

Relationship of Water and Nitrogen Inputs to Occurrence of Arsenic and Uranium in the Deep Unsaturated Zone and Local Groundwater

Arindam Malakar¹, Chittaranjan Ray¹, Matteo D'Alessio², Jordon Shields³, Craig Adams³, Marty Stange⁴, Karrie Weber⁵, and Daniel D Snow¹

¹University of Nebraska

²University of Mississippi

³University of Nebraska-Lincoln

⁴Hastings Utilities

⁵University of Nebraska-Lincoln

November 21, 2022

Abstract

The unsaturated zone serves as reservoir for geogenic and anthropogenic contaminants to local groundwater. Biogeochemical processes in this zone can be affected by nitrogen and water infiltration mobilizing contaminants, ultimately affecting groundwater quality. In this large-scale study, we evaluated the effects of estimated water and nitrogen inputs to the unsaturated zone of a public water supply wellhead protection (WHP) area with respect to subsurface occurrence and transport of nitrate, ammonium, arsenic, and uranium. Thirty-two coring sites were sampled and grouped by water application volume, irrigated – sprinkler (n=20), gravity (n=4) and non-irrigated land use. Unsaturated zone sediments were evaluated for the potential to mobilize arsenic and uranium in relation to nitrogen and water use. Sediment nitrate and ammonium had strong significant ($p < 0.05$) correlation under all water application. Nitrate concentrations were lower beneath sprinkler-irrigated sites but had statistically higher ammonium concentrations than gravity-irrigated. Sediment nitrate concentrations were significantly ($p < 0.05$) different among water application types, suggesting a strong effect of water volume on the changing nitrate concentration. Sediment arsenic presumably attenuated by iron ($r = 0.32$ $p < 0.05$). Uranium in sediments of unsaturated zone was negatively correlated to increase in sediment nitrate ($r = -0.23$ $p < 0.05$) and ammonium ($r = -0.19$ $p < 0.05$). Water application types were found to significantly influence sediment arsenic and uranium. While the groundwater arsenic and uranium concentration were below maximum contaminant levels, the highest uranium concentrations were observed in samples from WHP area. The study suggests that irrigation has an impact on unsaturated zone geochemistry with the potential to ultimately affect groundwater quality.

Hosted file

hastings_as_u-wrr-final_supporting information.docx available at <https://authorea.com/users/527046/articles/596543-relationship-of-water-and-nitrogen-inputs-to-occurrence-of-arsenic-and-uranium-in-the-deep-unsaturated-zone-and-local-groundwater>

1 **Relationship of Water and Nitrogen Inputs to Occurrence of Arsenic and Uranium in**
2 **the Deep Unsaturated Zone and Local Groundwater**

3 **Arindam Malakar¹, Chittaranjan Ray², Matteo D'Alessio^{3,†}, Jordan Shields¹, Craig**
4 **Adams^{1,‡}, Marty Stange⁴, Karrie Weber^{5,6}, and Daniel D. Snow^{7,*}**

5 ¹Nebraska Water Center, part of the Robert B. Daugherty Water for Food Global Institute, Water
6 Sciences Laboratory, University of Nebraska, Lincoln, NE 68583-0844, USA.

7 ²Nebraska Water Center, part of the Robert B. Daugherty Water for Food Global Institute 2021
8 Transformation Drive, University of Nebraska, Lincoln, NE 68588-6204, USA.

9 ³Nebraska Water Center, part of the Robert B. Daugherty Water for Food Global Institute, Keim
10 Hall 135, University of Nebraska, Lincoln, NE, 68583-0915, USA.

11 ⁴Hastings Utilities, 1228 N. Denver Avenue, Hastings, NE 68901

12 ⁵School of Biological Sciences, University of Nebraska—Lincoln, Lincoln, NE

13 ⁶Earth and Atmospheric Sciences, University of Nebraska—Lincoln, Lincoln, NE 68588, USA

14 ⁷School of Natural Resources and Nebraska Water Center, part of the Robert B. Daugherty
15 Water for Food Global Institute, 202 Water Sciences Laboratory, University of Nebraska,
16 Lincoln, NE 68583-0844, USA.

17
18 *Corresponding author: Daniel Snow (dsnow1@unl.edu)

19
20 †Present Address: Department of Civil Engineering, 204 Carrier Hall, University of Mississippi,
21 University, MS 38677, USA.

22 ‡Present Address: Burns & McDonnell, 1111 N 13th St #300, Omaha, NE 68102, USA.

23
24 **Key Points:**

- 25 • Unsaturated zone serves as a dynamic reservoir for inorganic nitrogen and geogenic
26 contaminants.
- 27 • Nitrogen transport and transformation can affect occurrence of geogenic contaminants.
- 28 • Irrigation water application can affect nitrogen and geogenic contaminant mobilization
29 and transport.
30

31 **Abstract**

32 The unsaturated zone serves as reservoir for geogenic and anthropogenic contaminants to local
33 groundwater. Biogeochemical processes in this zone can be affected by nitrogen and water
34 infiltration mobilizing contaminants, ultimately affecting groundwater quality. In this large-scale
35 study, we evaluated the effects of estimated water and nitrogen inputs to the unsaturated zone of
36 a public water supply wellhead protection (WHP) area with respect to subsurface occurrence and
37 transport of nitrate, ammonium, arsenic, and uranium. Thirty-two coring sites were sampled and
38 grouped by water application volume, irrigated – sprinkler (n=20), gravity (n=4) and non-
39 irrigated land use. Unsaturated zone sediments were evaluated for the potential to mobilize
40 arsenic and uranium in relation to nitrogen and water use. Sediment nitrate and ammonium had
41 strong significant ($p<0.05$) correlation under all water application. Nitrate concentrations were
42 lower beneath sprinkler-irrigated sites but had statistically higher ammonium concentrations than
43 gravity-irrigated. Sediment nitrate concentrations were significantly ($p<0.05$) different among
44 water application types, suggesting a strong effect of water volume on the changing nitrate
45 concentration. Sediment arsenic presumably attenuated by iron ($r=0.32$ $p<0.05$). Uranium in
46 sediments of unsaturated zone was negatively correlated to increase in sediment nitrate ($r=-0.23$
47 $p<0.05$) and ammonium ($r=-0.19$ $p<0.05$). Water application types were found to significantly
48 influence sediment arsenic and uranium. While the groundwater arsenic and uranium
49 concentration were below maximum contaminant levels, the highest uranium concentrations
50 were observed in samples from WHP area. The study suggests that irrigation has an impact on
51 unsaturated zone geochemistry with the potential to ultimately affect groundwater quality.

52

53

54 **Plain Language Summary**

55 The unsaturated zone, comprising the soil layer between Earth's surface and water table, is one
56 of the most important and least understood regions. This reservoir serves as filter protecting the
57 groundwater table from geogenic and anthropogenic contaminants, including nitrate, arsenic and
58 uranium. Unsaturated zone geochemistry and hydrology controls mobility and loading of many
59 contaminants. Land-use such as, agriculture, fertilizer application, and irrigation all affect
60 processes controlling the mobility of trace elements and may promote movement within this
61 zone. In the present study, the influence of surface processes such as, irrigation method, and
62 nitrogen fertilizer use was compared to existing occurrence and mobility of arsenic and uranium
63 within the unsaturated zone. Correlation of geogenic contaminant occurrence concurrent with
64 anthropogenic contaminants such as nitrate and ammonium suggests the unsaturated zone is
65 affected by surface irrigation and fertilizer use and has the potential to impact local groundwater
66 quality. Understanding of unsaturated processes impacted by irrigation water application may
67 help stakeholders devise plans to protect the water quality of the corresponding aquifer.

68

69 **1 Introduction**

70 Over the last several decades world-wide annual fertilizer nitrogen (N) input rate has
71 increased substantially, and significantly altered the global N-cycle (Burow et al., 2010). This
72 surge in N-input has resulted in global degradation of water resources and especially the quality
73 of shallow groundwater in agriculturally intensive areas (Burow et al., 2010). Groundwater
74 accounts for almost 37% of the water used by public water systems (Dieter et al., 2018), and
75 nearly half the population of the U.S. including 99% of rural population use groundwater for
76 drinking (Nolan & Hitt, 2006). Nebraska is an agriculturally intensive state and accounts for 15%
77 of the total irrigated land in the U.S. Roughly 79% of Nebraska public water systems use
78 groundwater as drinking water source (Dieter et al., 2018). Groundwater throughout Nebraska
79 has been found to contain elevated nitrate concentrations above the EPA regulatory maximum
80 contaminant level (MCL) of 10 mg L^{-1} for drinking water, and consequently ranks among the
81 highest for USEPA Safe Drinking Water Act violations (Pennino et al., 2017). Juntakut et al.
82 (2019) recently reported that groundwater exceeds the 10 mg L^{-1} MCL beneath more than
83 1,096,026 ha in the state. In addition to nitrate violations, seven Nebraska public water supply
84 systems have implemented treatment systems for source water uranium concentrations in excess
85 of the $30 \text{ } \mu\text{g L}^{-1}$ MCL (NDEQ, 2018) and seventy-five have reported arsenic concentrations in
86 source water above the $10 \text{ } \mu\text{g L}^{-1}$ (Gosselin et al., 2004). Further, around 36% of wells in the
87 Southern High Plains region of the Ogallala aquifer exceed the MCL of $10 \text{ } \mu\text{g L}^{-1}$ for arsenic
88 (Reedy et al., 2007). Clearly, there is growing conflict between groundwater quality and intended
89 use in this region.

90 The unsaturated, or vadose zone is considered as a natural filter for infiltrated water as it
91 recharges groundwater and may also serve as a reservoir for both anthropogenic and geogenic

92 contaminants (Huan et al., 2020). Intensive irrigation water use and fertilizer application at the
93 surface increases recharge water input and N-input, which can impact unsaturated zone
94 biogeochemistry mobilizing contaminants (Cassiani et al., 2007; Scanlon et al., 2005). Recharge
95 through intensive irrigation can affect redox-sensitive microbial processes modifying behavior,
96 distribution and mobilization of trace elements such as arsenic or uranium in the unsaturated
97 zone (Chi et al., 2018; Tesoriero et al., 2019). Trace element contaminants present in
98 groundwater can accumulate in the surface soil when used for irrigation and further increase the
99 concentration of these contaminants in the unsaturated zone (Farooq et al., 2019). Elevated
100 volume of groundwater use for irrigation can fluctuate water table and affect arsenic mobility in
101 the unsaturated zone (Xiao et al., 2018).

102 Contaminants occurring in local groundwater are generally linked to surface soils and
103 subsurface geology. The concentration of arsenic varies widely in soil, and arsenic in Earth's
104 crust is estimated to range from 1 to 40 $\mu\text{g g}^{-1}$ (Chou et al., 2002). Arsenic in soil can also come
105 from previous arsenic-based pesticide use (Reedy et al., 2007). When dissolved in water
106 inorganic arsenic primarily exists as reduced arsenite (As(III)) and oxidized arsenate (As(V))
107 oxyanions, these species of arsenic can be associated with solid-phase minerals such as iron
108 oxides, and iron oxy(hydroxides) and precipitate in soils (Malakar et al., 2016). However,
109 equilibrium forms and mobilization of arsenic species are sensitive to redox and pH changes of
110 the system. The uranium content in soil ranges from 0.3 – 10.7 $\mu\text{g g}^{-1}$ around the world
111 (Vodyanitskii, 2011). Inorganic uranium exists in soils and groundwater primarily as redox
112 determined complexes of U(IV) and U(VI), while the oxidized U(VI) as UO_2^{2+} is considered to
113 be the most mobile and soluble form (Vodyanitskii, 2011). Phosphate fertilizers can also be a
114 source of uranium, (Yamaguchi et al., 2009). However, at the present study site arsenic and

115 uranium concentrations mainly arise from the geogenic history of the region (Brown et al.,
116 2007), as well as chemical weathering and drainage from the uraniferous regions of the Rocky
117 Mountains (Nolan & Weber, 2015; Snow & Spalding, 1994), and are known to be significantly
118 high in the soils of Nebraska. The prior information of arsenic and uranium present in the
119 unsaturated zone can serve as a proactive measure for groundwater protection in this region.

120 The importance of agricultural activities, soil composition and unsaturated zone
121 properties on groundwater arsenic and uranium occurrence has been well recognized and studied
122 from multiple perspectives (Lopez et al., 2021). Negatively charged nitrate produced from
123 nitrogen fertilizer application is mobile and may rapidly leach below the root zone (Wells et al.,
124 2018). Nitrate in the unsaturated zone pore water is known to impact the mobility of arsenic and
125 uranium under both oxic and anoxic conditions (Herath et al., 2016; Nolan & Weber, 2015;
126 Smith et al., 2017). A recent review by Collins and Rosso (2017) suggests that mobilization of
127 uranium in groundwater and the unsaturated zone is likely related to anthropogenically-driven
128 biogeochemical processes including denitrification and iron reduction. Iron transformation in the
129 unsaturated zone is known to impact the mobility of arsenic and uranium, as many forms of these
130 elements are strongly bound to iron oxides (Roberts et al., 2017). Further, excess water input
131 from irrigation can increase soil saturation, generating anoxic microsites within the bulk
132 unsaturated zone (Keiluweit et al., 2016, 2017; Malakar et al., 2020). Anoxic microsites can act
133 as redox hotspot in the deep unsaturated zone leading to mobilization of nutrients and trace
134 element contaminants (Keiluweit et al., 2018; Malakar et al., 2020; Warrinnier et al., 2020).

