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The role of sediment properties and solution pH in the adsorption of uranium(VI) to 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 (≤ 50 µm), 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

1. Introduction

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

3

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.

2.2. Test solutions

131   Stock solutions of U(VI) were prepared from uranyl nitrate hexahydrate ($UO_2(NO_3)_2 \cdot 6H_2O$) (Strem

132   Chemicals, Inc., Newburyport, MA, USA) and ultra-pure water (18 MΩ-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).

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-µm filtered (polyethersulfone membrane) supernatant. All

163 treatments were rapidly prepared and immediately capped to minimize exchange of CO_2 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***

7

173   Samples for analysis of Fe, Mn, and U were acidified to a pH of ~2 (HNO_3) 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^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, Cl^-, PO_4^{3-}, and NO_3^-) 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 (µg/g) and in the solution (µg/ml) at

185   equilibrium (after 48 h) using the equation:

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

187   where C_0 is the concentration of U in the initial solution (µg/ml), C_e is the concentration of U in

188   solution at equilibrium (µg/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 $\log_{10}$

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 $Fe(III)(OH)_3$, UO_2 and $CaUO_4$ was allowed to occur if

217 saturation products were exceeded; however, no precipitation of either UO_2 or $CaUO_4$ 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 µm; 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 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   ($\leq$ 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 µg/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 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 µg/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 µg/L treatments ranged from 0.12 to 150 µg/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 µg/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 µg/L; CCME, 2011). Additionally, the lowest initial U concentration

303　　tested (23 µg/L) falls within the range of the long-term and short-term Canadian Water Quality

304　　Guidelines (CWQG) for U of 15 µg/L and 33 µg/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*

13

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 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 [$\log K_d(U) = -1.02$ 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 [$\log K_d(U) = -0.77$pH + 7.73, $R^2 = 0.30$, Vandenhove

335   et al., 2009b; $\log K_d(U) = -1.18$pH + 10.8, $R^2 = 0.65$, Vandenhove et al., 2007; $\log K_d(U) = -1.07$pH

336   + 9.80, $R^2 = 0.41$, Sheppard et al., 2006; $\log K_d(U) = -1.29$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 [$\log K_d(U) = -21.22 + 7.97$pH $- 0.63$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

15

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 ≥ 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

17

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 $Ca_2UO_2(CO_3)_3$ and

455 $CaUO_2(CO_3)_3^{2-}$ being greatest at pH 7 and 8, and UO_2CO_3 and $UO_2(CO_3)_2^{2-}$ 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 CO_2

483 free or low CO_2 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 CO_2 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 µg/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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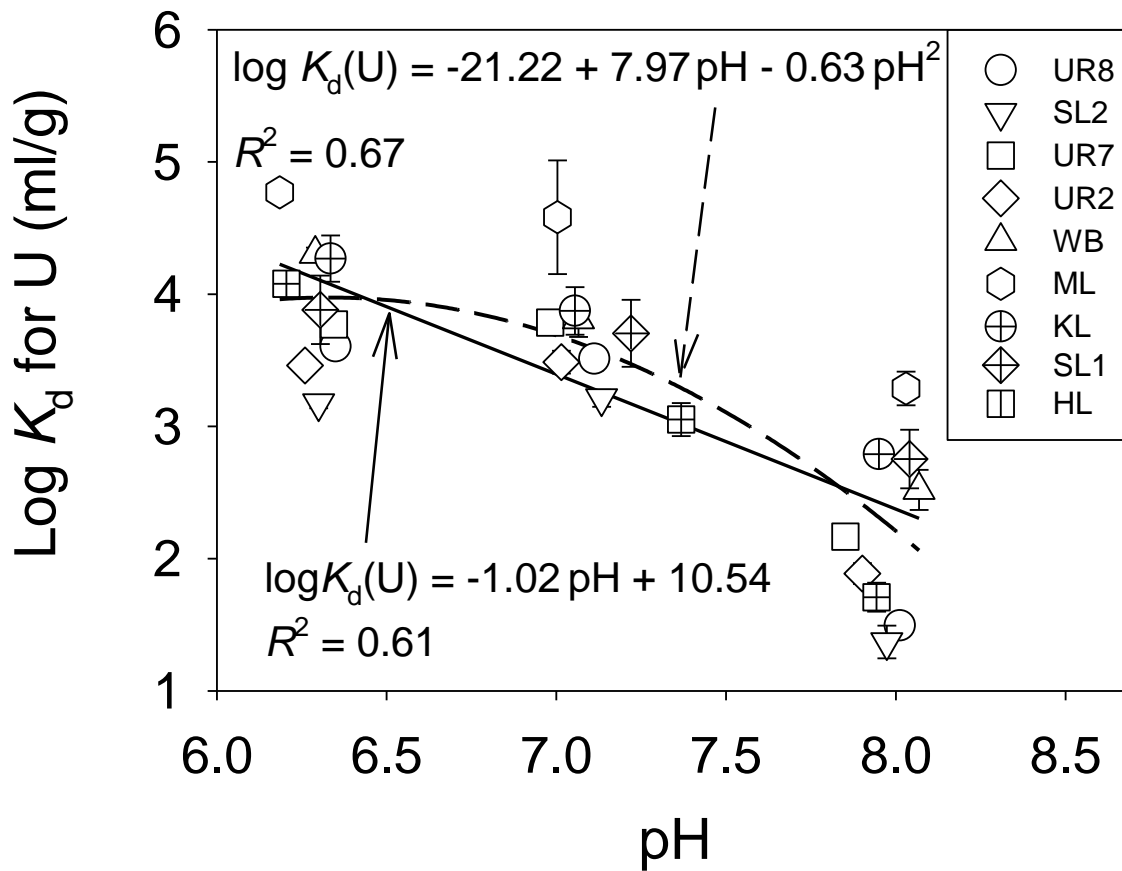722   uranium concentration. Environ. Pollut. 145, 587-595.

