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TECHNICAL ARTICLE

Development of a Geochemical Model to Predict Surface Water Discharge Compositions in Northern Saskatchewan: Applications of PHREEQC and PhreePlot to Identify Active Geochemical Processes

John Mahoney[1] · **Ryan Frey**[2] · **Valerie Plagnes**[2,3] · **Brett Mitchell**[2] · **John Rowson**[2]

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Abstract
Geochemical models were developed using PHREEQC to estimate the composition of three downstream water bodies that accept uranium (U) mill discharge waters and additional mine-related waters. The models included: mixing; dilution by rain, snow, and groundwater; evapoconcentration; equilibration with selected phases; and surface complexation reactions. Starting with a water balance that quantified the flux of the discharged waters, the models used monthly sample compositions collected from the major discharge sources, as well as constant composition samples that represent ground and surface water sources. A 5 year period was evaluated. Mixing and dilution played the dominant role in attenuation of the major ions. Conservative elements included Na, K, Cl, and Mg and attenuation was noted for some metals. Hydrous ferric oxide (HFO) forms in the discharge zone, resulting in a drop in Fe concentrations. However, concentrations were not consistent with the published solubility constant for ferrihydrite, which was modified using a smaller HFO site density than is typically reported to better fit the observed As concentrations in Sink Lake, using PhreePlot to match the observed Fe concentrations. The models were also evaluated for U using PhreePlot's fitting capabilities. For 4 years, U acted as a conservative element with little attenuation, but later, U displayed some attenuation.

Keywords Surface water discharge · PhreePlot · Arsenic · Molybdenum · Uranium

Introduction

The quantitative prediction of environmental impacts to surface water bodies is an important aspect in the permitting of many mining and milling operations throughout the world. When detailed hydrologic data is coupled with a geochemical modeling program such as PHREEQC (Parkhurst and Appelo 2013), more accurate predictive models can be prepared that incorporate well-documented geochemical processes. Further understanding of the nature and extent of active geochemical processes can be gleaned when selected model parameters are optimized through data fitting through programs such as PhreePlot (Kinniburgh and Cooper 2011).

In Canada, uranium (U) mine and mill projects are required to predict the long-term surface quality of water in downstream environments throughout operations, and up to 10,000 years into the future. Capturing important geochemical processes in a modelling program has enabled companies to commit to processing additional ore sources, knowing that regulatory commitments will continue to be achieved. Modelling provides the capacity to back-calculate the remedial capacity of the natural receiving environment, creating meaningful limits of effluent release and associated milling production.

The JEB Mill at Orano Canada's McClean Lake Operation produces yellowcake U from various ores located in the eastern Athabasca Basin in northern Saskatchewan, Canada (Fig. 1). Many of these high grade ores contain trace metals such as

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JohnMahoney: Deceased.

✉ Ryan Frey
ryanfrey427@gmail.com

Brett Mitchell
Brett.Mitchell@Orano.group

[1] Mahoney Geochemical Consulting LLC, 892 S. Newcombe Way, Lakewood, CO, USA

[2] Orano Canada (formerly AREVA Resources Canada) Inc., PO Box 9204-817, 45th St.,, Saskatoon, SK S7K 3X5, Canada

[3] Sorbonne Université, UPMC Univ. Paris 06, CNRS, EPHE, UMR 7619 Metis, 4 Place Jussieu, 75005 Paris, France

arsenic (As) and molybdenum (Mo). Dedicated treatment systems have been implemented within the plant to stabilize trace metals into solid phases that are disposed with the tailings in the JEB tailings management facility (TMF) (Mahoney et al. 2007). Tailings, consisting of processed ores and discharge water, are disposed through a sub-aqueous system into the former JEB pit, where a barge is used to disperse the tailings throughout the TMF. An underdrain collection system and dewatering operations were implemented to help control the water level in the JEB TMF pit lake. Additionally, large quantities of water are handled through various milling operations; this water is treated and ultimately discharged to the surface water system as part of the Sink Vulture treated effluent management system (SVTEMS; Fig. 2). The hydrologic setting and description of the water balance used in the model described below, as well as a simple conceptual model of the water balance were described by Plagnes et al. (2017). Water derived from the mining and milling operations are discharged into an area above Sink Reservoir, which flows into Vulture Lake, and finally into McClean Lake. Most of the chemical reactions occur in the discharge area as the waters are mixed and exposed to the atmosphere. Dilution, in the form of mixing with ambient waters, further reduces concentrations along the flow path.

The purpose of this effort was to develop a model of the hydrogeological and geochemical processes operating in the SVTEMS to estimate long term concentrations of major and trace constituents [mainly As, Mo, selenium (Se), and U] in the surface water system near the McClean Lake operation. One of the requirements of a predictive model is a detailed understanding of the geochemical processes that control the various dissolved constituents along the discharge pathway. A simple proof of concept model, using annual average solution compositions and 12 timesteps (Mahoney and Frey 2014) demonstrated that this overall approach had merit, and so a larger, more detailed model was prepared, based on 60 months of continuous data.

Conceptual Model

The SVTEMS operation is a straightforward discharge system and so a relatively simple conceptual model was developed. The model mixes the three primary waters in the drainage area immediately above Sink Reservoir: the JEB TMF dewatering water, the JEB water treatment plant (WTP) discharge, (which tends to have the greatest dissolved load), and the SUE water treatment plant discharge. Geochemical processes are permitted in this mixing zone. These processes include equilibration with atmospheric O_2 and CO_2, formation of ferrihydrite, and surface complexation reactions with the ferrihydrite surface. The equilibrated solution is saved and mixed with the water in Sink Reservoir, along with contributions from groundwater, runoff, and precipitation (rainfall mainly). Equilibration and precipitation of oversaturated phases is the next process. Evapoconcentration, which occurs only during the warmer months, and the associated removal of any oversaturated phase is permitted. Although the second mixture is allowed to equilibrate and oversaturated minerals can precipitate, the water is less concentrated than the first mixture, so the solution is further diluted, and removal of dissolved constituents is not likely except for changes in gas phases.

Further mixing and dilution of the Sink Reservoir solution takes place in Vulture Lake where the influent Sink Reservoir solution mixes with the ambient Vulture Lake waters. More dilution occurs through groundwater influx, runoff, and precipitation that feed Vulture Lake. The same equilibration and evapoconcentration processes are included in this step, but the additional dilution has rendered most phases undersaturated.

Finally, the Vulture Lake solution enters McClean Lake and undergoes even further dilution. Much of this dilution is from Collins Creek, which contributes 35–75 % of the diluting water in this mixing step.

The rationale for selecting the mineral equilibration reactions was based on a review of saturation indices, and comparison of the observed concentrations to the modeled solution compositions generated after mixing. Equilibration with O_2 and CO_2 gas was included. Another objective was to keep the model as simple as possible, with a minimum number of precipitating phases. A considerable effort was spend updating the thermodynmic database used in these models; details are included as a Supplemental Information file.

Much of the surface water and groundwater are dilute and have little potential to precipitate mineral phases. The JEB WTP discharge had the potential to precipitate gypsum ($CaSO_4 \cdot 2H_2O$) and $CaMoO_4$ under some conditions. The pit dewatering solution had some ferrous iron, which had the capability to oxidize and precipitate as ferryhydrite [$Fe(OH)_3$]. The concentrations of As, U, and Se were generally too low to allow the precipitation of end member phases, such as scorodite [$FeAsO_4 \cdot 2H_2O$] or schoepite [$UO_2(OH)_2 \cdot H_2O$]. Consequently, surface complexation reactions, using the diffuse layer model on hydrous ferric oxide (HFO), were used to lower trace metal concentrations.

