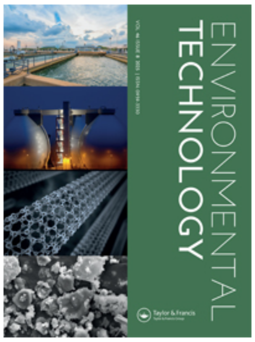

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Metal uptake in wetland plants from oil sands process-affected waters: a case study

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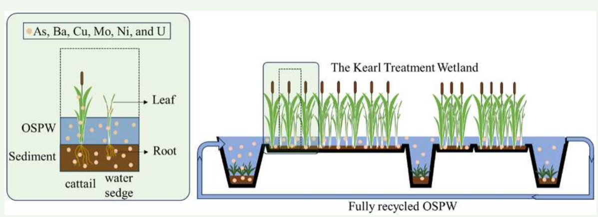
ABSTRACT
Treatment wetlands have emerged as a potential remediation option for oil-sands process affected waters (OSPW) which contains a suite of organic and inorganic constituents of potential concern. The aim of this study was to evaluate the fate of metals in a treatment wetland exposed to OSPW. Data was collected over three operational seasons testing freshwater and OSPW inputs at the Kearl Treatment Wetland in northern Alberta. Overall, results show that OSPW from the Kearl oil sands mine has relatively low concentrations of metals and trace elements compared to other industrial OSPW. Of the inorganic constituents introduced into the wetland from OSPW, six analytes (As, Ba, Cu, Mo, Ni, and U) were found to depurate by wetland treatment, were distributed among wetland media (water, sediment, plants), and translocated into water sedge and cattail tissue. Depuration of these analytes from the OSPW occurred mainly through sorption to sediment, while Mo and Cu had higher uptake and storage within plant tissue compared to the other analytes. No significant differences in metal uptake were observed between cattails and water sedge; root concentrations were higher than leaf concentrations. Root and leaf concentration factors were similar across years indicating that mechanisms of plant uptake were not impacted by exposure to OSPW and that bioconcentration was mainly a function of exposure. These findings support continued investigation into the application of treatment wetlands for OSPW remediation and underscore the need for further studies to optimize these systems for diverse OSPW types.



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Bioconcentration factor; oil sands process-affected water; metals; plant uptake; treatment wetland

1. Introduction

Oil sands process-affected water (OSPW) refers to the water that is used, produced, or impacted during oil sands mining operations and includes water used in the mining or extraction process and water that becomes mixed with tailings. As a result, OSPW is comprised of a complex and highly variable mixture of solids (sand and clay), water, dissolved organic and inorganic constituents. OSPW treatment therefore requires a dynamic and resilient system capable of treating a wide range of pollutants, including metals and trace elements, polycyclic aromatic hydrocarbons, and naphthenic acids.

Treatment wetlands have emerged as a potential remediation option for OSPW due to the array of natural biogeochemical processes present in wetland systems that contribute to the removal of pollutants from OSPW [1–7]. Wetland vegetation is a key component of treatment wetlands due to their role in regulating and facilitating many of these different biogeochemical processes [8–10]. Wetland plants are directly involved in the removal of pollutants from water through processes of immobilization, biotransformation, and evapotranspiration [11]. Wetland plants also contribute indirectly to pollutant removal. For example, the roots of wetland plants oxygenate

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sediment in the rhizosphere and provide a habitat for microorganisms that degrade pollutants [12–18].

Recently, treatment wetlands were found to remove polycyclic aromatic hydrocarbons [2] and naphthenic acids [1,3] from OSPW. However, the distribution and accumulation of inorganic OSPW pollutants in wetland media, and their effects on wetland vegetation has not been fully investigated despite their potential to pose an ecological risk (e.g. [19–21]). Therefore, we focus our investigation on inorganic constituents associated with OSPW and bitumen extraction.

This study aims to evaluate the fate of metals in a treatment wetland exposed to OSPW. Specifically, we investigate (1) the loading of dissolved metals into the wetland, (2) their depuration through wetland treatment, and (3) the distribution and translocation of these metals among wetland media (water, sediment, plants).

2. Methods and materials

2.1. Site description

The Kearl Treatment Wetland (KTW) is located on the Kearl Oil Sands site and operates annually from May to September. The wetland consists of six cells-in-series containing three deep pools (1.7 m deep) with mainly submerged vegetation and three shallow areas (0.4 m deep) with emergent vegetation (Figure S1). At the start of the 2021 and 2022 operational seasons, standing water in the KTW was removed to a depth of < 0.5 m and approximately 6200 m^3 of source OSPW was pumped into the KTW inlet bay (May 10, 2021; June 13, 2022). In 2022, supplemental source OSPW was added to the KTW on July 8 and August 28 to balance water loss from evapotranspiration and maintain adequate water levels for operation. The subsequent addition of OSPW in 2022 loaded additional contaminant mass into the wetland. Therefore, wetland depuration during this operational season is likely underestimated. OSPW is fully recycled during each operational season at 5 L/s using a recirculation pump in the outlet to aim for a 14-day retention time in the wetland.

Wetland vegetation in the shallow cells is dominated by common cattail (cattail; *Typha latifolia*) and water sedge (*Carex aquatilis*). Cattail is a prolific emergent perennial wetland plant that grows in ponded water, is commonly used in treatment wetlands [6], can adapt to OSPW [22,23], and increase the performance of constructed wetland systems [24]. Water sedge is a widespread perennial wetland plant that forms dense colonies in shallow water and has been found to tolerate and reduce the toxicity of OSPW in treatment wetlands [7,25,26]. Additional details on the design and operation of the KTW can be found in Cancelli and Gobas [2,3] and Cancelli et al. [4].

In 2020, no OSPW was introduced into the KTW due to logistical challenges related to the COVID-19 pandemic. In 2021 and 2022, OSPW was sourced from a tailings pond at the Kearl Oil Sands site and pumped directly into the inlet of the KTW. This OSPW is classified as fresh effluent tailings from oil sands operations and therefore contains a suite of different organic and inorganic contaminants. For information on the organic chemical contents and their removal in the KTW, refer to Cancelli and Gobas [2,3]. Hourly and daily weather data (temperature, precipitation, relative humidity, wind) were collected at the Imperial Kearl Lake Weather station near the KTW. Local weather data was compared to 30-year climate normals at the Fort McMurray weather station (1981–2010; Figure S2) [27].

Average daily air temperatures from May to September at the KTW ranged from 13.8 °C to 15.2 °C. Overall, the temperature profile throughout each study period was similar to 30-year climate normals for the region [27]. Heavy precipitation occurred at the KTW in 2020 resulting in significantly higher than normal total rainfall (477 mm) from May to September. Most of the rainfall occurred in June (121 mm) and July (147 mm) of 2020, but since no source OSPW was added to the KTW in 2020 the above average rainfall and average seasonal temperatures likely buffered any potential negative effect on wetland functions from a lack of supplemental water inputs. Conversely, total rainfall from May to September in 2021 and 2022 at the KTW was 218 and 201 mm, respectively (30-year normal total rainfall = 283 mm).

