

Geochemical Explanations for Strong Natural Attenuation of Molybdenum, Selenium, and Lithium in a Groundwater Plume

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KEYWORDS: Natural Attenuation, Coal Combustion Residuals (CCR), Molybdenum, Selenium, Lithium

ABSTRACT

Molybdenum (Mo), selenium (Se), and lithium (Li) are Appendix IV constituents that are required to be monitored under the coal combustion residuals (CCR) rule. Mo and Li are highly soluble in water, usually present in the form of an ion, relatively weak in terms of sorption onto geological media, and require more extreme geochemical conditions to form a precipitate. Because of these chemical properties, natural attenuation is often considered ineffective for Mo and Li. In contrast, natural attenuation may considerably limit Se transport when groundwater redox conditions are mildly reducing due to the formation of a precipitate of elemental Se. Here, a natural attenuation case study of a plume containing Mo, Li, and Se is presented. The contaminant plume, sustained by a CCR-containing material pile for approximately 20 years, is situated in a shallow alluvial aquifer consisting of mainly fine-grained sediments. Based on results of the natural and extent investigation, Mo, Li, and Se migration was limited to a relatively short distance (less than 35 meters [approximately 120 feet]). This indicates the occurrence of significant attenuation. In contrast, very limited attenuation was observed for boron. Based on geochemical evaluation and modeling assessment, it is concluded that the iron-reducing conditions, powellite (CaMoO_4) formation, adsorption to clayey soil, and matrix diffusion are the likely primary attenuation mechanisms responsible for observed natural attenuation of Mo, Li, and Se at the site.

INTRODUCTION

Several constituents present in coal ash can serve as indicators of a release from a coal ash management area to groundwater and they have been used by U.S. Environmental Protection Agency (USEPA) to design the groundwater monitoring program under the final CCR Rule.¹ Groundwater monitoring at CCR sites often show detections of various

Appendix III and Appendix IV constituents. Among these constituents, selenium, molybdenum, and lithium are constituents that have been found at levels above their groundwater protection standards at numerous CCR sites. Since the physicochemical properties of these three constituents are distinctly different, their tendencies to be naturally attenuated in the environment can vary significantly.

Interestingly, at a coal-fired power plant (the Site), concurrent attenuation of selenium, molybdenum, and lithium in an impacted shallow aquifer have been observed. Results of the nature and extent investigation show that selenium, molybdenum, and lithium are all attenuated to their groundwater protection standards (GWPSs) within approximately 35 meters of the CCR-containing material pile boundary at the Site. To better understand how site-specific conditions contribute to observed natural attenuation, a geochemical evaluation was conducted to assess the potential attenuation mechanisms, including redox-associated mineral precipitation, precipitation due to mineral oversaturation, adsorption, and ion exchange enhanced matrix diffusion.

In this proceedings paper, we first describe general geochemical properties of selenium, molybdenum, lithium, and boron. Then the Site hydrogeology, surroundings of the CCR-containing material pile, and the extent of impacted groundwater are discussed. These provide a framework for the natural attenuation evaluation. For selenium and molybdenum, groundwater chemical data are then used to determine geochemical precipitation reactions that are likely responsible for observed attenuation of selenium and molybdenum. Since lithium is not subject to any precipitation reaction under site groundwater conditions, the potential of matrix diffusion coupled with ion exchange is assessed for observed lithium attenuation. A conclusion section is then provided to summarize the key natural attenuation mechanisms evaluated.

GENERAL GEOCHEMICAL PROPERTIES OF SELENIUM, MOLYBDENUM, LITHIUM, AND BORON

In this section, general geochemical properties of selenium, molybdenum, lithium, and boron are provided to provide a framework to assess relevant natural attenuation mechanisms for these constituents.

Selenium: Dissolved selenium is generally in the form of oxyanions (e.g., selenate – SeO_4^{2-} and selenite – SeO_3^{2-}). The aqueous speciation and potential formation of selenium minerals under a spectrum of the electro-potential (Eh) and pH conditions are shown in Figure 1. Under neutral pH (pH between 6 and 8) and very oxic groundwater conditions, selenium is expected to be present in the form selenate (Figure 1). Transport of selenate under oxic conditions are likely subject to adsorption to aquifer sediments, including metal oxide minerals and clay minerals. The magnitude of adsorption generally decreases with pH.² Under iron/sulfate-reducing conditions, selenium can form precipitate as elemental selenium or ferrous selenide (FeSe).³ Selenium has also been reported to adsorb to sulfide minerals or form co-precipitation in sulfide minerals.⁴ In calcium-rich groundwater (e.g., > 400 milli-grams per liter [mg/L]),

calcium selenite precipitate may form when selenite concentrations are higher than 1.5 mg/L.³ The adsorption behavior of selenium is also linked to its oxidation state. At the oxidation state of +6 (e.g., selenate), the adsorption constant (K_d) values may range from 0.01 Liter/Kilogram (L/Kg) to 100 L/Kg with a mean value of approximately 0.5 L/Kg.⁵ At the oxidation state of +4, selenite, based on limited data, the mean K_d values are higher (= 20 L/Kg). Sheppard et al. (2009) evaluated a large set of selenium soil desorption data and found that the K_d values for Canadian till and peat soils ranged from 10 to 140 L/Kg.⁶ A more detailed thermodynamic modeling study shows that selenite is generally more strongly adsorbed to aquifer solids (Goldberg, 2014).²

