

TECHNICAL MEMORANDUM

DATE February 2019

TO Jessica Mackie
Teck Coal Limited

CC

FROM Adrian de Bruyn

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BIOACCUMULATION ANALYSIS IN SUPPORT OF THE 2019 IMPLEMENTATION PLAN ADJUSTMENT

Golder Associates Ltd. (Golder) is pleased to provide Teck Coal Limited (Teck) with the following analysis of potential selenium bioaccumulation in support of the 2019 Implementation Plan Adjustment (IPA).

1.0 BACKGROUND

In 2013, Teck developed a valley-wide selenium bioaccumulation model in support of the Elk Valley Water Quality Plan (EVWQP). The model was developed in consultation with a technical advisory committee with representation from British Columbia Ministry of Environment, Environment Canada, the Ktunaxa Nation Council (KNC), United States Environmental Protection Agency, and Montana Department of Environmental Quality. Steps were taken in model development to reduce and account for uncertainty, including comparing a range of possible statistical approaches and model structures, evaluating data quality prior to inclusion, and incorporating margins of safety to offset residual uncertainty. The final model (hereafter 'the EVWQP model') consisted of a set of statistical equations describing observed patterns of selenium bioaccumulation through aquatic species in the Elk Valley. The EVWQP model was derived from a large dataset of tissue and aqueous selenium measurements collected throughout the Elk Valley over several decades of monitoring. Supporting analyses conducted during model development confirmed that bioaccumulation data collected in Koocanusa Reservoir conformed to the EVWQP model, and it was concluded that a separate bioaccumulation model was not required for the reservoir.

Following implementation of the West Line Creek Active Water Treatment Facility (WLC AWTF) at Teck's Line Creek Operation (LCO), it became apparent that active water treatment can change selenium speciation in a way that affects bioaccumulation. Selenium in areas of the Elk Valley not affected by active water treatment is predominantly (usually >99%) found as the oxyanion selenate (SeO_4 , oxidation state +6). AWTF effluent was found to contain a higher proportion of selenite (SeO_3 , oxidation state +4) and organoselenides (oxidation state -2), which have higher bioavailability than selenate. To address this change in speciation, Teck investigated, piloted, and is in the process of implementing an advanced oxidation process (AOP) that returns selenium speciation in AWTF effluent to a selenate-dominated condition.

To account for potential changes in patterns of bioaccumulation in areas affected by active water treatment, Teck engaged subject matter experts to develop a new selenium bioaccumulation tool that explicitly accounts for selenium speciation. The speciation bioaccumulation tool is described in Golder (2018), a copy of which is provided as Attachment A. The analysis reported in Golder (2018) utilized a number of data sources:

- 1) observed selenium bioaccumulation at monitoring stations in the Elk Valley, including in Line Creek prior to and during the operation of the WLC AWTF
- 2) selenium speciation data from watercourses in the Elk Valley, including water samples collected from Line Creek upstream and downstream of the WLC AWTF, effluent from the WLC AWTF, and effluent from the AOP system pilot
- 3) laboratory tests of algal selenium uptake conducted using Line Creek waters, WLC AWTF effluent, AOP system pilot effluent, and selenate- and selenite-spiked laboratory waters

The analysis provided a basis for calculating expected selenium bioaccumulation in waters containing a mixture of selenium species.

As outlined in Attachment A, the main change between the EVWQP model and the new selenium bioaccumulation tool consists of an update to the equation describing the initial uptake step from water to periphyton, which is the step at which speciation effects occur. Bioaccumulation to aquatic species at higher trophic levels then follows the same equations as included in the EVWQP model (Teck 2014).

In both the EVWQP model and the new bioaccumulation tool, bioaccumulation from water to periphyton can be expressed using the variable K_d , which represents the ratio of selenium concentrations in periphyton tissue to selenium concentrations in water. However, the definition of K_d changes between the EVWQP model and the new tool. In the EVWQP model, selenium uptake by periphyton is calculated from total selenium in water. Therefore, the K_d inherent in the EVWQP model expresses periphyton selenium concentrations relative to total selenium in water. In the new tool, K_d considers the concentrations of individual selenium species in water, and has therefore been renamed $K_{d,mixture}$. The equation describing uptake from water to periphyton in the EVWQP model is expressed as a regression equation, but can be rearranged to give:

$$[Se]_{peri} = K_d \times [Total Se]_{aq} \quad \text{(Equation 1)}$$

In the new bioaccumulation tool, this calculation is modified as:

$$[Se]_{peri} = K_{d,mixture} \times [Total Se]_{aq} \quad \text{(Equation 2)}$$

where $K_{d,mixture}$ is calculated from K_d values for selenate, selenite, and other selenium species and the proportions (P , expressed as dimensionless fractions) of total aqueous selenium that are in each form:

$$K_{d,mixture} = (K_{d,selenate} \times P_{selenate}) + (K_{d,selenite} \times P_{selenite}) + (K_{d,other} \times P_{other}) \quad \text{(Equation 3)}$$

Because selenium is an essential element for all life, K_d values tend to be highest when aqueous concentrations are relatively low (as organisms strive to meet their physiological requirements) and decline at higher aqueous concentrations (as organisms partially regulate their selenium uptake). K_d values for selenite, selenate and other forms of selenium were defined as detailed in Attachment A. In brief:

- The K_d of selenite was characterized using results of a laboratory algal uptake experiment conducted by Nautilus Environmental, evaluated in the context of relevant and reliable published studies. The selenite K_d was expressed as a function of aqueous selenite concentration, and was found to vary from 1,000 at an aqueous selenite concentration of 1 micrograms per litre ($\mu\text{g/L}$) to 4,000 at an aqueous selenite concentration of 0.1 $\mu\text{g/L}$.
- The K_d of selenate was characterized with an analysis of Elk Valley monitoring data collected at sites where selenate and selenite were the only two detected species. Observed bioaccumulation in biota was adjusted to factor out the contribution of selenite, and the remaining pattern was attributed to selenate. K_d of selenate was expressed as a function of aqueous selenate concentration, varying from 20 at an aqueous selenate concentration of 100 $\mu\text{g/L}$ to 200 at an aqueous selenite concentration of 10 $\mu\text{g/L}$. It is acknowledged that this relationship likely reflects the effect of sulphate, which is correlated with selenate in Elk Valley waters.
- A combined K_d for other selenium species was characterized using a combination of monitoring data from Line Creek downstream of the WLC AWTF and laboratory algal uptake tests with WLC AWTF effluent with and without AOP, evaluated in the context of relevant and reliable published studies.

The new bioaccumulation tool reflects the best information currently available to understand and predict selenium bioaccumulation in waters affected by biologically-based active water treatment.

2.0 OBJECTIVE AND APPROACH

During the development of the EVWQP, the EVWQP model was applied to calculate protective long-term targets for selenium that subsequently were adopted as Site Performance Objectives (SPOs) in Permit 107517, issued under the British Columbia *Environmental Management Act*. The long-term targets were calculated as aqueous total selenium concentrations that, if attained as a monthly average, would result in tissue selenium concentrations in sensitive biota lower than protective tissue-based effects benchmarks. Because the SPOs were derived using the EVWQP model, their protectiveness may be negatively affected by active water treatment and its effect on selenium speciation. In other words, although active water treatment may result in long-term total selenium concentrations that are at or below the SPOs outlined in Permit 107517, selenium concentrations in the tissues of aquatic species may be higher than would have been expected, due to selenium speciation changes and resulting higher bioaccumulation than was forecast during development of the EVWQP.

The objective of the present analysis was to evaluate whether selenium speciation changes could result in higher bioaccumulation than was forecast during development of the EVWQP. The analysis involved comparing projected selenium concentrations in benthic invertebrate tissues developed for a water treatment scenario using first the EVWQP model and then the new bioaccumulation tool. If tissue concentrations projected by new bioaccumulation tool were equal to or less than those projected by the EVWQP model, then the long-term SPOs expressed as total selenium concentrations would continue to provide the same level of protection as outlined in the EVWQP.

3.0 METHODS

The 2017 Regional Water Quality Model (RWQM), as described in Teck (2017) and changed as outlined in Annex B, was used to generate projections of monthly average total aqueous selenium concentrations ($[Se]_{total}$; $\mu\text{g/L}$) and percent treated water ($P_{effluent}$; %) at 14 representative modelling locations on Line Creek, Michel Creek, the Fording River, the Elk River, and Koocanusa Reservoir. The set-up of the RWQM included 199,600 m^3/d of active water treatment capacity distributed through time and across Teck’s operations (Table 1) and reflected the Permitted Development Scenario described in Section 2 of the 2019 IPA Report (Teck 2019).