2.2. Sample collection and analysis

2.2.1. Water

Bulk water samples were collected directly from the tailings pond on the Kearl Oil Sands site (source OSPW), from the KTW in 2020 when only freshwater was present in the wetland (KTW FW), and from the KTW in 2021 and 2022 when OSPW was introduced into the wetland (KTW OSPW; Figure S1). All water samples (source OSPW, KTW FW, and KTW OSPW) were collected, preserved, stored, handled, and analyzed in accordance with procedures outlined in the Protocols Manual for Water Quality Sampling in Canada [28] and Standard Methods for the Examination of Water and Wastewater [29]. Samples were collected in lab-specified jars, immediately stored at < 4 °C, and then shipped on wet ice to the laboratory for analysis within 72 h to meet holding time requirements. All water samples were analyzed by Bureau Veritas (formerly Maxxam Analytics; Calgary, AB) for conventional parameters and major and trace elements following standard methods provided in Table S1. Method blank, blank spike, matrix spike, and laboratory duplicate analyses were performed for each batch of water samples submitted, and at a frequency of no less than one in 20 samples. For each analyte, the reporting detection limits are presented in Table S2.

Source OSPW samples were used to identify 29 inorganic constituents above detection limits. Once source OSPW was introduced into the KTW, KTW OSPW samples were collected from the KTW inlet roughly every two weeks during the operational season and were used to monitor the concentration of metals and trace elements in the KTW OSPW over time. For this analysis, sample collection from the inlet was sufficient to assess water quality and changes to OSPW chemistry over time as the water was recirculated in the KTW throughout the season. The number of samples collected at the KTW in each year varied. In 2020, three samples were collected from June 13 to September 12 (91 days). In 2021, ten samples were collected from May 30 to August 26 (88 days). In 2022, eight samples were collected from June 18 to September 25 (99 days).

Constituents of interest were determined by comparing the concentration of these inorganic constituents in KTW OSPW in 2021 and 2022 to their concentration in KTW FW 2020. KTW FW samples were used as a baseline for concentrations of inorganic constituents since no source OSPW was introduced in 2020. Rainfall contributed approximately 7000 m^3 of water into the wetland during this period which closely resembled the volume of source OSPW introduced during 2021 and 2022. Therefore, we believe 2020 observations are a good representation of natural conditions with a similar water budget to 2021 and 2022 operations. Constituent concentrations in KTW OSPW 2021 and 2022 that exceeded their concentration in KTW FW 2020 were designated as constituents of interest. The inorganic constituents with concentrations that were found to decrease through the KTW throughout each operational season were of particular interest in this study. The removal and distribution of these select constituents of interest among wetland media in the KTW in 2021 and 2022 were further explored.

2.2.2. Sediment

Sediment samples were collected in triplicate each year from two shallow cells of the KTW (Cell 02a and Cell 04a; Figure S1). A sample of the top 10 cm (0-10 cm) was collected using a blunt ended multi-stage sampler to standardize sampling area. Roots, litter, and large organic matter pieces were removed by hand and/or with a sieve. The samples were stored in amber glass jars and placed in plastic bags and into a cooler with wet ice for submission to Bureau Veritas for laboratory analysis within the specified holding times. Sediment samples were analyzed for metals and trace elements by Bureau Veritas using standard methods provided in Table S1. A total of six sediment samples were collected and analyzed each year (2 locations x 3 replicates). Method blank, blank spike, matrix spike, and laboratory duplicate analyses were performed for each batch of sediment samples submitted, and at a frequency of no less than one in 20 samples. For each analyte, the reporting detection limits are presented in Table S2.

2.2.3. Plant roots and leaves

Plant tissue was collected from cattail and water sedge in late-summer (late-July to mid-August) in-parallel to sediment sample collection (Figure S1; Table S3). Three different individual plants of each species were randomly selected each year from established 1 x 1 m plots in Cell 02a (near the inlet) and Cell 04a (near the outlet) of the KTW.

Tissue from live aboveground leaves and belowground roots were collected from each individual plant. A 20-gram sample of leaves were collected by clipping several full mature leaves at the base of the shoot. From the same plant, a 10-gram sample of roots were collected from the top 10 cm of length. Once collected, plant tissues were kept frozen in a plastic freezer bag and shipped in a cooler with ice to Bureau Veritas for laboratory analysis of metals and trace elements using standard methods listed in Table S1. A total of 24 samples were collected and analyzed each year (2 tissue types x 2 species x 2 locations x 3 replicates). Method blank, blank spike, matrix spike, and laboratory duplicate analyses were performed for each batch of plant tissue samples submitted, and at a frequency of no less than one in 20 samples. For each analyte, the reporting detection limits are presented in Table S2.

2.3. Plant uptake and translocation

Plant uptake of analytes in cattail and water sedge were evaluated using bioconcentration factors for both root and leaf components relative to the KTW sediment. The root concentration factor (RCF) and leaf concentration factor (LCF) were calculated as:

$$\mathrm{RCF} = C_{\mathrm{root}}/C_{\mathrm{sediment}}$$

$$\mathrm{LCF} = C_{\mathrm{leaf}}/C_{\mathrm{sediment}}$$

where C_{root} and C_{leaf} ($\mathrm{mg/kg_{dw}}$) represent the concentration of the analyte in the root and leaf tissue, respectively, and $C_{sediment}$ (mg/kg_{dw}) is the concentration of the analyte in sediment immediately surrounding the plant roots. The translocation of analytes through the plants was evaluated with a translocation factor (TF) which compares the concentration in the leaf to that in the root:

$$TF = C_{leaf}/C_{root}$$

2.4. Statistical methods

Data were analyzed with a one-way analysis of variance (ANOVA) to test the null hypothesis of no time effect for concentrations in OSPW, and in wetland media (sediment, roots, leaves). Post ANOVA mean comparisons using Dunnett's Test were completed when there was significant year effect, with year 2020 serving as the control (KTW FW) against which the mean concentration from 2021 and 2022 (KTW OSPW) were compared. Dunnett's test was chosen for its superior statistical power compared to other post-hoc tests when evaluating multiple treatments against a single control, as it involves fewer comparisons [30]. Wetland treatment was quantified by the first-order rate of decrease in concentration over time (day) during each study period (2020, 2021, and 2022). The removal of CoCs over time was evaluated using their first-order rate (k) of removal from OSPW (i.e. depuration), where: $k = \ (ln\ C_t \ - ln\ C_0)/t$, where C_t and C_0 arethe concentrations of analyte in KTW water at time t and time 0, respectively, and t reflects the length of time the OSPW was continuously recycled through the KTW (i.e. length of treatment). Negative k values represent the concentration of a major or trace element in KTW water that is decreasing over time during treatment. Significance was determined for the slope (k) of least squares regression relationship $\ln C_t = \ln C_0 + k.t$ using a regression t-test. To satisfy the assumption of homogeneity of variances, all tests were completed on log transformed data using JMP v16.1 software, and results were deemed significant when p-values were below 0.05. Mean values ± standard errors (SE) are depicted in figures and are reported throughout.

3. Results and discussion

3.1. Water chemistry

Table 1 presents water quality data for the KTW when only freshwater from precipitation was present (KTW FW; 2020), from water samples collected directly from the source tailings pond (source OSPW), and from water samples collected from the KTW when OSPW was introduced (KTW OSPW; 2021 and 2022) from May

Table 1. Water quality summary of KTW freshwater (FW), source OSPW, and KTW OSPW.