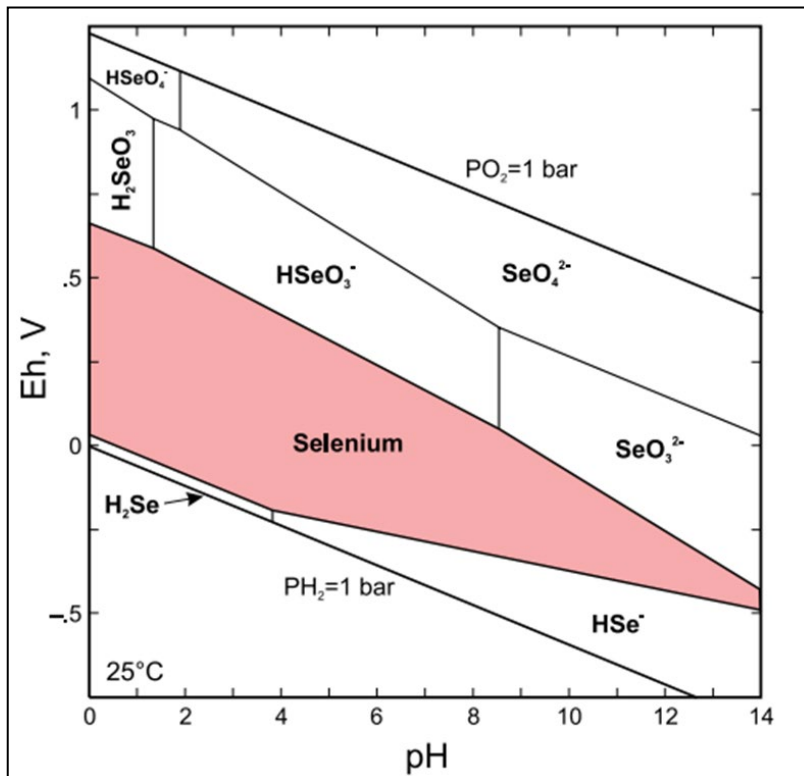


Figure 1: Selenium Eh-pH diagram for selenium-oxygen-hydrogen system, adapted from USEPA (2007). Solid stability field for elemental selenium is shaded pink.

Molybdenum: Dissolved molybdenum in typical oxic groundwater conditions is generally in the form of an oxyanion (molybdate – MoO_4^{2-}). The aqueous speciation and potential formation of Mo-related minerals under a spectrum of the electro-potential (Eh) and pH conditions are shown in Figure 2. Under strong sulfate reducing conditions, molybdenum disulfide (or molybdenite, MoS_2) can form and precipitate. Under oxic and neutral pH conditions, the dominant form of molybdenum is molybdate (MoO_4^{2-}). The affinity for molybdenum to adsorb to the geologic matrix can be affected by factors such as pH, redox conditions, mineral contents of aquifer solids, organic matter abundance, and the presence of organic ligands in the groundwater system. In calcium-rich groundwater and/or high Mo concentration in groundwater (e.g., >1 mg/L), the mineral,

powellite (CaMoO_4), may form and precipitate in the aquifer matrix, as shown in Figure 3. The presence of nickel, lead, and ferric ions may also produce Mo containing minerals, such as nickel molybdate, wulfenite, and ferrimolybdite. The dissolution constants for these molybdenum containing minerals are summarized in Table 1. The adsorption of molybdenum to aquifer solids has been studied on a variety of minerals, sediments, soils, and crushed rock materials. The extent of adsorption is greatly influenced by pH; generally, the degree of adsorption decreases with an increase in pH.⁶

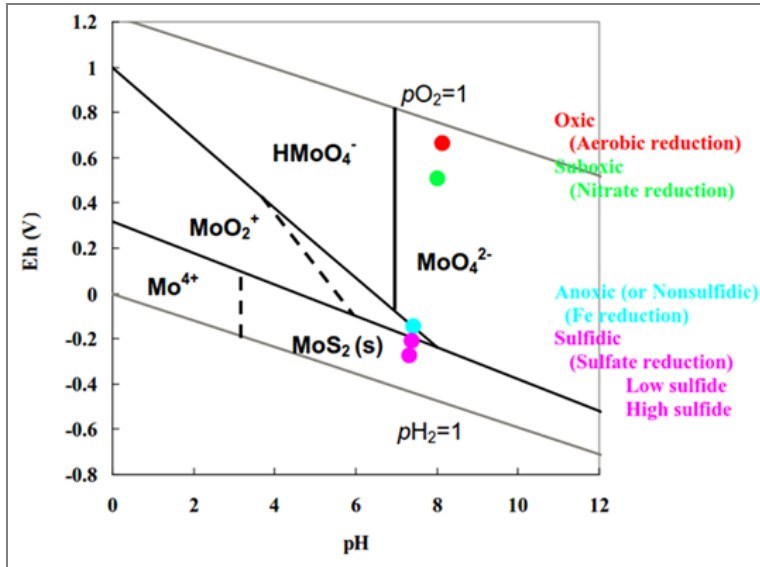


Figure 2: Molybdenum Eh-pH Diagram for a molybdenum-sulfur-oxygen-hydrogen system. The pH-Eh calculated for different redox conditions assuming activity of dissolved molybdenum (Mo)= 10^{-7} M, and Sulfide= 10^{-3} M, adapted from Wang (2007).⁷

