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1 **The role of sediment properties and solution pH in the adsorption of uranium(VI) to**
2 **freshwater sediments**

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39 **Abstract**

40 Uranium (U) can enter aquatic environments from natural and anthropogenic processes,
41 accumulating in sediments to concentrations that could, if bioavailable, adversely affect benthic
42 organisms. To better predict the sorption and mobility of U in aquatic ecosystems, we investigated
43 the sediment-solution partition coefficients (K_d) of U for nine uncontaminated freshwater
44 sediments with a wide range of physicochemical characteristics over an environmentally relevant
45 pH range. Test solutions were reconstituted to mimic water quality conditions and U(VI)
46 concentrations (0.023 to 2.3 mg U/L) found downstream of Canadian U mines. Adsorption of
47 U(VI) to each sediment was greatest at pH 6 and 7, and significantly reduced at pH 8. There were
48 significant differences in pH-dependent sorption among sediments with different physicochemical
49 properties, with sorption increasing up until thresholds of 12% total organic carbon, 37% fine
50 fraction ($\leq 50 \mu\text{m}$), and 29 g/kg of iron content. The K_d values for U(VI) were predicted using the
51 Windermere Humic Aqueous Model (WHAM) using total U(VI) concentrations, and water and
52 sediment physicochemical parameters. Predicted K_d -U values were generally within a factor of
53 three of the observed values. These results improve the understanding and assessment of U
54 sorption to field sediment, and quantify the relationship with sediment properties that may
55 influence the bioavailability and ecological risk of U-contaminated sediments.

56 **Keywords:** Uranium; sorption; distribution or partition coefficients; sediment; Windermere
57 Humic Aqueous Model, WHAM; speciation.

58 **Capsule:** The sorption of uranium(VI) was significantly influenced by solution pH and
59 physicochemical properties of sediment, and was modeled well with the geochemical speciation
60 model, WHAM7.

61

62 **1. Introduction**

63 Uranium (U) is an actinide element important in the nuclear fuel cycle, where it is both an initial
64 fuel source and final waste component. Northern Saskatchewan, Canada, is home to some of the
65 richest deposits of U in the world, making Canada the second largest producer (approx. 15%) of
66 U globally (OECD-NEA and IAEA, 2014). Introduction of U into aquatic environments can occur
67 in areas with U mining and nuclear processing, as well as in areas with high geological background
68 concentrations of U. In freshwater ecosystems, under oxic conditions, U is predominantly found
69 in the U(VI) state, either complexed to ligands or present as the aqueous hexavalent uranyl ion
70 (UO_2^{2+}), the latter of which has been suggested to be the major species responsible for U toxicity
71 in aquatic organisms (CCME, 2011; Markich, 2002; Sylwester et al., 2000). However, the uranyl
72 ion strongly interacts with solid phases, such as suspended solids, sediments and various minerals,
73 which tends to lead to large accumulation of U in depositional sediments downstream of U mine
74 and mill sites, in some cases exceeding 1000 mg U/kg d.w in the sediment (Hart et al., 1986;
75 Neame et al., 1982). Such accumulation of U in sediments can have adverse effects on benthic
76 invertebrates (Alves et al., 2008; Dias et al., 2008; Lagauzère et al., 2009; Liber et al., 2011;
77 Thompson et al., 2005) and as a result the Sediment Quality Guideline (SQGs) that exist (i.e.,
78 lowest effect level, probable no-effect concentration) have been set at approximately 100 mg U/kg
79 d.w. (Thompson et al., 2005; Sheppard et al., 2005). The degree of sorption of contaminants to
80 sediments influences the degree to which contaminants may be taken up by organisms (their
81 bioavailability), and subsequently their toxicity (Alves et al., 2008; Smit and Van Gestel, 1998;
82 Van Gestel and Ma, 1990). Thus, quantifying U sorption behaviour is important in understanding
83 the mobility and bioavailability of U in freshwater environments.

84 Uranium, in comparison to most cationic metals, has a relatively complex solid-aqueous chemistry,
85 which depends on a number of factors that influence the partitioning of U between the aqueous
86 and solid phases (Ames et al., 1983; Catalano and Brown Jr, 2005; CCME, 2011; Langmuir, 1978;
87 Markich, 2002; US EPA, 1999). Many ligands, such as phosphate, carbonate, and humic and fulvic
88 substances can form complexes that are readily soluble and mobile in aquatic systems (Cheng et
89 al., 2006; Franke et al., 2000; Schaller et al., 2008). However, transport of U can be limited by
90 strong adsorption onto solid phases. Specifically, a number of studies have demonstrated the
91 importance of single mineral or solid phases, such as montmorillonite and kaolin clay minerals,
92 organic carbon, goethite, and Fe oxides in the sorption of U (Bhattacharyya and Gupta, 2008;
93 Catalano and Brown Jr, 2005; Cheng et al., 2004; Mibus et al., 2007; Morrison et al., 1995; Ren
94 et al., 2010; Sachs and Bernhard, 2008; Zhirong and Shaoqi, 2010). However, the use of pure
95 mineral/solid phases may not appropriately represent more chemically complex field sediments.
96 The number of complexing agents and/or specific types of solid phases present in a system will
97 influence the degree of adsorption. Thus, there is often large variation in the sediment-solution
98 partition (or distribution) coefficients (K_d values) for U reported in the literature, which typically
99 range from <1 to 1×10^6 ml/g under various solid-aqueous conditions (CCME, 2011; US EPA,
100 1999). A limited number of studies have investigated the adsorption of U(VI) to field sediment
101 with variable total organic carbon (TOC), fine fraction (clay and silt particle size), iron (Fe) and
102 manganese (Mn) oxides contents, as well for sediments with varying cation exchange capacity
103 (CEC) (Barnett et al., 2000; Dong et al., 2012). Additionally, sorption of U is strongly influenced
104 by pH (Barnett et al., 2000; Markich, 2002), but few studies have investigated the importance of
105 pH in conjunction with physicochemical properties of sediment.

106 In the present study, we investigated the sorption of U(VI) onto nine field sediments in several
107 sorption experiments, as a function of U concentration and solution pH. The sediments were
108 collected from reference sites around U mines in northern Saskatchewan, Canada and exhibited a
109 wide range of common sediment physicochemical properties, such as TOC, particle size, CEC,
110 and Fe contents. Sorption experiments were conducted at three U concentrations and three pHs
111 that are environmentally relevant to areas surround U mining and milling activity in Canada. The
112 specific objectives were to: (i) measure the effects of U concentration and pH on the adsorption of
113 U to sediment, (ii) quantify the adsorption of U onto nine field sediments from northern
114 Saskatchewan representing different physical, chemical, and mineralogical properties, and (iii)
115 model U sorption to field sediments using a computer model (Windermere Humic Aqueous Model)
116 and compare model predictions to experimental observations. Our overall goal was to develop an
117 improved understanding and predictive capability of U sorption behaviour under conditions typical
118 of U mine sites in northern Saskatchewan, in order to better characterize U bioavailability and
119 improve risk assessment for U-contaminated sediments.