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731

The figure shows a plot of $\log K_d$ for U (ml/g) versus pH with the following annotations:

$$\log K_d(U) = -21.22 + 7.97\,pH - 0.63\,pH^2$$

$$R^2 = 0.67$$

$$\log K_d(U) = -1.02\,pH + 10.54$$

$$R^2 = 0.61$$

Legend: UR8, SL2, UR7, UR2, WB, ML, KL, SL1, HL

732

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
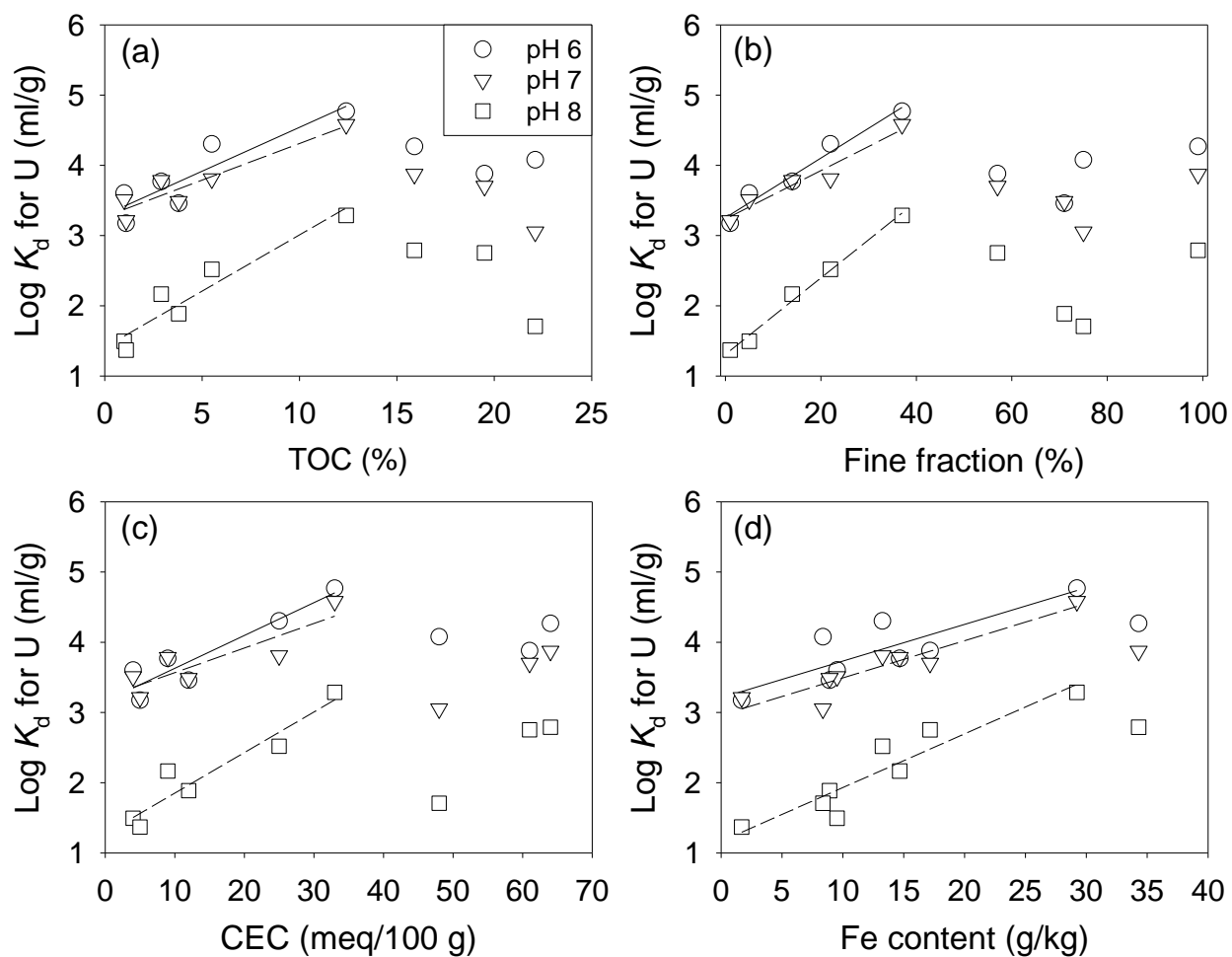
Fig. 2 Mean K_d for U (log ml/g) as a function of solution pH (nominal of 6, 7, and 8) and sediment