135 In the present study, the deep unsaturated zone of a wellhead protection (WHP) area, a
136 protected area defined by a 50-year time of groundwater travel for public supply wells in the city
137 of Hastings, Nebraska, was evaluated for the occurrence and potential mobility of nitrate,

138 ammonium, arsenic, and uranium in relation to historical land use based on water application and
139 changes in stored nitrogen. Changes in unsaturated zone nitrate concentrations were related to
140 differences in uranium and arsenic distributions within the unsaturated zone and evaluated with
141 respect to potential redox reactions that may be controlling contaminant mobility. This data
142 provides a unique and detailed framework for evaluation of the geochemistry in the unsaturated
143 zone beneath agriculturally intensive irrigated crops and subsequent impact on groundwater
144 quality in similar agricultural settings around the world. Understanding the impact of associated
145 geogenic elements such as arsenic and uranium contamination in the groundwater rising from
146 intensive agriculture can provide the basis to strategize best management practices to protect the
147 groundwater quality.

148 **2 Materials and Methods**

149 **2.1 Study Site Description**

150 **2.1.1 Site Location and Water Application Pattern**

151 Hastings is located within Adams County in southcentral Nebraska. The Hastings WHP
152 area (Figure 1) provides a source of drinking water for the city serving a population of 24,822 as
153 of 2018 and is intended to provide a framework to encourage residential and agricultural best
154 management practices to ensure safe drinking water quality. As nitrate is the primary cause for
155 drinking water quality impairment, unsaturated zone coring sites were selected across the WHP
156 area to evaluate changes in nitrogen storage under a variety of water application volume. Thirty-
157 two coring locations include twenty sites with sprinkler (pivot) irrigated cropland, four gravity
158 (furrow) irrigated sites (Table 1). Corn and soybeans are the primary crops grown on all of these
159 sites. Three responses from producer surveys suggest that current fertilizer application rates

160 average nearly 200 kg N ha⁻¹ in the WHP area (Adams, 2018) though it was not possible to
 161 distinguish rates for pivot from gravity-irrigated crops. The remaining eight sites fall under non-
 162 irrigated (residential lawns or dryland agricultural) water volume use. The classification of water
 163 application volume was based on water use estimates and records. From 2011 to 2016, in the
 164 irrigated regions average annual water application was around 46.2±4.4 cm ha⁻¹ yr⁻¹. Water
 165 application volumes in agricultural sites of Hasting WHP area varies according to weather
 166 conditions, and drought conditions require higher than average water volume (Adams, 2018).
 167 Average annual rainfall for the area is 71.1 cm, which is not accounted for in irrigation water
 168 applications but likely serves as the baseline for the entire area. The water application volume for
 169 pivot and gravity irrigated sites is not reported, however, water application volume in gravity
 170 irrigated fields are nearly double compared to pivot irrigated sites (USDA, 2019), which is also
 171 the case at Hastings WHP area (Adams, 2018). Under the non-irrigated site, two residential
 172 lawns received water while the rest had no external water application and annual average water
 173 application volume is around 5.2±3.2 cm ha⁻¹ yr⁻¹, much lower compared to irrigated sites.

Table 1. Shows different site IDs and the corresponding water application volume.

Water application volume (Low to high)	Site IDs
Non-irrigated sites (n=8)	HC2, HC3N, HC3S, HC4, HC5, HC6, HC7, HC8
Pivot Irrigation (n=20)	HC9N, HC9S, HC10N, HC10S, HC11E, HC11W, HC13NE, HC13SW, HC14E, HC14W, HC15N, HC15S, HC16N, HC16S, HC17N, HC17S, HC18E, HC18W, HC20E, HC20W
Gravity Irrigation (n=4)	HC1E, HC1W, HC12E, HC12W

N=North, S=South, E=East, W=West

174 2.1.2 Sediment and Groundwater Sampling

175 Sediment sampling was done following recommended unsaturated zone sampling
 176 practices (ASTM, 1999). Soil cores from HC3N, HC3S, HC4, HC5 and HC6 were collected

177 utilizing a Geoprobe Model 66DT (Salina, KS, USA) direct push coring system. A CME
178 (Central Mine Equipment Co, Earth City, MO USA) hollow stem auger with split spoon sampler
179 was used in the remaining sites. Cores (0.053 m diameter by 0.76 m length) were collected in
180 acrylic liners, capped and placed into a cooler immediately after removal from the core sampling
181 barrel. Intact cores were transported on ice and stored in a walk-in freezer at -20 °C. Sediment
182 cores were described and processed using several chemical characterization methods to evaluate
183 inorganic nitrogen forms and the potential to mobilize geogenic contaminants and their affinity
184 to impact local groundwater quality. The occurrence and distribution of arsenic and uranium
185 concentrations were then characterized relative to a measured increase or decrease in nitrate
186 storage in the unsaturated zone in comparison to the 2011 study (Spalding & Toavs, 2012) and
187 whether the primary land use based on water application volume was pivot, gravity, or non-
188 irrigated. HC10N and HC10S changed from gravity to pivot around 2011, and HC11E and
189 HC11W in 2015. These sites can help assess the effect of lower water application of pivot
190 irrigation to nitrate leaching and trace element mobility. Groundwater samples were collected
191 from monitoring wells located near the coring sites using a submersible pump, filtered with 0.22
192 µm filter, preserved in the field (Malakar et al., 2020) and stored at 4 °C prior to analysis.

193 2.1.3 Sediment Lithology and Texture

194 Coring sites, marked in Figure 1, were selected from a previous study of the WHP area
195 by Spalding and Toavs (2012) and published in a recent study describing the relationship of
196 unsaturated zone nitrate on groundwater quality in the area (Spalding et al., 2019). Interpretive
197 cross-sections of unsaturated zone texture and lithology beneath the WHP area are shown as a
198 block diagram in Figure 1, along with the map of the location of Hastings in the state of
199 Nebraska and WHP area region (red border). The interpretative cross-sectional lithology shows a

200 Holocene age surficial layer of clayey sediment with intercalated sand, silt, and gravel units
 201 within the unsaturated zone (Adams, 2018) and are primarily alluvial sands with interbedded
 202 overbank silts and clays. The dashed line shown in Figure 1 represents the approximate location
 203 of the water table and the arrow shows the regional groundwater flow.

204 Surface soil samples were classified based on the web soil survey (USDA, 2014). In the
 205 gravity and pivot sites, the surface soil is made up of wide variety such as Holder silt loam,

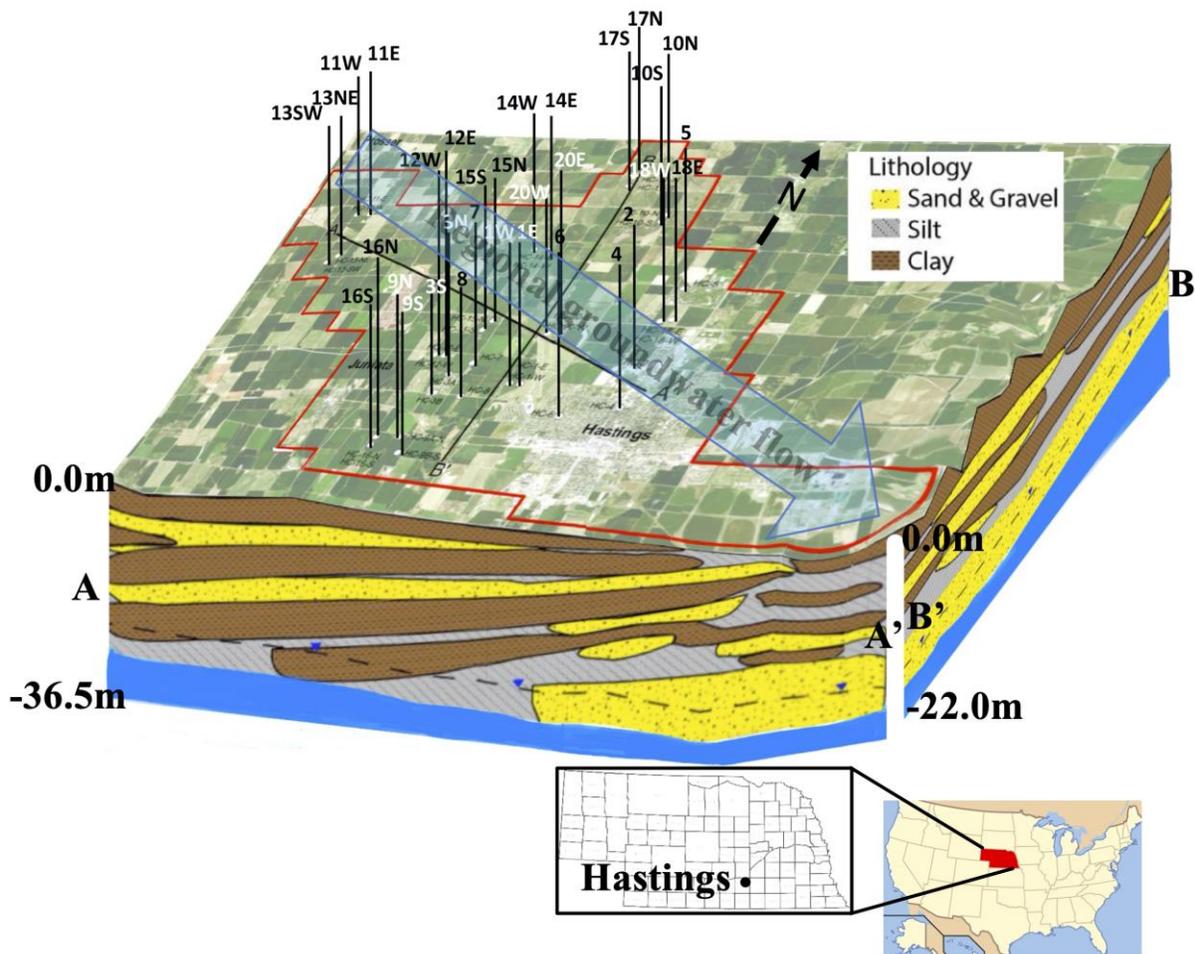


Figure 1. Shows map of wellhead protection (WHP) area located at Hastings, Nebraska, USA. Different locations were cored and are marked in the map of WHP area. Lithology of the WHP areas across AA' and BB', is also presented, shows a Holocene age surficial layer of clayey sediment with intercalated sand, silt, and gravel units within the unsaturated zone (Adams, 2018) and are primarily alluvial sands with interbedded overbank silts and clays.. Regional groundwater flow direction is marked with the arrowhead across the WHP area. The dashed line near the bottom marks the water table at the study site. A gradual decline in water table depth is observed from A to A' region in the WHP area.

206 Holder loam, Holder silty clay loam, and Crete silt loam. The soils on non-irrigated sites at the
207 Hastings WHP area mainly consists of Hastings silt loam. These soil forms are all moderately
208 well to well-drained soils in loess, having slopes ranging from 0-17% for Hastings and Crete
209 soils and less than 4% for Holding soils (Adams, 2018). The geology of the underlying
210 unsaturated sediments consists of early Cretaceous-age to Tertiary-age bedrock overlain by
211 Pliocene-age to Quaternary-age alluvial and aeolian sediments. Sandy layers in the deeper
212 sediments are likely to be alluvial, while silt-rich zones may be aeolian or reworked loess. The
213 primary aquifer for the Hastings well field is the High Plains Aquifer, and includes both the
214 Quaternary unconsolidated sands, silts and clays overlying the Ogallala bedrock at this location
215 (Keech & Dreeszen, 1968).