Output from the RWQM was reviewed and the years and months with maximum projected $P_{effluent}$ were selected for the present analysis to assess the potential influence of AOP effluent on selenium bioaccumulation (accounting for the influence of selenium speciation) compared to the EVWQP selenium bioaccumulation model (which did not account for selenium speciation). The review identified that $P_{effluent}$ reached maximum values in Line Creek and Michel Creek in 2034, and in the Fording River and Elk River in 2049. For each of the 14 locations, the months in 2034 and 2049 with maximum projected $P_{effluent}$ were selected for inclusion in the analysis.

Table 1: Summary of Active Water Treatment Considered in the Analysis

Location	Fully Effective Date	Hydraulic Capacity (m^3/d)
WLC Phase I	Dec-2018	6,000
	Dec-2019	1,100
FRO-S Phase I	Dec-2021	20,000
EVO Phase I	Sep-2022	20,000
FRO-N Phase I	Dec-2023	35,000
WLC Phase II	Dec-2025	12,500
EVO Phase II	Dec-2027	20,000
FRO-S Phase II	Dec-2029	5,000
GHO Phase I	Dec-2031	2,500
WLC Phase III	Dec-2033	32,500
FRO-S Phase III	Dec-2035	20,000
LCO Dry Creek Phase I	Dec-2037	2,500
FRO-N Phase II	Dec-2039	15,000
EVO Phase III	Dec-2043	5,000
LCO Dry Creek PII	Dec-2049	2,500

Notes: EVO = Elkview Operations; FRO-N = Fording River Operations Active Water Treatment Facility North; FRO-S = Fording River Operations Active Water Treatment Facility South; GHO = Greenhills Operations; LCO = Line Creek Operations; m^3/d = cubic metres per day; WLC = West Line Creek.

Next, the $P_{effluent}$ information was used in combination with the total selenium projections to estimate the relative proportion of selenate, selenite, and other selenium species at each location, and then to calculate projected selenium concentrations in benthic invertebrate tissue. These calculations involved the following four steps:

- 1) Calculating a total projected selenium concentration at each location in each of two categories: that associated with water that had passed through a treatment facility and that associated with untreated ('background') water.
- 2) The total selenium concentration in each category was sub-divided into component selenium species (i.e., selenate, selenite, and other).

- 3) Common components were then added together across the two categories to estimate the concentrations of selenate, selenite, and other selenium species projected to be present at each location.
- 4) The EVWQP model (using total aqueous selenium concentration) and the new bioaccumulation tool (using the component selenium species) were then applied to estimate selenium concentrations in benthic invertebrate tissues.

Further detail on how each step was executed is as follows:

- Step 1 - The concentration of selenium that had been treated by an AWTF ($[Se]_{\text{treated}}$; $\mu\text{g/L}$) was estimated as the product of P_{effluent} and the selenium concentration in AWTF effluent ($[Se]_{\text{effluent}}$), which was assumed to be $30 \mu\text{g/L}$ for the purposes of this analysis. The percentage of selenium that would be treated by an AWTF ($P_{\text{Se,treated}}$; %) was then calculated by dividing $[Se]_{\text{treated}}$ by the projected $[Se]_{\text{total}}$.
- Step 2a – Untreated Water: Speciation in untreated Elk Valley waters was characterized as background percent selenite ($P_{\text{SeIV,bg}}$; %), which was estimated for each location using receiving environment speciation data collected by Teck in 2017. Background percent selenite was calculated as the ratio of reported selenite concentration to the sum of selenite and selenate. The remainder of selenium was present as selenate; other non-selenate species were negligible in untreated waters. Where multiple speciation samples were available for a given location, the average of available data was used. Because no speciation data were available for Elko Reservoir or Kooacanusa Reservoir, speciation in the reservoirs was assumed to be the same as Elk River location EV_ER4. Background speciation at the LCO Compliance Point (LC_LCDSSLCC) was estimated using data from Line Creek upstream of the WLC AWTF (LC_LCUSWLC) to avoid speciation changes associated with the WLC AWTF.
- Step 2b – Treated Water: Speciation in treated water was estimated assuming AOP technology was in use at each facility, and was calculated as the average of speciation data collected during pilot AOP testing simulating normal operation of the AOP with effluent from the WLC ($n = 53$ samples)¹ and Fording River AWTFs ($n = 29$ samples). Average percent selenite was 1.7% during pilot AOP testing with WLC AWTF effluent and 0.9% during testing simulating Fording River AWTF effluent. The higher of these values (1.7%) was used in the present analysis. Average percent other selenium species (P_{other} ; %) was 1.64% during pilot AOP testing with WLC AWTF effluent and 1.0% during testing simulating Fording River AWTF effluent. The higher of these values (1.64%) was used in the present analysis. The remainder of selenium (after accounting for percent selenite and percent other selenium) was present as selenate.
- Step 3 – Speciation at each location was estimated by blending the speciation of untreated and treated water. Percent selenite at each location was calculated as a weighted average of background percent selenite at that location (from Step 2a) and percent selenite in treated water (from Step 2b), weighted by the percentage of selenium at that location that had been treated by an AWTF (from Step 1). A similar calculation was used to estimate percent selenate and percent other selenium.

¹ Two anomalous speciation samples were excluded from this calculation because they had reported concentrations of selenite and/or other non-selenate species that were 10-fold higher than the remaining 53 samples. It was assumed that these anomalous samples were not representative of normal operation of the AOP. No such anomalous samples were observed in testing that simulated Fording River water.

- Step 4 – K_d values for selenate, selenite, and other non-selenate species were calculated according to equations in Attachment A. K_d of the mixture of selenium species ($K_{d,mixture}$) was then calculated as a weighted average of the three K_d values, weighted by the estimated percent of each species (from Step 3). This calculation was carried out for each location. Benthic invertebrate selenium concentrations were then calculated in two ways: 1) by applying the bioaccumulation tool with location-specific speciation information as described in Attachment A (results denoted $[Se]_{benthos}$ in Section 4.0); and 2) by applying the EVWQP model to the total aqueous selenium concentration (results denoted 'EVWQP Model' in Section 4.0).

4.0 RESULTS

Results of the analysis are shown below for 2034 (Table 2) and 2049 (Table 3). At each location in both snapshots, the new bioaccumulation tool predicted tissue concentrations in benthic invertebrates that were similar to and slightly lower than the EVWQP model. Thus, effects of biologically-based active water treatment on selenium speciation are not expected to result in higher bioaccumulation than was characterized by the EVWQP model, provided AOP technology is used. Consequently, the long-term SPOs and limits in Permit 107517, expressed as total selenium concentrations, remain appropriate for an implementation plan that incorporates active water treatment with AOP.

Table 2: Selenium Bioaccumulation Tool Calculations for Modelled Water Quality in 2034

Location	P _{Se,treated} (%)	P _{Effluent} (%)	[Se] _{total} (µg/L)	P _{SeIV,bg} (%)	P _{SeVI} (%)	P _{SeIV} (%)	P _{other} (%)	K _{d,SeVI}	K _{d,SeIV}	K _{d,other}	K _{d,mix}	[Se] _{benthos} (mg/kg dw)	EVWQP Model
FRO Compliance Point (FR_FRCP1)	34.3%	39.3%	34.4	0.39%	98.6%	0.84%	0.56%	56	2,248	2,248	86	8.3	9.5
Fording River Downstream of Greenhills Creek (GH_FR1)	16.2%	22.6%	41.9	0.64%	98.9%	0.81%	0.26%	46	2,034	2,034	68	8.0	9.9
Fording River Above of Chauncey Creek (FR_FRABCH)	32.1%	35.6%	33.2	0.23%	98.7%	0.70%	0.53%	57	2,557	2,557	88	8.2	9.5
Line Creek Downstream of South Line Creek (LC_LCDSSLCC)	64.9%	36.6%	16.9	0.50%	97.6%	1.28%	1.06%	107	2,669	2,669	167	7.9	8.4
Fording River Downstream Line Creek (LC_LC5)	26.0%	23.3%	26.9	0.85%	98.5%	1.07%	0.43%	70	2,255	2,255	103	7.7	9.1
GHO Elk River Compliance Point (GH_ERC)	15.7%	1.3%	2.4	3.00%	96.9%	2.79%	0.26%	634	5,404	5,404	780	5.3	5.8
Elk River Upstream of Boivin Creek (GH_ER1)	15.3%	1.2%	2.3	0.94%	98.6%	1.06%	0.25%	656	10,029	10,029	778	5.0	5.8
Elk River Upstream of Grave Creek (EV_ER4)	25.7%	10.0%	11.6	0.71%	98.6%	0.96%	0.42%	150	3,975	3,975	203	6.6	7.8
EVO Harmer Compliance Point (EV_HC1)	0%	0%	46.4	0.62%	99.3%	0.62%	0.00%	42	2,256	2,256	56	7.3	10.1
Michel Creek downstream of CMO (CM_MC2)	0%	0%	7.7	2.22%	97.7%	2.22%	0.00%	218	3,064	3,064	281	6.1	7.2
EVO Michel Creek Compliance Point (EV_MC2)	29.8%	11.1%	11.2	1.31%	98.0%	1.42%	0.49%	155	3,207	3,207	213	6.7	7.7
Elk River Downstream of Michel Creek (EV_ER1)	30.4%	8.5%	8.4	4.12%	96.1%	3.39%	0.50%	206	2,273	2,273	287	6.7	7.3
Elko Reservoir (RG_ELKORES)	27.9%	5.6%	6.1	0.71%	98.5%	0.99%	0.46%	270	5,805	5,805	350	5.9	6.9
Koocanusa Reservoir (RG_DSELK_Inflow)	31.5%	1.3%	1.3	0.71%	98.4%	1.02%	0.52%	1,126	14,621	14,621	1,333	4.7	5.2

Notes: EVWQP = Elk Valley Water Quality Plan; EVO = Elkview Operations; Se = selenium; % = percent; µg/L = micrograms per litre; mg/kg dw = milligrams per kilogram dry weight.