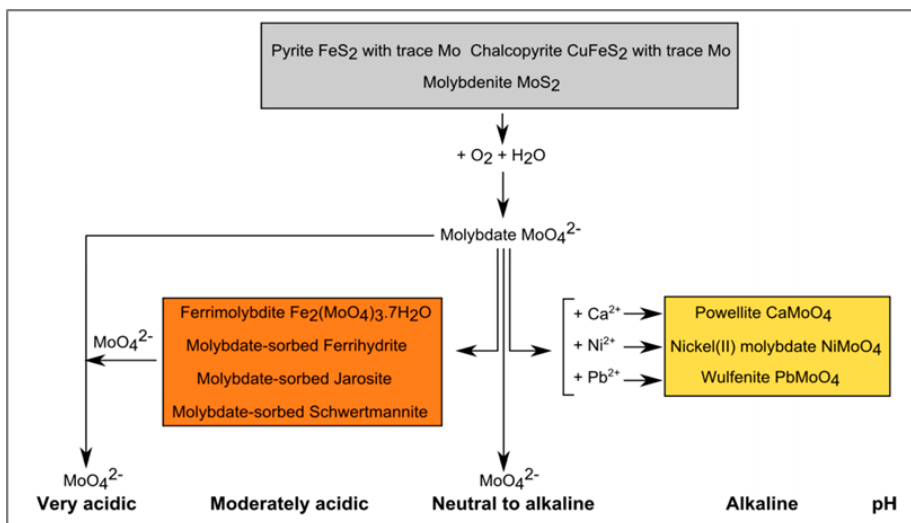


Figure 3: Occurrence of common molybdenum-containing minerals, adapted from Frascoli, F. and Hudson-Edwards, K. (2018).⁸

Table 1: Molybdenum Containing Minerals and Their Dissolution Constants

Mineral Name	Chemical Formula	Molecular Weight (g/mol)	Solubility Product Constant (Log Ksp) or Solubility
Powellite	CaMoO ₄	200.02	Ksp from -7.19 to -8.5
Wulfenite	PbMoO ₄	367.14	Ksp from -9.72 to -15.89
Molybdite	MoO ₃	143.95	Solubility (18°C) = ~ 1 g/L
Ferrimolybdite	Fe ₂ (MoO ₄) ₃	573.49	Ksp = -26.1
Molybdenite	MoS ₂	160.07	Generally insoluble in water
Note: Data obtained from Vlek and Lindsay (1977). ⁹			

Metal oxides (iron, manganese, and aluminum oxides) in aquifer solids are shown to play a major role in Mo adsorption; the K_d values reported by Goldberg et al. (1996) for oxide minerals range from 10 to 10³ Liter/Kilogram (L/Kg).¹⁰ Adsorption on a weight basis of iron oxide minerals increased in the order: hematite < goethite < amorphous Fe oxide < poorly crystalline goethite; adsorption on a weight basis for clay minerals increases in the order: well crystallized kaolinite < poorly crystallized kaolinite < illite < montmorillonite.

Lithium: It is a common element of nearly all igneous rocks but does not occur in the metallic state in nature. Under most pH and redox conditions in groundwater environments, lithium is present in the form of a cation with the valence state of +1. Lithium may also be concentrated in clays, in which it correlates strongly with aluminum.¹¹ The extent of lithium adsorption to amorphous aluminum hydroxides increases with pH for the pH range between 6.5 and 8.¹² The cation exchange characteristics of a soil are also influential in retaining lithium. This factor is a function of the clay mineral and organic content in soil material, as well as the chemistry of other mineral components of the soil system. Any lithium attached as an exchangeable cation is expected to be very weakly held. Based on published results for lithium transport field studies, K_d may range from 0.03 to 5 L/Kg.^{13, 14, 15}

Boron: Boron is a naturally occurring element that can be found extensively in nature. Boron is classified as a nonmetal and is typically found in the environment combined with oxygen in compounds called borates. In groundwater, boron is one of the most mobile inorganics associated with CCR material. The various species of boron throughout the pH and Eh range found in most aquifer systems is presented in Figure 4. Within pH ranges of 6 to 8 (the pH range of most groundwater) the predominate form of boron is relatively inert boric acid (H₃BO₃). Boron can be absorbed by many different mineral and soil surfaces (such as kaolinite, illite clay, organic matter, lime content) forming weak, labile bonds.^{16,17} The mobility of boron in a groundwater is generally a function of the amount of fine-grained materials and the presence of certain iron and aluminum oxides which decrease boron's mobility.¹⁸ The adsorption of borates and boric acids to soils is also controlled by the presence of aluminum and iron oxides, and, to a lesser extent, organic matter. Soils rich in these oxides can experience significant adsorption of available borates. In some environments, adsorption to soil particles may be irreversible. The extent of boron adsorption is affected by pH; between pH 6 and pH 9, the extent of adsorption generally increases with pH.¹⁹ Reported boron K_d values for

a variety of soil types (e.g., sandy, silty, and clayey soils) are generally lower than 2 L/Kg.