216 **2.2 Measurement of Sediment Physical and Chemical Parameters**

217 2.2.1 Water Content, Particle Size, Nitrate and Ammonium Concentrations

218 Sediment cores were taken out of freezer storage and allowed to thaw for no more than
219 12 hours. Sediments extruded from each liner were laid out in order of increasing depth, and the
220 core interval was described with respect to texture and lithology. A measured 2.5 cm subsection
221 was removed and used for measurement of bulk density and gravimetric water content. The
222 remaining sediment was then homogenized and allowed to dry overnight at room temperature.
223 Once dried, the sample was ground with a Thomas Wiley mill and passed through a 2 mm sieve
224 (Thomas Scientific, Swedesboro, NJ, USA). A 10.0 g portion of each composite sample was
225 mixed with 100 mL of 1 M potassium chloride (ACS Certified, Fisher Chemicals, Waltham,
226 MA, USA) capped and placed on a wrist action shaker (Burrell Corp., Pittsburgh, PA, U.S.A.)
227 for 1 hour. The extract was filtered with a vacuum flask and a Whatman 42 filter paper (GE

228 Healthcare, Chicago, IL, USA) with a pore size of 2.5 μm . The extract was acidified ($\text{pH}<2$)
229 with sulfuric acid (Fisher Chemical, Waltham, MA, USA) and analyzed on a 2-channel Lachat
230 Quikchem 8500 (Hach, Loveland, CO, US) flow injection analyzer using Cd-reduction and
231 salicylate methods for nitrate and ammonium, respectively. The total nitrate in the unsaturated
232 zone was calculated by summing the total nitrate stored beneath each profile as total kg-N ha^{-1} . If
233 stored nitrate in the unsaturated zone was found to be more than 2011 (Spalding and Toavs,
234 2012) for a particular site, it is marked as increase in nitrate storage or increased nitrate input and
235 the increased amount was obtained by subtracting the present concentration from previous
236 concentration. When nitrate concentration was found less than 2011 that site is marked as
237 decrease in nitrate storage, and the amount decreased was obtained by subtracting the 2011 value
238 with the present value. Particle size composition (clay, silt, and sand), detailed in supporting
239 information (Text S1), was determined by a combination of wet-sieve and settling in
240 hexametaphosphate dispersant (Kettler et al., 2001).

241 2.2.2 Acid Digestion and Measurement of Sediment Arsenic and Uranium

242 One hundred sixty-four ($n=164$) samples were selected at 1.5 m intervals from all coring
243 locations for measurement of acid leachable arsenic and uranium. Microwave digestion of air-
244 dried ground soil samples was carried out following method 3051A of EPA (U.S. EPA, 2007).
245 Briefly, 0.5 g portion of each sample was weighed out into a Teflon[™] microwave digestion tube
246 (CEM, Matthews, NC, USA) and mixed with concentrated nitric acid (TraceMetal[™] Grade,
247 Fisher Chemical, Waltham, MA, USA), hydrochloric acid (TraceMetal[™] Grade, Fisher
248 Chemical, Waltham, MA, USA), and hydrogen peroxide (Sigma-Aldrich, St. Louis, MO, USA).
249 Samples were digested using the MARS Xpress microwave digester (CEM, Matthews, NC,
250 USA) by ramping to 175 $^{\circ}\text{C}$ for 10 minutes and holding the temperature for another 10 minutes.

251 After digestion, the Teflon™ tubes were allowed to cool. Each digest was allowed to settle,
252 filtered (0.45 µm, PES w/PP, Whatman GD/XP™ Syringe Filters, GE Healthcare, Chicago, IL,
253 USA), added 0.500 mL of 100 µg-In L⁻¹ was added and diluted to a final volume of 50.0 mL
254 ultrapure deionized water (18.2 MΩ) obtained from a Millipore Milli-Q® system (Millipore
255 Sigma, Burlington, MA, USA). Filtered digests were analyzed using inductively coupled plasma
256 mass spectroscopy (Thermo iCAP-RQ ICP-MS, Thermo Fisher Scientific, Waltham, MA, USA).
257 Calibration standards were prepared and digested with samples and quality assurance included
258 analysis of certified reference materials (Sigma-Aldrich, St. Louis, MO, USA) which were used
259 throughout the analytical work.

260 2.2.3 Hot Water Extractable Organic Carbon in Sediments

261 Hot water extractable organic carbon (HWEOC) was measured using the method
262 described by Ghani et al. (2003). The hot water extracted carbon from soil, which strongly
263 correlates to soil microaggregate characteristics, represents assimilative component of total
264 organic matter and can be a good indicator for labile organic carbon content compared to cold
265 water extractable organic carbon (Ćirić et al., 2016; Hamkalo & Bedernichek, 2014; Lambie et
266 al., 2019; Šeremešić et al., 2013). Briefly, 10.0 g sediment was mixed with 50 mL of purified
267 reagent grade water and heated for 90 minutes on a heating block at 80 °C. The mixture was
268 allowed to cool, centrifuged, and filtered (0.45 µm, GMF, Whatman GD/X Syringe Filters, GE
269 Healthcare, Chicago, IL, USA) for DOC by the persulfate oxidation method on a OI Model 2020

270 TOC analyzer (OI Analytical, College Station, TX, USA). The resulting concentration was
271 expressed relative to dry sediment weight.

272 2.2.4 Analysis of Major Elements in Sediments by X-ray Fluorescence Spectroscopy

273 Thirty-nine air-dried and ground sediment samples were subjected to X-ray fluorescence
274 (XRF) analysis (Rigaku Supermini200 WDXRF Spectrometer, Tokyo, Japan) to characterize
275 changes in gross elemental composition. Concentrations of major elements are reported as a
276 mass percentage (%) and were compared with acid-leachable arsenic and uranium
277 concentrations.

278 **2.3 Statistical Analysis**

279 Nitrate and ammonium concentrations measured in the 18.2 m below ground surface
280 (bgs) of unsaturated zone were compared to the 2011 study at the same locations (Spalding &
281 Toavs, 2012) for evaluation of changes in nitrogen occurrence and movement. Results from
282 samples (n=821) were grouped into three categories for water application volume – sprinkler or
283 pivot and gravity or furrow, and non-irrigated water sites. Depth weighted average nitrate and
284 ammonium under the different water application volume categories were compared to acid-
285 leachable arsenic and uranium measured in the samples under same category. The arsenic and
286 uranium concentration data normality test was considered (Ghasemi & Zahediasl, 2012), and if
287 needed, distributed using a log function. The arsenic and uranium concentration data were
288 analyzed for the top 18.2 m by using One-Way and Two-Way ANOVA for factors including
289 water application volume (pivot, gravity and non-irrigated) and nitrate concentrations change

290 between 2011 and 2016. Statistical analysis and correlation coefficients were carried out in
291 Origin Pro Version 2020 software by Origin Lab (Northampton, MA, USA).

292 **3 Results and Discussions**

293 **3.2 Influence of Water Application Type on Changes in Unsaturated Zone Nitrogen**

294 3.2.1 Nitrate in the Unsaturated Zone

295 Nitrate movement in the unsaturated zone is well-known to be affected by water
296 application in the surface soil, which is dependent on various land-uses (Wells et al., 2018).
297 Irrigated agricultural sites will generally have higher water inputs compared to non-irrigated
298 sites, which is the case in the present study site. To evaluate the effect of nitrate movement,
299 coring sites were divided on the basis of estimated water application volume. The mean
300 concentration of nitrate beneath pivot irrigated sites was $2.0 \pm 1.9 \mu\text{g-N g}^{-1}$, whereas in gravity
301 irrigated sites was $2.4 \pm 2.2 \mu\text{g-N g}^{-1}$ (Figure 2b) and non-irrigated sites was $1.6 \pm 1.6 \mu\text{g-N g}^{-1}$
302 (Figure 2c). The depth weighted average concentrations of unsaturated zone nitrate and
303 ammonium in 2016 under different applied water volume is shown in Figure 2. In all three sites
304 *viz.*, (a) pivot, (b) gravity and (c) non-irrigated shown in Figure 2, the top soil showed higher N
305 content (nitrate and ammonium), which is expected due to surface fertilizer application
306 especially for agricultural sites. The amount of ammonium available in the unsaturated zone was

307 comparable to nitrate. Total nitrate (Figure 2a) amount associated with soils in the sites irrigated
 308 using a pivot is lower relative to the gravity irrigated sites (Figure 2b) with low variability.

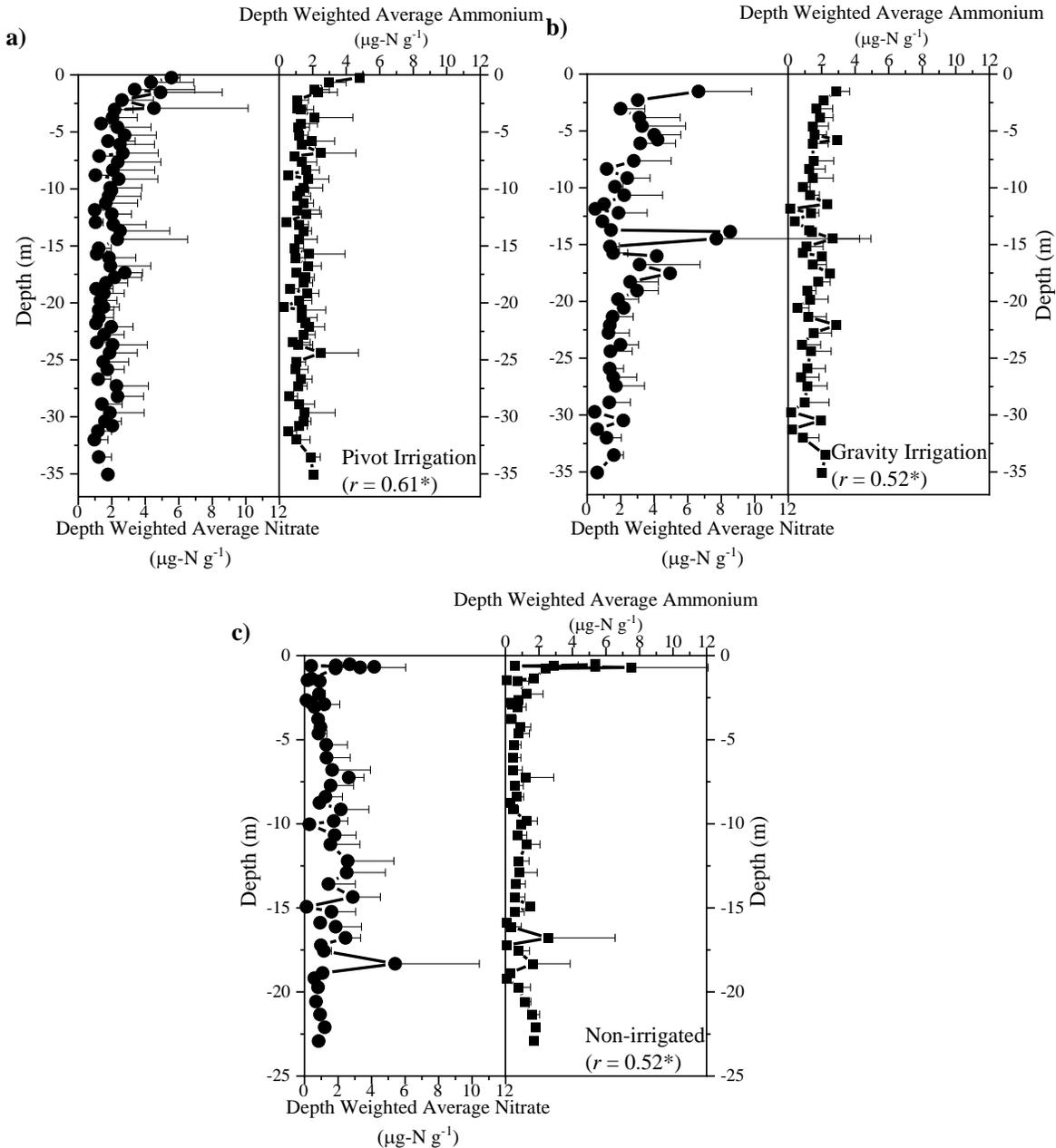


Figure 2. Shows depth weighted average and standard deviation of nitrate and ammonium concentrations under (a) pivot or sprinkler irrigated fields (b) gravity or furrow irrigated fields and (c) non-irrigated sites. The non-irrigated sites are relatively shallower water table depth compared to irrigated sites. “ r ” is the correlation coefficient between nitrate and ammonium, which has been marked with * for significance ($p < 0.05$). Among the different water application types, unsaturated zone beneath pivot irrigated sites has lowest sediment nitrate concentration but has highest sediment ammonium concentration. The unsaturated zone beneath gravity irrigated sites has the lowest concentration of sediment associated nitrate and non-irrigated sites have lowest concentration of sediment associated ammonium.