Model Setup

To estimate the different proportions of water in any location at any time, a detailed water balance was prepared using the monthly flow rates for the different waters that entered the lakes (Plagnes et al. 2017). This water balance was developed and calibrated at a daily time step for the period 2004–2015 and validated for 2016–2017. A mass balance model was developed for conservative elements,

Fig. 1 Site location map. McClean Lake area is in red

such as chloride (Cl), for the same period to validate the proportion of inputs and outputs of water in the water balance model; once calibrated, the water balance model was run for monthly time steps. For the model parameters, the monthly model still perfomed very well (Nash and Sculitte criteria reaches 0.91). The water balance for earlier samples, starting in 2000, was based on monthly summaries in the environmental monitoring reports. In this respect, the water balance model is similar to a version of the geochemical model called the discrete model, described below. The geochemical models were set up using PHREEQC (version 3), allowing reactions to be included and defined based on well documented processes, such as mineral precipitation and surface complexation. Furthermore, the predictive model(s) uses solution compositions derived from earlier steps in the modeling process.

The availability of geochemical modeling programs such as PHREEQC and the fitting capabilities in PhreePlot provide a set of methodologies that permit the rigorous fitting of various model parameters such as solubility product constants by adjusting saturation indices, as well as site densities for surface complexation reactions. The optimization capabilities provided in PhreePlot provide a new tool to better quantify the nature and extent of reactions in models of this type.

The models are limited to a series of batch reactions, and some of these assumptions do not fully represent the complexity of this system. However, the mixing zone can be

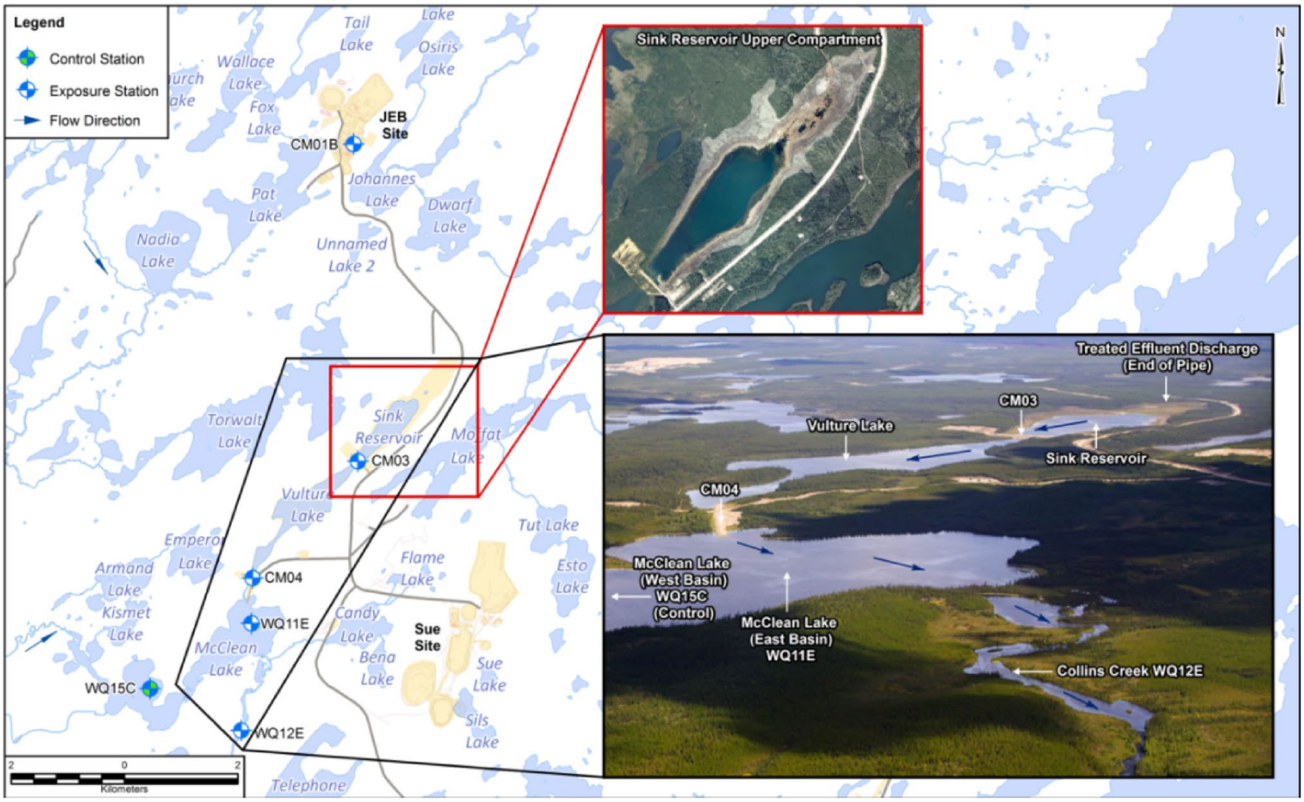

Fig. 2 Close up view of the SVTEMS discharge area. Discharge (mixing zone) is the open area northeast of Sink Reservoir

considered to be a batch reactor with a limited residence time; it was assumed that reactions do not always reach a final equilibrium state. These models used PHREEQC's equilibrium_phase and surface keyword blocks[1] to handle the most likely chemical reactions. In most of the scenarios, the precipitated phases were removed from further calculations; the initial list of phases was then used for the next step. There is a mixing zone at the start of the model setup and phases tend to drop out in this zone, which means that they are not available to react in subsequent steps. When dealing with a flowing and reacting system, reaction rate information may be used to further improve the model. However, kinetic processes were not incorporated in this model because the most reliable kinetic information is related to dissolution reactions and this model occasionally uses precipitation processes, which are more difficult to model. To some extent, the fittings performed by PhreePlot, specifically the adjustment to the saturation indices for $Fe(OH)_3$, provide a work around. In evaluation of trace metal attenuation properties, the model was designed to provide a self-consistent synthesis of the observed data. Only solution compositions were used as input data.

Water Compositions

Several different water sources are discharged at the northern end of Sink Reservoir, including the JEB WTP treated waters and waters from a secondary treatment plant located at the SUE mining operations, which consists of several open pit mines (Fig. 3). A Piper trilinear diagram, based on the same data, was used to generate Stiff diagrams (Supplemental Fig. S-1) in the Supplemental Information file. Waters from the JEB pit dewatering operation also contribute, although currently dewatering has ceased. The largest percentage of water originates from the JEB water treatment plant (JWTP), which also contributes most of the loading to the SVTEMS.

The low mineralized waters representing the JEB TMF dewatering sample and the ambient groundwater sample are based on a limited number of samples: periodic analyses indicate that these concentrations have remained constant, so it was decided not to add further complications. Based on their TDS concentrations, ambient waters, such as the surface water runoff and waters from Collins Creek, are considered to be dilute and tend to have a calcium-bicarbonate "fingerprint". The waters impacted by JWTP discharge tend to have a calcium-sulfate "fingerprint" and higher total dissolved solids (TDS) concentrations.

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[1] In this paper, we will use upper case to represent PHREEQC keywords.