Year		2020		2021		2022			
Sample Location		KTW FW		Source OSPW	KTW OSPW	Source OSPW		KTW OSPW	
Number of Samples		n=3		n=1	n = 10	n=2		n = 8	
	Units	Mean (sd)	Min – Max	Mean	Mean (sd)	Min – Max	Mean (sd)	Mean (sd)	Min – Max
Alkalinity (Total as CaCO3)	mg/L	260 (35)	220 – 80	250	289 (33)	240 – 320	315 (106)	315 (47)	230 – 360
Conductivity	µS/cm	1029 (126)	940 – 1118	1028	1163 (95)	1027 – 1307	1413 (15)	**1383 (155)**	1118 – 1663
Dissolved Oxygen (DO)	mg/L	8.4 (1.3)	7.5 – 9.3	-	6.0 (2.9)	1.1 – 9.4	6.6 (1.4)	6.2 (2.3)	3.0 – 9.0
Hardness (Total as CaCO3)	mg/L	513 (50)	460 – 560	250	**336 (52)**	230 – 380	225 (7)	**354 (52)**	220 – 380
Naphthenic Acids[1]	mg/L	< 2.0	-	41	**11.4 (4.9)**	6.6 – 21	30.5 (13)	**13.4 (3.8)**	10 – 22
pH	-	8.05 (0.20)	7.9 – 8.3	8.12	8.13 (0.10)	8.0 – 8.3	7.92 (0.08)	8.04 (0.18)	7.7 – 8.3
Total Dissolved Solids (TDS)	mg/L	947 (92)	840 – 1000	900	857 (72)	750 – 980	1040 (85)	**1100 (53)**	1000 – 1200
Turbidity	NTU	0.41 (0.06)	0.36 – 0.47	3.7	5.0 (7.5)	1.0 – 21	13	4.9 (5.9)	1.2 – 17

[1] Represents total naphthenic acids, measured by Fourier transform infrared (FTIR) spectroscopy.
2020 samples collected from June 13 to September 12; 2021 samples collected from May 30 to August 6; 2022 samples collected from June 18 to September 26
Bold – Parameter measurements are statistically different from KTW FW (2020) values ($p < 0.05$).
– – parameter not measured.
sd – standard deviation.

to September of each year. Alkalinity, dissolved oxygen (DO), and pH did not differ significantly between years or water types (i.e. FW, source, OSPW) and no differences were observed between KTW OSPW from 2021 and 2022. The average alkalinity in KTW OSPW ranged from 289 to 315 mg/L $CaCO_3$, which meets the GoA [31] water quality guidelines for the protection of aquatic life (minimum 20 mg/L) and is below typical values for OSPW [32]. The average DO concentration in KTW OSPW (2021 and 2022) was below the GoA [31] chronic water quality guideline (6.5 mg/L) but was found to be highly variable during the three study periods. The KTW is designed to help oxygenate OSPW as it passes over interior berms between wetland cells. However, during periods with low rainfall in 2021 and 2022 (Figure S2) and high evapotranspiration, the volume of water in the wetland decreased which led to slower flow rates through the wetland. During these periods, OSPW did not evenly flow over interior berms, reducing the surface area available for oxygen diffusion and limiting reoxygenation of OSPW. pH was slightly alkaline but within the range typical for OSPW at the reported hardness and alkalinity and was within the GoA [31] guidelines for the protection of aquatic life in surface waters. The average turbidity in KTW OSPW did not differ significantly from KTW FW; however, turbidity did decrease over time in the KTW OSPW as the solids that were initially suspended in the water during the turbulent conditions created when pumping OSPW into the wetland eventually settled over time (Figure S5).

The conductivity of KTW OSPW 2022 and the concentration of dissolved solids (TDS) in KTW OSPW 2022 were greater than in KTW FW and were found to increase in the KTW each year. Relatively high conductivity and TDS occurs as a result of relatively high concentrations of major ions prevalent in source OSPW; however, TDS concentrations in the KTW OSPW (698 to 1019 mg/L) and source OSPW (750 to 1000 mg/L) in this study were relatively low compared to other OSPW sources throughout the industry (2000 to 2500 mg/L; [32,33]). Hardness was significantly lower in KTW OSPW (2021 and 2022; 336 to 354 mg/L as CaCO3) and source OSPW (225 – 250 mg/L as CaCO3) compared to KTW FW (460 – 560 mg/L as CaCO3) due to the water softening of OSPW caused by use of caustic agents during bitumen extraction.

The concentrations of total naphthenic acids (analyzed by FTIR) were below detection limits in all samples of KTW FW. Higher concentrations of total naphthenic acids were observed in KTW OSPW compared to KTW FW, but concentrations were lower compared to the source OSPW in both years. Treatment wetlands have been shown to reduce the concentration of naphthenic acids over time ([1,3]; Figure S5). Reported EC50s (median effective concentration) for the hatch success of fathead minnows exposed to naphthenic acid fraction compounds from OSPW range from 5-12 mg/L (measured by LC/QtoF-MS; [34]), suggesting the OSPW entering the KTW may initially elicit a toxicological response in some wetland biota. However, an assessment of toxicological risk is challenging since the data is generated using two different analytical methods and equipment. Further, a KTW vegetation assessment reported no phytotoxic effects [4].

3.2. Profile of inorganic constituents in the KTW

Figure 1 illustrates the aqueous profile of inorganic constituents in the KTW FW (2020) and KTW OSPW (2021 and 2022). The concentration of metals and trace elements in KTW FW are viewed as reference values as they primarily represent concentrations of analytes in freshwater that accumulated in the KTW through precipitation. KTW OSPW is compared against KTW FW concentration measurements to assess contaminant-loadings by OSPW introduction into the KTW. Figure 1 is ordered by decreasing concentration of metals and trace elements in KTW FW, i.e. SO4 > S > Ca > Na > Mg > Cl- > K > Si > Sr > F- > B > Fe > Li > Ba > NO3 > NO2 > Mn > tAl > tS2 > Zn > Ni > V > Mo > Sb > As > Cu > U > Co > Se (Figure 1; Table S2). The concentrations of most metals and trace elements were lowest in KTW FW among the three study periods since OSPW was not introduced in 2020, and metal and trace element concentrations were often greatest in KTW OSPW 2022 which follows industry trends on OSPW quality over time [32,33,35]. However, the concentration of Ca in KTW FW was greater than in KTW OSPW 2021 and the concentration of Mg in KTW FW was greater than in KTW OSPW 2022 ($p < 0.05$). Concentrations of Ca (97.5 SE 15.4 mg/L) and Mg (40.3 SE 7.2 mg/L) in KTW FW resemble concentrations observed in surface waters of extreme-rich fens [36] but were substantially higher than concentrations reported in the Athabasca River in 2015 (55 mg–Ca/L, 17 mg-Mg/L; [37]). The presence of Ca and Mg in the freshwater environment is not unusual given the alkaline nature of wetland substrate [38].