309 Nitrate accumulation and storage in the unsaturated zone was compared with nitrate
310 storage in these sites from a prior study conducted five years ago (Spalding & Toavs, 2012)
311 (Table S1). Total mass of nitrate in the unsaturated zone sediments under pivot-irrigated sites
312 increased (mean increase 318 ± 170 kg-N ha⁻¹) in twelve cores (HC9N, HC9S, HC13NE, HC15N,
313 HC15S, HC16N, HC16S, HC17S, HC18E, HC18W, HC20E, and HC20W). The mass of stored
314 nitrate decreased (mean decrease 156 ± 110 kg-N ha⁻¹) in the other eight pivot irrigated sites
315 (HC10N, HC10S, HC11E, HC11W, HC13SW, HC14E, HC14W, and HC17N). Four of the eight
316 sites (HC10N, HC10S, HC11E and HC11W) in which a decreased was observed were
317 transitioned from gravity to pivot irrigation. HC10N and HC10S converted to pivot system in
318 2011, HC11E and HC11W changed to pivot system in year 2015. Nitrate increased (mean
319 increase 423 ± 572 kg-N ha⁻¹) in soils collected from three of the gravity irrigated sites (HC1E,
320 HC12E, and HC12W) whereas a decrease was observed in one site (HC1W) (226 kg-N ha⁻¹).
321 The largest decrease in nitrate storage was observed at the non-irrigated sites, with an average
322 decrease of 494 ± 743 kg-N ha⁻¹ at three sites (HC2, HC5, and HC6) and five sites (HC3N, HC3S,
323 HC4, HC7, and HC8) showed an average increase (308 ± 49 kg-N ha⁻¹) in nitrate storage from
324 2011. The one-way ANOVA test was considered for different water application type (pivot,
325 gravity or non-irrigated) as factor and nitrate concentrations of the unsaturated zone were
326 compared. The analysis revealed that the concentration of nitrate stored beneath different water
327 application types are significantly different ($F=6.7$ at 0.05 level), indicating a strong effect of
328 water application type on the amount of nitrate stored in the unsaturated zone.

329 Nitrification processes converts applied ammonium based fertilizer to nitrate which is
330 coupled to the reduction of molecular oxygen (Brock et al., 2003). The resulting anion nitrate
331 poorly adsorbs to surfaces and can readily mobilize with an increase in soil moisture (Sopilniak

332 et al., 2017). Nitrate formed in surface soil is known to leach at higher rate once it travels below
333 the root zone (~2.5 m bgs) (Exner et al., 2014; Spalding and Kitchen, 1988; Wells et al., 2018;
334 Wang et al., 2019). The unsaturated zone beneath gravity irrigated sites contained less nitrate in
335 the root zone sediments (~2.5 m bgs) compared to pivot sites, which may be due to the increased
336 deep percolation of water generated by high volume of water application in gravity irrigated sites
337 compared to pivot irrigated sites (Biscaia Ribeiro da Silva et al., 2018; Yitayew et al., 1985).
338 Further, the sandy sediments in the unsaturated zone at the Hastings WHP area (Figure 1) likely
339 leads to rapid nitrate leaching beneath the root zone under irrigated crops (Stagnitti et al., 1999).
340 Nitrate concentrations did show negative correlation ($r=-0.26$, $p<0.05$) to the percentage of sand
341 in the lithology of the unsaturated zone. The negative correlation may indicate lower retention of
342 nitrate within the sandy layers, which would promote enhanced transport of nitrate through the
343 unsaturated zone.

344 3.2.2 Ammonium in the Unsaturated Zone

345 Sediment associated ammonium concentrations within the unsaturated zone published
346 prior ($0.4\pm 0.6 \mu\text{g-N g}^{-1}$) (Spalding & Toavs, 2012) were generally lower than measured in our
347 current study ($1.8\pm 8.4 \mu\text{g-N g}^{-1}$). Depth-weighted soil ammonium concentrations were found to
348 have significant ($p<0.05$) correlation with depth-weighted soil nitrate concentration within the
349 unsaturated zone of all three sites (Figure 2), ammonium, with correlation coefficients of $r=0.61$
350 for pivot irrigation, $r=0.52$ under gravity, and non-irrigated sites. These depth-weighted
351 correlations between nitrate and ammonium may indicate co-occurrence of nitrate and
352 ammonium within the sediment profiles of the unsaturated zone in the Hastings WHP area.
353 However, a different picture is presented when mean sediment ammonium concentrations in the
354 unsaturated zone of these three sites are compared to mean sediment nitrate concentrations.

355 Sediment ammonium concentration was found to follow an opposite trend compared to nitrate
356 concentration, where sediment ammonium concentration was highest in the pivot sites (1.5 ± 1.0
357 $\mu\text{g-N g}^{-1}$). Average ammonium concentration in the non-irrigated sites was lowest ($0.9\pm 1.4 \mu\text{g-N}$
358 g^{-1}), followed by gravity sites ($1.4\pm 0.9 \mu\text{g-N g}^{-1}$). Further, the one-way ANOVA test on sediment
359 ammonium concentration with water application type (pivot, gravity or non-irrigated) as the
360 factor revealed the sediment ammonium content to be significantly different ($F=23.6$ at 0.05
361 level), indicating a strong effect of water application on the amount of ammonium present in the
362 unsaturated zone. Two-way ANOVA test on sediment ammonium concentrations were
363 considered by having water application type as one factor and change in unsaturated zone nitrate
364 storage that is either increase or decrease in stored nitrate at a coring site compared to five years
365 ago (Table S1), as the second factor. The test revealed significant differences ($F=3.2$ at 0.05
366 level) in levels of sediment associated ammonium concentration between the sites where there
367 was increase in stored nitrate within the unsaturated zone and sites where there was a decrease in
368 stored nitrate within the same water application type.

369 The presence of elevated sediment ammonium in the deep unsaturated zone is interesting,
370 as the pH of all the soil cores was below 7.5, with a mean of 7.1 ± 0.6 . At this pH, ammonium is
371 in cationic form and readily sorbed to soil colloids (Sato et al., 2009). Ammonium was found to
372 correlate significantly ($r=0.32$, $p<0.05$) with iron concentration (Table S2) in the unsaturated
373 zone. Transport of ammonium ion through iron-rich unsaturated zone sediments would be slow
374 and dependent on pH and ionic strength (Li et al., 2016; Sopilniak et al., 2017). Moreover,
375 ammonium transport from surface soil through clay-rich and colloid-rich unsaturated sediments
376 should be heavily retarded by the presence of mono or bivalent cations such as sodium or
377 calcium, which are presumably high in agricultural leachate (Li et al., 2016). There is a

378 possibility of ammonium transportation to the unsaturated zone from surface applied anhydrous
379 ammonia or other ammonium bearing fertilizers through very sandy sediments where it is known
380 to rapidly transport (Wang & Alva, 2000). However, the surface soil at the Hastings WHP area is
381 mostly silty loam and ammonium would preferentially sorb at the surface soil (Sopilniak et al.,
382 2017). Geogenic nitrate and ammonium at elevated levels are also known to be present naturally
383 in the loess deposits of deep unsaturated zone in southwestern and central Nebraska (Boyce et
384 al., 1976). Previous studies of geogenic ammonium and nitrate in North America suggest that
385 these deposits are remnants of reduced nitrogen accumulations in the root zone or subsoil during
386 drought periods (McMahon et al., 2006). However, Nitrate ¹⁵N-isotope studies in the
387 groundwater and unsaturated zone of the WHP area (Snow et al., 2020; Spalding et al., 2019),
388 suggests that nitrate is primarily derived from commercial fertilizer or livestock nitrogen sources
389 and not geogenic sources. Further, changes in ammonium concentrations compared to the
390 previous study indicate that movement of ammonium or transformation to ammonium may be
391 occurring in the unsaturated zone.

392 Possible explanations for changes in unsaturated zone ammonium include leaching of
393 surface-applied ammonia fertilizer into the unsaturated zone, subsurface mineralization of
394 organic nitrogen, or conversion of leached nitrate to ammonium, which may be through
395 dissimilatory nitrate reduction to ammonium (DNRA), fermentative nitrate reduction, biological
396 reduction of nitrate to nitrite and then abiotic oxidation by iron(II), or abiotic reduction of nitrate
397 by reduced iron minerals within anoxic microsites of unsaturated zone (Cole & Brown, 1980;
398 DeSimone & Howes, 1998; Hansen et al., 1996; Jamieson et al., 2018; Shan et al., 2016; Smith
399 et al., 2017; S. Wang et al., 2019; Weber et al., 2001; Weber, Urrutia, et al., 2006; Zhu &
400 Getting, 2012). In the present study, it is not possible to predict which biogeochemical

401 mechanisms predominate. However, these probable biogeochemical reactions may affect the
402 distribution of redox-sensitive geogenic contaminants such as arsenic and uranium (Herath et al.,
403 2016; Malakar et al., 2020; Neil et al., 2014; J. Nolan & Weber, 2015; Smith et al., 2017; Weber
404 et al., 2011).

405 **3.2 Distribution of Arsenic and Uranium in the Unsaturated Zone of WHP Area**

406 3.2.1 Major Elemental Composition of Unsaturated Zone Sediments

407 XRF provides means for characterizing gross changes in elemental composition with
408 depth. Unsaturated sediments were found to be primarily aluminosilicate (silicon averaged
409 $61.3\pm 3.2\%$; aluminum averaged $13.6\pm 0.8\%$) with high levels of iron ($9.0\pm 2.6\%$) and potassium
410 ($7.8\pm 0.6\%$). Other elements which were present in lower amount in decreasing order are calcium
411 ($3.2\pm 0.6\%$), magnesium ($1.6\pm 0.4\%$), sodium ($1.3\pm 0.3\%$), titanium ($1.2\pm 0.2\%$), phosphorus
412 ($0.2\pm 0.0\%$), and manganese ($0.1\pm 0.1\%$). Detailed elemental composition obtained from XRF is
413 shown in Table S2 of supplementary information. Scatter plot of uranium, arsenic, iron, % clay
414 and ammonium among the samples analyzed by XRF are shown in Figure S1 of supplementary
415 information. Iron is a very important element supporting a variety of redox processes, and XRF
416 analyses confirms high levels of iron throughout the unsaturated zone, ranging from 3.6 to
417 14.8%. Iron species were not measured in the present study but sediment iron concentrations
418 were found to significantly correlate ($r=0.54$, $p<0.05$) to clay content and was found to be more
419 concentrated in the 14 m bgs of the unsaturated zone. Scatter plot of uranium, arsenic, iron, %

420 clay and ammonium among the samples analyzed by XRF are shown in Figure S1 of
421 supplementary information.

422 3.2.2 Distribution of Sediment Associated Arsenic and Uranium in the Unsaturated Zone under 423 Different Water Application Volume

424 Analysis of sediment samples for total arsenic and uranium was undertaken given the
425 natural presence in soils in this region (Brown et al., 2007; Snow & Spalding, 1994) and
426 potential to impact local groundwater quality. One hundred and sixty-four (164) sediment core
427 samples were analyzed for arsenic and uranium – 129 were beneath intensive row-crop irrigated
428 sites (107 samples from pivot irrigated sites and 22 samples from gravity irrigated sites), while
429 the remaining samples were from non-irrigated sites. These sediment cores were 1.5 m apart,
430 were air-dried, homogenized and analyzed for trace element concentration. The depth-wise
431 arsenic and uranium profiles for the coring sites are shown in the supplementary information
432 Figure S2 to S7. The mean value of arsenic was found to be $3,600 \pm 1000 \mu\text{g kg}^{-1}$ and uranium
433 was found to be $300 \pm 400 \mu\text{g kg}^{-1}$. Averages from fourteen core sites out of thirty-two showed
434 arsenic concentrations above a total mean value of $3,600 \mu\text{g kg}^{-1}$, which is below the global
435 average value reported for soils $\sim 5,000 \mu\text{g kg}^{-1}$ (Chou et al., 2002). Depth weighted average of
436 acid leachable arsenic concentrations ranged between a low of $400 \mu\text{g kg}^{-1}$ to a maximum of
437 $21,200 \mu\text{g kg}^{-1}$. The highest concentrations of arsenic were found in cores to the west of the
438 Hastings city limits at site HC20E at 29 m bgs which was also found to have high iron content
439 with distinct brown patches.