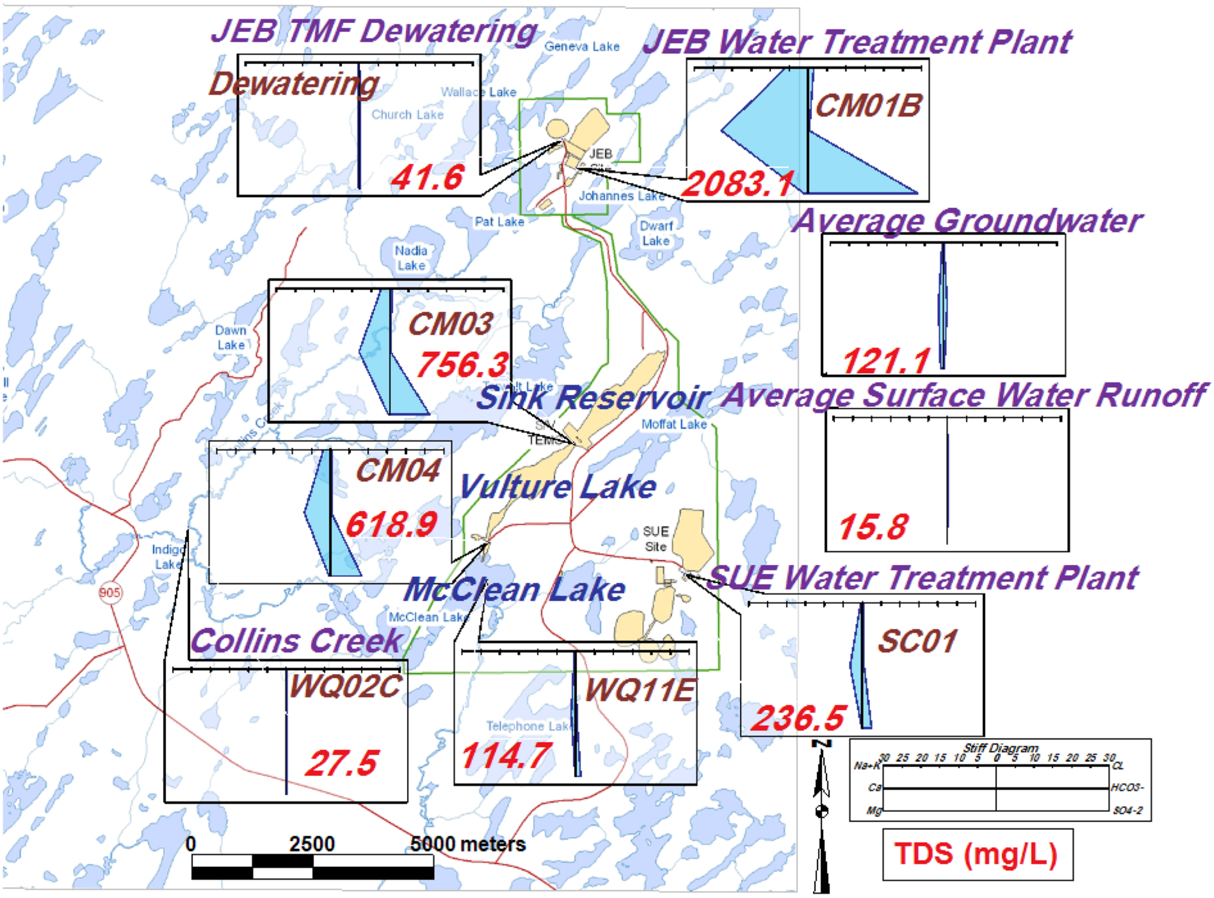

Fig. 3 Detailed sample locations and Stiff Diagrams of waters in this study. Average concentrations used to calculate values in this figure. Samples collected from as early as 1998 (month not specified) through October 2013. Ground water and surface water runoff do not have specific locations. Average TDS values (in mg/L) are included in red. The locations that identify the permitting designations are also included

Uranium extraction at the McClean Lake mill uses sulfuric acid, and neutralization of tailings and raffinates is performed using lime.

Surface waters have the lowest TDS values and are represented by the surface water runoff and the Collins Creek sample (WQ02C); their dominant anion is bicarbonate. The next group of samples are the two groundwaters. The first sample represents the average groundwater composition near the discharge area. The second groundwater is from the JEB TMF (pit) dewatering operations. Compared to the surface waters, the groundwaters have slightly more sulfate, but they are still dominated by bicarbonate. The cation signatures are similar to the surface waters. The final group of samples represent the two mining-related discharges. The discharges include CM01B from the JEB water treatment plant and SC01, representing the SUE water treatment plant effluent. The three surface water bodies (Sink Reservoir, Vulture Lake, and McClean Lake) retain high proportions of sulfate and calcium. Precipitation (rain water and snow melt) was also included in the PHREEQC models.

Model Details

The model is predominantly a mixing model that allows for equilibration with solid phases (minerals) and gas phases (CO_2 and O_2) as well as surfaces, in the form of surface complexation reactions. The mixing proportions are based on a detailed water balance (Plagnes et al. 2017), which consists of flow rates for the different water sources for the 60 months the model represents. Evaporation during the warmer months is also included in the water balance and in the PHREEQC-based model. To accommodate requirements in PHREEQC, the water balance data were converted to percentages of the different source waters, and these percentages define the mixing proportions for each time step used for the PHREEQC model. Pertinent sections of the water balance provided the mixing proportions of the different solutions that enter Sink Reservoir, Vulture Lake, and finally McClean Lake.

Evapoconcentration is included as part of the water balance and model. We used the monthly evapotranspiration observed at the Brochet Lake, MB station in northern Manitoba (Environment Canada). It comprises evapotranspiration over the catchment area and direct evaporation over the water bodies from May to September for each year. The greatest amount of evapotranspiration was set at 120 mm/month for June and July. September has the least amount of evapotranspiration with 54 mm/month. Because the water bodies have different exposed surface areas, the amounts of evaporated water in each water body are proportional to their surface area. When evaporation was required, water was removed from the modeled solution using the REACTION keyword.

The water balance details were originally prepared at the daily time step using GoldSim® and recalculated at the monthly time step for the geochemical model. The tabulated data was exported into an Excel® Spreadsheet, which greatly facilitated the PHREEQC model setup, as the mixing proportions required for the PHREEQC models were calculated in Excel®. Eventually, as the models developed more detail, the complete PHREEQC models were prepared in Excel®. In preparation for the final simulation(s), a version of IPHREEQC.com (Charlton and Parkhurst 2011) was employed that runs within Excel®. The model used up to seven water sources that enter Sink Reservoir (waters 1 through 6 and 9). Additional waters representing the Vulture and McClean Lake compositions were also required for the later steps in the model(s). The waters used in the model included:

