Spencer Foramtion |
| | Tlbs | Tyee Formation, Baughman member |
| | Twc | White Tail Ridge Formation, Coquille River member |
| | Twr | White Tail Ridge Formation, Remote member |
| | Dp | Deflation plain |
| | Tbsc | Bushnell Rock Formation, Slater Creek member |
| | Tem | Eugene Formation, micaceous, quartz sandstone |
| | Terrace | Qtg |
| QTg | | Weathered terrace gravel |
| Qal | | Terrace gravel |
| Qt | | High terrace gravels |
| Qoft | | Older fluvial terrace deposits |
| Qtl | | Quaternary lower terrace |
| Qt | | Terrace and fan deposits |
| QTg | | Terrace gravel |
| Tuffs and volcaniclastics | Tlt | Little Butte Volcanic Series; tuff |
| | Tu | Tuffaceous sedimentary rocks, basalt flows, and tuffs, undivided |
| | Tv | Volcanic Group, undifferentiated volcanic rocks |
| | Tlt | Little Butte Volcanics, tuffaceous volcaniclastic rocks |
| | Tt | Tuff, lapilli tuff, agglomerate, and volcanic sandstone |
| | Te | Eugene Formation, volcanic sandstone and tuff |
| | Tp1 | Pyroclastic deposits and associated sediments |
| | Tvs | Volcanolithic sandstone, conglomerate, and laharic breccia |
| | Tov | Oligocene volcanic rocks |
| | Ttw | Tuff of South Willamette Street |
| | Ttf | Tuff of Fox Hollow |
| | Turbidite | Tt |
| Tty | | Tyee Formation |
| Tmss | | Tenmile Formation, turbidite sandstone |
| Tmsm | | Tenmile Formation, turbidite sandstone and mudstone |
| KJdd | | Dothan Formation, phyllitic siltstone and metagraywacke |
| KJda | | Dothan Formation, turbidite sandstone broken formation |
| Trs | | Roseburg member, turbidite sandstone and mudstone |
| Tmms | | Tenmile Formation, mudstone and turbidite sandstone |
| Tm | | Tenmile Formation, undivided |
| Tet3 | | Tyee Formation, Baughman Lookout member |
| Ttts | | Tyee Mountain member |