120 **2. Materials and methods**

121 *2.1. Characterization of field sediment*

122 The field-collected sediments used in this study were previously characterized and used in 10-d
123 U-spiked sediment bioaccumulation tests (Crawford and Liber, 2016). In brief, sediment was
124 collected from the top 10-cm layer of surficial sediments using an Ekman grab from 18
125 uncontaminated reference sites surrounding U mines in northern Saskatchewan, Canada
126 (Wollaston Lake area, 58°N, 103°W). Nine of these 18 sediments were selected for use in the
127 present study, chosen to represent a wide range in common physicochemical properties (Table S1).

128 Each of the sediment samples were air-dried, sieved through a 2-mm sieve, and thoroughly
129 homogenized prior to use and analysis.

130 ***2.2. Test solutions***

131 Stock solutions of U(VI) were prepared from uranyl nitrate hexahydrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Strem
132 Chemicals, Inc., Newburyport, MA, USA) and ultra-pure water (18 M Ω -cm). Test solutions were
133 reconstituted from ultra-pure water with 0.01 M NaNO_3 -0.005 M CaSO_4 to mimic water quality
134 conditions (i.e., conductivity, total hardness, alkalinity, and major ions; Table S2) found
135 downstream of Saskatchewan U mining and milling operations (EARMP, 2014; Goulet et al.,
136 2015).

137 ***2.3. Adsorption batch equilibrium experiments***

138 Sorption tests were conducted using a batch equilibrium approach following OECD 106 guidelines
139 (OECD, 2000). Tests were conducted at room temperature (~22 °C) in 50-ml polypropylene
140 centrifuge tubes, in duplicate. The tubes were prepared by adding 0.75 g d.w. of sediment and 30
141 ml of test solution (plus an extra 5 ml for water chemistry sampling prior to the test), producing a
142 fixed solid-to-solution ratio (SSR) of 25 g/L. The pH of the suspensions were adjusted daily with
143 0.1 M HNO_3 and/or NaOH (less than 0.05% of the total solution volume) to the desired pH values
144 of 6, 7 and 8 until a stable pH was achieved (maximum up to 10 days). These pH values represent
145 the range of overlying water pH typically found downstream of Saskatchewan U mines (EARMP,
146 2014; Goulet et al., 2015).

147 Immediately prior to spiking, 5-ml aliquots of centrifuged (4000 g, 5 min), pH-steady suspensions
148 were removed to determine initial conductivity, pH, total hardness, and alkalinity. At test initiation,
149 100- μl aliquots of U stock solutions were added to test tubes to achieve initial overlying water
150 concentrations of 0.023, 0.23, and 2.3 mg U/L. These U concentrations are environmentally

151 relevant to areas surrounding Saskatchewan U mines and mills and/or within the range of sub-
152 lethal U concentrations found in the overlying water of previous U-spiked sediment tests
153 (Crawford and Liber, 2016; Crawford and Liber, 2015; Environment Canada, 2003; Hynes et al.,
154 1987; Muscatello and Liber, 2010). Tests included additional duplicates of (i) *negative controls*
155 with no added U or sediment to ensure there was no contamination, (ii) *sediment controls* with
156 each sediment and no added U to determine if natural background U desorbed from sediment, and
157 (iii) *U controls* with added U but no sediment to ensure spiking accuracy. The sorption experiments
158 were conducted with all nine sediments at three U concentrations for all three pH conditions;
159 except pH 6 treatments, which were only tested at 0.23 mg U/L based on insignificant differences
160 among U concentrations obtained from pH 7 and 8 tests (see Results and Discussion section).
161 Immediately after spiking, dissolved U concentrations were determined from 1-ml aliquots of
162 centrifuged (4000 g, 5 min) and 0.45- μ m filtered (polyethersulfone membrane) supernatant. All
163 treatments were rapidly prepared and immediately capped to minimize exchange of CO₂ with the
164 atmosphere. Samples were then gently agitated on a rocking platform shaker for 48 h, which had
165 been established as an adequate time to achieve pseudo-equilibration under our experimental
166 conditions and in previous research (Barnett et al., 2000; Cheng et al., 2004; Payne et al., 2004).
167 The samples were removed from the shaker, centrifuged, and 1-ml aliquots of supernatant were
168 filtered for measurement of dissolved U concentrations. Additional aliquots of 10 ml were filtered
169 from the supernatant to quantify dissolved organic carbon (DOC; Shimadzu TOC-V CPN model
170 5000). The remaining suspensions were analyzed immediately for conductivity, pH, total hardness,
171 alkalinity, and major ions.

172 ***2.4. Chemical analysis and calculations***

173 Samples for analysis of Fe, Mn, and U were acidified to a pH of ~2 (HNO₃) and analyzed by
174 inductively coupled plasma-mass spectrometry (ICP-MS; X-series II spectrometer with
175 PlasmaLab software and collision cell technology, Thermo Electron Ltd., Mississauga, ON, CAN).
176 Certified reference materials (SLRS-5; National Research Council of Canada and 1640e; National
177 Institute of Standards and Technology), blanks, and duplicates were included with all analyses to
178 ensure analytical accuracy and validity. The minimum method detection limits for Fe, Mn, and U
179 were 1.34, 0.68, 0.05 mg/L, respectively, with instrumental and method recoveries of 80-120%.
180 All major ions in solution (i.e., K⁺, Na⁺, Ca²⁺, Mg²⁺, SO₄²⁻, Cl⁻, PO₄³⁻, and NO₃⁻) were analyzed by
181 Ion Chromatography (Dionex ICS-3000 dual Ion Chromatography System, Sunnyvale, CA, USA)
182 following U.S. Environmental Protection Agency Method 300.1 (US EPA, 1997).

183 The sediment-solution partition coefficient (K_d , ml/g) was calculated for U in each sediment, as
184 the ratio of the total concentration of U in the sediment ($\mu\text{g/g}$) and in the solution ($\mu\text{g/ml}$) at
185 equilibrium (after 48 h) using the equation:

$$186 \quad K_d = [(C_0 - C_e)/C_e] V/m \quad (1)$$

187 where C_0 is the concentration of U in the initial solution ($\mu\text{g/ml}$), C_e is the concentration of U in
188 solution at equilibrium ($\mu\text{g/ml}$), V is the volume of the solution (ml), and m is the mass of the
189 sediment (g) (CCME, 2011; OECD, 2000; Pandit et al., 2012).

190 ***2.5. Statistical analysis and modeling***

191 Statistical analyses were performed and plotted with Sigmaplot[®], version 11 (San Jose, CA, USA).
192 All tests were conducted adopting a significance value of $\alpha = 0.05$ after checking for compliance
193 with parametric assumptions of normal distribution (Shapiro-Wilk test) and homogeneous
194 variance (Levene's test). Since K_d values were log-normally distributed, all K_d -U values were log₁₀
195 transformed and analyzed using one-way analysis of variance (ANOVA) followed by Tukey's

196 post-hoc tests. If data did not meet the normality and homogeneity of variances assumptions, then
197 a non-parametric Kruskal-Wallis one-way ANOVA on ranks was used, followed by the Dunn's
198 method pairwise multiple comparison post-hoc test. The effects of sediment physicochemical
199 characteristics and pH on K_d -U were analyzed by linear (simple and quadratic) regression.
200 Pearson's product-moment tests were also used to identify correlations among sediment properties.
201 The root mean square error (RMSE) was calculated as a measure of the absolute errors between
202 the model estimates and the observed values.