1. Water from the JEB Water Treatment Plant. The model uses monthly composite samples for this water source. This solution composition is used in the Sink Reservoir mixing calculation. This treated mill-generated water contains high sulfate and calcium concentrations, along with some trace metals, and provided most of the dissolved constituent load to the model. Its location is identified as CM01B on Fig. 3. The average flow rate for this source was 124,000 m^3/month. The maximum flow rate was 153,000 m^3/month, with a minimum flow rate of 67,200 m^3/month.
2. Water from the SUE Water Treatment Plant - The model uses monthly compositions for this water source. This water is more dilute than the JWTP solution. The location is identified as SC01 on Fig. 3. The average flow rate was 61,300 m^3/month. The maximum flow rate was 196,400 m^3/month, with a minimum flow rate of 0.0 m^3/month, when the plant was not operating.
3. Water from the JEB TMF dewatering operation—This was essentially dilute groundwater collected from a series of dewatering wells around the JEB pit. Pumping rates were adjusted to maintain the water level in the "pit lake". It retained a constant composition for the 5 years evaluated in the model. The average flow rate was 149,400 m^3/month. The maximum flow rate was 196,400 m^3/month, with a minimum flow rate of 0.0 m^3/month during a three-month period, when maintenance operations required a shut-down of the pit dewatering system.
4. Groundwater—This represents an average concentration of groundwater feeding the three lakes. It is also defined as having a constant composition. Average groundwater flows into Sink Reservoir, Vulture Lake, and McClean Lake were 57,000, 58,000, and 97,400 m^3/month, respectively.
5. Runoff (surface water)—This represented water that entered the lakes by surface runoff. It has a constant composition. Average runoff flows into Sink Reservoir, Vulture Lake and McClean Lake were 67,000, 85,400, and 108,700 m^3/month, respectively.
6. Water in Sink Reservoir at the start of the time step—the monitoring point is CM03 (Fig. 3). The discrete model uses monthly samples collected from this location. In the carryover model, the composition of the water in the Sink Reservoir at the start of the next time step is represented by the previous model-generated composition for Sink Reservoir.
7. Water in Vulture Lake at the start of the time step—the monitoring point is CM04. The model uses the solution composition of corresponding monthly samples for the discrete model. In the carryover model, the water in Vulture Lake is represented by the previous model-generated solution composition.
8. Water in McClean Lake at the start of the time step—the monitoring point is identified as WQ11E. The model uses monthly samples from this source in the discrete model. In the carryover model, the water in McClean Lake is represented by the previous model-generated solution composition.
9. Precipitation—This represented rainwater that fell on the lake surfaces in the warmer months. The model prepared a composition based on equilibration of pure water with CO_2 at 0.0004 atmospheres and O_2 at 0.21 atmospheres. No other major ions or trace metals were included.
10. Surface water from Collins Creek (WQ02C) was also added to the model. This dilute water only enters McClean Lake.

Waters 1 and 2 have variable compositions based on monthly samples collected using continuous samplers. The next three waters used constant compositions. The Sink Reservoir, as well as the Vulture and McClean Lake samples were also collected using continuous samplers. This provides a better sample than grab samples, given the residence time in these water bodies as well as the generally slow changes in load. Short term changes in the JWTP feed were the greatest potential issue related to disequilibrium, but for the most part, the averaging processes during mixing appear to limit potential excursions.

The initial modeling exercise (Mahoney and Frey 2014) provided a proof of concept that a reasonable model could be developed. That model used averaged annual compositions for the source waters and did not have enough resolution to assess seasonality issues. During the first 5 years of operation, starting in January 2000 up to December 2004, detailed samples of the lakes and other source terms were collected and provided a dataset that was robust enough to identify trends in the data.

Ultimately, two different models were developed. The first was a discrete model and used the measured concentrations in Sink Reservoir as well as Vulture and McClean Lakes to provide the ambient concentrations in each lake for each time step. Additional source term water compositions were included to make up the final modeled concentration. Since this approach used measured water compositions, which constituted 50, 75, and ≈ 70% of the water in Sink Reservoir, Vulture, and McClean Lakes respectively, the agreement between the models' predicted and observed concentrations were inherently better than using an alternative means to predict the concentrations. Inclusion of these measured water compositions tends to dampen model fluctuations, and the differences between the modeled and observed concentrations tended to be less than in the carryover model.

The carryover model, after the first time step, used previously modeled compositions from Sink Reservoir, Vulture Lake, and McClean Lake to estimate the modeled compositions for those terms in the subsequent time step. Because it did not rely on measured concentrations in the three bodies of water, the carryover model had greater predictive abilities, although the match between observed and modeled concentrations was poorer than with the discrete model. Despite this issue, the overall fits for the carryover model are considered reliable.

In developing such a large and complicated model, the final PHREEQC models relied heavily on the logical line separator (;) capability in PHREEQC. Rather than prepare a typical PHREEQC model that can require over 100 lines for each time step and then repeat that for 60 more time steps, the model can be prepared in Excel® and one row can define all of the model steps for each time step. Ultimately, the model was run using a PHREEQC version that is a component object module (*.com file) that uses a macro in Excel® to run the model (Charlton and Parkhurst 2011). This approach also simplified the updating of water balances as well as preparing numerous alternative models and updating of figures and tables. All these models used the default temperature of 25 °C. Temperature data is more difficult to estimate for the monthly grab samples. Also, not all reactions in the thermodynamic database included enthalpies or analytical temperature functions to adjust equilibrium constants. This is particularly the case for the surface complexation reactions. The lack of reliable temperature data, particularly for the surface complexation reactions, is an issue that would need to be resolved before a more detailed temperature function could be included.

Model Results

Conservative Elements

Various elements were classified as conservative when the model results visually matched the observed concentrations in Sink Reservoir, Vulture Lake, and McClean Lake, without a requirement to cite a geochemical process to adjust the concentrations. These elements included sodium (Fig. 4), potassium (supplemental Fig. S-2, in supporting information), magnesium (Supplemental Fig. S-3), and chloride (Fig. 5). Each figure includes the discrete model and carryover model results as well as the JWTP source, followed by the results from Sink Reservoir, Vulture Lake, and finally McClean Lake. For most constituents, the waters from the JWTP source remain unmodified in the model and so differences between the measured (observed) concentrations and modeled concentrations were not expected.

The fits, based on a qualitative visual evaluation, were very good for the discrete model, demonstrating the consistency (quality) of the water balance estimates. The carryover model also provided an acceptable fit, based on a visual comparison.

Figure 6 shows the observed and modeled calcium concentrations. For this time frame, both calcium and sulfate (Supplemental Fig. S-4) are considered to be conservative. The similar variations in calcium and sulfate reflect the mill operations and the relationship between sulfuric acid, which is used to leach uranium from the ore, and calcium hydroxide, which is used to neutralize the raffinate. Increased amounts of acid require more calcium hydroxide to neutralize this solution prior to release to the JEB TMF. Much of the sulfate and calcium are removed by gypsum precipitation in the tailings neutralization system (Mahoney et al. 2007). Therefore, these solutions are saturated with respect to gypsum when disposed with the tailings in the TMF. The underdrain and reclaim pond collects this water, and it is directed to the JWTP process, resulting in dilution from additional treatment waters; this results in a predominantly undersaturated solution with respect to gypsum in the CM01B discharge.