Table 3: Selenium Bioaccumulation Tool Calculations for Modelled Water Quality in 2049

Modelling Location	P _{Se,treated} (%)	P _{Effluent} (%)	[Se] _{total} (µg/L)	P _{SeIV,bg} (%)	P _{SeVI} (%)	P _{SeIV} (%)	P _{other} (%)	K _{d,SeVI}	K _{d,SeIV}	K _{d,other}	K _{d,mix}	[Se] _{benthos} (mg/kg dw)	EVWQP Model
FRO Compliance Point (FR_FRCP1)	36.7%	49.7%	40.5	0.39%	98.5%	0.87%	0.60%	48	1,990	1,990	77	8.7	9.8
Fording River Downstream of Greenhills Creek (GH_FR1)	18.1%	30.4%	50.2	0.64%	98.8%	0.83%	0.30%	39	1,797	1,797	59	8.3	10.2
Fording River Above of Chauncey Creek (FR_FRABCH)	34.1%	44.6%	39.3	0.23%	98.7%	0.73%	0.56%	49	2,257	2,257	78	8.6	9.8
Line Creek Downstream of South Line Creek (LC_LCDSSLCC)	63.8%	36.6%	17.2	0.50%	97.6%	1.27%	1.04%	105	2,658	2,658	164	7.9	8.4
Fording River Downstream Line Creek (LC_LC5)	26.7%	28.0%	31.5	0.85%	98.4%	1.07%	0.44%	61	2,044	2,044	91	8.0	9.4
GHO Elk River Compliance Point (GH_ERC)	15.1%	1.2%	2.4	3.00%	96.9%	2.80%	0.25%	625	5,339	5,339	768	5.3	5.9
Elk River Downstream of Michel Creek (GH_ER1)	14.7%	1.1%	2.3	0.94%	98.7%	1.05%	0.24%	646	9,957	9,957	766	5.0	5.8
Elk River Upstream of Grave Creek (EV_ER4)	27.4%	12.1%	13.2	0.71%	98.5%	0.98%	0.45%	133	3,639	3,639	183	6.8	8.0
EVO Harmer Compliance Point (EV_HC1)	0%	0%	60.0	0.62%	99.3%	0.62%	0.00%	33	1,932	1,932	45	7.6	10.5
EVO Michel Creek Compliance Point (CM_MC2)	0%	0%	8.0	2.22%	97.7%	2.22%	0.00%	211	3,005	3,005	273	6.1	7.3
EVO Michel Creek Compliance Point (EV_MC2)	24.2%	8.6%	10.7	1.31%	98.2%	1.40%	0.40%	162	3,331	3,331	219	6.6	7.7
Elk River Downstream of Michel Creek (EV_ER1)	29.5%	9.0%	9.2	4.12%	96.1%	3.41%	0.48%	190	2,143	2,143	266	6.8	7.5
Elko Reservoir (RG_ELKORES)	26.9%	5.9%	6.6	0.71%	98.5%	0.98%	0.44%	251	5,560	5,560	326	6.0	7.0
Koocanusa Reservoir (RG_DSELK_Inflow)	30.6%	1.4%	1.4	0.71%	98.4%	1.01%	0.50%	1,052	14,056	14,056	1,249	4.7	5.3

Notes: EVWQP = Elk Valley Water Quality Plan; FRO = Fording River Operations; Se = selenium; % = percent; µg/L = micrograms per litre; mg/kg dw = milligrams per kilogram dry weight.

5.0 CLOSURE

We trust that the information provided in this technical memorandum is sufficient for your present needs. Should you need anything further, please do not hesitate to contact the undersigned.



Adrian de Bruyn, Ph.D., R.P.Bio.
Associate

AMD/JPB/tt/jlb



J.P. Bechtold, M.A.Sc., P.Biol.
Principal

Attachment: Attachment A - Selenium Bioaccumulation Tool Version 1.1

[https://golderassociates.sharepoint.com/sites/22006e/p1792554teckimplanupdate/shared documents/sirs/ipa_rd3/reporting/08_annex g - selenium/annexg_sebioaccumulation.docx](https://golderassociates.sharepoint.com/sites/22006e/p1792554teckimplanupdate/shared%20documents/sirs/ipa_rd3/reporting/08_annex%20g%20-%20selenium/annexg_sebioaccumulation.docx)

6.0 REFERENCES

- Golder (Golder Associates Ltd.). 2018. *Selenium Species Bioaccumulation Tool Version 1.1*. Prepared by Golder. Submitted to Teck Coal Limited on May 23, 2018.
- Teck (Teck Coal Limited) 2014. *Elk Valley Water Quality Plan*. Prepared by Teck Coal Limited and submitted to the British Columbia Minister of Environment. July 2014.
- Teck. 2017. *2017 Elk Valley Regional Water Quality Model Update Overview Report*. Prepared by Teck Coal Limited and submitted to the British Columbia Minister of Environment. October 31, 2017.
- Teck. 2019. *Elk Valley Water Quality Plan - 2019 Implementation Plan Adjustment*. Prepared by Teck Coal Limited.

ATTACHMENT A

**Selenium Bioaccumulation Tool
Version 1.1**

TECHNICAL MEMORANDUM

DATE 23 May 2018

Project No. 1791695

TO Marty Hafke
Teck Coal Limited

CC Christine Deynaka, Teck Resources Limited

FROM Adrian de Bruyn

EMAIL adebruyn@golder.com

SELENIUM SPECIES BIOACCUMULATION TOOL VERSION 1.1

Golder Associates Ltd. (Golder) is pleased to provide Teck Coal Limited (Teck) with the following predictive selenium bioaccumulation tool that accounts for speciation in receiving waters downstream of Teck's existing and planned active water treatment facilities (AWTFs).

1.0 BACKGROUND

Selenium in aquatic environments occurs predominantly as the oxyanions selenate (SeO_4^{2-} , oxidation state Se^{6+}) and selenite (SeO_3^{2-} , oxidation state Se^{4+}). In well-oxygenated surface waters such as those that predominate in the Elk Valley, selenate is the dominant species (typically $\geq 99\%$ of total selenium). Conditions that promote the formation of selenite and more reduced species such as organoselenides (oxidation state Se^{2-}) tend to be rare in the Elk Valley and associated with lentic (still water) environments and mine-contact waters immediately adjacent to source such as waste rock seeps and some pit waters. As a result, the majority of selenium monitoring data that have been collected by Teck in receiving environments, and the selenium bioaccumulation model derived from those data for the Elk Valley Water Quality Plan (EVWQP), predominantly reflect the bioaccumulation of selenate (Teck 2014). Data from some lentic areas have been shown to exhibit higher bioaccumulation relative to elsewhere in the Elk Valley (Orr et al. 2012; Teck 2014), and this has been attributed to the formation and retention of more bioavailable reduced forms of selenium in those areas.

It has been identified that the West Line Creek (WLC) AWTF has the unexpected consequence of changing the speciation of aqueous selenium from predominantly selenate in influent water to a greater proportion of selenite and various organic and unidentified selenium species in AWTF effluent. This shift in speciation has been shown to increase the bioavailability of the remaining selenium for uptake by periphyton downstream of the WLC AWTF. To address this issue, Teck has piloted an advanced oxidation process (AOP) that will reverse the shift in selenium speciation in AWTF effluent and return the effluent to a selenate-dominated condition. Speciation analysis and laboratory uptake tests indicate that post-AOP effluent contains predominantly selenate and has lower selenium bioavailability than pre-AOP AWTF effluent, consistent with the expectation for a selenate-dominated speciation.

Given the potential for changes to selenium speciation associated with operation of existing and planned treatment facilities, Teck retained Golder to develop the following selenium bioaccumulation tool that explicitly accounts for selenium speciation.

2.0 BIOACCUMULATION TOOL

The bioaccumulation tool presented herein considers differences in bioavailability of selenium species in the initial uptake step from water to periphyton. The approach predicts the total uptake of selenium into periphyton by calculating the expected uptake of different selenium species, proportional to their presence in the mixture. Uptake is expressed as the periphyton/water concentration ratio, denoted K_d . Separate estimates of K_d are derived for selenate and selenite, and an approach is provided for modelling the combined contribution of other selenium species. The 'other species' term could easily be split further to explicitly model additional selenium species if information becomes available to characterize their concentrations and expected uptake.