203 The Windermere Humic Aqueous Model (WHAM7), version 7.0.4 (Lofts and Tipping, 2011;
204 Tipping, 1994) was used to estimate the chemical speciation of U in the experimental aqueous
205 media and predict K_d -U values under our experimental conditions. Speciation of U(VI) for the
206 different field sediments and test conditions was calculated using WHAM7 with the most current,
207 critically reviewed thermodynamic stability constants for U(VI) complexes presented in Table S3.
208 The WHAM7 model includes the Humic Ion-Binding Model VII, a discrete site/electrostatic
209 submodel of cation binding to humic substances (Tipping et al., 2011) and a surface complexation
210 model (Lofts and Tipping, 1998) for ion binding to mineral oxides. These submodels are
211 parameterized for the binding of 46 cations, including U(VI), to humic and fulvic acids and
212 amorphous Fe(III) oxide, optimized using the same value of protonation-dissociation constants
213 and surface site density. The solution complexation and particulate hydrous Fe oxide binding
214 parameters used were those of Lofts et al. (2015), specifically adjusted for U(VI) (Table S3). Free
215 Fe(III) and Al activities were computed assuming them to be in equilibrium with Fe(III)(OH)₃ and
216 Al(OH)₃, respectively. Precipitation of Fe(III)(OH)₃, UO₂ and CaUO₄ was allowed to occur if
217 saturation products were exceeded; however, no precipitation of either UO₂ or CaUO₄ was
218 predicted in the present sorption tests.

219 The input variables required for WHAM7 were based on measured physicochemical properties of
220 the test sediments and solutions (Tables S1 and S2; pH, TOC, Fe content, DOC, alkalinity, total
221 hardness, dissolved major ion concentrations, total U concentration in overlying water). Iron(III)
222 oxide contents of sediments were determined from measured Fe content by assuming that all
223 measured sediment Fe was contained in amorphous Fe(III) oxide and that 1 mole of Fe (55.85 g)
224 corresponded to 90 g of oxide (Dzombak and Morel, 1990). Fe oxide contents were further
225 converted to solution concentrations for input into WHAM7 as particulate hydrous Fe oxide by
226 accounting for the sediment concentration (i.e., 25 g/L SSR). Concentrations of TOC were
227 converted to solution concentrations for input into WHAM7 by accounting for the sediment
228 concentration, with the additional assumption that organic matter was comprised of 50% carbon,
229 and consisted of 50% particulate HA and FA. For measured DOC concentrations, complexation
230 was accounted for by assuming that dissolved organic matter (DOM) was comprised of 50%
231 carbon, with 65% of the DOM active with respect to cation binding (represented by FA), and input
232 into WHAM7 as colloidal FA (Tipping, 1998; Tipping and Lofts, 2015). The carbonate system
233 was simulated from measured alkalinity.

234 **3. Results and discussion**

235 *3.1. U(VI) adsorption batch equilibrium experiments*

236 *3.1.1. Physicochemical parameters of test sediment and water*

237 Sediments used in the sorption tests were collected from northern Saskatchewan, and represented
238 a wide range of TOC (1 to 22%), fine fraction ($\leq 50 \mu\text{m}$; 1 to 99%), CEC (4 to 64 meq/100 g), and
239 Fe content (5 to 34 g/kg) as presented in Table S1. All sediments had low background
240 concentrations of U ($\leq 3 \text{ mg U/kg d.w.}$) which were similar to or below the median sediment U
241 concentrations of 3.7 mg U/kg d.w. reported for northern Saskatchewan (Environment Canada,

242 2003). Furthermore, the sediments resulted in negligible concentrations of U in the test solutions
243 (≤ 0.002 mg U/L) as measured in the sediment controls (sediment with no added U).
244 Concentrations of U in the negative controls (no added sediment or U) were below the limit of
245 detection of U in solution (i.e., U-LoD < 0.05 μ g/L). Additionally, spiking efficiencies were within
246 $\pm 4\%$ of nominal concentrations in the U controls (U with no added sediment), with negligible loss
247 of U to the container walls over the 48-h equilibration period, which is consistent with other U
248 sorption investigations (Barnett et al., 2000; Cheng et al., 2004; Chisholm-Brause et al., 1994).

249 Water chemistry parameters for the controls and each sediment-pH treatment are summarized in
250 Table S2 and were used as input parameters for WHAM7. These values are within the range of
251 water quality characteristics representative of Saskatchewan waters receiving U mine and mill
252 effluent (Goulet et al., 2015). Uranium speciation and sorption are thought to be affected by water
253 hardness because the competitive binding of Ca and Mg to carbonate ions decreases the amount
254 of carbonate species available for binding U (Goulet et al., 2015). However, contrasting literature
255 exists regarding the importance of hardness in altering the sorption and bioavailability of U.
256 Previous accounts of increased hardness reducing toxicity is often confounded by co-varying
257 changes in alkalinity, or has been species-specific (Borgmann et al., 2005; Riethmuller et al., 2001;
258 Van Dam et al., 2012). A review by Sheppard et al. (2005) suggested that sensitivity of fish to U
259 under varying conditions of alkalinity and hardness was not due to the influence of hardness but
260 instead to low alkalinity. This conclusion is in agreement with a recent study by Goulet et al.
261 (2015) that concluded hardness was not the main driver for changes in toxicity as free uranyl ion
262 concentrations remained constant despite increasing hardness, and instead that alkalinity and pH
263 were the stronger influences. Low alkalinity results in greater free uranyl ion concentrations,
264 whereas greater alkalinity leads to uranyl complexation with carbonate and bicarbonate ions (i.e.,

265 Section 3.2). In our study, alkalinity tended to increase with pH with simultaneous decreases in
266 hardness, particularly for sediments with more silt, loam and TOC (Table S2). The goal of this
267 study was not to investigate the specific influence of hardness and alkalinity on U speciation and
268 mobility, as the test water was reconstituted, as closely as was feasible, to reflect the high hardness
269 and low alkalinity conditions found downstream of U mines in Saskatchewan. Thus, no
270 conclusions from the study can be made on the role of alkalinity and hardness.