CASE STUDY SITE: HYDROGEOLOGY SETTINGS

The project site (the Site) is located at a coal-fired power generation plant close to an ocean shoreline. CCR material generated by the facility has been used to manufacture a construction product for beneficial use. The product has been temporarily stored in a stockpile area on site. The Site is underlain by fill material to a depth of approximately 3.3 meters (10 feet) below ground surface (bgs) and an upper water bearing unit consisting of sandy clay and clay sand to a depth of approximately 7.6 meters (25 feet) bgs. The upper water bearing unit is bounded/underlain vertically by a stiff clay layer. Slug tests performed in the upper water bearing unit indicate that the hydraulic conductivity values range from 1.2×10^{-5} to 2.4×10^{-4} centimeters per second (0.035 to 0.67 feet per day). The groundwater hydraulic gradient beneath the stockpile area is approximately 0.005 to 0.011 (meter per meter). Selenium, molybdenum, and lithium were detected above the site-specific GWPSs (0.05 mg/L, 0.1 mg/L, and 0.04 mg/L, respectively) in the shallow groundwater immediately downgradient of the stockpile area. The nature and extent of impacted groundwater was investigated using the transect approach (Figure 4). The distance between two transects are approximately between 30 meters (~100 feet) and 40 meters (~130 feet). All transect monitoring wells are screened in the upper water bearing unit.

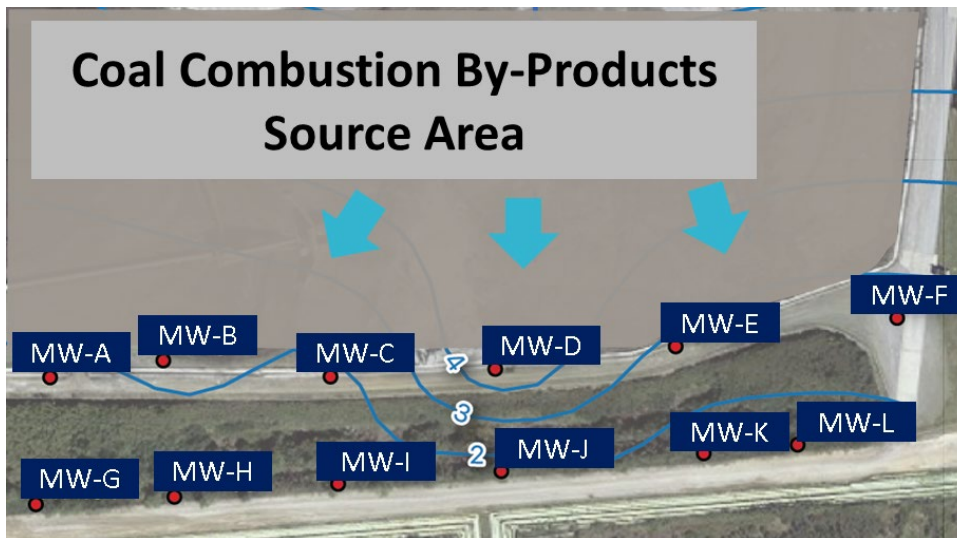


Figure 4: Transect wells for the nature and extent investigation. The transect monitoring wells immediately adjacent to the stockpile source area are MW-A through MW-F. The transect monitoring wells further downgradient are MW-G through MW-L. The blue contour lines show the potentiometric head contours. The blue arrows show the predominant groundwater flow directions.

EVIDENCE OF CONCURRENT ATTENUATION OF LITHIUM, MOLYBDENUM, AND SELENIUM

The pH range of shallow groundwater is generally between 6.5 and 7.5; the dissolved oxygen concentrations are generally lower than 1 mg/L; the observed field oxidation-reduction potential (ORP) values were typically negative (lower than 0 milli-volts). The chemical concentrations of selenium, molybdenum, lithium, boron, and calcium in the transect monitoring wells are shown in Figure 5.