3.3. Wetland treatment of inorganic constituents

The metals and trace elements loaded into the KTW by source OSPW were monitored to explore the potential of depuration from OSPW by wetland treatment. The concentration of SO4, S, F-, B, Si, NO3, Li, and Fe in

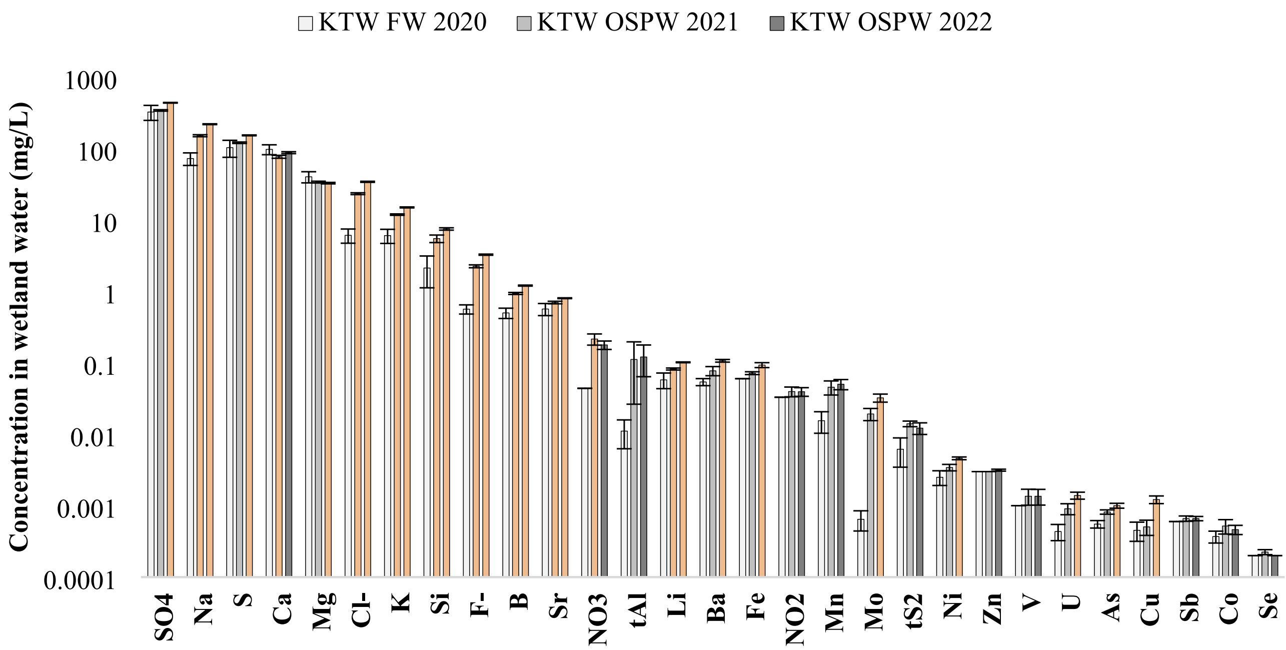

Figure 1. Mean (+/− standard error of the mean) concentration of metals and trace elements in KTW FW in 2020 (n = 3) and KTW OSPW in 2021 (n = 10) and 2022 (n = 8). Concentrations represent dissolved analytes, except for tS2 = total Sulphide; tAl = total Aluminum. *Orange bars* indicate analyte concentrations of KTW OSPW in 2021 and 2022 that are statistically different than analyte concentrations in KTW FW in 2020 ($p < 0.05$; results in Table S5). Error bars represent standard error of mean concentrations. The concentration of SO4, S, Na, Cl-, K, Si, Sr, F-, B, Fe, Li, Ba, NO3, Ni, Mo, As, Cu, and U was greater in KTW OSPW (2021 or 2022) compared to KTW FW (2020; $p < 0.05$) suggesting that these analytes are above background concentrations and were loaded into the wetland through the introduction of source OSPW. Given the higher concentrations in the KTW OSPW, these 18 analytes are considered to be of interest and were evaluated for their fate and removal by wetland treatment.

KTW OSPW showed no effect from wetland treatment (were not effectively removed), as no change in the concentration of these substances in KTW OSPW was observed over time ($p > 0.05$). The concentrations of Na, Cl-, K, and Si were found to increase ($p < 0.05$) in KTW OSPW over time, suggesting that these metals and trace elements are either being added to the KTW OSPW, perhaps from the wetland sediment, or concentrating in KTW OSPW due to water loss by evapotranspiration. Salt-tolerant plants, like many wetland plants, have been shown to excrete salts that were taken up through salt glands in plant leaves [39,40]. Through this mechanism, metals can also be co-excreted in salt crystals thereby returning metals and trace elements back into their surrounding environment [41]. The ionic nature of analytes such as Na and Cl- also makes them highly prevalent in OSPW throughout the industry. Their concentrations in OSPW tend to increase throughout the lifespan of a tailings pond [32,42] so that older mining operations typically produce OSPW that contains higher concentrations of these ions than newer operations. A similar trend observed in the KTW suggests there may be a limit to wetland treatment of OSPW if these analytes continue to accumulate in KTW OSPW throughout operation.

The concentrations of As, Ba, Cu, Mo, Ni, and U in KTW OSPW were found to decrease over time ($p < 0.05$) in the KTW, indicating these six analytes are good target constituents for wetland treatment of OSPW. These substances are further evaluated for the chemical fate and effects in treatment wetlands to explore their distribution among wetland media and identify mechanisms that contribute to their removal from OSPW. Figure 2 demonstrates the decrease in concentration of these analytes in KTW FW and OSPW over time. First-order rates of depuration in KTW OSPW were calculated to quantify their removal by wetland treatment, which range from 0.0005 to -0.021 d^{-1} in KTW OSPW 2021 and -0.003 to -0.014 d^{-1} in KTW OSPW 2022. In order of increasing average rates of depuration are: As < Ni < Cu < Ba < U < Mo, where Mo has the fastest rate of depuration in both KTW OSPW 2021 and 2022 among these six analytes.

3.4. Distribution of select metals among wetland media

Since As, Ba, Cu, Mo, Ni, and U were found to depurate in OSPW by wetland treatment, we explore their distribution among wetland media to investigate