271 Final pH measurements after 48-h showed little change (< 0.05 pH drift) from the starting solution
272 pH for each pH treatment. Mean measured pH values (Table S2) were mostly within 0.1 pH units
273 of the nominal value, except for pH 6 treatments which were consistently 0.2 to 0.3 pH units greater
274 than the nominal. Major ions measured in the reconstituted overlying water consisted of NO_3^- ,
275 SO_4^{2-} , Ca^{2+} , and Na^{2+} , ions that are common in treated effluent from U mining and milling activities
276 in northern Saskatchewan as a result of the U ore extraction and effluent treatment processes (i.e.,
277 lime, barium chloride, and sulfuric acid; EARMP, 2014; Goulet et al. 2015). Concentrations of
278 DOC ranged from 5.7 to 67.0 mg/L and increased with sediment TOC content (slope = 1.83, $R^2 =$
279 0.68 , $n = 27$, $p < 0.001$). Additionally, DOC increased as pH increased for most sediments and
280 coincided with a decrease in K_d -U values. This is consistent with a study by Ren et al. (2010),
281 which demonstrated that for solutions with $\text{pH} > 6.5$, negatively charged FA and HA resisted
282 adsorption to clays due to electrostatic repulsion and remained in solution as pH increased. Thus,
283 greater pH may allow for more complexation between DOC and U, which would decrease sorption
284 to sediment (i.e., more U in solution present as U-DOC complexes). This is further supported by
285 a study of Van Dam et al. (2012), which concluded that U toxicity was reduced to a variety of
286 freshwater organisms by 6 to 9% with each addition of 1 mg/L of DOC (up to 30 mg/L DOC).

287 Thus, DOC and water chemistry are important modifiers of U sorption behaviour and should be
288 documented in all U-sorption studies.

289 ***3.1.2. U(VI) adsorption at different U concentrations***

290 The K_d values for the three U concentrations investigated at each pH treatment are presented for
291 all nine sediments in Fig. S1. Although K_d -U values differed among sediment types at each pH,
292 the three U concentrations did not have a significant effect on K_d -U values for each sediment
293 treatment at pH 7 and 8 ($p > 0.05$; one-way ANOVA). Due to the negligible effect of U
294 concentration on K_d -U, these values for the remainder of the paper are presented as an average K_d -
295 U for all three U concentration treatments for pH 7 and 8 (mean \pm SD, $n = 6$); only one U
296 concentration (230 $\mu\text{g/L}$) was used to determine K_d at pH 6 ($n = 2$). The final U concentrations
297 measured in the overlying water of the nominal 230 $\mu\text{g/L}$ treatments ranged from 0.12 to 150 $\mu\text{g/L}$
298 (Table S2). It is worth restating that these initial added U test concentrations ($t = 0$ h) and final U
299 concentrations ($t = 48$ h) are environmentally relevant to areas surrounding U mining and milling
300 activity. For example, the initial 230 $\mu\text{g/L}$ test U concentration is within the range of U
301 concentrations reported for surface water at decommissioned mines in Beaverlodge Lake,
302 Saskatchewan (200 to 400 $\mu\text{g/L}$; CCME, 2011). Additionally, the lowest initial U concentration
303 tested (23 $\mu\text{g/L}$) falls within the range of the long-term and short-term Canadian Water Quality
304 Guidelines (CWQG) for U of 15 $\mu\text{g/L}$ and 33 $\mu\text{g/L}$, respectively (CCME, 2011). The highest
305 concentration tested (2.3 mg/L) was included as concentrations > 3 mg/L were historically
306 measured in northern Saskatchewan U mine effluent discharge (Hynes et al., 1987) and represents
307 a very high, but possible pore water U concentration.

308 ***3.1.3. U(VI) adsorption as a function of pH***

309 The degree of U adsorption for each sediment was significantly dependent on aqueous pH, with
310 greater K_d -U values observed at pH 6 and 7, followed by a sharp, significant decrease at pH 8 for
311 all sediment treatments (Fig. 1; $p < 0.001$). The maximum adsorption ($K_d > 1000$ ml/g), observed
312 at all pH values between 6.2 and 7.4, was likely the result of a greater number of negatively charged
313 binding sites (compared to pH 8) available on mineral surfaces due to the release of protons
314 (CCME, 2011). Alternatively, the formation of uranyl-carbonate complexes at pH 8 may also
315 decrease adsorption of U (i.e., low K_d -U values; Fig. 1) due to negligible interactions of such
316 complexes with solid phases. The formation of soluble uranyl-carbonate complexes and low
317 sorption at alkaline pH conditions is in agreement with previous literature for a number of other
318 substrates, including pure Fe-minerals and amorphous Fe hydroxides (Barnett et al., 2000;
319 Langmuir, 1978; McKinley et al., 1995; Payne et al., 2004; Vandenhove et al., 2007; Waite et al.,
320 1994). Speciation of U, dissolution and precipitation processes, and surface charge or availability
321 of binding sites on organic matter and oxide clay minerals are known to change as a function of
322 pH (CCME, 2011; Maity et al., 2013). These characteristics and processes alter the availability of
323 cationic metals and influence complexation to solid phases (Barnett et al., 2002; Ren et al., 2010).
324 Although not investigated in our study, adsorption is also reported to be low at $\text{pH} < 6$ due to
325 competition for binding sites between H^+ ions and the free UO_2^{2+} ion that predominates at lower
326 pH conditions (CCME, 2011; Markich et al., 2000; Riethmuller et al., 2001). Thus, sorption of U
327 within the environmentally relevant pH range is unlike many other cationic metals; changes in pH
328 lead to a relationship with sorption increasing as pH increases, to a maximum sorption at
329 circumneutral pH conditions, followed by a decrease in sorption as pH increases further (i.e.,
330 sorption envelopes).

331 A negative relationship, which could be represented by a linear equation, was observed between
332 K_d -U and pH [$\log K_d(U) = -1.02 \text{ pH} + 10.54$, $R^2 = 0.61$, $n = 27$, $p < 0.001$; Fig. 1, solid black line].
333 This trend is in general agreement with previous literature examining the relationship between pH
334 (6 to 9) and U sorption to sediments and soils [$\log K_d(U) = -0.77 \text{ pH} + 7.73$, $R^2 = 0.30$, Vandenhove
335 et al., 2009b; $\log K_d(U) = -1.18 \text{ pH} + 10.8$, $R^2 = 0.65$, Vandenhove et al., 2007; $\log K_d(U) = -1.07 \text{ pH}$
336 $+ 9.80$, $R^2 = 0.41$, Sheppard et al., 2006; $\log K_d(U) = -1.29 \text{ pH} + 11.0$, $R^2 = 0.76$, Echevarria et al.,
337 2001]. General similarities in the observed relationship to other published findings confirm that
338 pH is a significant modifier of U sorption despite differences in experimental conditions among
339 the different studies (e.g., SSRs, U concentrations, soil vs. sediment substrate, incubation time,
340 water chemistry). However, the K_d -U values reported here for the pH 6 and 7 treatments were not
341 significantly different, except for sediments WB, KL and HL which had ~2- to 10-fold greater K_d -
342 U values at a nominal of pH 6 than 7 ($p < 0.05$). As a result, the linear regression shown does not
343 predict the K_d -U values at pH 7 accurately. This trend may also have been present in other
344 published research, but masked by the variability in sediments/soils and conditions examined. One
345 strength of the present research is that U sorption was investigated under different pH conditions,
346 but for the same sediments, thus allowing for a less confounded investigation of the effects of pH
347 on U sorption. For the present data, a quadratic function [$\log K_d(U) = -21.22 + 7.97 \text{ pH} - 0.63 \text{ pH}^2$,
348 $R^2 = 0.67$, $n = 27$, $p < 0.001$; Fig. 1, dashed line] provided a slightly better fit than the linear
349 relationship, at least within the pH range investigated. But it is evident from Fig. 1 that pH alone
350 does not solely dictate K_d -U for the number of sediments investigated.