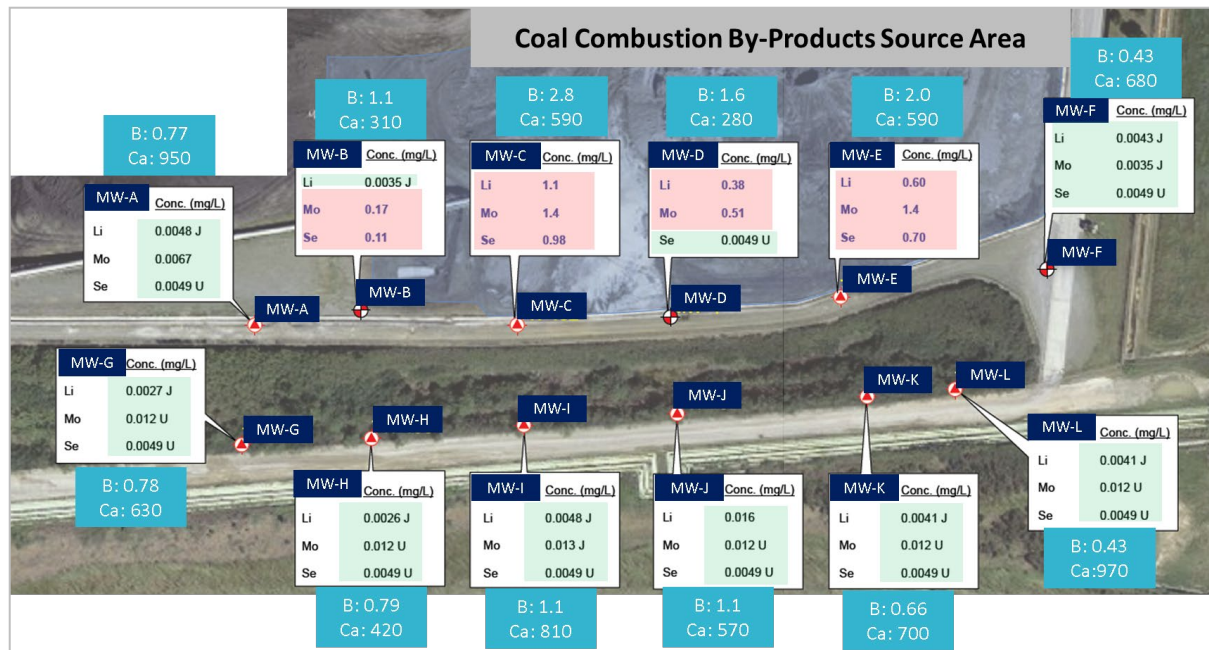


Figure 5: Chemical concentrations of selenium (Se), molybdenum (Mo), lithium (Li), boron (B), and calcium (Ca) found in transect monitoring wells. All concentrations are in the unit of mg/L. J stands for an approximate result that is less than the reporting limit, but greater than or equal than the method detection limit. U stands for no detection at the indicated method detection limit. The red highlighted concentration values for Se, Mo, and Li are higher their GWPSs. The green highlighted concentrations values are lower than the GWPSs.

For the transect monitoring wells (Transect 1 wells) adjacent to the stockpile area (MW-A through MW-F), the average boron concentration is 1.45 mg/L. For the transect monitoring wells further downgradient (Transect 2 wells), the average boron concentration is lower (0.81 mg/L), showing some extent of boron attenuation. In contrast, the average calcium concentration for Transect 1 wells (567 mg/L) are lower than that of the Transect 2 wells, showing no sign of calcium attenuation in the upper water bearing unit.

For selenium, molybdenum, and lithium, a concentration higher than the corresponding groundwater protection standard were found at multiple Transect 1 wells (MW-B

through MW-E). The high-end concentrations are approximately 10 to 20 times higher than their respective GWPSs. To the contrary, all concentrations of selenium, molybdenum, and lithium were found below their GWPSs at Transect 2 wells, indicating significant attenuation occurring between two transects.

SELENIUM PRECIPITATION UNDER SITE GEOCHEMICAL CONDITIONS

When the site-specific selenium Eh-pH diagram for the selenium-oxygen-hydrogen system was generated using measured representative concentrations of relevant chemical species, the measured Eh and pH values at key Transect 1 and Transect 2 wells are plotted in the region of elemental selenium (Figure 6). The results indicate that the current site geochemical conditions favor the formation of elemental selenium precipitation, which will be removed from impacted groundwater during transport. Since this attenuation mechanism is related to the prevailing site redox conditions, which is expected to last for an indefinite timeframe, the attenuation capacity of the aquifer for selenium is considered unlimited.