2.1 Overview of Tool

In this approach, periphyton selenium concentration ($[Se]_{peri}$; mg/kg dw) is calculated from aqueous total selenium concentration ($[Se]_{aq}$; $\mu\text{g/L}$) and the overall K_d of the selenium species mixture ($K_{d,mixture}$) according to:

$$[Se]_{peri} = K_{d,mixture} \times [Se]_{aq} \quad (\text{Equation 1})$$

where $K_{d,mixture}$ is calculated from K_d values for selenate, selenite, and other species and the proportion (P , expressed as a dimensionless fraction) of total aqueous selenium that is in each form:

$$K_{d,mixture} = (K_{d,selenate} \times P_{selenate}) + (K_{d,selenite} \times P_{selenite}) + (K_{d,other} \times P_{other}) \quad (\text{Equation 2})$$

Periphyton selenium concentrations calculated using Equations 1 and 2 can then be used as inputs to the EVWQP selenium bioaccumulation model or other model to calculate predicted concentrations in other aquatic species. Analyses presented below use a trophic transfer factor (per Presser and Luoma 2010) to calculate selenium concentrations in benthic invertebrates from modelled concentrations in periphyton. Note that Equation 1 is simply a rearrangement of the definition of K_d as a periphyton/water concentration ratio.

The following subsections provide methods to estimate K_d for selenate, selenite, and combined other species for a particular set of environmental conditions. Note that K_d can vary by orders of magnitude as a function of aqueous selenium concentration, concentrations of modifying factors such as sulphate, selenium speciation, periphyton growth rates, and other site-specific conditions. Therefore, estimates of K_d for one set of environmental conditions cannot be assumed to apply under other conditions.

Two approaches to estimating K_d are discussed below: 1) extrapolation of results from published or site-specific laboratory uptake studies; and 2) inference from analysis of site-specific field bioaccumulation and speciation data. Each of these approaches has strengths and limitations that depend on the quantity and quality of available information for the selenium species in question. Uncertainties in each approach are discussed in Section 3.0.

2.2 Estimation of K_d for Selenate

Selenate uptake by algae declines with increasing concentrations of sulphate and aqueous selenate (Williams et al. 1994; Bailey et al. 1995; Riedel and Sanders 1996; Lo 2014; Van Geest et al. 2016). Because selenate and sulphate concentrations are highly correlated in coal mine-affected waters, it has not been possible to separately characterize the effect of these two factors on selenium bioaccumulation in the Elk Valley. Therefore, uptake of selenium into periphyton was characterized in the EVWQP model as a statistical regression equation relating periphyton selenium concentration to aqueous total selenium concentration, inherently reflecting the combined effect of selenate and associated sulphate concentrations. Total selenium in receiving waters of the Elk Valley is predominantly (usually $\geq 99\%$) selenate, but the EVWQP model does inherently reflect the contributions of both selenate and the small proportion of selenite that is present.

The following analysis uses field data from the Elk Valley to estimate the K_d of selenate by factoring out the contribution of selenite to total bioaccumulation. Field-collected bioaccumulation data are expected to provide a direct and site-relevant characterization of total selenium bioaccumulation under conditions in the Elk Valley. This analysis was conducted by parameterizing Equation 2 with data collected by Teck in receiving waters not affected by the WLC AWTF, as follows:

- The contribution of selenium species other than selenate and selenite (P_{other}) was assumed to be negligible because no species other than selenate and selenite has been detected in Elk Valley receiving waters not affected by the WLC AWTF. This assumption involves setting the right-most term in Equation 2 to zero.
- The remainder of Equation 2 was rearranged to solve for $K_{d,selenate}$ to give:

$$K_{d,selenate} = (K_{d,mixture} - K_{d,selenite} \times P_{selenite}) / P_{selenate} \quad \text{(Equation 3)}$$

- $K_{d,mixture}$ was calculated from 18 paired aqueous total selenium and benthic invertebrate selenium concentrations collected by Teck at locations where selenium speciation was also measured. Data were collected in 2017 under the regional aquatic effects monitoring program (RAEMP) and the Fording River and Line Creek local aquatic effects monitoring programs (LAEMPs) at monitoring stations on the Elk River, Fording River, Michel Creek, and their tributaries (Table 1). Data were also included in the analysis from monitoring in Line Creek in 2012, prior to operation of the WLC AWTF. Selenium speciation in Line Creek in 2012 was estimated from monitoring in Line Creek in 2016 and 2017 upstream of the AWTF.

Benthic invertebrate tissue selenium data were used because these are expected to provide a more reliable estimate of average site-specific bioaccumulation than periphyton selenium concentrations. Benthic invertebrates are longer-lived and slower-growing than periphyton, and therefore less subject to short-term temporal variation in aqueous selenium concentrations, selenium speciation, and growth conditions. Benthic invertebrate data are also less prone to potential confounding effects of sediment or calcite inclusion in samples. $K_{d,mixture}$ was estimated by dividing measured benthic invertebrate selenium concentrations by an average trophic transfer factor of 2.8 (Presser and Luoma 2010) to estimate periphyton concentrations, and then dividing the calculated value by the concurrent aqueous total selenium concentration. The adopted trophic transfer factor is consistent with values observed in the Elk Valley at similar selenium concentrations (Teck 2014).

- $K_{d,selenite}$ was calculated using Equation 5 (Section 2.3).
- $P_{selenate}$ and $P_{selenite}$ were calculated from selenium speciation data collected by Teck in 2017 at the same biological monitoring stations (Table 1). Proportions were calculated as the ratio of measured concentration to the sum of quantified selenium species. Non-detected species should not be included in this calculation (e.g., as the detection limit) unless there is reliable evidence that a species is present and a basis for estimating its concentration. In the present analysis, the sum of detected species was similar to the measured total selenium concentration, indicating that other selenium species are not present. Measured total selenium concentration should be used as the denominator in this ratio with caution because different analytical methods are used for total selenium and selenium species, and the sum of selenium species can exceed measured total selenium (which would give erroneous estimates of P).

- The resulting calculated $K_{d,selenate}$ values were analyzed in a regression analysis against associated selenate concentration (Figure 1). The resulting equation ($p < 0.0001$; $r^2 = 0.85$) was:

$$\log_{10}K_{d,selenate} = 3.14 - 0.908 \times \log_{10}[Se(VI)]_{aq} \quad (\text{Equation 4})$$

Table 1: Calculation of $K_{d,selenate}$ from Elk Valley Monitoring Data

Site	Sampling Date	Benthos [Se] (mg/kg dw)	Total [Se] ($\mu\text{g/L}$)	Selenite ($\mu\text{g/L}$)	Selenate ($\mu\text{g/L}$)	$K_{d,mixture}$	$K_{d,selenite}$	$K_{d,selenate}$
EV_ER1	17-Sep-17	5.6	11.2	0.103	11.1	178	4,092	142
EV_ER4	13-Sep-17	5.5	9.0	0.060	8.9	219	5,672	182
FR_FRABCH	Sep-17	5.4	57.3	0.121	57.1	34	3,710	26
FR_FRCP1	Sep-17	6.4	51.1	0.183	51.0	45	2,906	34
GH_FR1	9-Dec-17	6.1	48.6	0.320	48.3	45	2,077	31
LC_LC5	27-Apr-17	6.6	30.1	0.200	30.0	78	2,756	60
	13-Sep-17	8.9	33.5	0.284	33.2	95	2,229	77
LC_LC6	27-Apr-17	7.0	42.1	0.511	41.6	59	1,570	41
	13-Sep-17	8.1	38.4	0.411	38.0	75	1,789	57
CM_MC2	14-Sep-17	2.9	6.6	0.074	6.5	157	4,987	102
EV_HC1	16-Sep-17	11.0	23.9	0.197	23.7	164	2,777	143
CM_CC1	14-Sep-17	4.3	19.3	0.168	19.2	79	3,054	53
EV_MC2	13-Sep-17	6.5	5.7	0.095	5.6	405	4,295	340
LC_DCDS	17-Sep-17	7.9	6.7	0.174	6.6	420	2,991	351
LC_DC1	17-Sep-17	7.0	3.4	0.066	3.3	745	5,340	653
LC_LC3	12-Sep-12	7.0	79.7	0.070	79.6	31	5,155	27
LC_LCDSSLC	12-Sep-12	8.1	54.1	0.048	54.1	53	6,499	48
LC_LC4	12-Sep-12	8.1	44.7	0.039	44.7	65	7,285	58