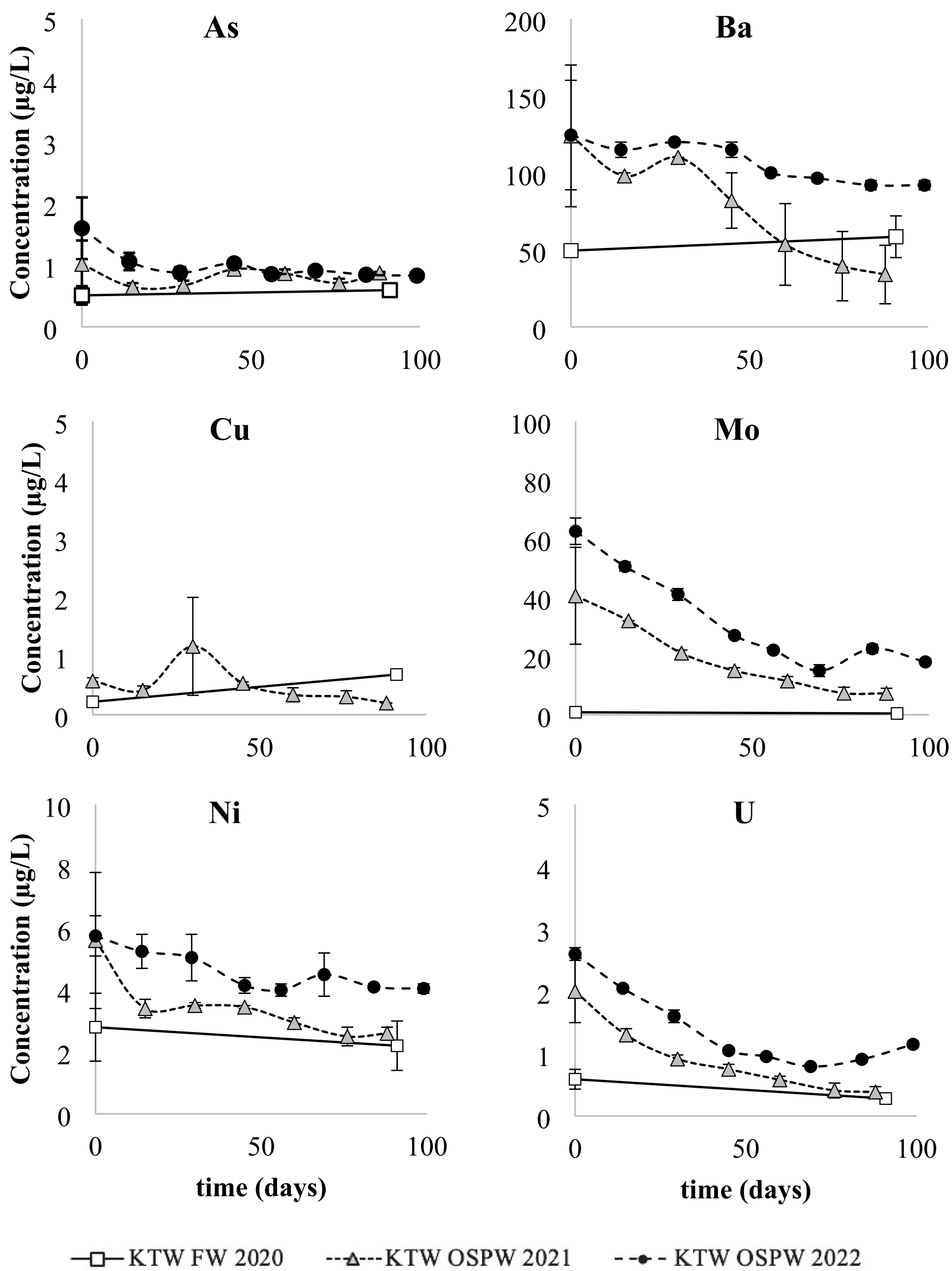

Figure 2. The concentration of As, Ba, Cu, Mo, Ni, and U in KTW FW (2020) and KTW OSPW (2021 and 2022) over the study periods in the KTW.

mechanisms of their removal from OSPW. Wetland mechanisms of chemical removal primarily involve sorption to wetland sediment, uptake into plant roots, and translocation from plant roots to leaves. The capacity to distribute these analytes among wetland media by these mechanisms reflects the potential for wetland treatment to sequester these metals from OSPW. Therefore, we assess their distribution among wetland media in conjunction with their rates of depuration measured in the KTW OSPW, noting that these wetland processes are sensitive to environmental conditions such as temperature, and water chemistry such as pH and oxidation–reduction potential, which can alter metal speciation and bioavailability of these analytes for plant uptake.

In general, concentrations of these analytes in sediment remained relatively stable throughout the study despite larger contaminant loadings into the wetland via KTW OSPW (2021 and 2022) compared to KTW FW (2020). However, large variability in analyte concentrations in wetland plant tissue was observed, but still with no overall effect of year (p > 0.05) on BCFs. The variability in plant tissue concentrations suggests varying uptake rates of analytes or environmental changes that affect bioavailability of analytes in wetland water and sediment.

3.4.1. Arsenic

The mean concentration of dissolved As in KTW FW was 0.6 (SE 0.07) ug/L and concentrations of dissolved As in KTW OSPW ranged from 0.8 to 1.0 ug/L (< 1.1 ug/L total As), both of which are below the water quality guideline of 5 ug/L for the protection of aquatic life [31,43]. Concentrations of As in the KTW sediment ranged from 1.4 to 1.8 mg/kg and remained below the lowest effects level (6 mg/kg) reported in Persaud et al. [44] which represents the concentration threshold that has no effect on the majority of sediment-dwelling organisms. The concentration of As in plants roots ranged from 0.5 – 3.1 mg/kg, and similar accumulation in plant roots has also been observed in several other wetland studies (e.g. [45–47]). The concentration of As was greatest in cattail roots ($p < 0.05$) compared to all other plant tissues. The concentration of As in plant leaves ranged from 0.04 to 0.37 mg/kg and no differences between cattail and water sedge leaves were observed, suggesting As accumulation in aboveground plant tissue is low for cattails and water sedge [48].

The overall removal of As from KTW OSPW occurs mainly by sorption to sediment, with little removal from plant uptake. Lizama-Allende et al. [49] reported similar findings for As from synthetic mine water in wetland microcosms, where plant uptake into *P. australis* contributed less than 3% to the total As removal. This mechanisms of sequestration in sediment occurs due to the formation of iron plaques on the surface of plant roots to which As sorbs, storing As within the rhizosphere but limiting root uptake [45,50,51]. As sequestration by iron plaque formation has been shown to inhibit the translocation of As from plant roots to leaves [52], which explains the relatively low concentration of As measured in cattail and water sedge leaves compared to roots in the KTW.

3.4.2. Barium

The mean concentration of dissolved Ba in KTW FW was 54 (SE 6.1) ug/L, and concentrations of dissolved Ba in KTW OSPW ranged from 77 to 107 ug/L (total Ba concentration < 110 SE 6.3 ug/L). No water quality guidelines for Ba are available, however maximum acceptable concentrations for total barium in drinking water is 2,000 µg/L [53], suggesting these concentrations in OSPW are not likely a toxicological concern to aquatic organisms. The concentration of Ba in KTW sediment range from 88 to 108 mg/kg, which are below the Tier 1 remediation guideline for agricultural and sensitive land areas [54]. The concentration of Ba in plant roots range from 18 to 80 mg/kg and in plant leaves range from 9.4 to 26 mg/kg, indicating low translocation of Ba from root to leaf tissue.

The removal of Ba by wetland treatment has been found to be highly variable, with removal efficiencies ranging from 26 to 74 % in constructed wetlands treating municipal wastewater with similar Ba concentrations (72 ug/L) in the Czech Republic [55], and ranging from no removal (0%) to 49% removal of total Ba in a constructed wetland treating leachate in New York, USA [56]. The reduction of Ba from KTW OSPW in both 2021 and 2022 ranged from 8 to 34 % over 45-days of wetland treatment. The mechanisms of Ba removal and retention in wetland systems is poorly understood, but overall Ba doesn't appear to be a very mobile analyte among soil-plant systems in this study especially given the low concentrations reported in plant tissue.