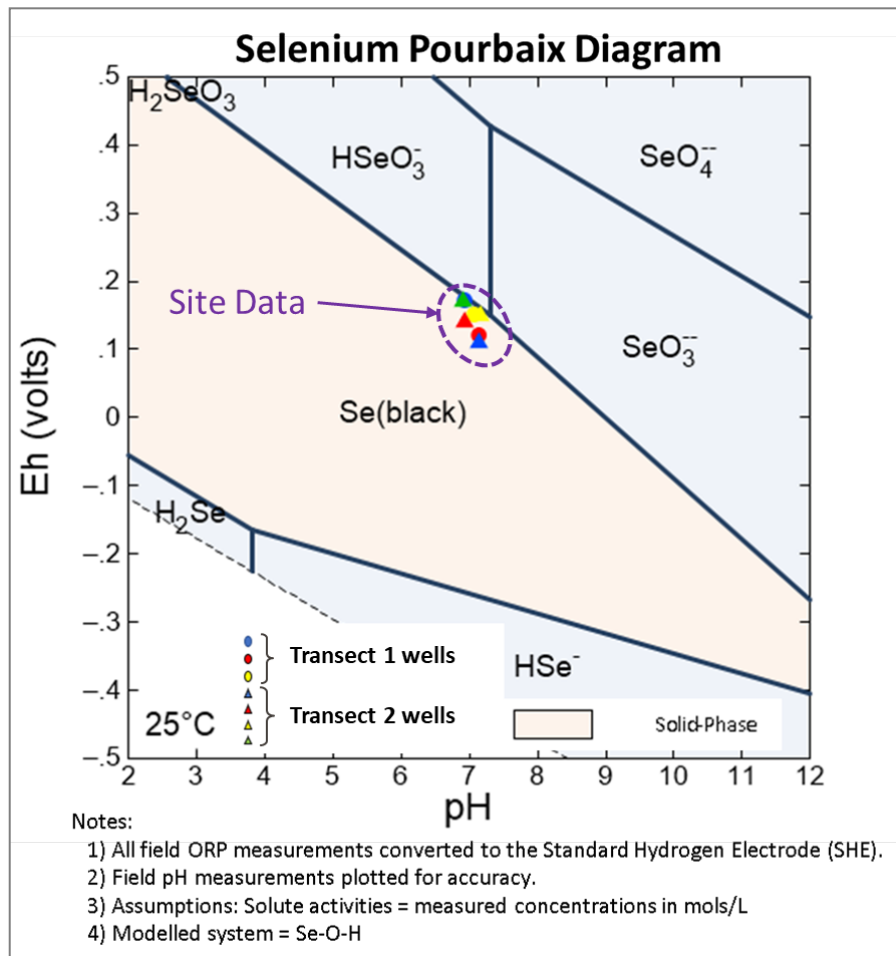


Figure 6: Site-specific selenium Eh-pH diagram with field measured Eh and pH data plotted for selected transect wells.

MOLYBDENUM PRECIPITATION POTENTIAL UNDER SITE GEOCHEMICAL CONDITIONS

The site-specific molybdenum Eh-pH diagrams for the molybdenum-oxygen-hydrogen-sulfur system was generated using measured representative concentrations of relevant chemical species at two different levels of molybdenum concentrations (Figure 7). The Site Eh-pH conditions are not expected to produce molybdenite precipitation (MoS_2), since the Site redox conditions (or Eh) are not sufficiently negative to produce sulfide-associated minerals. Under the high molybdenum concentration conditions ($\text{Mo} = 1.4 \text{ mg/L}$; See MW-C concentrations in Figure 5), powellite precipitation can form [Panel (A) of Figure 7]. However, at a lower molybdenum concentration ($\text{Mo} = 0.4 \text{ mg/L}$), molybdenum prefers being in the form of an oxyanion – molybdate. Therefore, the formation of powellite cannot attenuate molybdenum in impacted groundwater to a level below the GWPS ($= 0.1 \text{ mg/L}$); it is only a partial attenuation mechanism. Thus, one or multiple other attenuation mechanism(s) must also occur to help limit the migration of molybdenum from Transect 1 to Transect 2.

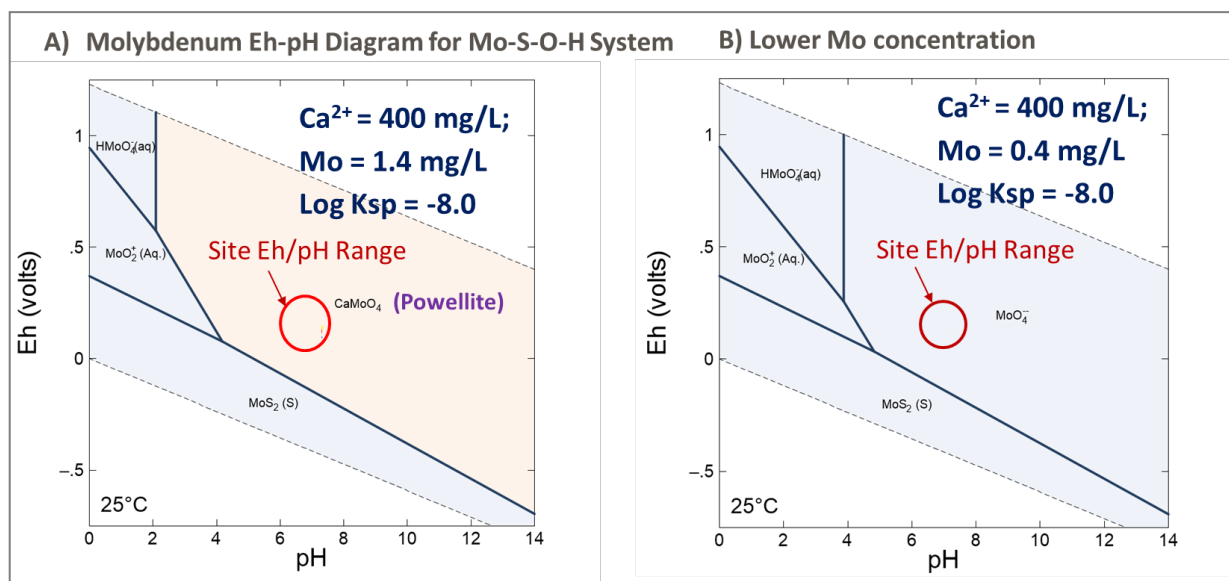


Figure 7: Site-specific molybdenum Eh-pH diagrams under (A) the high and (B) the low molybdenum concentration conditions. The logarithm of powellite solubility product was assumed to be -8.0.

HOW IS LITHIUM ATTENUATED UNDER SITE GEOCHEMICAL CONDITIONS?

Considering the fact that lithium is not expected to form precipitation under Site conditions but experienced significant attenuation, adsorption of lithium to Site sediments is the only possible mechanism that can play an important role for lithium attenuation. Based on our evaluation below, matrix diffusion together with adsorption to fine-grained aquifer sediments is the likely attenuation mechanism for lithium. Note that

this mechanism may also play an important role for molybdenum attenuation, which help retard molybdenum migration.