351 Generally, K_d values are an indication of the adsorption of a compound to solid phases (via ion
352 exchange processes and surface complexation formation) and subsequent mobility and thus
353 bioavailability of a compound in an aqueous system. The mobility of contaminants is generally

354 small for compounds with K_d values > 1000 ml/g as sorption to sediments is great. In contrast,
355 mobility can be considered high when K_d values are ≤ 10 ml/g due to the negligible partitioning to
356 sediment (Sheppard, 2011). The K_d -U values calculated in the present study ranged over three
357 orders of magnitude from ~ 20 to $> 20,000$ ml/g depending on the pH and sediment type (Fig. 1).
358 Adsorption of U to sediments was $\geq 97\%$ at pH 6 and 7 treatments, while adsorption ranged from
359 43 to 97% for the pH 8 treatment depending on the sediment used. The greater K_d -U values ($>$
360 1000 ml/g), and the extent of adsorption at pH 6 and 7, suggest that mobility of U may be of limited
361 interest in some environmental assessments, as most U under such conditions would have a
362 tendency to bind to sediment. In contrast, greater concentrations of U in solution at pH 8, as
363 indicated by K_d -U values < 500 ml/g, suggest that the potential for U transport may be greater at
364 higher pH values. Greater concentrations of dissolved U may also increase the potential uptake of
365 U by organisms depending on the water chemistry, type of organism, exposure route, and type of
366 sediment (Crawford and Liber, 2016; Liber et al., 2011). The results from the present study
367 demonstrated the strong influence of pH on U adsorption at pH conditions (6 to 8) representative
368 of northern Saskatchewan U mining areas, suggesting that increased U mobility and transport are
369 more likely the higher the pH of the system.

370 **3.1.4. U(VI) adsorption and sediment physicochemical properties**

371 The effect of sediment properties on U sorption is demonstrated in Fig. 2a-d for four common
372 sediment properties (TOC, fine fraction, CEC, and Fe content). The K_d -U values varied by orders
373 of magnitude at a specific pH as a function of sediment type, with greater fine fraction and Fe
374 content sediments (ML, KL, SL1) having greater K_d -U values than sandier sediments (SL2 and
375 UR8). In particular, there appeared to be an interaction between pH and sediment type, as an 80-
376 fold change in K_d -U values occurred at pH 8 while only approximately a 14-fold change in K_d -U

377 values was observed at pH 6 and 7 for the same sediments. Sheppard (2011) reported a similar
378 trend with a 250-fold higher K_d -U for soils containing 35% clay compared to 5% clay at pH 5.5,
379 while at pH 6.5 only a 3-fold change in K_d occurred for the same range in clay content.
380 Additionally, K_d -U values have previously been proposed for sand (40 ml/g), loam and clay (200
381 ml/g), and organic soils (2000 ml/g) (Sheppard et al., 2006), but K_d values for U can typically
382 range from <1 to >500,000 ml/g (Campana et al., 2013; Echevarria et al., 2001; Maity et al., 2013;
383 Pandit et al., 2012; Van Dam et al., 2012; Van Gestel, 2008; Vandenhove et al., 2007). Conversely,
384 some studies have reported no effect of sediment properties such as CEC or TOC on U sorption
385 (Echevarria et al., 2001; Vandenhove et al., 2007), likely due to differing pH conditions and the
386 limited range in sediment/soil properties investigated (i.e., only examined approx. <1 to 3%
387 organic carbon).

388 Significant positive relationships were evident between sediment properties and K_d -U values (R^2
389 > 0.71, $p < 0.05$, Fig. 2 and Table S4) until either a threshold was reached or negative relationships
390 were observed. These inflection points were clear for sediments with greater than 12% TOC, 37%
391 fine fraction, and 33 meq/100 g CEC (Fig. 2a-c), and to a lesser extent for sediments with 29 g/kg
392 of Fe content (Fig. 2d). Vandenhove et al. (2007) demonstrated a strikingly similar positive
393 relationship between increasing K_d -U values and greater soil organic matter ($R^2 = 0.70$) and Fe
394 content ($R^2 = 0.63$). However, the latter study did not document a threshold after which a negative
395 relationship was observed, as the maximum ranges examined were only approximately 15%
396 organic matter and 20 g/kg of Fe content (Vandenhove et al., 2007), which are near or below the
397 thresholds at which negative relationships appeared in our study. Exceptions to the positive
398 relationships between sediment characteristics and K_d -U values in our study were observed for
399 sediments with the greatest TOC, fine fraction, and CEC (i.e., SL1, HL, and KL). The decreasing

400 K_d -U values associated with these sediments contradicts information from the literature that
401 suggest that these sediments should offer the greatest number of binding sites for contaminants
402 (Davis et al., 2004; Pabalan and Turner, 1996; Simpson et al., 2011). However, the lower K_d -U
403 values observed for these organic carbon- and mineral-rich sediments (Fig. 2) may be, in part, due
404 to desorption of complexing agent such as DOC, colloids, and carbonates from the sediment. Such
405 desorption would increase dissolved U and lower K_d -U values, but without necessarily increasing
406 U bioavailability. This is supported by results from previous experiments with the same organic-
407 and mineral-rich sediments (SL1, HL, KL) that resulted in the lowest bioaccumulation of U by *C.*
408 *dilutus* larvae (Crawford and Liber, 2016), demonstrating that much of the U was not bioavailable.
409 These results suggest that U may be in solution and mobile even for sediments with large
410 concentrations of some binding phases, but that the variability in dissolved U does not necessarily
411 correlate with U bioavailability to aquatic organisms. Therefore, bioaccumulation tests
412 complement investigations of U sorption and information on the presence of colloids, DOC and
413 other ligands that could be released from sediment should be provided.

414 The sorption tests demonstrated that all sediment properties evaluated here were important
415 modifying factors of U sorption (Fig. 2); however, the use of a combination of multiple factors
416 may have limited practicality for modeling U bioavailability in sediment. Fe content (Fig. 2d) was
417 the factor that explained the greatest variation in K_d -U across the entire range of parameters
418 examined here (at least up until ~29 g/kg), excluding the additional influence of pH. Barnett et al.
419 (2000) also suggested that Fe oxide content exerted significant control over sorption of U across
420 three bulk substrates with similar Fe oxide contents, as K_d values were similar despite having
421 significant differences in fine fraction and organic matter content. Uranium species can adsorb to
422 the surface sites of Fe oxides, and can become structurally incorporated into the oxide structure

423 through repeated dissolution-precipitation cycling of amorphous or poorly crystalline Fe oxides
424 (Vandenhove et al., 2007). Thus, Fe oxides in sediment can be an important adsorption-controlling
425 phase for U, and may overcome the challenges of predicting U bioavailability associated with the
426 presence of dissolved U-complexes from complexing agents such as DOC and colloids.
427 Additionally, Fe content of sediment has previously been observed to correlate with fine fraction,
428 CEC, and TOC for the sediments used in this study ($r = 0.84$ to 0.97 , $p < 0.001$; Crawford and
429 Liber, 2016), as well as for other sediments and soils (Bradham et al., 2006; Payne et al., 2011;
430 Vandenhove et al., 2007; Waite et al., 1994). The binding of U and other metals to sediments is
431 not only influenced by the presence of Fe/Al oxides, but also by pH and TOC, which influence the
432 binding properties (surface area, charge and binding sites). Properties such as CEC are intrinsically
433 accounted for through correlation with parameters such as sediment TOC and fine fraction, which
434 are routinely measured in conjunction with field-collected sediment samples (Bradham et al.,
435 2006; Criel et al., 2008). Recent studies have also supported the use of K_d values normalized for
436 specific surface area (Davis et al., 2004; Pabalan and Turner, 1996; Wang et al., 2011). However,
437 sorption can be controlled by interactions with specific surface sites, the abundance of which are
438 not reflected by the specific surface area (Payne et al., 2011).