440 Figure 3 shows depth-weighted average arsenic and uranium concentrations grouped by
441 water application volumes (agricultural – gravity, pivot, and non-irrigated sites). The results in

442 Figure 3 are sub-categorized, within the water application volume, by an increase or decrease in
 443 total unsaturated zone nitrate storage in the top 18.2 m over a period of five years. The vinculum
 444 above the bar graph with ‘**’ sign indicates that the interaction between the factors is
 445 significantly different. Concentrations were analyzed utilizing Two-way ANOVA, considering
 446 water application, and change in nitrate storage in last five years (Table S1). Arsenic
 447 concentration in the unsaturated zone was found to be significantly different (at 0.05 level)
 448 among water application type. However, within the same water application type, change in
 449 nitrate concentration from the previous study did not find any differences between arsenic

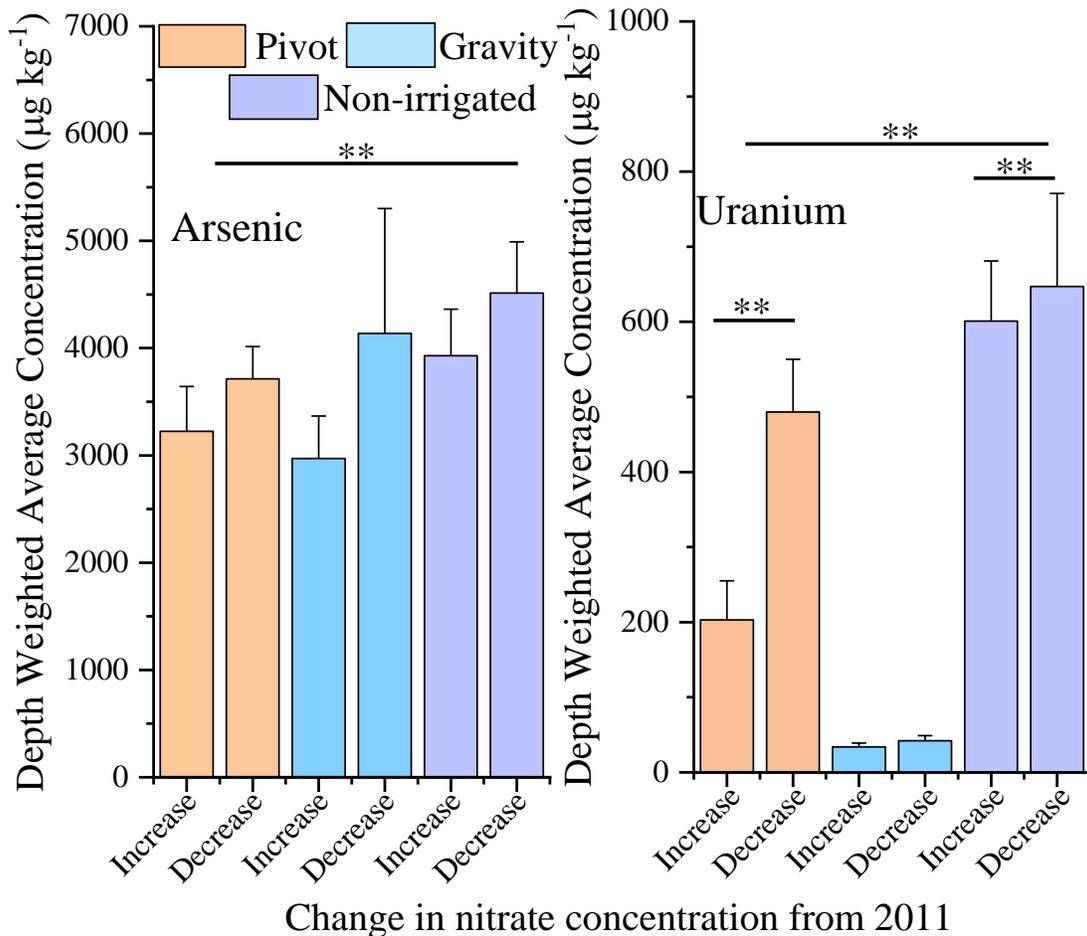


Figure 3. Depth weighted average concentration of arsenic and uranium for different sites under different water application volume, which has been divided according to increase or decrease in nitrate storage in the unsaturated zone over a period of five years. The error bar represents standard deviation. Wherever ** is present it means the interaction among them is significantly different at 0.05 level.

450 concentrations. Sediment arsenic concentrations were found to be highest beneath non-irrigated
451 areas, irrespective of decrease or increase in nitrate content in the unsaturated zone. Sediment
452 arsenic concentrations beneath the gravity irrigated sites were the next highest and the pivot-
453 irrigated sites showed the lowest concentrations of arsenic in the unsaturated zone (Figure 3, S2-
454 S7).

455 Sediment uranium concentrations in the unsaturated zone was found to be significantly
456 different among different water application type (Figure 3). Similar to arsenic, the highest
457 concentrations for uranium were found in cores collected from non-irrigated areas (Figure 3).
458 Further, within the same water application type, when sediment uranium concentration was
459 categorized according to change in stored nitrate concentration over a period of five years, pivot-
460 irrigated sites and non-irrigated sites presented significantly different sediment uranium
461 concentration at 0.05 level (Figure 3). However, no significant differences were found for
462 uranium concentration based on change in nitrate content in the unsaturated zone beneath the
463 gravity irrigated sites. This observation may be due to overall low concentration of uranium in
464 the gravity irrigated sites. The unsaturated zone beneath pivot irrigated sites were found to
465 contain ~ 200 and $\sim 500 \mu\text{g kg}^{-1}$ uranium, for areas that showed a decrease and increase in nitrate
466 content, respectively (Figure 3). Twelve coring sites had average uranium concentrations above
467 the mean value of $300 \mu\text{g kg}^{-1}$, which is lower than average for U.S. surface soils (Vodyanitskii,
468 2011). Uranium concentration ranged between below detection to $1,600 \mu\text{g kg}^{-1}$. Core location
469 HC14W contained the highest levels of uranium at 1.34 m bgs and sediments were characterized
470 by high silt and clay content. Notably, unsaturated zone nitrate decreased by 105 kg-N ha^{-1}
471 between 2011 and 2016 at HC14W. In general, the distribution of uranium throughout the

472 Hastings WHP area was found to be related to water application volume and change in stored
473 nitrate in the unsaturated zone.

474 3.2.3 Detailed Arsenic and Uranium Sediment Core Profiles

475 Water application volume was found to be a significant factor for variation in sediment
476 arsenic and uranium concentration within the unsaturated zone. Further, these pivot and non-
477 irrigated sites also presented significant difference for uranium concentration with respect to
478 change in nitrate storage over a period of five years. Therefore, sites HC3N (non-irrigated) and
479 HC14E (pivot), which had measurable amount of arsenic and uranium concentration in the
480 unsaturated zone, were selected for hot water extractable organic carbon measurement and the
481 concentrations are shown together with sediment arsenic, sediment uranium, gravimetric water
482 content, sediment nitrate, sediment ammonium, particle size distribution and percentage (%)
483 saturation in Figure 4 and 5, respectively. HC3N, a non-irrigated site, showed a 95% increase in
484 nitrate input into the unsaturated zone from five years ago, and represents shallow depth to water
485 table. HC14E, a pivot irrigated site, showed decrease in nitrate storage by 9% from the earlier
486 study, and represents a deeper unsaturated zone. Both sites contain higher than average sediment
487 uranium and arsenic concentrations for Hastings WHP area. Core samples from HC3N contained
488 on an average $36.2 \pm 26.6 \mu\text{g-C g}^{-1}$ and ranged between 9.9 to $144.0 \mu\text{g-C g}^{-1}$. HC14E contained
489 on an average $14.2 \pm 12.4 \mu\text{g-C g}^{-1}$ and range was between 1.2 to $48.2 \mu\text{g-C g}^{-1}$. For both sites the
490 highest amount of hot water extractable organic carbon was found in shallow unsaturated zone
491 depth near the topsoil, though substantial concentrations of hot water extractable organic carbon
492 were present throughout the cores. Hot water extractable organic carbon for depth below 9 m
493 ranged between 9.9 to $55.2 \mu\text{g-C g}^{-1}$ and 1.2 to $41.8 \mu\text{g-C g}^{-1}$ for HC3N and HC14E,
494 respectively. The moisture profile in these two sites was similar to the previous study and most

495 of the gravimetric moisture content range was within the values observed earlier. The percentage
 496 saturation was found to be on the higher side at few depths within the unsaturated zone as seen
 497 from Figure 4 and 5. HC14E, the pivot irrigated site, which received added water during
 498 irrigation presented multiple depths where the conditions were saturated. If compared to HC3N,
 499 within a depth of 20 m bgs, irrigated site HC14E presented two depths where percentage
 500 saturation was close to ~100%, representing fully saturated zones. Fully saturated conditions
 501 within the unsaturated zone may be transient in nature and dependent on the movement of the
 502 water front (Malakar et al., 2020). The gravity irrigated sites, where deep percolation rate of

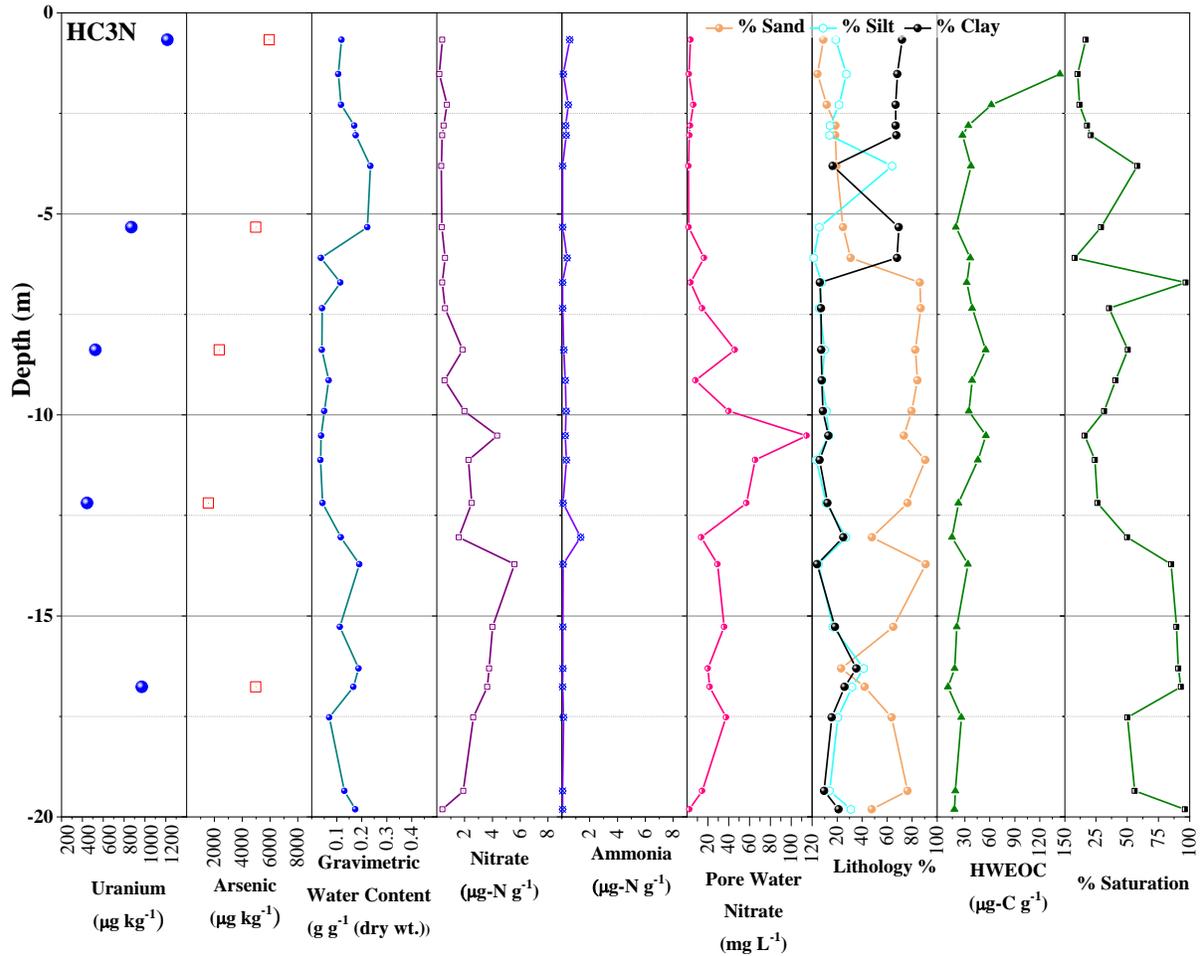


Figure 4. Shows arsenic, uranium, gravimetric water content, nitrate, ammonium, pore water nitrate, lithology, hot water extractable organic carbon (HWEOC), and % saturation profile of site HC3N (Non-irrigated site) against depth. As water application in this site is only rainfall so there is only one site with 100% saturation within the unsaturated zone. Higher clay content in the lithology favors saturation and can act as the hotspot for redox based geochemical reactions.