The conceptual model of how matrix diffusion works with adsorption to retard solute transport are shown in Figure 8. Significant matrix diffusion effects often happen where connected permeable zones (high K zones) are embedded in more voluminous low permeability zones (low K zones), which generally are fine-grained material or rock matrix. While the main solute transport pathway along the groundwater flow direction is through the connected high K zones, individual solute molecules may migrate into and out of the low K zones through diffusion. The timescale or probability of a solute to be trapped into the low K zones affects the apparent traveling velocity of the solutes along the general groundwater flow direction. A more tortuous yet connected pore structure of the low K zones and a higher adsorption affinity of the low K material to a solute are expected to produce more pronounced retardation effects.

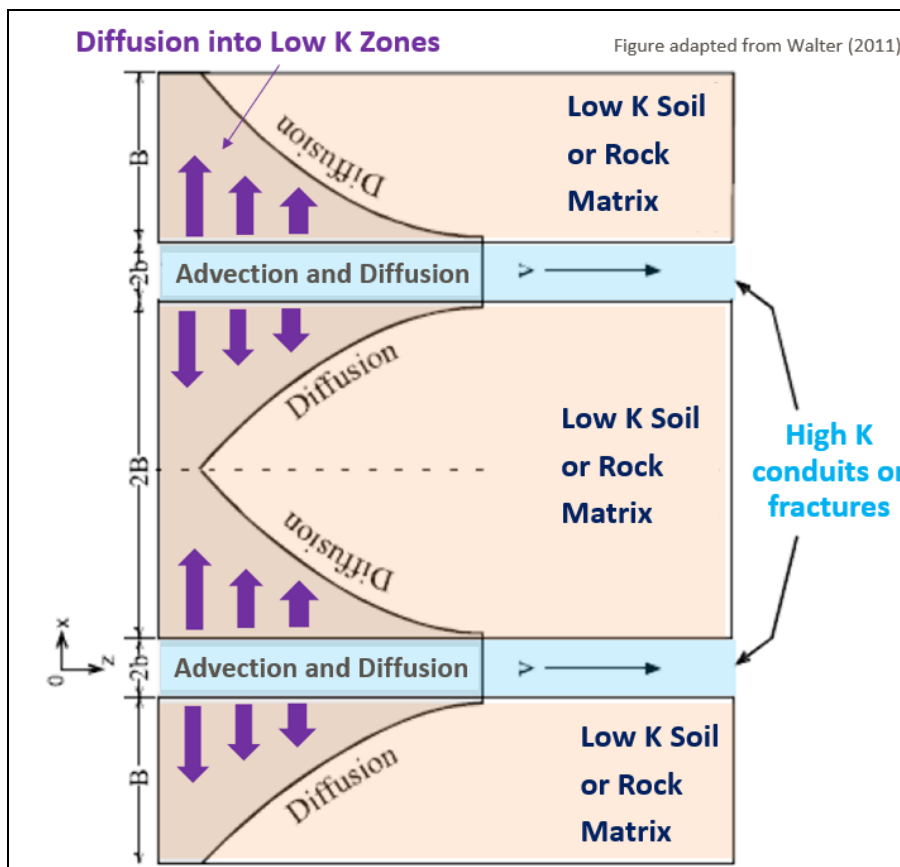


Figure 8: A schematic of matrix diffusion process.

The methodology used to assess the combined matrix diffusion and adsorption to the low K sediments is described here. The REMChlor-MD semi-analytical model (<https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Persistent-Contamination/ER-201426>) was used to assess where the use

of an idealized site geological conditions and a reasonable K_d value for lithium can explain the attenuation observed at two transects. The idealized three-dimensional model domain is shown in Panel (A) of Figure 9. The idealized vertical representation is shown in Panel (b) of Figure 9, signifying an approximately 3-foot (or 90 cm) thick connected high K sand zone embedded in a much thicker unit of low K clayey sediments at the Site. The initial lithium concentration at the source was assumed to be 1 mg/L. The duration of the lithium mass loading to the aquifer was assumed to last for 28 years, followed by a complete source removal (zero concentration at the source). After the source removal period, the REMChlor-MD model would simulate back diffusion of the lithium mass stored in the low K zones during the active source period.