439 An exception to the positive linear relationship between Fe content and K_d -U was observed with
440 the KL sediment, which had a slightly lower K_d -U value, despite having the greatest Fe content
441 (34 g/kg; Fig. 2d). However, the KL sediment also had the only detectable CaCO_3 content (1.13%),
442 which Pandit et al. (2012) have demonstrated to have a strong negative correlation with K_d for
443 soils collected around U mines due to the formation of uranyl-carbonate complexes. Sheppard
444 (2011) also suggested that carbonates were more likely to persist in fine-textured soils and KL had
445 the highest content of clay (28%) among the sediments tested. The lower sorption in the KL

446 sediment may therefore be a result of the formation of soluble uranyl-carbonate complexes.
447 Overall, sediment properties, particularly Fe content, were significant modifiers of U sorption,
448 resulting in up to an 80-fold change in K_d -U values for sediments collected from the same general
449 area of northern Saskatchewan.

450 ***3.2. Modeling aqueous U(VI) speciation***

451 The abundance of aqueous U species was estimated as a function of pH using WHAM7 for selected
452 sediments that covered a wide range of physicochemical properties (Table S1) and water
453 chemistries (Table S2). These U species are presented in Fig. S2. The major aqueous U species
454 were dominated by the (calcium)-uranyl-carbonate complexes, with $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ and
455 $\text{CaUO}_2(\text{CO}_3)_3^{2-}$ being greatest at pH 7 and 8, and UO_2CO_3 and $\text{UO}_2(\text{CO}_3)_2^{2-}$ being greatest at pH
456 6. The dominance of these aqueous U(VI) species is in agreement with previous modeling efforts
457 in the primary literature (Lofts et al., 2015; Wang et al., 2011). Thus, these speciation calculations
458 support the observed reduction in K_d values at pH 8, which were likely due to the formation of
459 uranyl-carbonate complexes that predominate under alkaline conditions and inhibit adsorption to
460 the sediment solid phase.

461 ***3.3. Modeling of U(VI) adsorption***

462 While using the relationship between Fe content of sediment and K_d -U is useful for estimating
463 changes in U bioavailability, a more universally applicable tool is desirable for the prediction and
464 modeling of U sorption behaviour in aquatic systems. A number of studies have supported the use
465 of surface complexation models (SCMs) for the modeling of U sorption (Barnett et al., 2000; Davis
466 et al., 2004; Dong et al., 2012; Pabalan and Turner, 1996; Payne et al., 2004; Romero-González et
467 al., 2007; Waite et al., 1994). Adsorption parameters may be derived directly by fitting to the solid
468 material (the generalized composite approach), which provides optimal site-specific model

469 performance at the expense of general applicability. A more flexible method is the assemblage
470 approach, where adsorption is modeled on the basis of the solid phase composition using a
471 collection of adsorption models parameterized on synthesized or isolated components (substrates)
472 of the solid phase such as organic matter, sesquioxides and clays (Dong et al., 2012; Groenenberg
473 and Lofts, 2014; Waite et al., 1994). In this study WHAM7 was applied to predict sediment K_d
474 values using the assemblage approach, using adsorption models for particulate organic matter and
475 Fe(III) oxide. This allowed for prediction of the variability of U sorption across the field sediments
476 and water characteristic of U mining areas in Saskatchewan, incorporating multiple solid-
477 adsorbing parameters. The phase models used in the present study for ion binding to HA, FA, and
478 hydrous Fe oxide allow both specific (inner-sphere) and diffuse layer binding. These binding
479 mechanisms are supported by recent studies that have demonstrated that adsorption of U species
480 onto clay mineral surfaces occurs via the formation of bidentate inner-sphere surface complexes
481 at near-circumneutral pH conditions (Dong et al., 2012; McKinley et al., 1995; Pabalan and Turner,
482 1996; Sylwester et al., 2000). However, some of the previous studies were conducted under CO₂
483 free or low CO₂ conditions which means the role of uranyl-carbonate ternary surface complexes
484 was not investigated (McKinley et al., 1995; Pabalan and Turner, 1996; Sylwester et al., 2000).
485 Carbonate complexes with uranyl can be very important for systems containing CO₂ and have been
486 reported as important sorption processes for U onto montmorillonite clay and different soils
487 (Catalano and Brown Jr, 2005; Dong et al., 2012; Pandit et al., 2012).

488 Modeling yielded a strong 1:1 relationship between the predicted and observed U concentrations
489 in solution (at equilibrium) in the various sorption tests (Fig. 3a; slope = 1.02, $R^2 = 0.961$, $p <$
490 0.001 , RMSE = 42 $\mu\text{g/L}$). This demonstrated that the model can predict, generally within a factor
491 of three, the concentration of U in solution based on the expected binding/partitioning of U to the

492 solid phases (i.e., sediments). Previous studies have reported issues with greater variation between
493 the observed and predicted U concentrations near adsorption edges, where concentrations change
494 sharply with pH (i.e., pH 8) (Barnett et al., 2002). A model examined by Barnett et al. (2002)
495 overestimated the K_d -U by up to two orders of magnitude in the pH range of maximum adsorption
496 (pH 6 to 7). Model predictions would be most sensitive to uncertainties in the measured pH near
497 adsorption edges. However, aqueous U concentrations were well predicted by WHAM7 under our
498 test conditions and parameters. The WHAM-predicted K_d -U values were generally within a factor
499 of three of the observations for all the sediment-pH treatments (Fig. 3b; slope = 1.07, $R^2 = 0.94$, p
500 < 0.001, RMSE = 0.47 ml/g log unit), with only slight deviations from the 1:1 line at the low K_d
501 values. One possible reason for the slight overestimation of U solubility at pH 8 may be due to an
502 underestimation of the total number or binding affinity of reactive surface sites, and/or
503 overestimation of complexation in solution. Regardless, the similarity between the predicted and
504 observed K_d -U values validates the trends presented in Fig. 2 (including the inflection points) for
505 U sorption as a function of different sediment properties. This further demonstrates the influence
506 of TOC, DOC, and Fe oxides, common input parameters for WHAM7, on U binding and
507 complexation. Thus, WHAM7 is able to account for the complex interactions between uranyl
508 binding to ligands on the solid sediment and in the solution in freshwater systems with a wide
509 range of sediments and conditions characteristics of northern Saskatchewan U mining areas.