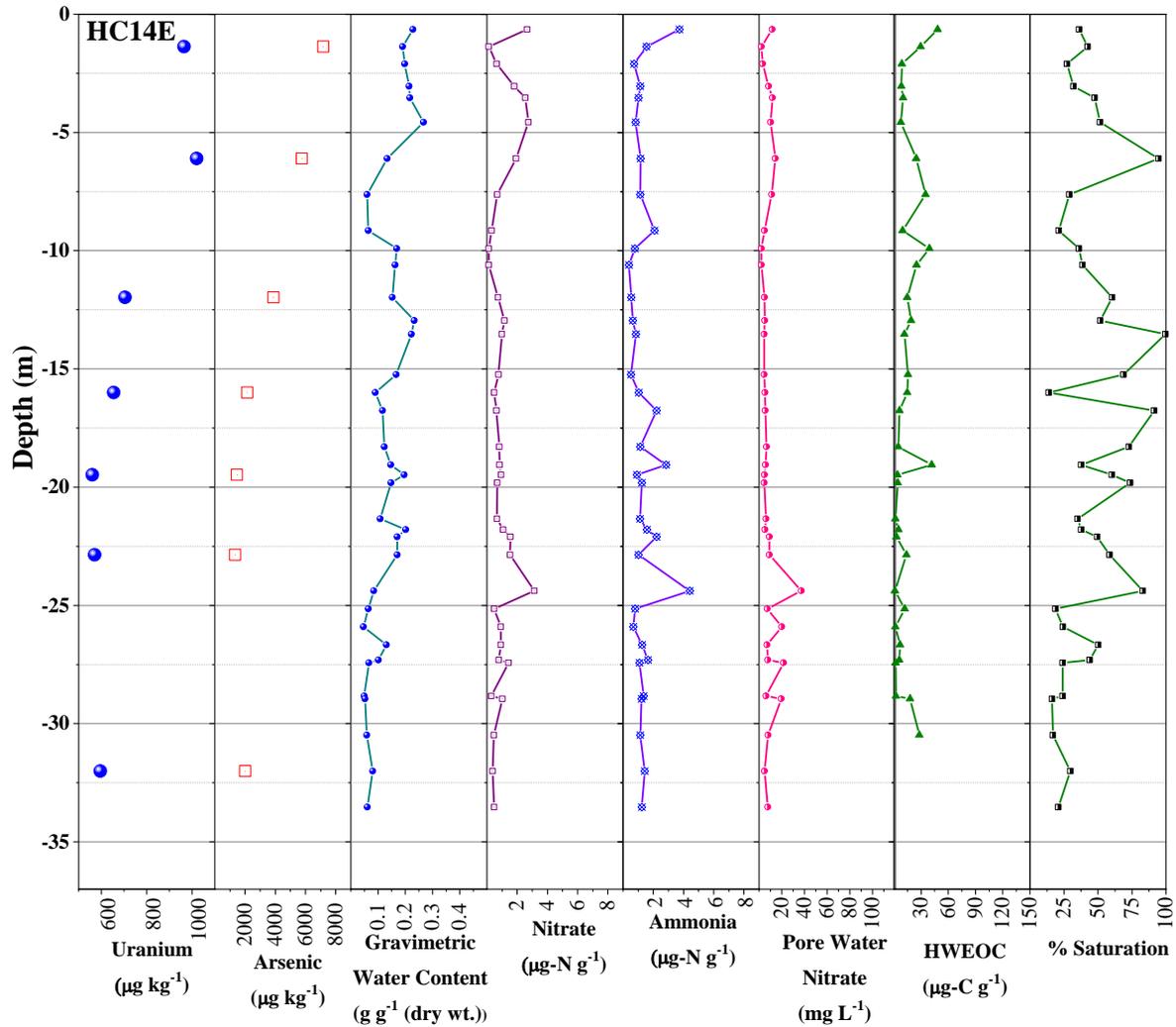


Figure 5. Arsenic, uranium, gravimetric water content, nitrate, ammonium, pore water nitrate, hot water extractable carbon (HWEOC) and percentage saturation profile of site HC14E (Pivot irrigated site) against depth. Although the profile is unsaturated, there are spots where water saturation level is $\sim 100\%$, these sites can create transient saturated zone and present unique redox conditions. The number of highly saturated spots in HC14E may be higher due to higher water application in the irrigated field.

503 water is higher compared to pivot irrigated sites, may present higher number of saturated zones
 504 within the sediment profiles. These saturated zones within the sediment profiles also contained
 505 measureable hot water extractable organic carbon. These transiently saturated zones within the
 506 seemingly bulk unsaturated conditions can give rise to anoxic microsites and can be the hotspot

507 for redox driven geochemical reactions (Keiluweit et al., 2017, 2018; Malakar et al., 2020;
508 Warrinnier et al., 2020).

509 **3.3 Influence of Water Application Volume and Nitrogen Species on Unsaturated Zone** 510 **Arsenic and Uranium Mobility**

511 Processes at the land surface have a long-term influence on the chemical composition of
512 the unsaturated zone (Lopez et al., 2021). Irrigation and fertilization have been linked with
513 enhanced weathering and impact on carbon fluxes (Chao et al., 2017; Kim et al., 2020). Gravity
514 irrigation (volume of water used $\sim 2837 \text{ m}^3$) utilizes almost twice as much water from pivot
515 irrigation (volume of water used $\sim 1480 \text{ m}^3$) (USDA, 2019). Irrigation method correlated well
516 with the quantity of nitrate in the unsaturated zone cores in the Hastings WHP area (Adams,
517 2018) that can be due to the rate of water infiltration, which is dependent on the water
518 application volume of the two irrigation methods (Biscaia Ribeiro da Silva et al., 2018; USDA,
519 2019). The rate of water transport through unsaturated zone is higher in gravity irrigation
520 (Bosch-Rubia, 2015; Spalding et al., 2001), which can influence the weathering processes in the
521 unsaturated zone and mobility of arsenic and uranium. Arsenic and uranium attenuation in the
522 unsaturated zone are also likely to be affected by recharge, nitrate concentrations, pore water
523 ionic strength, pH, carbonate, and potentially from recurrent microbial activity driven by
524 changing moisture profile and readily available organic carbon in pore water. Occurrence of
525 transiently saturated conditions in the bulk unsaturated zone may give rise to movement of trace
526 elements.

527 Sediment arsenic concentrations varied significantly with respect to estimated water
528 application volume (Figure 3), but the change in nitrate input to the unsaturated zone did not

529 seem to correlate to arsenic concentration in the unsaturated zone. Depth of the unsaturated zone
530 showed a weak correlation with arsenic concentration which was found to be significant ($r=0.35$
531 $p<0.05$), indicating an increase in sediment arsenic concentration in deeper unsaturated zone.
532 Sediment arsenic concentrations show significant weak positive correlation with uranium
533 concentrations ($r=0.19$ $p<0.05$), which may indicate co-occurrence of both the geogenic
534 contaminant via depositional processes or mechanisms retaining sediment arsenic and uranium
535 may be similar. Sediment arsenic showed a positive correlation with mass% of iron in the
536 sediments ($r=0.32$ $p<0.05$), indicating that arsenic is preferentially bound to iron minerals in the
537 sediments, which also explains the positive correlation between arsenic and clay content ($r=0.58$
538 $p<0.05$) as most of iron seem to be clay bound (Figure S1).

539 Arsenic is known to strongly adsorb to iron oxide minerals (Wang et al., 2018). The high
540 concentration of arsenic in the unsaturated zone suggests that the unsaturated zone may attenuate
541 arsenic. The sediment pH is near-neutral to slightly basic which may lead to less mobility of
542 arsenic, especially the charged species. However high levels of organic carbon can bring about
543 reductive dissolution of iron oxides promoting arsenic mobilization and leaching (Rawson et al.,
544 2016). Transiently saturated conditions can create fluctuation between reducing and oxidizing
545 conditions. Higher levels of organic carbon in the unsaturated zone can act as electron donor and
546 higher nitrate concentration can act as electron acceptors, which can bring about redox-based
547 transformation such as reductive dissolution of iron oxides (Oppong-Anane et al., 2018; Mejia et
548 al., 2016) coupled with change in the N-species (Chen et al., 2018).

549 Sediment uranium concentrations in the unsaturated zone were found to be influenced by
550 water application type and changes in nitrate concentration in the unsaturated zone (Figure 3).
551 Uranium concentration was tenfold higher in pivot sites compared to gravity and further 1.3 fold

552 increase from pivot to non-irrigated sites, signifying that the unsaturated zone can immobilize
553 uranium better in pivot or non-irrigated sites, which corresponds to low water application
554 volume. There was more leaching loss of uranium in soils that had higher rate of water
555 application at the land surface. Sediment uranium concentrations were weakly correlated with
556 depth ($r=0.22$ $p<0.05$), suggesting higher sediment uranium concentration at deeper unsaturated
557 zone. Uranium present in sediments showed a weak negative correlation with N-species
558 (sediment nitrate ($r=-0.23$ $p<0.05$) and sediment ammonium ($r=-0.19$ $p<0.05$)) of the
559 unsaturated zone.

560 In contrast to arsenic, uranium concentrations did not correlate with iron and clay
561 content, which suggests that the form of iron oxides may not preferentially bind or weakly bind
562 to uranium species, and uranium immobilization, if any, in the unsaturated zone may be driven
563 by reduction to U(IV), in the presence of organic carbon. There is also a possibility of formation
564 ligand based uranium complexes such as calcium-uranyl-carbonate complexes (Nolan, 2016;
565 Stanley & Wilkin, 2019) in the unsaturated zone as, calcium was found to be the fourth largest
566 element in the unsaturated zone ranging from 2.5 to 6.2%. Surface soil organic and inorganic
567 carbon concentrations tend to increase over time due to cultivation-induced changes in soil
568 properties, water regime and carbonate-forming ion concentrations (Denef et al., 2008) and both
569 organic and inorganic forms of carbon likely accumulate in the deeper unsaturated zone.
570 Calcium-uranyl-carbonate complexes may provide mobility to uranium at the prevalent pH range
571 of the unsaturated zone (Stanley & Wilkin, 2019). The present data suggests less attenuation of
572 uranium in the unsaturated zone, specifically in sites with high infiltration rate of water and
573 nitrate such as gravity irrigated locations. High nitrogen and water input negatively correlated to

574 uranium concentrations. This may have promoted formation of uranyl carbonate complexes
575 enhancing mobility of uranium through the unsaturated zone.

576 Depending on its form, organic carbon in the unsaturated zone can support microbial
577 activity controlling oxidation state of iron and may likely influence arsenic and uranium
578 mobility. Biogeochemical processes in the unsaturated zone are controlled by moisture content
579 and organic carbon, which serve as a good predictor for potential pore water microbial activity
580 (Kaiser & Kalbitz, 2012). Investigations of unsaturated zone denitrification are limited, though
581 studies have indicated that subsurface microbial respiration can be significantly increased by
582 addition of water and organic carbon. For example, Chen et al (2018) show that incubation-
583 measured unsaturated zone denitrification rates are intended to be 2-3X higher under plots with
584 high fertilizer-derived nitrate to depths of 10 meters. Stimulation of denitrification required only
585 addition of moisture and carbon with carbon serving as the limiting factor (Chen et al., 2018).
586 Mobility and availability of nutrients and contaminants in surface soils are also largely
587 determined by organic carbon (Sopliniak et al., 2017). Extractable organic carbon concentrations
588 in soil have been related to the mobilization of arsenic and subsequent leaching to groundwater
589 (Mladenov et al., 2010). Elevated hot water extractable organic carbon occurs at the surface and
590 may be subsequently leached with recharging surface water. Hot water extractable organic
591 carbon leached from the surface or root zone soil will support microbial activity in the
592 subsurface (Baker et al., 2017). Organic carbon supported microbial respiration and redox
593 processes can control various biogeochemical processes such as denitrification, ammonification,
594 metal/radionuclide reduction, and mobilization/immobilization in the unsaturated zone (Oppong-

595 Anane et al., 2018; Soplinskiak et al., 2017). Microbial activity, if any, may be rapid, but
596 characterization of microbial populations was not possible in the current investigation.

597 **3.4 Comparison of Unsaturated Zone to Groundwater Arsenic and Uranium** 598 **Concentrations**

599 Groundwater collected in the Hastings WHP area reveals high concentrations of nitrate,
600 iron, and uranium but not arsenic in spite of the elevated concentrations found in the unsaturated
601 zone. In the groundwater samples, mean groundwater nitrate concentration were measured at
602 8.1 ± 7.4 mg-N L⁻¹, groundwater arsenic at 1.4 ± 1.2 µg L⁻¹ and groundwater uranium at 17.8 ± 6.7
603 µg L⁻¹. Near site HC20, highest value of groundwater arsenic (3.3 µg L⁻¹), uranium (27.9 µg L⁻¹)
604 and nitrate (19.5 mg L⁻¹), concentrations were observed, which coincides with lowest
605 groundwater iron concentration (2.8 mg L⁻¹). At HC-20 unsaturated zone sediment uranium
606 concentrations are lower, and there was an increase in sediment nitrate storage by 480 kg-N ha⁻¹
607 and 176 kg-N ha⁻¹ at HC20E and HC20W respectively (Table S1). Groundwater iron
608 concentration were measured at 84.4 ± 121.0 mg L⁻¹ and dissolved organic carbon were measured
609 at 0.7 ± 0.1 mg-C L⁻¹. Groundwater arsenic and uranium concentration showed a significantly
610 strong correlation ($r=0.98$, $p<0.05$), suggesting co-occurrence of these two geogenic
611 contaminants. Groundwater nitrate concentration also showed strongly significant correlation
612 with groundwater arsenic ($r=0.94$, $p<0.05$) and groundwater uranium ($r=0.93$, $p<0.05$)
613 concentrations. Groundwater at WHP area of Hastings contained elevated levels of uranium
614 compared to arsenic though sediment uranium concentration is ten times less compared to
615 sediment arsenic concentration in the unsaturated zone. This enhanced concentration may

616 indicate processes leading to preferential mobilization of uranium to the groundwater below,
617 which may impact water quality.