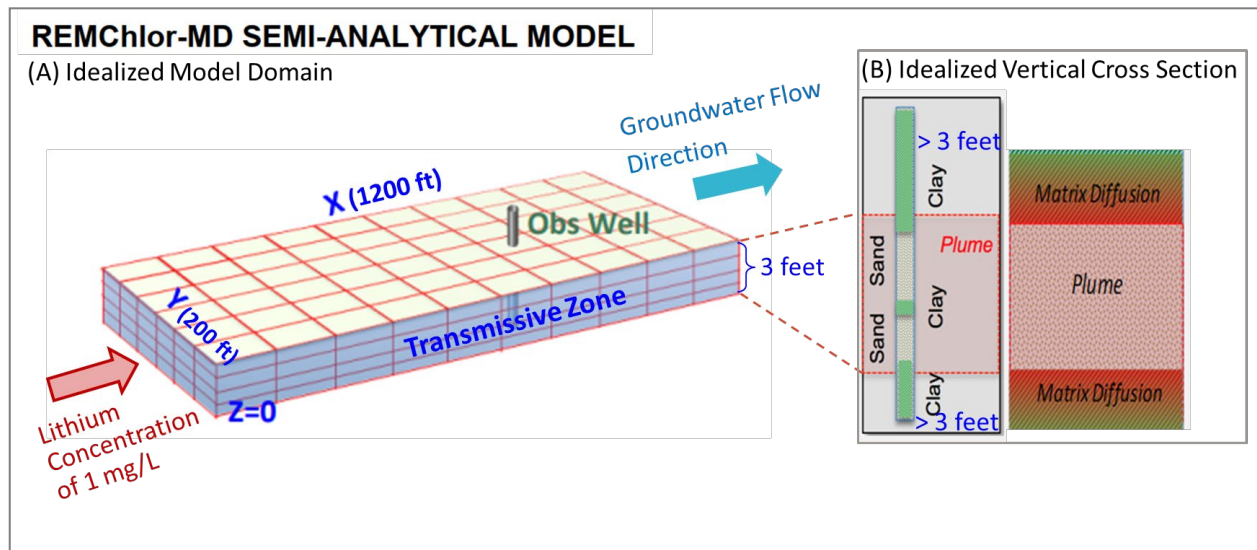


Figure 9: Model Domain for REMChlor-MD modeling.

Several reasonable pairs of the K_d values for the high K and low K zones were modeled; it was found that the K_d value of 0.1 L/Kg for the high K zone and the K_d value of 10 L/Kg for the low K zone produces the best results to the transect observations. The simulated concentration trends from the onset of the lithium loading to 300 years afterwards at two selected monitoring locations (30 meters [100 feet] downgradient and 240 meters [800 feet] downgradient) are shown in Figure 10.

Based on the modeling results for the observation point at 30 meters downgradient of the source, while the observed lithium concentrations at Transect 2 (approximately 30 meters [100 feet] downgradient of the source) are currently below the lithium GWPS (= 0.04 mg/L), it is expected that the concentrations will rise and exceed the GWPS within a decade (Panel [A] of Figure 10). Despite the planned source removal, the peak concentration at this monitoring location will arrive approximately 20 years after the source removal. Back diffusion can sustain the lithium concentration at this location for more than 100 years thereafter.

The simulated concentration trend at the observation point 240 meters [800 feet] downgradient shows no exceedance of the GWPS because there is a sufficient attenuation capacity between the source and this location to assimilate the overall lithium loading. Note that, without the source removal action, the simulated peak concentration at this location would be above the GWPS.

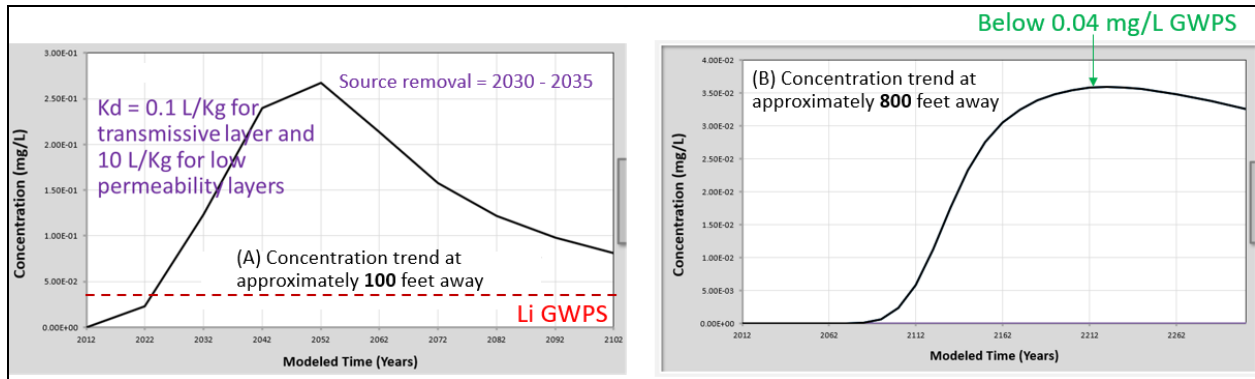


Figure 10: Simulated concentration trends at (A) 30 meters (100 feet) downgradient of the source and (B) 240 meters (800 feet) downgradient of the source.

CONCLUDING REMARKS

The case study presented above illustrates different mechanisms that may be responsible for the attenuation for lithium, molybdenum, and selenium in groundwater:

Lithium: The combination of matrix diffusion and stronger adsorption in the low K zone can produce noticeable attenuation effects for lithium. The case study signifies the importance of characterizing the K_d value for the low K zone. If there is sufficient buffering distance between the source and a compliance point, this attenuation mechanism may work with the source removal action to achieve the cleanup goal.

Molybdenum: At the case study site, the redox conditions are not sufficiently low to produce molybdenite precipitation. The combination of a high molybdenum (e.g., 1.4 mg/L) and a high calcium concentration (e.g., 400 mg/L) can promote powellite precipitation; however, this is only a partial attenuation mechanism for molybdenum since it cannot work at a lower molybdenum concentration (0.4 mg/L). The combination of matrix diffusion and adsorption in the low K zone may also provide significant additional attenuation.

Selenium: The site-specific prevailing redox conditions can result in elemental selenium precipitation, which is considered the major selenium attenuation mechanism because it is kinetically fast. While the combination of matrix diffusion and adsorption can provide additional aquifer assimilation capacity, most of selenium is expected to precipitate out before being attenuated through matrix diffusion.

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