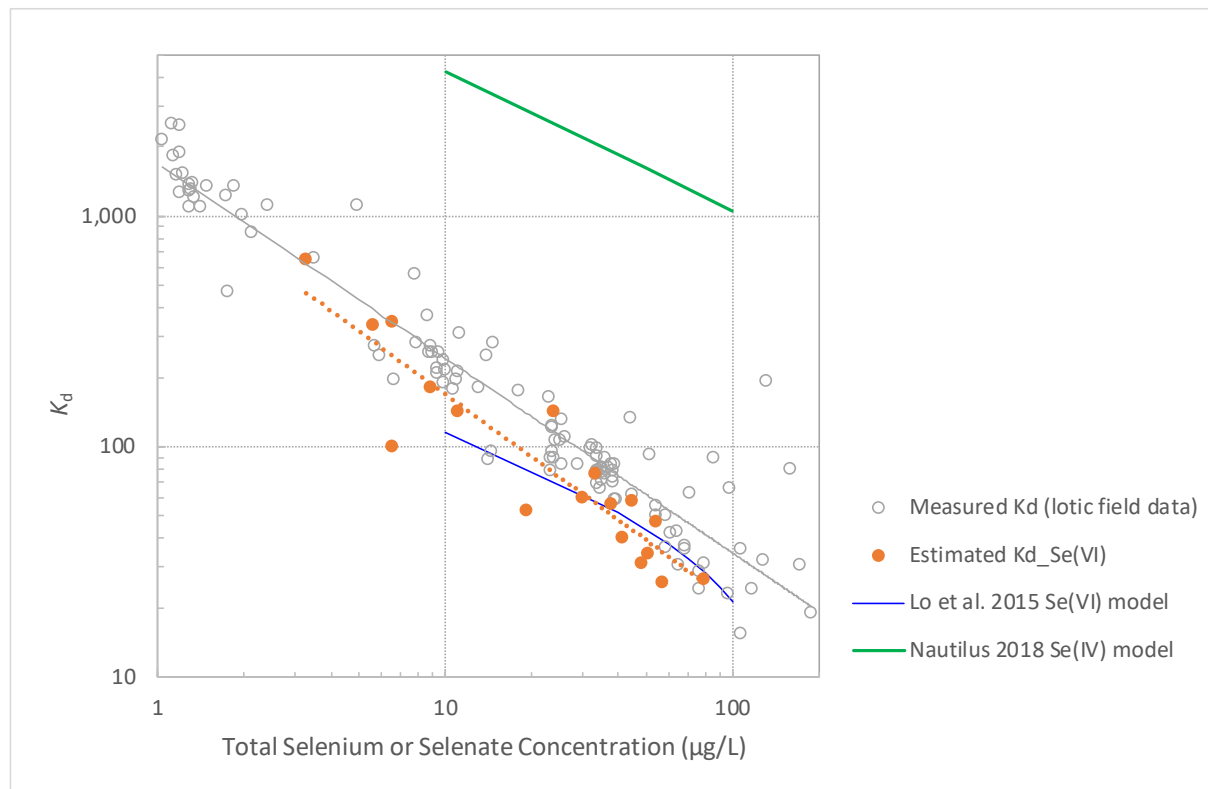


Figure 1: Comparison of estimated $K_{d,selenate}$ (Se(VI); filled symbols) to measured K_d from lotic sites in the Elk Valley (open symbols). Relationship between $K_{d,selenate}$ and aqueous selenate concentration (dotted line) is shown in comparison to field data (fine grey line), Lo et al. (2015) selenate model (blue line), and Nautilus (2018) selenite model (bold green line; calculated for 1% selenite).

Figure 1 shows the calculated $K_{d,selenate}$ estimates (Table 1) and the fitted regression (Equation 4) in comparison to measured data and existing models from laboratory studies of selenate and selenite. Measured K_d values were calculated from benthic invertebrate tissue selenium concentrations measured by the RAEMP in lotic areas in 2012 and 2015 (Minnow 2018). Laboratory-based $K_{d,selenate}$ estimates were calculated with the Lo et al. (2015) model, with sulphate concentrations estimated using a sulphate-selenium correlation derived by Van Geest et al. (2016). Laboratory-based $K_{d,selenite}$ estimates (Equation 5) were calculated from 10 to 100 $\mu\text{g/L}$ total selenium by assuming 1% selenite (i.e., 0.1 to 1 $\mu\text{g/L}$ selenite).

Equation 4 gives estimates of $K_{d,selenate}$ that range from approximately 200 at 10 $\mu\text{g/L}$ selenate to approximately 20 at 100 $\mu\text{g/L}$ selenate. These estimates are similar to $K_{d,selenate}$ values reported by laboratory studies of selenate uptake by the green alga *Pseudokirchneriella subcapitata* at sulphate concentrations greater than 100 mg/L, reflective of concentrations in mine-affected waters in the Elk Valley (Lo et al. 2015; Van Geest et al. 2016). The estimates calculated by Equation 4 are at the low end of the range of K_d values typically ascribed to selenate-dominated systems (e.g., 140 to 493 [Presser and Luoma 2010]; 100 to 200 [Teck 2014]), but the derivation described above shows how a small amount of selenite can have a measurable influence on observed K_d (Figure 1). Previous studies have not attempted to factor out the contribution of selenite.

Equation 4 is expected to provide reasonable estimates of $K_{d,selenate}$ under conditions in the Elk Valley. Because $K_{d,selenate}$ is a function of sulphate concentration, any change to the correlation between sulphate and selenium concentrations (e.g., downstream of an AWTF) would need to be accounted for in applying Equation 4. One approach would be to use Equation 4 to calculate $K_{d,selenate}$ for the untreated aqueous selenate concentration, which would provide a $K_{d,selenate}$ estimate that considers the expected effect of sulphate. This calculation may not reflect the dependence of $K_{d,selenate}$ on selenate concentration. However, the concentration dependence effect is expected to be relatively small compared to the effect of sulphate (Lo et al. 2015; Van Geest et al. 2016).

2.3 Estimation of K_d for Selenite

Uptake of selenite is not affected by aqueous sulphate concentration, although there is evidence that $K_{d,selenite}$ varies inversely with aqueous selenite concentration (DeForest et al. 2016; Nautilus 2018) and several studies have shown an inverse relationship with phosphate concentration (Riedel and Sanders 1996; Vriens et al. 2016). To our knowledge, the effect of phosphate on selenite uptake has not been quantified and data do not exist to derive a quantitative relationship. The effect of aqueous selenite concentration was characterized by Nautilus (2018) using laboratory algal uptake tests with selenite spiked into Elk Valley waters. Results of the Nautilus (2018) study are shown in Figure 2 and summarized below.

Nautilus (2018) measured selenite uptake in *P. subcapitata* 7-day tests and observed a negative correlation between K_d and aqueous selenite concentration between approximately 0.7 and 10 µg/L selenite (data reproduced in Figure 2). Previous studies with *P. subcapitata* have shown that 7 days is sufficient to approximate steady state under these test conditions (Van Geest et al. 2016). It was not possible to characterize the effect of conditions that differ between laboratory and field (e.g., phosphate concentration, algal growth rate). Therefore, for the present analysis it was assumed that the Nautilus (2018) laboratory data would provide a reasonable estimate of $K_{d,selenite}$ in field periphyton. Other published data (summarized below) give similar $K_{d,selenite}$ estimates to the Nautilus (2018) model. Uncertainty associated with this assumption is discussed in Section 3.0.

The Nautilus (2018) equation ($p < 0.0001$; $r^2 = 0.99$) is:

$$\log_{10}K_{d,selenite} = 3.02 - 0.598 \times \log_{10}[Se(IV)]_{aq} \quad (\text{Equation 5})$$

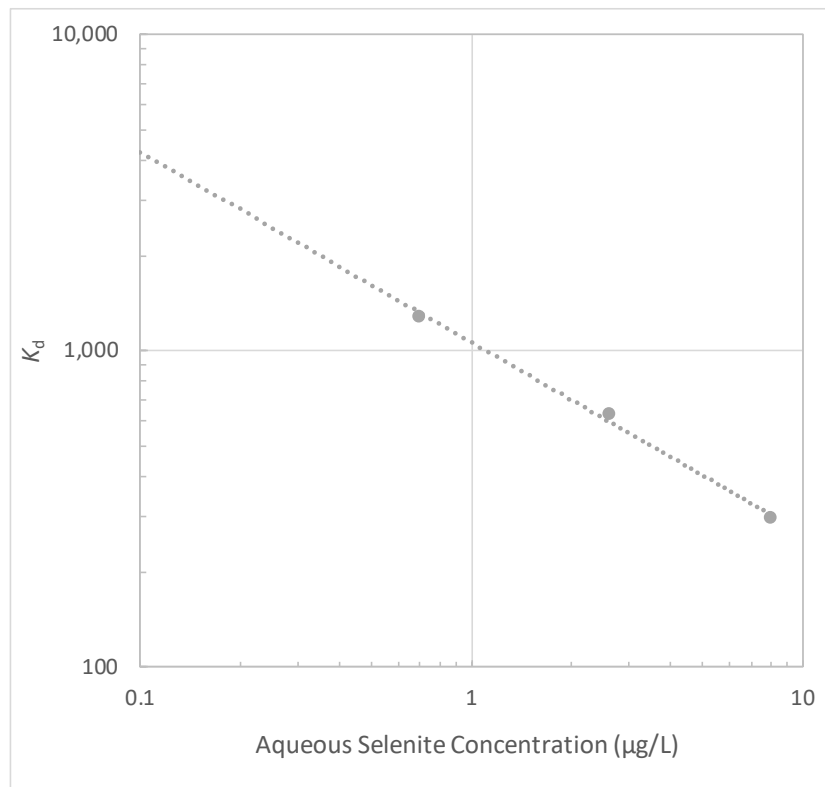


Figure 2: Measured selenite K_d and fitted regression from Nautilus (2018) uptake studies with Elk Valley waters.