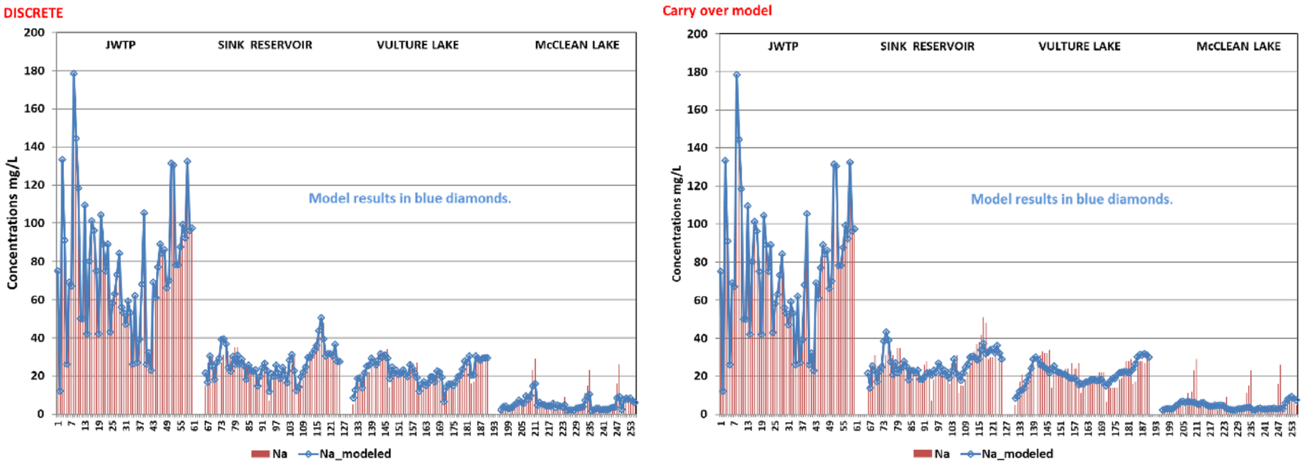

Fig. 4 Observed and modeled sodium concentrations for the discrete and carryover models. Vertical bars represent observed concentrations and the blue diamonds represent model results. The x axis labels are a simple row count and were retained to better track individual results. The first 60 samples represent the sodium concentrations from the JEB Water Treatment Plant for January 2000–December 2004. Similarly, the next 60 samples represent the measured and modeled concentrations for Sink Reservoir, followed by the Vulture Lake samples and McClean Lake

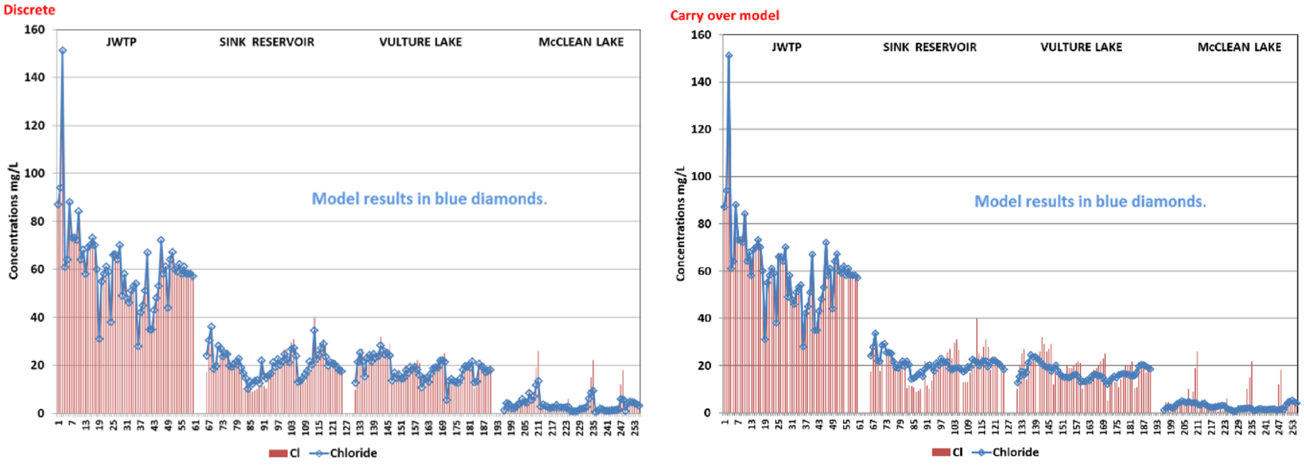

Fig. 5 Observed and modeled chloride concentrations for the discrete and carryover models. Vertical bars represent observed concentrations and the blue diamonds represent model results

Selenium appears to be conserved, although at these low values, an understanding of how reporting limits change is required to calculate average surface water and groundwater concentrations. Many of the surface water samples are estimated at or less than the laboratory reporting limits, and these values changed from 0.005 to 0.001 mg/L. Because one of the purposes of this model was to support licensing requirements, the laboratory reporting limits were used in the model. This can bias estimates of average concentrations for the ambient groundwater and surface waters such as from Collins Creek (Water 10). But any bias is upward and tends to produce possibly elevated concentrations (Supplemental Fig. S-5).

The agreement between the observed concentrations and their respective modeled concentrations for these seven parameters demonstrates the robust nature of the models. The agreement in the carryover models, particularly in Sink Reservoir and Vulture Lake, indicate a strong capability to predict the overall behavior of these conservative constituents. Simple mixing and dilution processes explain the behavior of these elements.

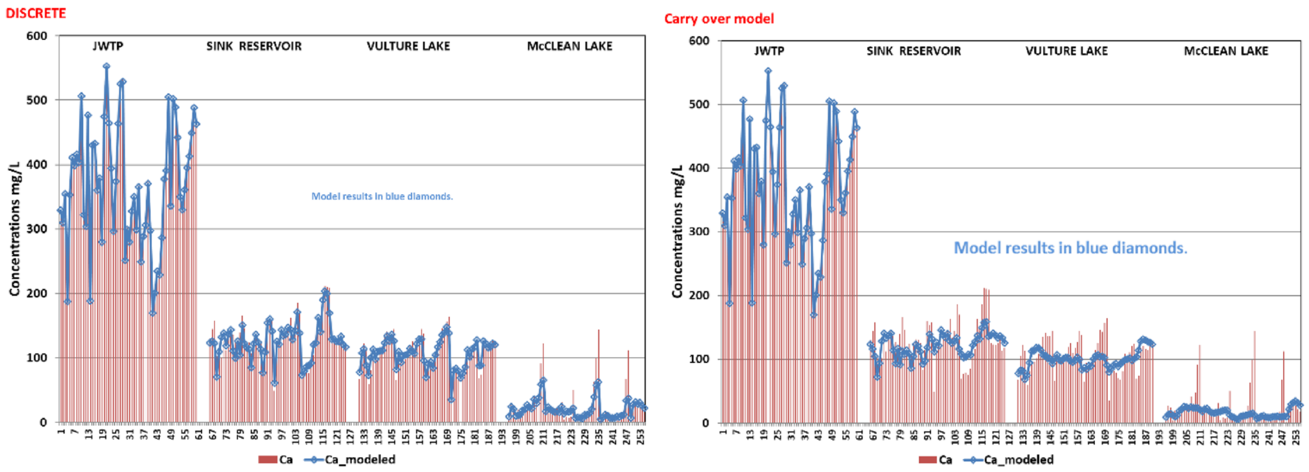

Fig. 6 Observed and modeled calcium concentrations for the discrete and carryover models. Vertical bars represent observed concentrations and the blue diamonds represent model results

Fitting of Model Parameters

Not all constituents are conserved in the subsequent mixtures. Non-conservative behavior is apparent when the concentrations estimated by a simple mixing model approach do not match the observed (measured) concentrations. These non-conservative constituents include pH, Fe, Mo, and As. These modeled concentrations, for both the discrete and carryover models, suggest that additional geochemical processes were acting on these constituents to lower concentrations to levels that cannot be explained by means of simple mixing and dilution.

To better quantify the nature and extent of likely geochemical processes, PhreePlot's fitting capabilities were used. PhreePlot allows the modeler to fit essentially any parameter in a PHREEQC-type model (Mahoney 2015). Solubilities were adjusted by fitting a saturation index for the specific phase. A similar approach was used to: (1) adjust pH by changing the CO_2 partial pressure, (2) better fit observed and modeled Fe concentrations by adjusting the solubility of ferrihydrite, (3) fitting molybdenum concentrations by adjusting the saturation index for powellite ($CaMoO_4$), and (4) adjust the site density function for the Hfo_wOH surface to match the observed arsenic concentrations in Sink Reservoir (Table 1).