(a) total organic carbon content (TOC, %), (b) fine fraction content ($\leq$ 50 µm, %), (c) cation

exchange capacity (CEC, meq/100 g), and (d) iron content (Fe, g/kg). Each symbol within a series

represents one of nine different sediments. Lines represent significant linear regressions up until a

threshold (Linear equations are presented in Table S4 of the supplementary material).

743
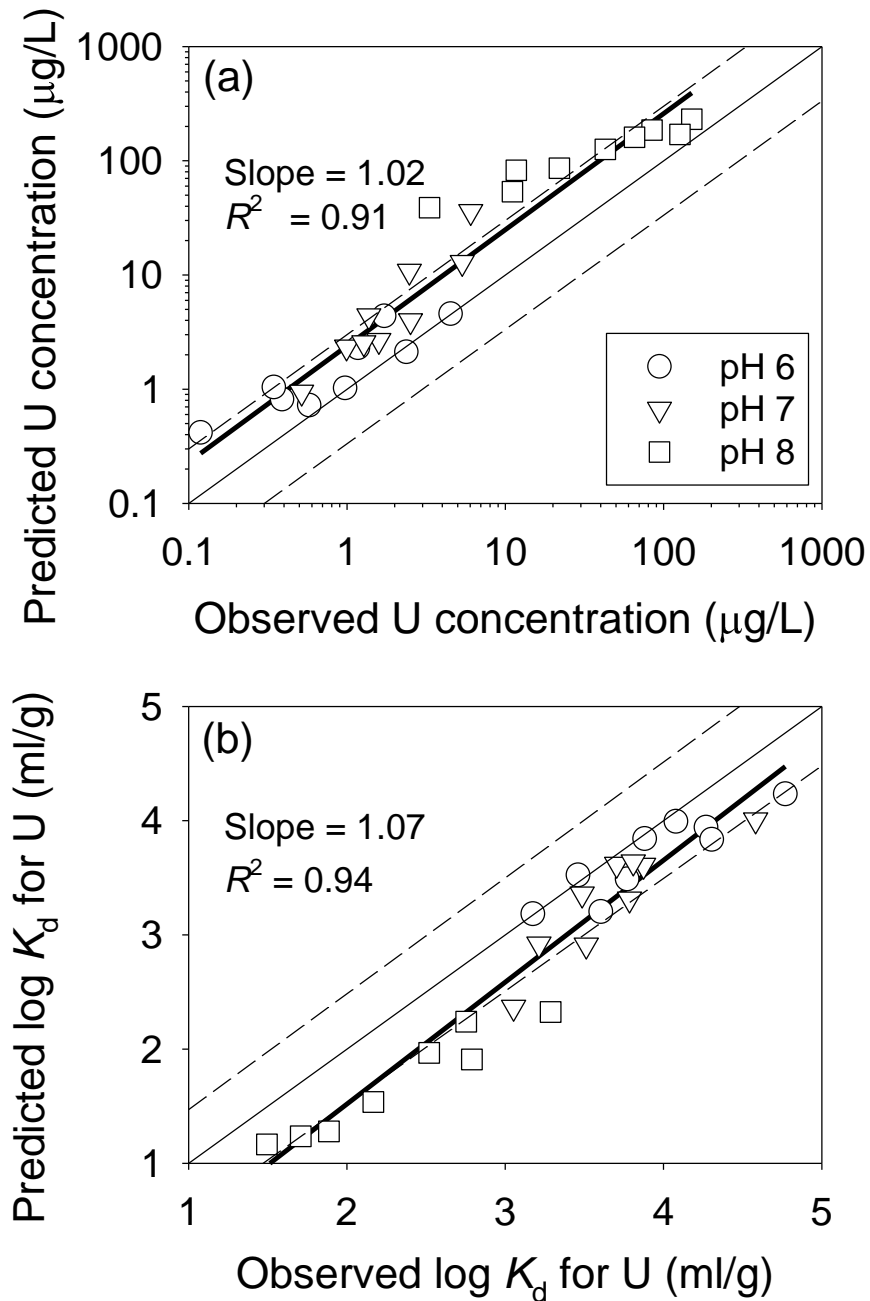
Fig. 3 WHAM-predicted versus observed (a) U concentration (µg/L) in the overlying water at

equilibrium, and (b) log K_d for U (ml/g) for all nine sediments at pH 6, 7, and 8. Thick solid line

represents the linear regression for all data points ($p < 0.05$); the 1:1 line is bracketed by dashed

lines representing a factor of three.