510 ***3.4. Implications for site characterization***

511 The present research confirms that K_d -U values are influenced by a number of sediment
512 components including TOC, fine fraction, CEC, and Fe content, water chemistry including pH,
513 and metal-complexing ligands such as carbonates. The extent of U adsorption was significantly
514 pH-dependent. Due to the complex nature of U sorption with multiple and correlating sediment

515 characteristics, it is difficult to recommend a simple relationship between the U concentrations in
516 solution and a single sediment parameter. However, the Fe content in sediment (within the range
517 of ~1 to 29 g Fe/kg sediment) was a consistent and strong modifier of U sorption behaviour with
518 a relationship modeled by the equations presented in Table S4 of the supplementary material. Fe
519 content, along with other common physicochemical parameters of sediments, provided useful
520 information for the application of an internationally recognized and user-friendly model, WHAM7,
521 to predict U sorption behaviour. It is therefore recommended that Fe content should be reported,
522 in addition to all other routinely measured sediment parameters, in site assessments where U-
523 contamination is a concern. Additionally, this research highlighted the conditions that enhance the
524 mobility of U in sediment, which will allow for further examination of these conditions to improve
525 the risk assessment of U-contaminated sites. Adsorption of U to sediment and other particulate
526 phases strongly influences the proportion of U available for transport and uptake by removing U
527 from the aqueous phase or by forming complexes that render U immobile and/or not bioavailable.
528 From this study, sediments in alkaline aquatic systems with low Fe content would favour greater
529 U concentrations in solution and thus likely greater U mobility and possible uptake in aquatic
530 organisms. Future work should focus on additional quantification and further validation of field
531 and/or site-specific physicochemical properties that could improve the use of WHAM7, which
532 may lead to more accurate risk assessments for U-contaminated sites and for development of
533 bioavailability influenced U-SQGs.

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541 **Appendix A. Supplementary data**