The observations, which were usually measured concentrations or pH, were compared to the equivalent model-generated values. PhreePlot calculates the residual sum of squares (RSS) between the set of model-derived values and their corresponding observations. In an iterative approach, the fitting solver adjusts the value of the model parameter and reruns the model; a new RSS is calculated. The solver routine continues to adjust the fitted parameter until no significant change was noted in the now minimized RSS value.

Fitting Average pH Values

Before the other non-conservative elements were evaluated, the modeled pH values in the three water bodies were adjusted. The partial pressures of CO_2 gas in the various water bodies were adjusted to better fit the observed pH values (Fig. 7). The pH values were generally greater than 7, with the average pH for the three surface water bodies being 7.5. It was decided that the simplest and most direct approach to adjusting the pH was to fix the partial pressures of CO_2 gas in the different waters bodies. The partial pressures were fit using PhreePlot (Table 1). There are five locations listed in Table 1, but only four locations in the figures. The mixing zone was added to the model in an unsuccessful attempt to improve the uranium results. The mixing zone did fit the physical setting better, and so it was retained in all subsequent models. However, water samples were not collected in the mixing zone and so there were no data for comparison. The final models separated the Sink Reservoir area into two sub-areas; the additional zone represented the initial discharge (mixing) zone and only included the three actively discharged solutions (JWTP effluent, SUE discharge, and the pit dewatering solution). These three solutions were mixed, with a subsequent step for the mixing of Sink Reservoir waters, groundwater, and seasonal precipitation, contributing an extra set of equilibration steps. It should be noted that one of the few seasonal effects is observed in the lake pH values (Fig. 7). This is particularly obvious in the McClean Lake samples, where the highest pH values are generally present in July or August, and the lowest values in late winter to early spring (March and April). There is a rough inverse relationship between Fe concentrations and pH, with the highest iron concentrations generally noted in March or April and the lowest Fe concentrations are in July

Table 1 Summary of model parameter fitting adjustments performed using PhreePlot

Fitted parameter	JWTP	Mixing zone	Sink reservoir	Vulture Lake	McClean Lake
Log partial pressure CO2(g) to adjust pH	– 3.19	– 2.11	– 2.67	– 2.67	– 2.67
Fitted average pH (standard deviation))	7.30 (0.134)	NA	6.49 (0.054)	7.12 (0.093)	6.81 (0.054)
Saturation index ferrihydrite	4.731	2.438	2.514	2.514	3.15
Saturation index $CaMoO_4$	Not included	– 0.0614	Not included	Not included	Not included
Hfo_wOH site density mol sites/mol HFO	Not fitted	0.0529	(0.0529)	(0.0529)	(0.0529)

In the fitting of the carbon dioxide partial pressures the Sink Reservoir, Vulture Lake and McClean Lake were grouped together as a single fitted value. For the saturation index calculations for ferrihydrite, Sink Reservoir and Vulture Lake were grouped together; McClean Lake was assigned its own EQUILIBRIUM_PHASES block because of elevated iron concentrations. Powellite (CaMoO4) only precipitated in the Mixing Zone, it was undersaturated in the other downflow locations. Sorption was only noted in the Mixing Zone although the same site density value was retained in the Sink, Vulture, and McClean water bodies

and August. It is believed that seasonal variations from the Collins Creek discharge to McClean Lake are responsible for these effects. Collins Creek is not monitored on a monthly basis so no further data was available. Sink Reservoir and Vulture Lake are probably too strongly affected by the mine-related discharge to display such an effect, but with a greater proportion of surface water influx from Collins Creek, this apparent seasonal effect is observed.

Fitting Ferrihydrite Solubility Product Constant

An understanding of the extent of the solubility of the precipitated HFO (ferrihydrite) is required to fit the observed iron concentration data with the modeled results. The amount of ferrihydrite is also required to assess the behavior of As, U, Mo, and other components that could form surface complexes on this phase. Dissolved Fe concentrations significantly decreased (Fig. 8) and most of the precipitation was observed to take place in the mixing zone. When ferrihydrite precipitation was disabled in the model, Fe concentrations remained elevated compared to the observed values in Sink Reservoir and in the other lakes. However, the measured concentrations of dissolved Fe in Sink Reservoir and the other locations showed a significant amount of oversaturation with respect to ferrihydrite. Therefore, fitting calculations were developed to better understand why these waters were oversaturated. One early model allowed for the precipitation of ferrihydrite, assuming a log K of 4.891 for the following reaction:

$$Fe(OH)_3 + 3H^+ = Fe^{+3} + 3H_2O \quad (1)$$

The given log K value clearly overestimated the stability of the ferrihydrite phase and tended to estimate Fe concentrations that were two to three orders of magnitude too low in Sink Reservoir, and the two downstream lakes (Fig. 8). Therefore, a model using PhreePlot was developed to adjust the log K value.

The PhreePlot calculations change the log K value by adjusting the saturation index for the ferrihydrite phase within the five equilibrium phase blocks used in the model. The SI values were added to the log K value of 4.891 to estimate the effective log K. The fitting calculations used the bound optimization by quadratic approximation (BOBYQA) method available in PhreePlot. The model adjusts the saturation index, which minimized the RSS for the observed and modeled Fe concentrations.

The ferrihydrite solubility constants were adjusted after the pH values were adjusted (Table 1). To obtain a minimum RSS, the fitting function selected a saturation index value for the CM01B samples (JWTP in Table 1) that was large enough so that all of the waters were oversaturated, preventing precipitation of ferrihydrite. In this situation, PhreePlot fit a saturation index that represented a value equal to or greater than the saturation index for the most oversaturated solution among the 60 CM01B samples. Therefore, none of

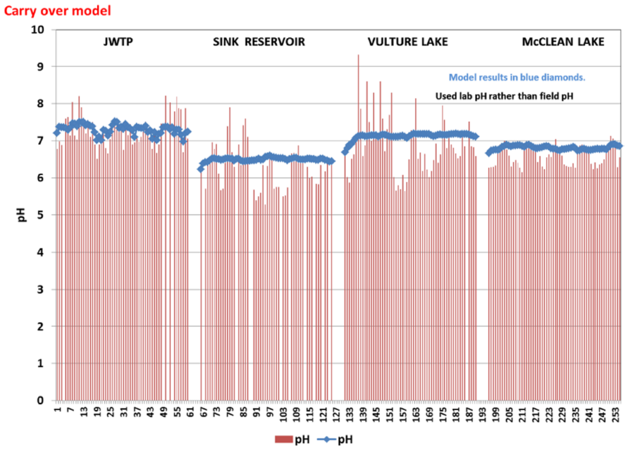

Fig. 7 Comparison of observed and modeled pH values using the carryover model. Vertical bars represent observed concentrations and the blue diamonds represent model results

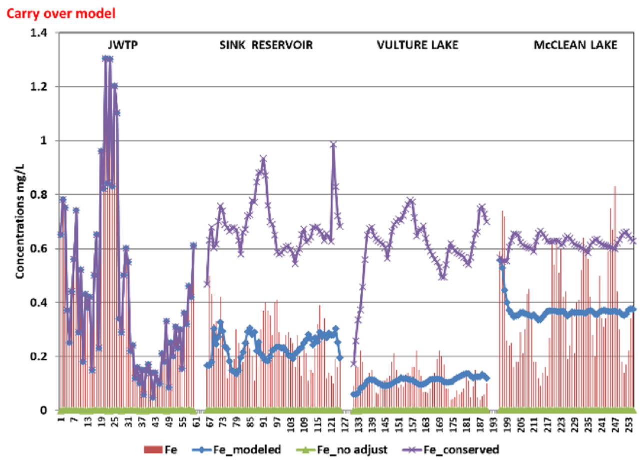

Fig. 8 Comparison of measured and modeled iron concentrations using the carryover model. Both a linear (LHS) and log scale (RHS) are shown. The figures include a conservative (no precipitation) model (upper purple crosses), the no adjustment model results (lower green triangles), and the selected model adjusted concentrations (blue diamonds) based on the PhreePlot fitting calculations

the JWTP samples precipitate ferrihydrite. The measured and observed concentrations were the same, so the RSS (except for rounding errors) was essentially 0.0 for the first group of samples (Fig. 8).