Equation 5 gives $K_{d,selenite}$ values of approximately 1,000 at an aqueous selenite concentration of 1 µg/L. Extrapolating Equation 5 down to 0.1 µg/L aqueous selenite gives a $K_{d,selenite}$ of approximately 4,000. The range of $K_{d,selenite}$ values calculated using Equation 5 is supported by the results of published studies. Conley et al. (2009, 2011, 2013) exposed mixed periphyton cultures to approximately 1 to 20 µg/L aqueous selenite in laboratory water. Data reported in Conley et al. (2009, 2011) indicate apparent $K_{d,selenite}$ values on the order of 1,000 to 4,000. However, aqueous selenite concentrations declined by up to 90% through the course of these experiments and Conley et al. (2013) reported shifts in selenium speciation in the test vessels, making it difficult to calculate reliable K_d values. Conley et al. (2009, 2011) also note that the duration of these exposures (between 5 and 9 days) did not appear to have been sufficiently long for the periphyton to achieve steady-state internal selenium concentrations. $K_{d,selenite}$ values measured at the end of these exposures may therefore underestimate what would be observed under longer-term exposures. Based on uptake and elimination rates estimated from data reported in Conley et al. (2013), DeForest et al. (2016) calculated a steady-state $K_{d,selenite}$ of 3,659 for the Conley et al. (2013) experiment. Applying similar calculations to those used by DeForest et al. (2016), Riedel and Cole (2001) estimated a steady-state $K_{d,selenite}$ of 1,647 for periphyton at 10 µg/L selenite. Graham et al. (1992) estimated a time-integrated $K_{d,selenite}$ of 2,800 for periphyton in a 318-day mesocosm experiment (aqueous selenite concentrations not reported). Applying the DeForest et al. (2016) approach to data reported by Besser et al. (1993) for the green alga *Chlamydomonas reinhardtii* exposed to selenite for 48 hours indicated a steady-state $K_{d,selenite}$ near 1,100 at 1 µg/L selenite and lower $K_{d,selenite}$ values at higher aqueous selenite concentrations.

2.4 Estimation of K_d for Other Selenium Species

Several organoselenium species have been detected in AWTF effluent that are not detectable in influent water. AWTF effluent contains dimethylselenoxide (DMSeO), methylseleninic acid (MSe(IV)), and a fraction of “missing” selenium (a consistent disparity between total or dissolved selenium quantified by mass spectrometry and the sum of detected species quantified by ion chromatography) that has tentatively been identified as dimethylselenide (DMSe). AOP treatment reduces concentrations of DMSeO and MSe(IV), often to non-detectable levels, and has no consistent “missing” selenium, but contains a detectable fraction of “unknown” selenium (a selenium peak in the chromatogram that has not been identified).

The influence of organoselenium and missing or unknown selenium species on K_d is illustrated in Figure 3 (modified from a figure prepared by Nautilus). Nautilus (2018) tested the uptake of selenium from AWTF effluent pre-AOP treatment and post-AOP treatment during AOP pilot testing. To evaluate the contribution of species other than selenate and selenite, observed K_d from these tests (reflecting all selenium species present) was plotted in comparison to a K_d calculated from measured concentrations of selenate and selenite only (i.e., P_{other} in Equation 2 was set to zero). Symbols near the 1:1 line on Figure 3 (observed = predicted) indicate that measured selenate and selenite concentrations alone were sufficient to explain observed uptake by algae, whereas symbols above the 1:1 line (observed > predicted) indicate that other selenium species are contributing meaningfully to uptake.

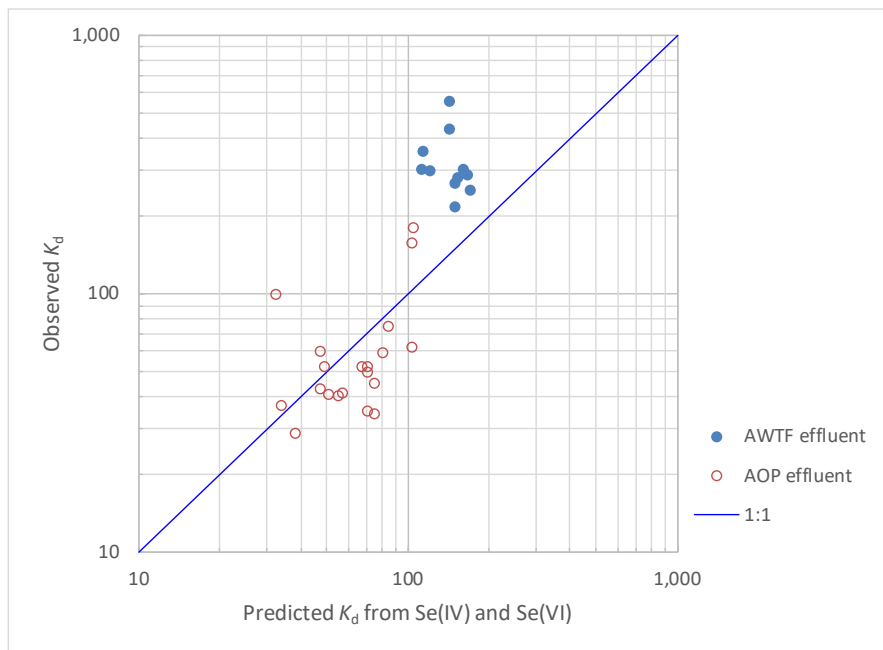


Figure 3: Comparison of observed and predicted K_d in laboratory algal uptake tests (Nautilus 2018).

2.4.1 $K_{d,other}$ for AWTF with AOP

Most results for AWTF effluent following AOP treatment fell near or below the 1:1 line on Figure 3, indicating that a model based on only selenate and selenite is sufficient to predict bioaccumulation. This finding indicates that organoselenium and unknown selenium species in AOP effluent are not contributing meaningfully to uptake by algae in this test. A small number of samples fell above the 1:1 line on Figure 3; however, concentrations of organoselenium and unknown selenium in those samples were similar to or lower than other tested samples (Nautilus 2018). To account for the potential contribution of other selenium species, it is recommended that a prediction tool for this effluent include a term for P_{other} and $K_{d,other}$. However, at present there is limited information available to estimate $K_{d,other}$. Given the generally good concordance on average between observed K_d and K_d calculated from selenate and selenite, it is expected that $K_{d,selenite}$ would provide a conservative estimate of $K_{d,other}$ for AWTF with AOP. It is recommended that this estimate be evaluated by comparison to field data collected after AOP is operational at the WLC AWTF.

2.4.2 $K_{d,other}$ for AWTF without AOP

All results for AWTF effluent without AOP treatment fell above the 1:1 line on Figure 3, indicating that AWTF effluent contains organoselenium or other selenium species that contribute meaningfully to uptake by algae. A prediction tool for this effluent would require an estimate of $K_{d,other}$.

Estimates of $K_{d,other}$ for AWTF effluent without AOP can be inferred from observed bioaccumulation and speciation data from Line Creek downstream of the WLC AWTF by using the calculation method in Section 2.2 to factor out the contribution of selenite and selenate to total bioaccumulation. This analysis was conducted by parameterizing Equation 2 with data collected by Teck in 2017, as follows:

- Equation 2 was rearranged to solve for $K_{d,other}$ to give:

$$K_{d,other} = (K_{d,mixture} - (K_{d,selenate} \times P_{selenate}) - (K_{d,selenite} \times P_{selenite})) / P_{other} \quad \text{(Equation 6)}$$

- $K_{d,mixture}$ was calculated from paired aqueous total selenium and benthic invertebrate selenium concentrations collected by Teck in 2017 in Line Creek downstream of the WLC AWTF (Table 2). $K_{d,mixture}$ was estimated by dividing measured benthic invertebrate selenium concentrations by an average trophic transfer factor of 2.8 (Presser and Luoma 2010) and then dividing the calculated value by the concurrent aqueous total selenium concentration.
- $K_{d,selenate}$ was calculated using Equation 4 (Section 2.2).
- $K_{d,selenite}$ was calculated using Equation 5 (Section 2.3).
- $P_{selenate}$, $P_{selenite}$, and P_{other} were calculated from selenium speciation data collected by Teck in 2017 at the same biological monitoring stations (Table 2). Proportions were calculated as the ratio of measured concentration to the sum of quantified selenium species for reasons discussed in Section 2.2.
- The resulting calculated $K_{d,other}$ values were 13,056 at LILC3 (near the point of discharge; at LC_LC3), 10,692 at LIDSL (downstream of the South Line Creek confluence; at LC_LCDSSLCC), and 23,375 at LI8 (near the mouth of Line Creek; at LC_LC4). Values calculated from LILC3 and LIDSL data may be more reliable estimates because loss terms such as dilution, uptake, and volatilization result in lower concentrations of all species at LI8 relative to upstream stations, increasing the potential to underestimate P_{other} (and thereby over-estimate $K_{d,other}$) due to some species being near or below detection. Alternatively,

these estimates may indicate that $K_{d,other}$ varies inversely with concentration, as has been observed for $K_{d,selenate}$ (Figure 1) and $K_{d,selenite}$ (Figure 2).