3.4.3. Copper

The mean concentration of dissolved Cu in KTW FW was 0.45 (SE 0.14) ug/L, and concentrations of dissolved Cu in KTW OSPW ranged from 0.5 to 1.2 ug/L, which are all below water quality guidelines for the protection of aquatic life (4 ug/L; [43]). The concentration of Cu in KTW sediment ranged from 3.3 to 3.7 mg/kg, which is lower than average concentrations of Cu observed in soils from natural areas near oil sands mining activities (12.6 SE 2 mg/kg; [57]). The concentration of Cu in KTW plant roots ranged from 1.6 to 13.3 mg/kg and in plant leaves ranged from 0.7 to 11 mg/kg highlighting the large variability in plant uptake and accumulation of Cu throughout the study. The highest concentrations of Cu were observed in cattail root and cattail leaf in 2021 (Figure 3), suggesting these plants are strong accumulators of Cu and important components of treatment wetlands intended for Cu remediation. Wetland plants have been shown to uptake and accumulate Cu [58].

Wetland treatment of Cu-contaminated wastewaters has been explored in several other studies, primarily in subsurface flow wetland designs (e.g. [59–63]). Removal efficiencies in the reported literature range from zero (i.e. no treatment; [59]) to 82% removal [61]. In this study, the concentration of Cu in KTW OSPW reduced 65% over 88-days of continuous wetland treatment in 2021. No assessment of removal was performed in KTW OSPW 2022 due to the large number of non-detectable concentrations in our dataset for this period. Concentrations of Cu were found to briefly increase around day 30 during KTW OSPW 2021 treatment. Given the large error around the average concentration estimate of this data point and the continued

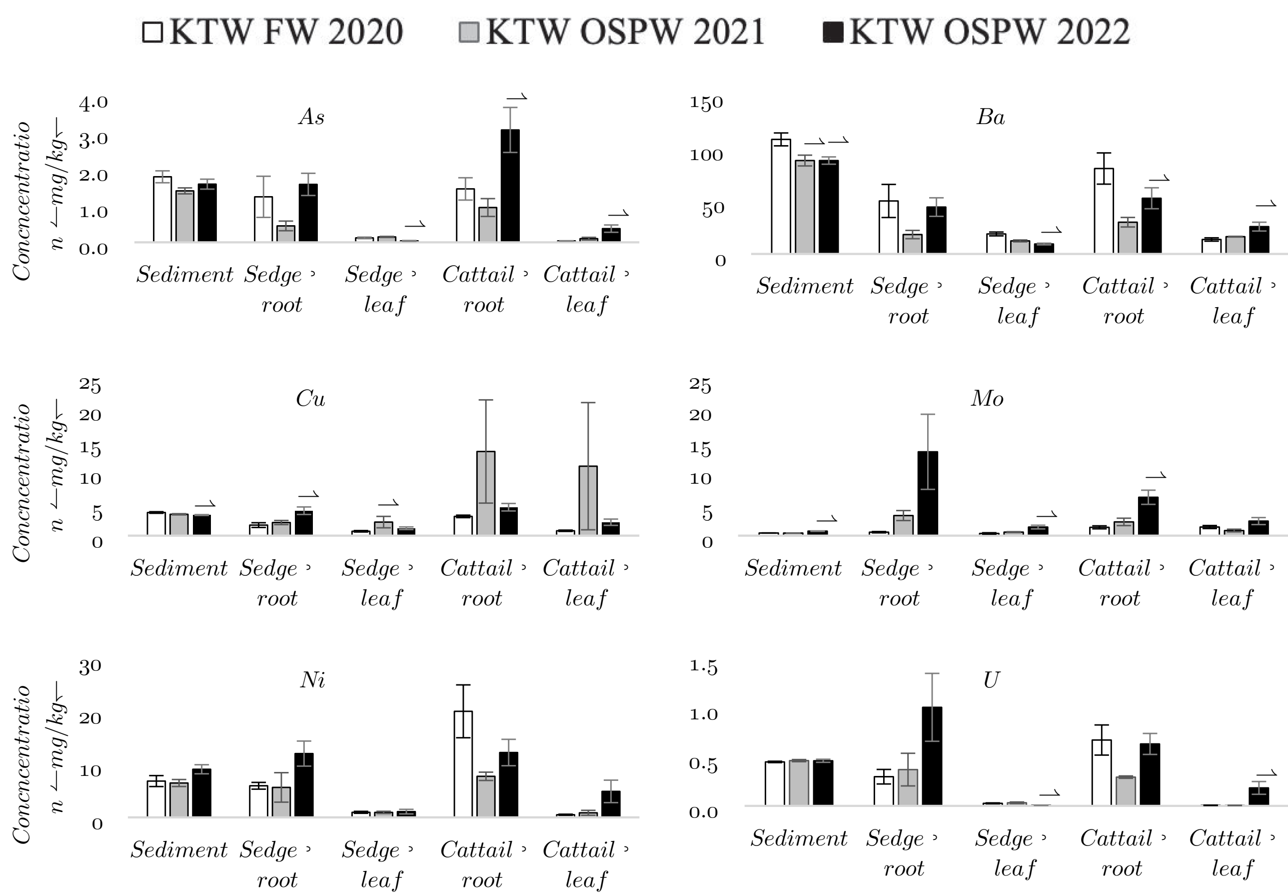

Figure 3. Concentrations of six metals in wetland media. Errors bars represent standard error of the mean concentration over the operational season year. The asterisk symbol (*) indicates that concentrations within wetland media in KTW OSPW 2021 or 2022 are statistically different ($p < 0.05$) from KTW FW 2020. Summary of results from ANOVA is provided in Table S4.

reduction in Cu concentration following this sample, we suspect the extreme value to be an outlier due to inconsistent sampling or laboratory analysis procedures.

3.4.4. Molybdenum

The mean concentration of dissolved Mo in KTW FW was 1.0 (SE 0.1) ug/L, and concentrations of dissolved Mo in KTW OSPW range from 19 to 32 ug/L (20 to 34 ug/L total Mo), which are all below the water quality guideline of 73 ug/L (total Mo) for the protection of aquatic life [31,43]. Concentrations of Mo in the KTW sediment range from 0.41 to 0.71 mg/kg, which is much lower than background concentrations of Mo in soils in Alberta, Canada (up to 3.8 mg/kg; [64]). The concentration of Mo in KTW plant roots ranged from 0.5 to 13.2 mg/kg and the concentration of Mo in plant leaves ranged from 0.3 to 2.3 mg/kg, with the concentration of Mo in water sedge roots significantly greater than all the other plant tissues ($p < 0.05$).

Mo exhibited the fastest rate of depuration among the six analytes assessed in the KTW, revealing the potential for treatment wetlands to effectively remove Mo from OSPW. The removal of Mo occurred mainly by sorption to sediment, whereas bioaccumulation in plants contributed little to overall removal of analyte mass from OSPW [65]. The removal of Mo has been shown to be dependent on pH, where lower pH tends to increase removal by adsorption to substrate [66,67]. Therefore, the slightly alkaline conditions of the KTW OSPW (mean of 7.7 to 8.3 pH across in both years) may have attenuated Mo removal, but greater removal of Mo may be possible under lower pH conditions.