618 While the initial deposition of sediment associated arsenic and uranium in the unsaturated
619 zone is likely geogenic, subsequent agricultural land-use and irrigation using groundwater can
620 encourage mobilization and leaching to groundwater (Xiao et al., 2018). Infiltration of irrigation
621 water containing high levels of nitrate and organic matter can affect biogeochemistry of the
622 unsaturated zone and influence arsenic and iron behavior, enhancing arsenic mobilization and
623 subsequent leaching (Xiao et al., 2018). Higher water application in gravity irrigated systems
624 will preferentially increase arsenic leaching processes in the unsaturated zone in comparison to
625 pivot irrigation system (Xiao et al., 2018). Anthropogenic activities such as irrigation,
626 fertilization, and nitrate input can influence the mobilization of arsenic and uranium to the
627 groundwater below (Chi et al., 2018; Collins & Rosso, 2017).

628 The application of water for irrigation and occluded water within soil pores of high
629 percentage saturation zones at intermediate and deeper depths of the soils can create temporary
630 saturated zone which can have anoxic microsites (Keiluweit et al., 2018; Malakar et al., 2020;
631 Warrinnier et al., 2020) within the overall bulk unsaturated zone. In the deep unsaturated zone,
632 clay rich elevated levels of organic carbon – a ready electron source and increased nitrate input, a
633 readily available electron sink can favor reduction and oxidation fluxes (Keiluweit et al., 2017,
634 2018; Mejia et al., 2016). These redox changes in the anoxic microsites of the unsaturated zone
635 will influence iron mineral transformation, which can play a key role in the mobilization of trace
636 elements (Malakar et al., 2020; Warrinnier et al., 2020). These anoxic microsites within the bulk
637 unsaturated zone can have distinct microcosm and geochemical activity, which can be the
638 hotspot of redox sensitive reaction, leading to release of immobile trace element such as arsenic

639 by reductive mineral dissolution but may attenuate uranium by precipitation to mineral forms
640 (Campbell et al., 2012; Hall & Huang, 2017; Janot et al., 2016; Küsel et al., 2002; C. Xiao et al.,
641 2020). However, even under iron reducing conditions prevalent in anoxic microsites, under
642 similar pH, uranium mobilization has been observed and linked with iron minerals such as
643 ferrihydrite (Belli & Taillefert, 2018; Burkhardt et al., 2010; Malakar et al., 2020; Wan et al.,
644 2005). Under reducing conditions, iron(III)-bearing minerals can act as the terminal electron
645 acceptor and drive the uranium(IV)/uranium(VI) redox potential in presence of calcium and
646 silica, both of which were present in elevated quantity in the sediments (Table S2), and can lead
647 to ternary calcium-uranyl-carbonate complex formation (Belli & Taillefert, 2018; Wan et al.,
648 2005).

649 Reduced iron at the anoxic-oxic interface of the unsaturated zone can mineralize to
650 reactive forms such as green rust, which may influence abiotic nitrate reduction to ammonium at
651 the prevalent pH in the anoxic microsites of the unsaturated zone (Hansen et al., 1996). Green
652 rust is difficult to sample and identify as it is easily oxidized, but has been identified in
653 groundwater (Christiansen et al., 2009) and unsaturated soils (Génin et al., 1998). Sediment cores
654 of the unsaturated zone of Hasting WHP area contained green intercalated layers throughout the
655 profile, which turned brown after overnight air drying may indicate presence of reduced iron
656 mineral in unsaturated cores. Iron reduction and denitrification may also occur intermittently
657 through changes in moisture content and organic carbon can drive pore water microbial
658 respiration in the unsaturated zone (Chen et al., 2018; Oppong-Anane et al., 2018; Rivett et al.,
659 2008; Weber, Achenbach, et al., 2006).

660 The processes leading to iron reduction and subsequent oxidation of mobile reduced iron
661 outside the anoxic microsites, within the largely unsaturated zone, can initiate arsenic and

662 uranium oxidation due to availability of molecular oxygen (Ding et al., 2018; Romanchuk et al.,
663 2020). Higher levels of oxygen in the unsaturated zone may lead to iron oxide-arsenate co-
664 precipitation effectively attenuating arsenic and sustain oxidized uranium with concurrent
665 formation of uranium(VI) ligands such as calcium-uranyl-carbonate complexes, making uranium
666 largely mobile (Hansen & Bender Koch, 1998; Luo & Gu, 2011; Rawson et al., 2016; Sani et al.,
667 2005; Stanley & Wilkin, 2019).

668 Figure 6 shows a simplified conceptual model of the various complex biogeochemical
669 processes in the unsaturated zone beneath irrigated cropland that can lead to ammonium in the
670 unsaturated zone and preferential uranium mobilization to the groundwater. Ammonium can be
671 transported from the surface or can be present naturally or formed from the nitrate already
672 present in the unsaturated zone. In the WHP area it seems transformation of nitrogen species
673 such as nitrate to ammonia may be the plausible, which may explain high levels of ammonium in
674 the sediments of unsaturated zone. Reduced iron in the anoxic microsites of transiently saturated
675 layers can mineralize, and may bring about abiotic reduction of nitrate present in the unsaturated
676 zone forming ammonium (Hansen et al., 1996). Biologically mediated ammonium production
677 can occur in the deep unsaturated zone, such as DNRA, if present, can bring about the
678 conversion of nitrate to ammonium (Gao et al., 2016). In the deep unsaturated zone, high levels
679 of hot water extractable organic carbon correspond to low levels of sediment nitrate and
680 increased sediment ammonium, may indicate biotic transformation of nitrate to ammonium. Both
681 abiotic and biotic processes can work concurrently to form ammonium in the unsaturated zone.
682 Microbial processes can lead to nitrite formation, which may be reduced to ammonium by
683 iron(II) species (Carlson et al., 2012; Summers & Chang, 1993; Weber, Achenbach, et al., 2006).
684 Increased water movement based on water application volume impacts the nitrate transportation

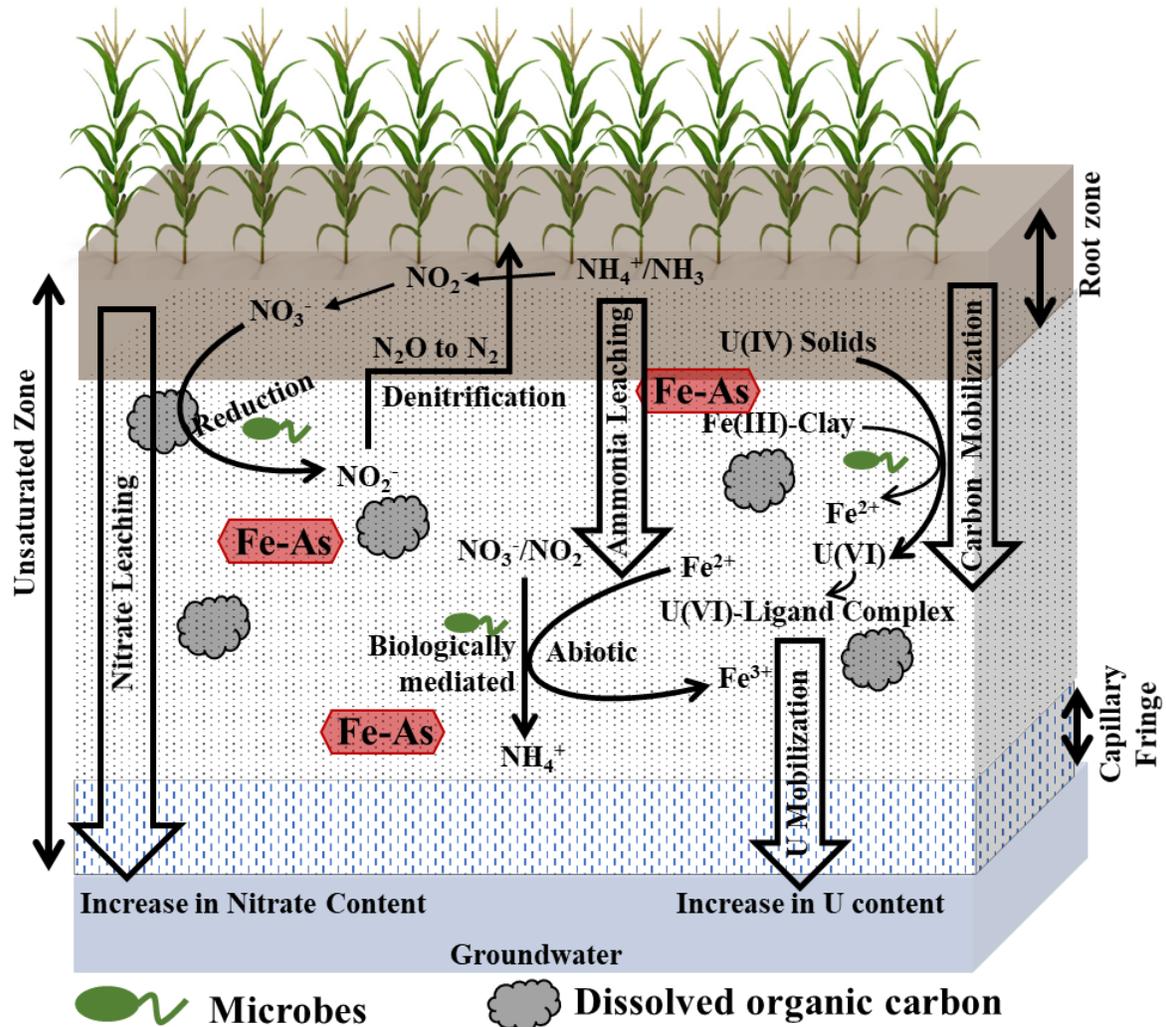


Figure 6. Conceptual model presenting probable pathways of uranium mobilization and occurrence of ammonium in the unsaturated zone. Ammonia-based fertilizer application in the surface soil can make way to unsaturated zone by preferential transport through the sediment layers of the WHP area, but given the charge this transport process will be relatively slow compared to nitrate. Nitrate applied in surface or formed at the root zone can leach rapidly as soon as it passes the root zone. High input of water can drive these leaching processes and can also increase soil moisture content to the point that sediment layers can be transiently saturated creating distinct redox sites, which can act as location for biogeochemical processes. Ammonium in sediments may come from nitrate in the pore water either formed by iron mediated abiotic process or biologically mediated processes. Arsenic will preferentially bound to iron oxides in the unsaturated zone outside the transiently saturated layers and remain attenuated. Reduced immobile uranium (IV) in sediments may be oxidized by iron-mediated oxidative dissolution and oxidized uranium in the unsaturated zone will preferentially from complexes, which will increase uranium mobility.

685 through the unsaturated zone, which can speed up due to sand layers present at the WHP area
 686 and impacts uranium chemistry. The main driving reaction may be mediated by iron based redox
 687 processes, which is abundant at WHP area unsaturated zone sediments. Iron oxides can attenuate
 688 arsenic movement as shown in the Figure 6, but its reduction can be made feasible by high level

689 of organic carbon and nitrate or nitrite within the transiently saturated zones, which may
690 mobilize arsenic. But predominantly higher level of oxygen in unsaturated system, can oxidize
691 arsenic and iron, which will preferentially make arsenic immobile. Iron minerals can support
692 oxidation of uranium by acting as terminal electron acceptor, which can be influenced by
693 calcium and silica present in the unsaturated zone (Belli & Taillefert, 2018; Wan et al., 2005).
694 Oxidative dissolution of immobile uranium(IV) can happen in the prevalent pH of the
695 unsaturated zone, where iron(III) oxides and iron(III)-bearing clays support as efficient oxidants
696 (Belli & Taillefert, 2018; Ginder-Vogel et al., 2010; Luan et al., 2014; Senko et al., 2005). The
697 oxidized uranium can readily form ligand-complexes enhancing the mobility of uranium within
698 the unsaturated zone. The WHP area unsaturated zone sediments contained measurable levels of
699 iron bound clay and iron-mediated geochemical processes seem relevant in mobilizing uranium
700 to the groundwater of the area.

701 **4 Conclusions**

702 The present study evaluates the occurrence of sediment arsenic and uranium in the
703 unsaturated zone within the framework of water application volume, irrigation and nitrate
704 leaching. The identification of the geochemical processes in the unsaturated zone will help in
705 conceiving proactive measures to prevent impact on groundwater quality. The presence of a
706 significant amount of ammonium in the deep unsaturated zone core is intriguing and needs
707 further investigation to ascertain the source of ammonium in deep sediment cores. The
708 occurrence and distribution of elevated levels of arsenic and uranium in the unsaturated zone of
709 the Hastings WHP area suggest that mobilization and leaching may lead to increasing levels in
710 the local groundwater. The change in uranium concentration of the unsaturated zone suggests
711 that nitrate and ammonium in unsaturated zone are acting as triggers for uranium mobilization.