542 Supplementary data related to this article can be found in the attached document.

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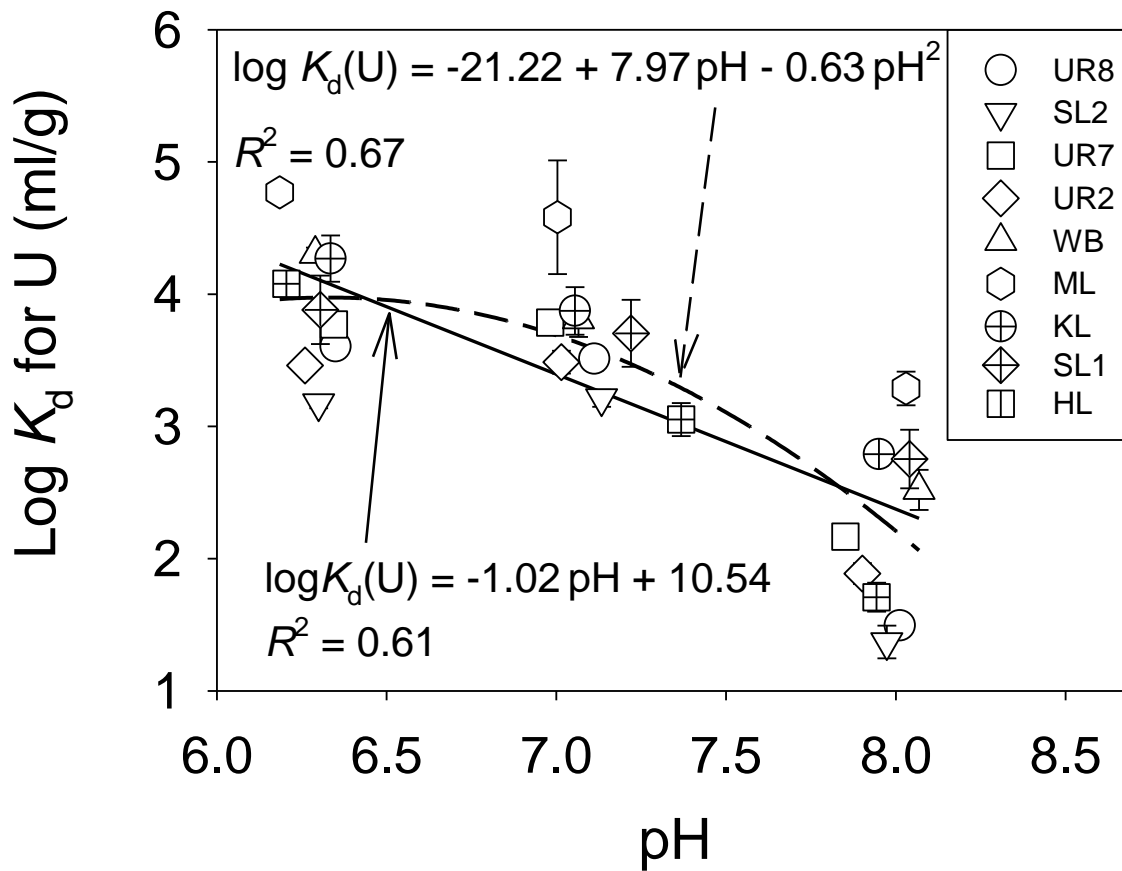
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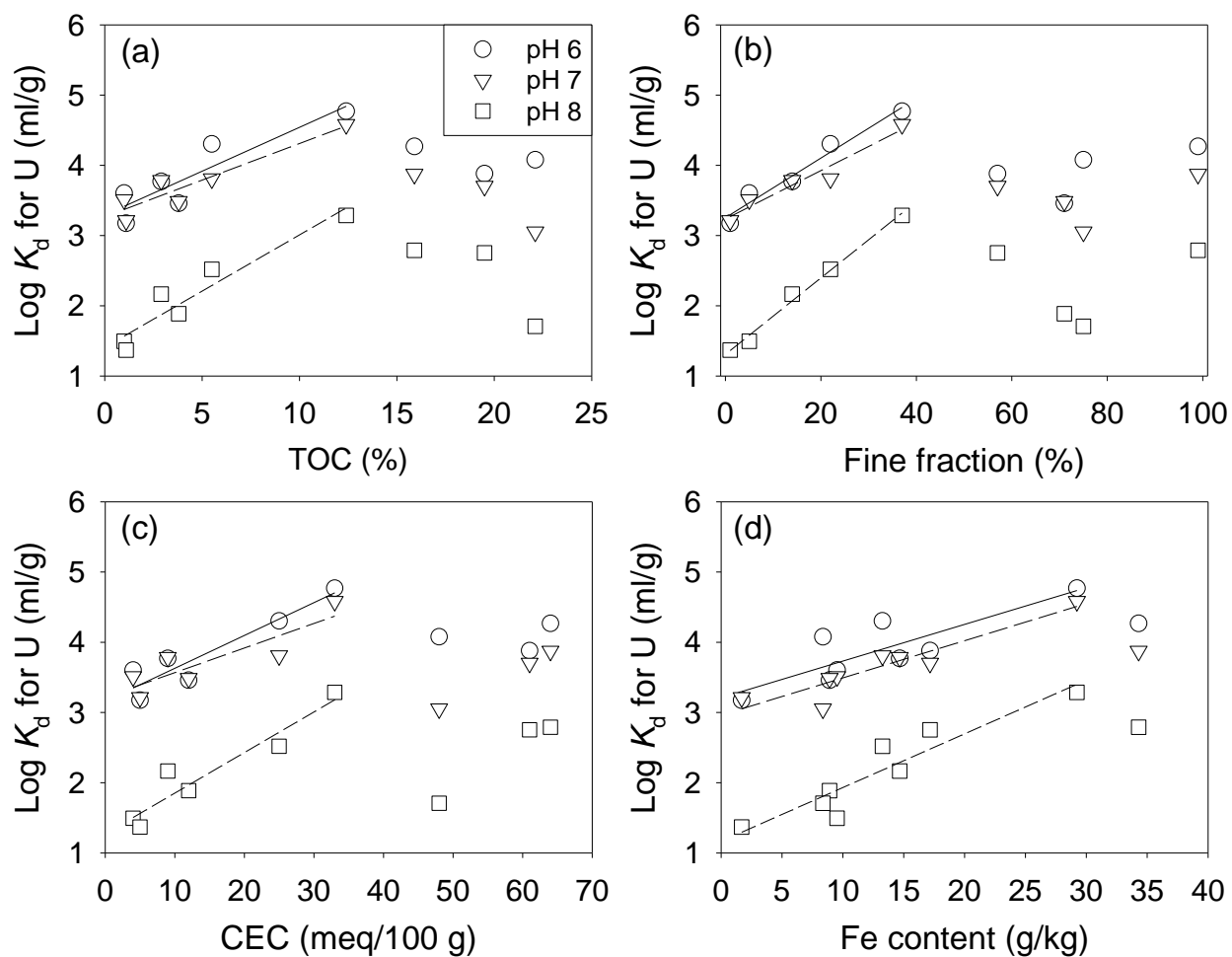
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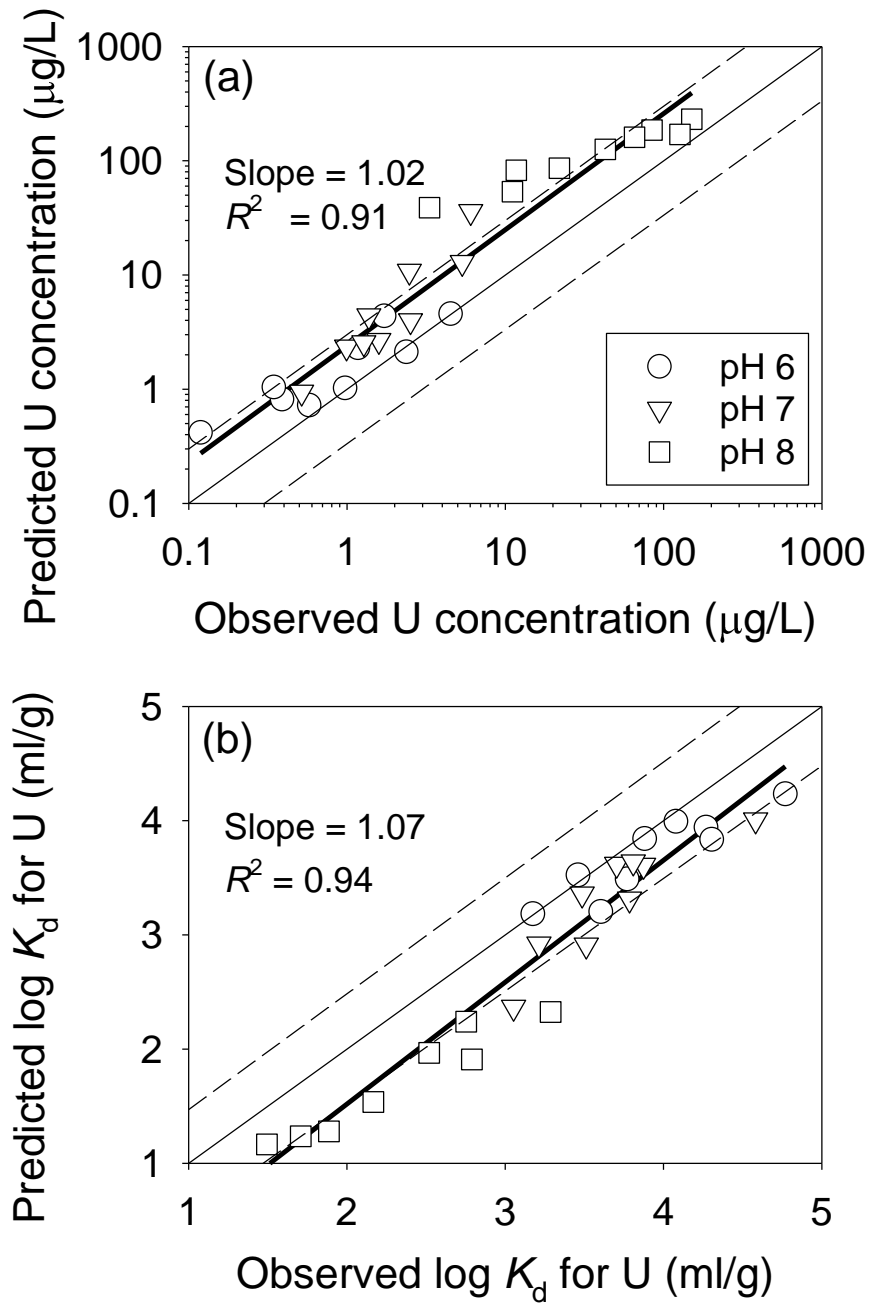
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733 Fig. 1 Mean (\pm SD, $n = 2-6$) K_d values for U (log ml/g) for all nine sediments as a function of pH
 734 for nominal pH treatments of 6, 7 and 8. The solid black line represents the negative linear
 735 regression and the dashed line represents the quadratic relationship between K_d -U and pH for all
 736 sediment treatments ($p < 0.001$).



737

738 Fig. 2 Mean K_d for U (log ml/g) as a function of solution pH (nominal of 6, 7, and 8) and sediment
 739 (a) total organic carbon content (TOC, %), (b) fine fraction content ($\leq 50 \mu\text{m}$, %), (c) cation
 740 exchange capacity (CEC, meq/100 g), and (d) iron content (Fe, g/kg). Each symbol within a series
 741 represents one of nine different sediments. Lines represent significant linear regressions up until a
 742 threshold (Linear equations are presented in Table S4 of the supplementary material).



743

744 Fig. 3 WHAM-predicted versus observed (a) U concentration ($\mu\text{g/L}$) in the overlying water at
 745 equilibrium, and (b) $\log K_d$ for U (ml/g) for all nine sediments at pH 6, 7, and 8. Thick solid line
 746 represents the linear regression for all data points ($p < 0.05$); the 1:1 line is bracketed by dashed
 747 lines representing a factor of three.