3.4.5. Nickel

The mean concentration of dissolved Ni in KTW FW was 2.5 (SE 0.6) ug/L, and concentrations of dissolved Ni in KTW OSPW ranged from 3.4 to 4.6 ug/L (< 5.3 ug/L total Mo), which are all well below the acute and chronic water quality guidelines for the protection of aquatic life (1290 and 140 ug/L, respectively) [31]. The concentration of Ni in the KTW sediments range from 6.5 to 9.1 mg/kg, below a lowest effect level of 16 mg/kg proposed by Persaud et al. [44]. The concentration of Ni in KTW plant roots ranged from 5.7 to 12.3 mg/

kg and in plant leaves from 0.9 to 4.9 mg/kg. Across all years, Ni was distributed among the plant tissue in decreasing order of concentration: cattail root > water sedge root > cattail leaf ∼ water sedge leaf ($p < 0.05$), with no difference between cattail and water sedge leaves.

Cattails have been shown to efficiently uptake Ni from wastewater (e.g. [68]) and have been identified as Ni accumulators suitable for its removal from wastewater in constructed wetlands [69,70]. Concentrations of Ni in KTW wetland media (water, sediment, plant tissues) closely resemble those reported in Klink et al. [71] as characteristic of industrial sites. Airborne emissions of Ni have been reported in regions close to oil sands mining activities [72], suggesting Ni deposition may have also contributed to Ni concentrations in KTW FW and KTW OSPW throughout the operation of the KTW.

3.4.6. Uranium

The mean concentration of dissolved U in KTW FW was 0.4 (SE 0.1) ug/L, and concentrations of dissolved U in KTW OSPW ranged from 0.9 to 1.4 ug/L, which are all below short- and long-term freshwater quality guidelines (i.e. 33 and 15 ug/L, respectively; [31,43]). The concentration of U in KTW sediment was consistent across years and with a narrow range from 0.45 to 0.46 mg/kg, which is below the average concentration of U in Canadian soils (1.2 mg/kg; [73]) and in soils near oil sands mining activities (1.5 mg/kg; [57]). The concentration of U in KTW plant roots ranged from 0.3 to 0.7 mg/kg, and in plant leaves from 0.005 to 0.03 mg/kg, demonstrating a similar trend in the capacity for immobilization in aquatic plants roots that was reported in Favas et al. [74]. At circumneutral pH (between 5.5 and 7.2), higher concentrations of U in the wetland plant rhizosphere are expected because U tends to co-precipitate with iron and form root plaques [75]. Wetland plants were also shown to play an important role by increasing microbial activity and Fe cycling in their rhizosphere leading to greater sequestration of U in sediment [75].

The concentration of U in tailings wastewater from a uranium processing plant reduced up to a 90% after 40-days of wetland treatment [76]. In this study, the concentration of U in KTW OSPW reduced by 60 - 63% after 45-days of wetland treatment. Groza et al. [76] also reports that water sedge exhibiting slightly higher uptake of U than cattail. Similar results are observed in this study, with water sedge root (0.37 to 1.0 mg/kg) containing slightly higher concentrations of U compared to cattail root (0.29 to 0.63 mg/kg). Water sedge leaves also had slightly higher concentration of U (0.01 to 0.18 mg/kg) compared to cattail leaves (0.01 to 0.03 mg/kg). Beyond plant uptake, U has a particularly strong affinity to sorb to organic matter [77] meaning that U removal from OSPW in sediment occurs mainly through sorption to the organic soil fraction [78]. Plant uptake of U occurs only to the bioavailable fraction of U in sediment, which is reduced significantly if organic matter content exceeds 3% [74].

3.5. Plant bioconcentration and translocation

Figure 4 presents the bioconcentration and translocation factors in cattail and water sedge for the six analytes determined to depurate from OSPW in the KTW. Overall, there were no differences in BCF metrics between cattail and water sedge ($p > 0.05$) indicating both exhibit similar uptake and translocation of the six analytes. A metals accumulation index (MAI) was calculated [79] to confirm this, resulting in an MAI ranging from 1.01 to 2.81 for cattail and 1.47 to 1.84 for water sedge. Similar MAIs observed for cattail and water sedge suggests both species perform similarly in their overall ability to accumulate metals in their leaves. However, both MAIs were relatively low compared to values reported in Haghnazar et al. [80] for cattail of 6.90, suggesting plant uptake in the KTW may not be a major mechanism of metals removal, partly because of the lower concentrations of metals available for plant uptake at the KTW compared to sites reported in Haghnazar et al. [80]. Similarly, no significant differences in BCFs metrics were observed for the six analytes between years ($p > 0.05$), indicating that uptake and translocation is primarily dependent on reference concentrations (i.e. sediment concentration for RCF and LCF, and root concentration for TF). Further, the consistent environmental conditions within the KTW and KTW OSPW chemistry throughout the study (Table 1), plant uptake mechanisms and bioavailability were seemingly constant between years resulting in consistent bioconcentration metrics. There were, however, significant differences in uptake and translocation between the six analytes, particularly in the RCFs.

RCFs observed for As in this study were typically less than one (0.32 – 1.0), with the exception of the RCF for As in cattails in 2022 (1.93). RCFs were consistently lower than those reported in Ben Salem et al. [81] (2.0 – 5.4); however, concentrations of As in sediment were roughly 10 – 100 fold lower in this study.

Ba experienced low RCF values in both cattail (0.34 – 0.75) and water sedge (0.21 – 0.50) compared to other analytes in this study, suggesting slow root uptake and low bioaccumulation potential of Ba within plant roots. Despite higher concentrations of Ba in water and