The precipitation process occurs in the mixing zone, but there were no data for that area. So the Sink Reservoir observed and the model-generated concentrations were compared. PhreePlot also estimated a saturation index of 2.438, producing the middle line (dark blue) in Fig. 8 for the Sink reservoir samples. The saturation indices in Sink Reservoir and Vulture Lake were set at the same value, which were slightly more saturated than the saturation index in the mixing zone. For the JWTP samples, this value represents a slightly oversaturated condition and Fe does not precipitate in Sink Reservoir, nor in Vulture Lake. The data set in McClean Lake showed an additional increase in dissolved Fe concentrations, so a separate fitting parameter value was specified for that water body. It is believed that the additional dissolved Fe concentrations observed in McClean Lake represent additional natural surface water and groundwater contributions to this furthest downstream lake.

The significance of the optimized ferrihydrite saturation indices is debatable. The simplest explanation is that the PhreePlot model was calculating an average saturation index for ferrihydrite for the different water bodies. Regarding the JWTP fitting calculations, the model determined a value large enough to prevent adjustment to the observed concentrations; the adjustment was 4.731 log units. This is reasonable; there was little reason to adjust these observed concentrations, as precipitation occurs after the waters are mixed within the mixing zone. For the mixing zone, PhreePlot then estimated a saturation index of 2.438 within the mixing zone. There was no independent method to confirm this value, but it suggests a less crystalline ferrihydrite solid is forming. Alternatively, the oversaturation may reflect other kinetic and transport effects, such as short residence times, in the mixing zone. This approach provides a simple ad hoc means to lower the amount of ferrihydrite. It demonstrates that some process actively limited the amount of precipitate. This is not a unique solution and other approaches could be employed.

Adjustment to Molybdenum Concentrations

The proof of concept model (Mahoney and Frey 2014) used only four sets of equilibrium_phases and surface keyword blocks. It contained only 12 samples representing simple annual average compositions. Elevated concentrations of Mo were noted in the first four samples of that data set, and an adjustment to the powellite ($CaMoO_4$) saturation index, assuming precipitation of the oversaturated CM01B solutions, lowered those concentrations to produce a better fit on Sink Reservoir and the other lakes. Some adjustment of the solubility product constant was calculated using PhreePlot and the solutions required approximately a 0.3 log unit degree of oversaturation. The carryover model allowed for powellite precipitation in the mixing zone. Figure 9 compares results for Mo for two model setups. The results represented by the blue diamonds assume that Mo is conserved and that precipitation does not occur. The green triangles show the precipitation of powellite in the upper mixing zone only; clearly this model is the better fit. The saturation index adjustment provided by PhreePlot was -0.0614 log units, indicating precipitation of powellite is a simple, equilibrium-controlled process. At 25°C, the log Ksp in the thermodynamic database for the $CaMoO_4$ dissolution reaction is -7.95.

Essentially, simple precipitation of powellite in the mixing zone removes the excess Mo in the CM01B discharge

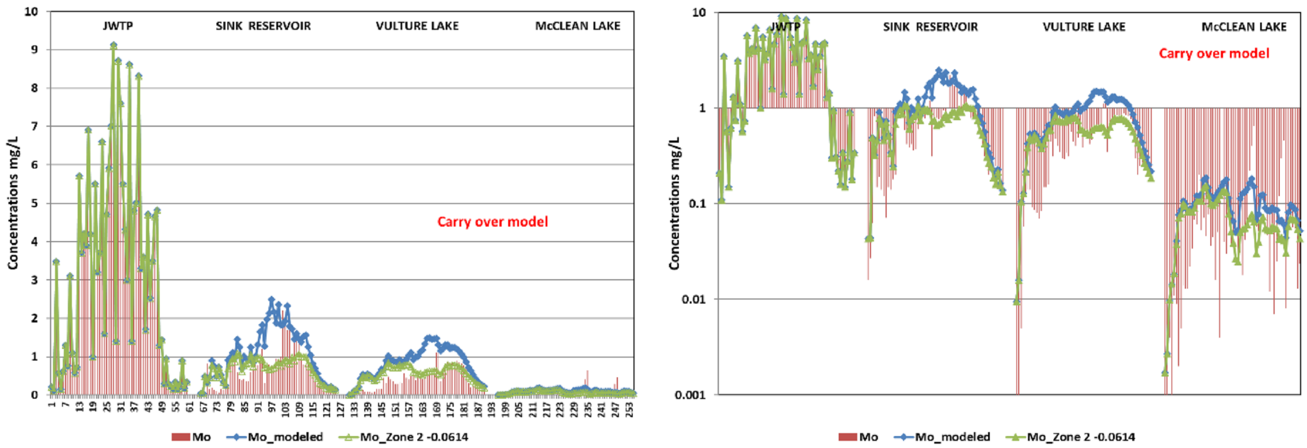

Fig. 9 Comparison of measured and modeled molybdenum concentrations using the carryover model. Both a linear (LHS) and log scale (RHS) are shown. The figures include a conservative (no precipitation) model (blue diamonds), the selected model adjusted concentrations (green triangles) based on the PhreePlot fitting calculations

samples. The mixing zone model of the powellite precipitation is superior to the earlier proof of concept version, as it eliminated possible issues related to the representativeness of the samples for the CM01B sampling point. In those models, there was a significant difference in the CM01B observed and the modeled concentrations. In the final version, the precipitation occurs in the mixing zone without any changes to the original CM01B results.

The $CaMoO_4$ precipitation process is now mainly of historical interest because in late 2003 to early 2004, the JWTP was modified. These modifications captured the Mo onto HFO, reducing its discharge to the SVTEMS area. Therefore, precipitation of powellite was no longer an active process in the SVTEMS.

Arsenic

Attenuation of As appears to be straightforward. Surface complexation onto the HFO surface provides reasonable fitting of the observed data, an improvement on the conservative model (Fig. 10). The surface complexation reactions of Gustafsson and Bhattacharya (2007) were used; these constants are about an order of magnitude greater than the values originally published in Dzombak and Morel (1990). The sorption takes place in the mixing zone and is concurrent with ferrihydrite precipitation. The density for weak sites (Hfo_wOH) was calculated using PhreePlot (Table 1). The site density value of 0.0529 sites/mole of HFO precipitated is significantly less than the value of 0.2 moles/mole HFO, as defined by Dzombak and Morel (1990). To maintain consistency with the assumptions in the original diffuse layer model, the strong site (Hfo_sOH) density was assumed to be 2.5 % of the weak site value (0.00132 mole/mole of HFO). The site density values were included in the surface keyword block for Sink Reservoir, and Vulture and McClean Lakes, but since ferrihydrite formation in these locations was negligible, there was no surface for sorption.