Table 2: Calculation of K_d for ‘Other’ Selenium Species in AWTF Effluent from 2017 Line Creek Monitoring Data

Site	Benthos [Se] (mg/kg dw)	Total [Se] ($\mu\text{g/L}$)	$P_{selenate}$	$P_{selenite}$	P_{other}	$K_{d,mixture}$	$K_{d,selenite}$	$K_{d,selenate}$	$K_{d,other}$
LILC3	23.9	40.8	97.5%	1.45%	1.08%	209	1,458	48	13,056
LIDSL	13.6	34.9	98.5%	0.83%	0.62%	139	2,242	55	10,692
LI8	11.4	28.0	99.2%	0.57%	0.26%	145	3,209	67	23,375

It is difficult to evaluate the estimates derived above relative to published studies because few studies have tested the uptake of species other than selenite and selenate, and to our knowledge no published data exist to characterize the K_d of DMSeO or MSe(IV) . The only organoselenium species that has been studied in laboratory uptake experiments is the amino acid selenomethionine (SeMet). Most of these studies have focused on short-term uptake kinetics and do not report sufficient information to estimate K_d . However, the available information (summarized below) indicates that the K_d for SeMet is likely on the order of 15,000 to 36,000, approximately 5 to 10 \times higher than the range of K_d for selenite.

Relevant studies of SeMet uptake are summarized below to provide an indication of a range of K_d values potentially relevant to organoselenium species:

- Riedel et al. (1991) compared uptake of radiolabelled selenate, selenite, and SeMet by three algal species (blue-green, green, and diatom) in a time course over a 24-hour exposure at aqueous concentrations ranging from 50 to 200 $\mu\text{g/L}$, and in a separate experiment following a 6-hour exposure at aqueous concentrations ranging from 1 to 50 $\mu\text{g/L}$. Uptake of SeMet in the time course experiment was faster than the inorganic forms and in two of the three algal species appeared to saturate after 6 to 12 hours. Algal SeMet concentrations also appeared to saturate in the 6-hour exposure experiment, with similar algal concentrations observed between 5 and 50 $\mu\text{g/L}$ SeMet in the green alga, and between 20 and 50 $\mu\text{g/L}$ in the blue-green alga (i.e., apparent K_d would have decreased with increasing aqueous SeMet concentration). SeMet did not saturate in the diatom species. Because algal concentrations were expressed as $\times 10^{-15}$ g/cell, K_d could not be estimated from these data. Algal concentrations following SeMet exposure were generally on the order of 10 \times to 100 \times higher than following exposure to selenate or selenite, but it is unknown whether this reflects similarly large differences in steady-state K_d or simply faster uptake of SeMet within the limited exposure period.
- Fournier et al. (2006) compared the uptake of selenate, selenite, and SeMet by a unicellular green alga (expressed as pg Se/ 10^5 cells) over a 1-hour exposure at aqueous concentrations ranging from 200 to 2,000 $\mu\text{g/L}$. Uptake of SeMet was faster than the inorganic forms and exhibited saturation, with similar algal concentrations observed across the entire tested range of aqueous SeMet concentrations (i.e., apparent K_d would have decreased 10-fold with increasing aqueous SeMet concentration). Uptake of SeMet over the 1-hour exposure was 5 \times to 50 \times higher than uptake of either inorganic species. However, it is unlikely that any of the treatments attained steady state, and it is unknown whether the very high aqueous concentrations tested are relevant to field conditions.

- Besser et al. (1993) compared the uptake of selenate, selenite, and SeMet by a green alga over a 24-h exposure. Algae were exposed for 48 hours but interpretation of data after 24 hours was confounded by 50 to 70% declines in aqueous selenite and SeMet concentrations. Apparent K_d of SeMet at 24 hours varied inversely with aqueous SeMet concentration, ranging from 36,300 at 0.1 $\mu\text{g/L}$ SeMet to 5,320 at 10 $\mu\text{g/L}$ SeMet. Apparent K_d values for SeMet were 5 to $10\times$ greater than those for selenite at the same aqueous concentration.
- Baines et al. (2001) compared the uptake of selenite and organoselenides by six species of marine algae over a 5-day exposure. Organoselenides were obtained by lysing algae cultured in radiolabelled selenite, and therefore represent a natural mixture of forms that may occur following biological reduction. Because algal selenium concentrations were expressed on a volumetric basis (ng/m^3), it was not possible to calculate K_d for either selenium species. However, Baines et al. (2001) showed similar uptake in the selenite and organoselenide exposures by all six algal species, indicating that K_d for organoselenides may be similar to $K_{d,\text{selenite}}$ under these conditions.
- Kiffney and Knight (1990) compared the uptake of selenate, selenite, and SeMet by a cyanobacterium over a 10-day exposure. The selenate and selenite treatments appeared to attain steady state within the exposure period, but tissue selenium concentrations in SeMet treatments were still increasing at the end of the experiment. These results have high uncertainty because the authors reported substantial loss of SeMet through the experiment and an “unpleasant odour” that they attributed to microbial methylation and volatilization of selenium. Also, apparent K_d would have been strongly influenced by exponential growth in the lower SeMet concentration treatments (0.3 to 0.7 d^{-1} growth), whereas the highest SeMet treatment exhibited negative growth. Kiffney and Knight (1990) reported apparent K_d values for SeMet approximately $5\times$ to $20\times$ higher than the apparent K_d of selenite, ranging from 1,500 to 20,000 at SeMet concentrations between 50 and 300 $\mu\text{g/L}$.

Overall, the basis for drawing conclusions about the K_d of SeMet or other organoselenium species is limited. Estimates range from equal to that of selenite (Baines et al. 2001) to $100\times$ higher (Riedel et al. 1991). The results of Fournier et al. (2006) and Riedel et al. (1991) further suggest that the K_d of organoselenides may decline with increasing aqueous concentration. An additional source of uncertainty is that most of the experiments described above used SeMet, which may not accurately reflect environmentally relevant organoselenide mixtures (LeBlanc and Wallschlager 2016). Estimates from the short-term experiments of Riedel et al. (1991) and Fournier et al. (2006) may not be reliable because of the potential for these data to be influenced by differences in short-term uptake kinetics among selenium species. Data from Besser et al. (1993) may also be influenced by short-term uptake kinetics, but provide an indication of how apparent K_d after a 24-hour exposure varies with aqueous selenium concentration. The longer-term experiments of Baines et al. (2001) and Kiffney and Knight (1990) are more relevant to steady-state K_d . Although the results of Baines et al. (2001) used an environmentally relevant mixture of organoselenides (algal lysate) and a range of algal species, insufficient data were provided to calculate K_d . Furthermore, it remains uncertain whether K_d estimates for SeMet accurately reflect uptake of the mixture of organoselenium species released from an AWTF, and published data do not currently exist to reduce this uncertainty.

Overall, the information summarized above indicates that a reasonable estimate of $K_{d,\text{other}}$ for AWTF effluent without AOP would likely be in the range of 10,000 to 20,000.

2.5 Evaluation of Performance

To provide an initial evaluation of the performance of the bioaccumulation tool, predicted K_d estimates were plotted in comparison to measured K_d in areas of the Elk Valley not affected by the WLC AWTF. Predicted K_d was calculated assuming 1% of reported aqueous total selenium was present as selenite. Measured K_d was calculated from benthic invertebrate tissue selenium concentrations reported by 2012 and 2015 RAEMP monitoring at lotic sites with aqueous total selenium concentrations ranging from 1 to almost 700 $\mu\text{g/L}$ (Minnow 2018; same data plotted on Figure 1; $n = 117$).