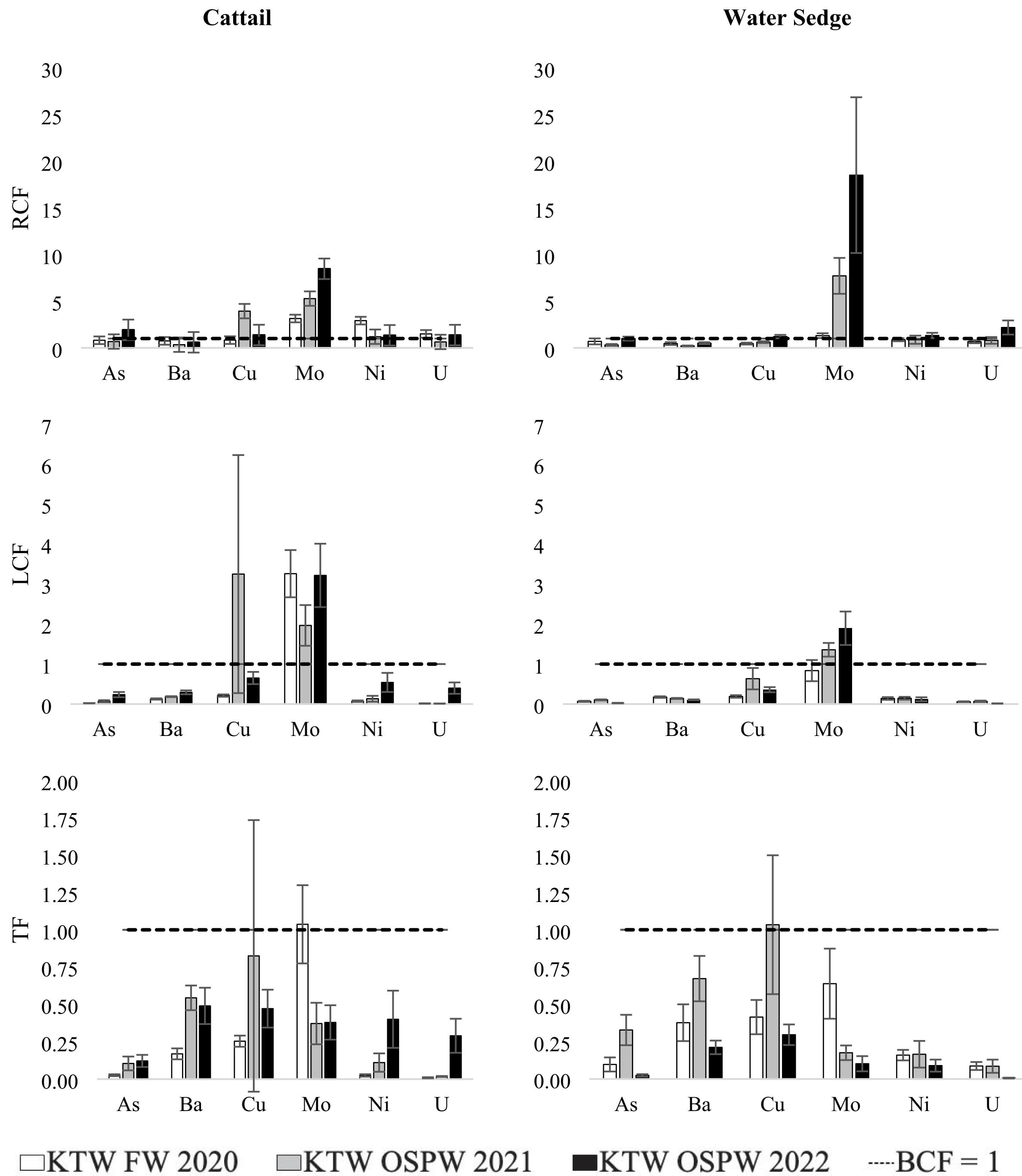

Figure 4. Root concentration factor (RCF), leaf concentration factor (LCF), and translocation factor (TF) for six metals in cattail and water sedge. BCF = Bioconcentration Factor. Error bars represent standard error of mean.

sediment in the KTW, RCFs remain relatively low indicating that Ba removal occurs primarily through sediment storage.

RCF values for Cu in cattails (0.83 – 3.94) and water sedge (0.46 – 1.21) were relatively high compared to most other analytes in this study. However, significantly higher RCFs for Cu are reported in Xue et al. [58] (RCF = 631 [*H. verticallata*] after 96-hours in 128 ug/L Cu solution) indicating Cu accumulation in certain plants can be rapid and substantial. The RCF for Cu in cattails and water sedge in this study is relatively low in comparison, but water concentrations were also substantially lower (0.45 (SE 0.14) ug/L).

Mo was consistently mobile within plants in this study and exhibited the highest RCF values, particularly in water sedge (18.5) compared to cattail (8.5) (KTW OSPW 2022) suggesting that water sedge are stronger bioaccumulators of Mo than cattails under KTW conditions. The efficiency of plant uptake of Mo may contribute to the relatively rapid depuration of Mo in KTW OSPW by wetland treatment. Although mechanisms of plant uptake and transport of Mo is still not well understood, it has been demonstrated that sulfate is an effective competitor to molybdate uptake [82,83]. Therefore, the relatively high concentrations of sulfate in KTW OSPW may inhibit Mo uptake in KTW plants.

The RCF for Ni in cattail in this study (1.35 – 2.92) are lower than the RCF for cattail reported in Klink [84] (5.14), but concentrations of Ni in sediment are roughly 3-fold greater in this study. The wide variability in RCFs suggests environmental conditions and water chemistry differences are important factors influencing Ni uptake into plants.

RCFs for U also varied widely (0.64 to 2.18) but tend to be greater for water sedge compared to cattail. However, these bioconcentration factors for U are significantly lower than (whole plant) mean bioconcentration factors for U in aquatic plants (ranging from 600 to 4000), but significantly greater than the bioconcentration factors for terrestrial plants (ranging from 0.02 to 0.2) reported in Favas et al. [74].

Little uptake of analytes into plant leaves occurred, as LCFs were observed as 1 > Ni > Ba > U >As for both cattail and water sedge, indicating relative immobility within plant systems. Cu and Mo were the only two analytes with LCFs greater than one (Cu: KTW OSPW 2021 [cattail only]; Mo: KTW FW 2020 [cattail only], OSPW 2021 [cattail and water sedge], and OSPW 2022 [cattail and water sedge]), highlighting the consistent plant uptake of Mo in the KTW that corresponds with its relatively rapid depuration from OSPW in this study. Mo (KTW FW 2020) and Cu (KTW OSPW 2021) were also the only analytes that exhibited TFs above one. Higher RCFs compared to LCFs and TFs often suggests that these analytes are phytostabilized in the rhizosphere, and not bioavailable for uptake and translocation to the leaves of cattail and water sedge under the prevailing environmental conditions in the KTW. These findings highlight the complexity of plant uptake and sensitivity of biogeochemical mechanisms to a range of environmental factors such as pH, redox potential, physicochemical interactions, and plant characteristics such as growth rate, tolerance thresholds, and nutrient requirements.

4. Conclusions

Wetland treatment and distribution of metals and trace elements found in oil sands process-affected waters (OSPW) in the KTW were explored over three years (2020 – 2022). Overall, concentrations of all metals and trace elements were relatively low in OSPW used for this study. Our findings indicate that the concentrations of 18 metals and trace elements were significantly higher in KTW OSPW (2021 and 2022) compared to KTW FW (2020), suggesting that contaminant-loading of these analytes into the KTW occurred through the introduction of source OSPW. Wetland treatment was effective in significantly reducing the concentrations of As, Ba, Cu, Mo, Ni, and U in OSPW. Their distribution among wetland media was explored to determine what biogeochemical processes may be contributing to their removal from OSPW by wetland treatment. Sorption to sediment was the primary removal mechanism for As and U since little plant uptake occurred for these analytes and both co-precipitate with iron to form root plaques. Mo experienced significant uptake in plant roots, particularly in water sedge, whereas Cu exhibited significant uptake in cattail roots and leaves. Mo bioavailability is highly influenced by pH and greater uptake would be expected under less alkaline conditions which are typical for OSPW. The bioconcentration and translocation factors demonstrated this trend, with Mo and Cu experiencing higher mobility within plant tissue compared to the other analytes, whereas Ni uptake into roots was observed but little translocation into leaves occurred and Ba was largely immobile within plant tissues in this study.

This work indicates that treatment wetlands can provide effective and safe removal of several metals from OSPW through a combination of removal pathways. Continued efforts into designing and implementing treatment wetlands for this purpose is warranted. Future treatment wetland projects applied to wastewaters with metal constituents should recognize the importance of the wetland substrate to treatment efficiency and consider the effects of environmental conditions (e.g. seasonality, vegetation type and maturity) and water chemistry (e.g. pH, redox potential) on metal bioavailability and distribution. The development and application of contaminant fate models for inorganics will also help to support our findings and explore the effects of environmental and water chemistry conditions on wetland treatment efficiency.

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Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials.

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