In the proof of concept model, the PhreePlot fitted site density was 0.09 moles/mole HFO for the first 6 years, increasing to 0.129 moles/mole HFO precipitated in the 6 to 12-year period. The site density discrepancy during these periods is attributed to the rate of pit dewatering activities. Groundwaters contain elevated concentrations of soluble Fe. However, the rate of pit dewatering decreased in subsequent years, resulting in less available Fe for subsequent HFO precipitation.

The fitted site density value of 0.0529 sites/mole of precipitated HFO may be in part due to the stronger surface complexation constants reported by Gustafsson and Bhattacharya (2007) used in these models. Other trace elements such as Mo and Se were permitted to sorb onto this surface. In the case of selenium, because the oxygen partial pressure is set at atmospheric pressure (≈ 20 %), the program calculates the Se valence as Se(6), which adsorbs less than Se(4). As both of these elements (Mo and Se) tend to have smaller surface complexation constants, the combination of low amounts of precipitated HFO, plus the lower site density, tends to limit the amount of sorption for these elements to small percentages of their total concentrations.

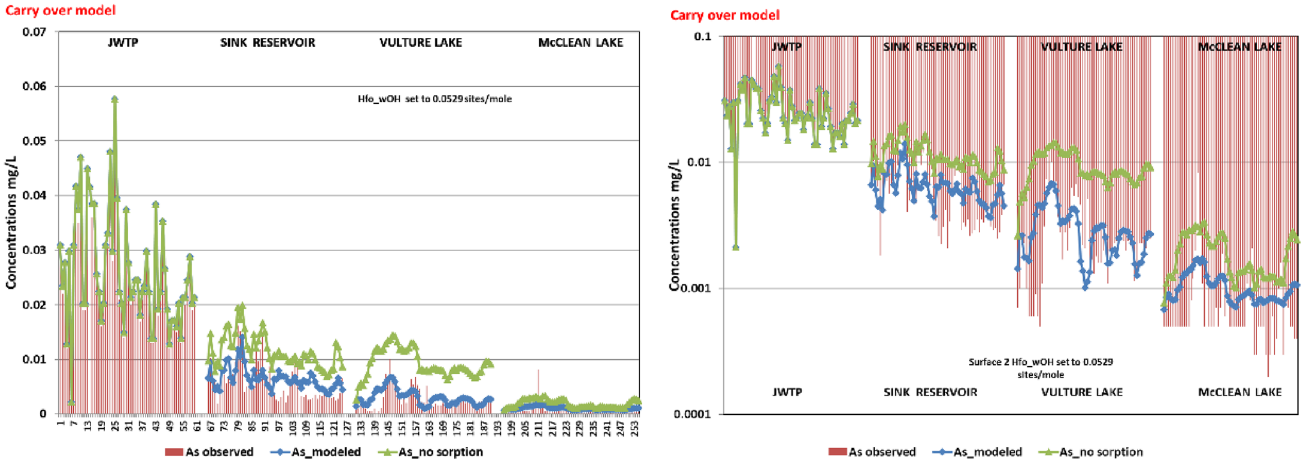

Fig. 10 Comparison of measured and modeled arsenic concentrations using the carryover model. Both a linear (LHS) and log scale (RHS) are shown. The figures include the selected model that uses surface complexation on HFO (blue diamonds), and a no attenuation conservative component model (green triangles). The Hfo_wOH site density of 0.0529 moles/mole of HFO precipitated was based on fitting with PhreePlot

Uranium

The geochemical behavior of U (Fig. 11) appears less straightforward than As and Mo. A comparison of the conservative, no-attenuation model with one using the 0.0529 site density, based on As sorption, showed essentially no differences in the modeled concentrations for the three surface water bodies. For about the first 4 years, U behaves as a conservative species whose concentrations are controlled primarily by mixing and dilution. The increase in the U concentrations, starting in February 2004, was tracked by the modeled concentrations in Sink Reservoir. The observed U concentrations were significantly less, suggesting that increased natural attenuation was occurring. Various surface complexation models were evaluated and none were provided an acceptable representation of these processes. It is likely that the stability of the two calcium uranyl carbonate complexes (Dong and Brooks 2006, 2008) keeps the uranium in solution and limits uranium sorption. At this point, it was decided to treat U as a nearly conservative species with limited attenuation.

Conclusions

A PHREEQC based geochemical model was developed to evaluate and predict the composition of three surface water bodies that received discharge waters from a U milling operation. Comparison of the modeled compositions to the observed concentrations for various elements indicated that the model captured the major processes that controlled water quality in these water bodies. The model demonstrated that mass loading from the treated water effluent system affected the downstream reservoirs and lakes. Most of the major elements were retained as dissolved constituents in the mixed solutions; mixing and dilution provide the primary control on these elements and are the only processes noted in the last two lakes.

Geochemical processes that controlled minor and trace element concentrations included precipitation of $CaMoO_4$, the precipitation of an amorphous HFO phase and surface complexation of arsenic on the HFO surface. These

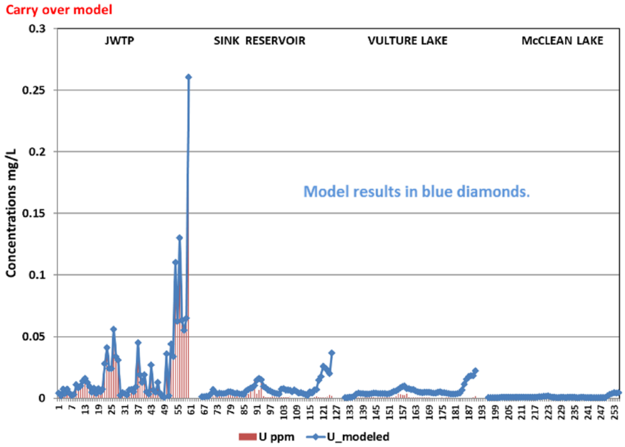

Fig. 11 Comparison of measured and modeled uranium concentrations using the carryover model. The model does allow for surface complexation of uranium, but the modeled concentrations are nearly identical to a simpler no sorption model

reactions appear to occur in the area of initial mixing of the three discharged solutions. Subsequent dilution prevents further precipitation reactions.

The model tended to overpredict U concentrations, particularly after the first 4 years of operations. It appears that there is a more complicated process within the system that attenuates U. In the early operational period, U appears to be conserved in solutions. Attempts to attenuate U in the models required unrealistically high surface site densities, thus lesser site densities based on the fitting of arsenic data were selected for the final model.

The apparent simplicity of the model is the result of an accurate water balance. Mixing and dilution among the mill-related discharges with the ambient surface waters and groundwater explain most of the changes in concentrations as the waters flow downstream. The geochemical reactions that were required to adjust Fe and As concentrations were basic, but well accepted processes, that involved mineral precipitation and surface complexation. Adjustments to the equilibrium constant for the ferrihydrite precipitation reactions and surface site densities were optimized using the fitting capabilities of PhreePlot. Although validation of any model is usually difficult to demonstrate, the abundant data available at this site and agreement between the modeled and measured concentrations suggests that, at the least, the model provides a reasonable representation of the conditions within the Sink Vulture treated effluent management system. It is understood that alternative reactions could be developed that might provide a better explanation of the Fe precipitation process. The agreement between measured and modeled concentrations in the three water bodies demonstrates that the carryover model provides a predictive tool that can be used in future license applications.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s10230-021-00759-1.

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