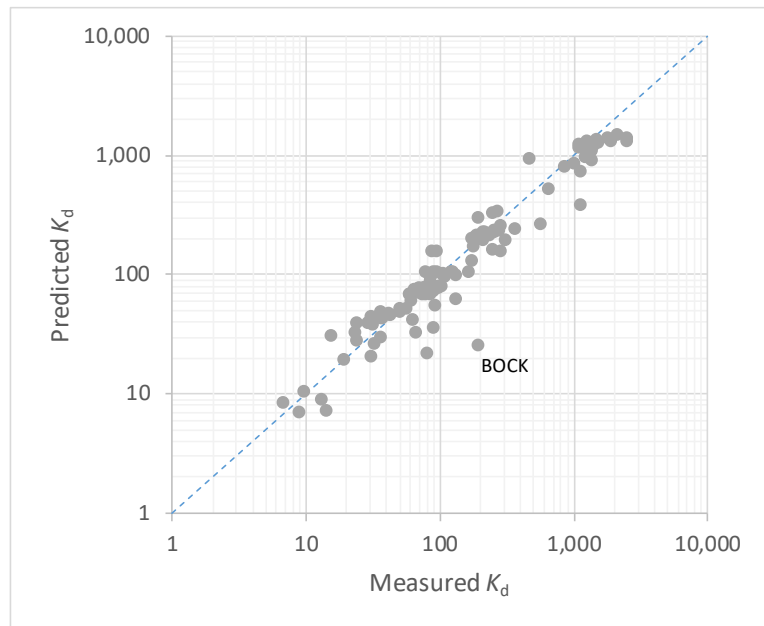


Figure 4: Comparison of predicted K_d to measured K_d at lotic sites in the Elk Valley.

Overall, Figure 4 indicates good agreement between predicted and measured K_d in mine-affected areas of the Elk Valley. More than half of predicted values were within a factor of 1.2 of measured (i.e., $\pm 20\%$) and 80% were within a factor of 1.5 (i.e., $\pm 50\%$). Some locations (notably Bodie Creek, annotated BOCK on Figure 4) exhibited several-fold higher measured K_d than predicted K_d , which may indicate that the proportion selenite is greater than 1% at these locations.

It is not possible at this time to evaluate performance of the tool in areas affected by AWTF effluent (because all available data were included in the derivation) or in areas affected by AOP effluent (because the AOP is not yet constructed).

3.0 UNCERTAINTY ASSESSMENT

The analysis presented herein combined available data from laboratory and field studies, each of which has particular strengths and limitations. Field data characterize actual bioaccumulation in the Elk Valley, reflecting water quality, biological community composition, and other factors that affect selenium bioaccumulation. However, field data are limited to characterizing only those combinations of selenium species and water quality factors that occur at the sampled sites. Field data are also subject to spatial and temporal variability in water quality, biological communities, and tissue selenium concentrations that may not be fully characterized by sampling. Laboratory studies provide greater control over selenium speciation and known modifying factors, but are necessarily

simplified systems that may not completely simulate all relevant conditions in the field. In particular, laboratory studies are conducted with single algal species or cultured periphyton communities, grown under optimized conditions, and exposed to selenium for periods that may not be sufficient to achieve steady state K_d .

The present analysis attempted to offset the limitations of each type of data by combining and comparing the results of laboratory and field studies. However, as with any predictive study, the results presented herein are affected by various types of uncertainty. The following bullets evaluate major identified sources of uncertainty in the analysis:

- **Additivity and Independence.** The framework for the bioaccumulation tool described in Section 2.1 assumes that each selenium species contributes to total bioaccumulation additively and independently of other species. These assumptions are consistent with the current understanding that different selenium species are taken up by algae via different mechanisms that are affected by different modifying factors (e.g., selenate and sulphate; selenite and phosphate), but that all selenium species are converted into the same organic forms within the algal cell. The analysis presented on Figure 3 supports these assumptions for selenate and selenite (i.e., an additive calculation of selenite and selenate uptake was able to explain observed total uptake). However, to our knowledge the assumptions of additivity and independence have never been directly tested by other investigators.
- **Selenate K_d Estimates.** The estimation method described in Section 2.2 relies on laboratory and field data, all of which are potentially affected by sampling and analytical error. This uncertainty was offset by including as many sampling events as were available into the analysis ($n = 18$) and was evaluated by comparing estimated K_d values against both field and laboratory data. Uncertainty associated with sampling and analysis of periphyton was avoided by basing the analysis on benthic invertebrate data. Overall, Equation 4 aligned well with laboratory data and was slightly lower than field data, consistent with the expected contribution of selenite in the field. The most important uncertainty in the estimation of $K_{d,selenate}$ is likely the input values for $K_{d,selenite}$ (discussed in the next bullet).
- **Selenite K_d Estimates.** The Nautilus (2018) data described in Section 2.3 reflect uptake of selenite spiked into Elk Valley waters, and therefore were selected as the most site-relevant data available. The algal uptake study method also allowed steady state to be attained within 7 days (Van Geest et al. 2016) and with minimal depletion of aqueous concentrations, reducing the confounding effects of variable exposure concentrations and shifts in selenium speciation that have been observed in other studies (e.g., Conley et al. 2013). However, Equation 5 is based on a small dataset ($n = 3$) at selenite concentrations higher than those typical of Elk Valley waters. The Nautilus (2018) method also involves culturing of algae under conditions that differ from the field (notably, with added phosphate and other nutrients). It is not possible with the information available to validate how well these laboratory-based $K_{d,selenite}$ estimates represent selenite uptake at lower concentrations and under field conditions. Other laboratory studies have reported $K_{d,selenite}$ values of similar magnitude at similar aqueous selenite concentrations. However, no laboratory studies were identified that studied selenite uptake at lower concentrations, and no field data are known to exist that reflect uptake of selenite alone.
- **K_d Estimates for Other Selenium Species in AOP Effluent.** Based on the analysis shown in Figure 3, it was concluded that other selenium species do not contribute meaningfully to selenium bioaccumulation at the concentrations present in AOP effluent. Because the selenium species present in AOP effluent have not been identified, it is not possible at this time to evaluate this conclusion further with laboratory testing. It is

also not known whether sample preparation and/or test conditions may have affected speciation or uptake of unknown selenium species in these samples. Adoption of $K_{d,selenite}$ as a preliminary estimate of $K_{d,other}$ for AOP effluent is expected to provide a conservative prediction of selenium bioaccumulation. This expectation should be validated with field data when the AOP is operational.

- **K_d Estimates for Other Selenium Species in AWTF Effluent.** The analysis presented in Section 2.4 used field data from Line Creek during AWTF operation to estimate the combined K_d of other selenium species present in AWTF effluent. This analysis was based on a small dataset ($n = 3$) and these data are potentially affected by sampling and analytical error. The analysis gave K_d estimates consistent with the limited published data from laboratory studies with organoselenides. However, the selenium species present in AWTF effluent have not been completely characterized and no studies are known to exist to characterize the uptake of the species that have been identified (DMSeO and MeSe(IV)).
- **Assumed Trophic Transfer Factor.** The calculations presented in Section 2.0 adopted a generic trophic transfer factor of 2.8 from Presser and Luoma (2010) to convert measured benthic invertebrate tissue selenium concentrations into estimated periphyton tissue selenium concentrations. This generic value is consistent with data compiled for the EVWQP that indicated trophic transfer factors ranging from approximately 2 to 4 within the concentration range considered herein (Teck 2014). The value adopted does not affect the interpretation of field data, as long as the same value is used consistently throughout.

4.0 SUMMARY

The selenium bioaccumulation tool presented herein is recommended for use as follows:

- In areas unaffected by AWTFs, selenium bioaccumulation can be modelled using Equations 1 and 2 with terms for selenate and selenite only (as in Section 2.5). $K_{d,selenate}$ would be estimated using Equation 4 and $K_{d,selenite}$ would be estimated using Equation 5. However, it is recommended that the EVWQP model remain the primary tool for predicting bioaccumulation in areas unaffected by AWTFs. The EVWQP model was derived from a larger dataset than could be considered in the present analysis, and therefore would be expected to make reliable predictions across a wider range of conditions.
- In areas affected by AWTF with AOP, selenium bioaccumulation should be modelled using Equations 1 and 2 with terms for selenate, selenite, and other species. $K_{d,selenate}$ would be estimated using Equation 4 and $K_{d,selenite}$ would be estimated using Equation 5. As discussed in Section 2.4.1, $K_{d,other}$ for AOP effluent would be estimated as equal to $K_{d,selenite}$.
- In areas affected by AWTF without AOP, selenium bioaccumulation should be modelled using Equations 1 and 2 with terms for selenate, selenite, and other species. $K_{d,selenate}$ would be estimated using Equation 4, $K_{d,selenite}$ would be estimated using Equation 5, and $K_{d,other}$ would be estimated in the range of 10,000 to 20,000.

5.0 CLOSURE

We trust that this technical memorandum is sufficient for your present needs. Should you have any questions or require anything further, please contact the undersigned.

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6.0 STATEMENT OF LIMITATIONS

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