712 In the WHP area, elevated levels of uranium are already being observed in the groundwater
713 below, and an increase in nitrate content in the unsaturated zone seems to accelerate the process
714 of uranium transport. Currently, arsenic concentrations in the unsaturated zone are higher than
715 global averages, but results suggest arsenic is well attenuated. Irrigation and nitrate leaching
716 from the surface are preferentially impacting uranium mobility in the unsaturated zone.

717 Continued monitoring of groundwater at the Hastings WHP area is necessary to ensure
718 that the trends of uranium mobilization to the groundwater are significant. The presence of high
719 iron in the sediments coupled with elevated levels of extractable organic carbon can influence
720 various microbial and abiotic processes, which can control mobilization or immobilization
721 process as iron oxides are known to influence arsenic and uranium mobility. The iron chemistry
722 in the deep unsaturated zone soil needs more rigorous study to understand their role in nitrate
723 conversion, tied with mobilization of trace elements. Further in-depth analysis of iron
724 geochemistry will provide more information about the biogeochemical processes controlling
725 trace element mobilization in the unsaturated zone. The occurrence of elevated ammonium and
726 potential transport or formation in the unsaturated zone calls for a more detailed study.
727 Recognizing the role of intensive irrigation practices on groundwater contamination by geogenic
728 elements such as uranium can promote efficient best management practices to protect the
729 groundwater quality.

730

731 **Acknowledgments**

732 Authors thank Dr. Sudeshna Dutta for helping to design figure 1. Authors thank Keith Miller
733 (City of Hastings, NE) for assistance in securing permission to collect core samples, and the

734 University of Nebraska School of Natural Resources Conservation and Survey Division drillers
735 Matt Marxsen and John Seamann for their efforts in collecting the unsaturated zone core
736 samples. Funding for this project was provided by the Nebraska Environmental Trust and City of
737 Hastings (Grant ID# 74649). The part of the laboratory work for this project was performed at
738 the University of Nebraska Water Sciences Laboratory core facility. Additional analyses were
739 conducted in the Nebraska Nanoscale Facility: National Nanotechnology Coordinated
740 Infrastructure and the Nebraska Center for Materials and Nanoscience, supported by the National
741 Science Foundation under Award ECCS: 1542182, National Science Foundation. EPSCoR
742 Center for Root and Rhizobiome Innovation Award OIA-1557471 to KAW and the Nebraska
743 Research Initiative.

744

745 The authors declare no conflict of interest.

746

747 **Data Availability**

748 Data supporting the conclusions in this paper is available at:

749 <https://digitalcommons.unl.edu/watercenterpubs/52/> and the attached supporting information file.

750

751 **References**

752 Adams, C. J. (2018). *The Impact of Land Use on Nitrate-N Movement and Storage in the Vadose Zone of the*
753 *Hastings' WHPA*. M.S. Thesis, University of Nebraska Lincoln.

754 ASTM. (1999). Standard guide for soil sampling from the vadose zone. *ASTM Standards International, D4700-15*.

755 Baker, A., Duan, W., Rutledge, H., McDonough, L., Oudone, P., Meredith, K., et al. (2017). Dissolved organic

- 756 matter in the unsaturated zone: the view from the cave. *American Geophysical Union Fall Meeting*. Retrieved
 757 from <https://agu.confex.com/agu/fm17/meetingapp.cgi/Paper/237005>
- 758 Belli, K. M., & Taillefert, M. (2018). Geochemical controls of the microbially mediated redox cycling of uranium
 759 and iron. *Geochimica et Cosmochimica Acta*, 235(5), 431–449. <https://doi.org/10.1016/j.gca.2018.05.027>
- 760 Biscaia Ribeiro da Silva, A. L., Hashiguti, H. T., Zotarelli, L., Migliaccio, K. W., & Dukes, M. D. (2018). Soil
 761 Water Dynamics of Shallow Water Table Soils Cultivated With Potato Crop. *Vadose Zone Journal*, 17(1),
 762 180077. <https://doi.org/10.2136/vzj2018.04.0077>
- 763 Böhlke, J.-K. K. (2002). Groundwater recharge and agricultural contamination. *Hydrogeology Journal*, 10(1), 153–
 764 179. <https://doi.org/10.1007/s10040-001-0183-3>
- 765 Bosch-Rubia, G. (2015). *Land Use and Water and Soil Management Practices Impacts on Potential Groundwater*
 766 *Recharge in Loess Regions of South Central Nebraska*. M.S. Thesis University of Nebraska - Lincoln.
 767 Retrieved from <https://digitalcommons.unl.edu/cgi/viewcontent.cgi?article=1054&context=biosysengdiss>
- 768 Boyce, J. S., Muir, J., Edwards, A. P., Seim, E. C., & Olson, R. A. (1976). Geologic nitrogen in pleistocene loess of
 769 nebraska. *Journal of Environment Quality*, 5(1), 93–96.
 770 <https://doi.org/10.2134/jeq1976.00472425000500010022x>
- 771 Brock, T. D., Madigan, M. T., Martinko, J. M., & Parker, J. (2003). *Brock Biology of Microorganisms*. Upper
 772 Saddle River, NJ: Prentice-Hill.
- 773 Brown, C. J., Jurgens, B. C., Katz, B. G., Landon, M. K., & Eberts, S. M. (2007). Arsenic and uranium in four
 774 aquifer settings : Occurrence , distribution , and mechanisms for transport to supply wells. In *2007 NGWA*
 775 *Naturally Occurring Contaminants COnference: Arsenic, Radium, Radon, Uranium*. Charleston, SC: NGWA.
 776 Retrieved from <https://pdfs.semanticscholar.org/24ca/4bd4ea61735fa97bb97884462364df0a8caf.pdf>
- 777 Burkhardt, E.-M., Akob, D. M., Bischoff, S., Sitte, J., Kostka, J. E., Banerjee, D., et al. (2010). Impact of
 778 biostimulated redox processes on metal dynamics in an iron-rich creek soil of a former uranium mining area.
 779 *Environmental Science & Technology*, 44(1), 177–183. <https://doi.org/10.1021/es902038e>
- 780 Burow, K. R., Nolan, B. T., Rupert, M. G., & Dubrovsky, N. M. (2010). Nitrate in groundwater of the united states,
 781 1991–2003. *Environmental Science & Technology*, 44(13), 4988–4997. <https://doi.org/10.1021/es100546y>
- 782 Campbell, K. M., Kukkadapu, R. K., Qafoku, N. P., Peacock, A. D., Leshner, E., Williams, K. H., et al. (2012).
 783 Geochemical, mineralogical and microbiological characteristics of sediment from a naturally reduced zone in

- 784 a uranium-contaminated aquifer. *Applied Geochemistry*, 27(8), 1499–1511.
785 <https://doi.org/10.1016/j.apgeochem.2012.04.013>
- 786 Carlson, H. K., Clark, I. C., Melnyk, R. A., & Coates, J. D. (2012). Toward a mechanistic understanding of
787 anaerobic nitrate-dependent iron oxidation: balancing electron uptake and detoxification. *Frontiers in*
788 *Microbiology*, 3(2), 1–6. <https://doi.org/10.3389/fmicb.2012.00057>
- 789 Chao, S., Changli, L., & Guilin, H. (2017). Impact of fertilization with irrigation on carbonate weathering in an
790 agricultural soil in Northern China: A column experiment. *Geochemical Journal*, 51(2), 143–155.
791 <https://doi.org/10.2343/geochemj.2.0447>
- 792 Chen, S., Wang, F., Zhang, Y., Qin, S., Wei, S., Wang, S., et al. (2018). Organic carbon availability limiting
793 microbial denitrification in the deep vadose zone. *Environmental Microbiology*, 20(3), 980–992.
794 <https://doi.org/10.1111/1462-2920.14027>
- 795 Chi, Z., Xie, X., Pi, K., Wang, Y., Li, J., & Qian, K. (2018). The influence of irrigation-induced water table
796 fluctuation on iron redistribution and arsenic immobilization within the unsaturation zone. *Science of The*
797 *Total Environment*, 637–638, 191–199. <https://doi.org/10.1016/j.scitotenv.2018.05.027>
- 798 Chou, S., Harper, C., Ingerman, L., Lladós, F., Colman, J., Chappell, L., et al. (2002). *Toxicological Profile for*
799 *Arsenic. ATSDR's Toxicological Profiles*. Atlanta. Retrieved from
800 <https://www.atsdr.cdc.gov/toxprofiles/tp2.pdf>
- 801 Christiansen, B. C., Balic-Zunic, T., Dideriksen, K., & Stipp, S. L. S. (2009). Identification of green rust in
802 groundwater. *Environmental Science and Technology*, 43(10), 3436–3441. <https://doi.org/10.1021/es8011047>
- 803 Ćirić, V., Belić, M., Nešić, L., Šeremešić, S., Pejić, B., Bezdán, A., & Manojlović, M. (2016). The sensitivity of
804 water extractable soil organic carbon fractions to land use in three soil types. *Archives of Agronomy and Soil*
805 *Science*, 62(12), 1654–1664. <https://doi.org/10.1080/03650340.2016.1165345>
- 806 Cole, J. A., & Brown, C. M. (1980). Nitrite reduction to ammonia by fermentative bacteria: A short circuit in the
807 biological nitrogen cycle. *FEMS Microbiology Letters*, 7(2), 65–72. [https://doi.org/10.1111/j.1574-](https://doi.org/10.1111/j.1574-6941.1980.tb01578.x)
808 [6941.1980.tb01578.x](https://doi.org/10.1111/j.1574-6941.1980.tb01578.x)
- 809 Collins, R. N., & Rosso, K. M. (2017). Mechanisms and rates of u(vi) reduction by fe(ii) in homogeneous aqueous
810 solution and the role of u(v) disproportionation. *Journal of Physical Chemistry A*, 121(35), 6603–6613.
811 <https://doi.org/10.1021/acs.jpca.7b05965>

- 812 Denef, K., Stewart, C. E., Brenner, J., & Paustian, K. (2008). Does long-term center-pivot irrigation increase soil
813 carbon stocks in semi-arid agro-ecosystems? *Geoderma*, *145*(1–2), 121–129.
814 <https://doi.org/10.1016/j.geoderma.2008.03.002>
- 815 DeSimone, L. A., & Howes, B. L. (1998). Nitrogen transport and transformations in a shallow aquifer receiving
816 wastewater discharge: A mass balance approach. *Water Resources Research*, *34*(2), 271–285.
817 <https://doi.org/10.1029/97WR03040>
- 818 Dieter, C. A. A., Maupin, M. A. A., Caldwell, R. R. R., Harris, M. A. A., Ivahnenko, T. I. I., Lovelace, J. K. K., et
819 al. (2018). *Estimated Water Use in the United States in 2015 (No. 1441)*. U.S. Geological Survey.
- 820 Dietrich, S., Bea, S. A., Weinzettel, P., Torres, E., & Ayora, C. (2016). Occurrence and distribution of arsenic in the
821 sediments of a carbonate-rich unsaturated zone. *Environmental Earth Sciences*, *75*(2), 1–14.
822 <https://doi.org/10.1007/s12665-015-4892-7>
- 823 Ding, W., Xu, J., Chen, T., Liu, C., Li, J., & Wu, F. (2018). Co-oxidation of As(III) and Fe(II) by oxygen through
824 complexation between As(III) and Fe(II)/Fe(III) species. *Water Research*, *143*(Iii), 599–607.
825 <https://doi.org/10.1016/j.watres.2018.06.072>
- 826 Exner, M. E., Perea-Estrada, H., & Spalding, R. F. (2010). Long-term response of groundwater nitrate
827 concentrations to management regulations in nebraska’s central platte valley. *The Scientific World Journal*,
828 *10*, 286–297. <https://doi.org/10.1100/tsw.2010.25>
- 829 Exner, M. E., Hirsh, A. J., & Spalding, R. F. (2014). Nebraska’s groundwater legacy: Nitrate contamination beneath
830 irrigated cropland. *Water Resources Research*, *50*(5), 4474–4489. <https://doi.org/10.1002/2013WR015073>
- 831 Farooq, S. H., Chandrasekharam, D., Dhanachandra, W., & Ram, K. (2019). Relationship of arsenic accumulation
832 with irrigation practices and crop type in agriculture soils of Bengal Delta, India. *Applied Water Science*, *9*(5),
833 1–11. <https://doi.org/10.1007/s13201-019-0904-1>
- 834 Gao, W., Kou, L., Zhang, J., Müller, C., Yang, H., & Li, S. (2016). Ammonium fertilization causes a decoupling of
835 ammonium cycling in a boreal forest. *Soil Biology and Biochemistry*, *101*, 114–123.
836 <https://doi.org/10.1016/j.soilbio.2016.07.007>
- 837 Génin, J.-M. R., Bourrié, G., Trolard, F., Abdelmoula, M., Jaffrezic, A., Refait, P., et al. (1998). Thermodynamic
838 equilibria in aqueous suspensions of synthetic and natural Fe(II)–Fe(III) green rusts: Occurrences of the
839 mineral in hydromorphic soils. *Environmental Science & Technology*, *32*(8), 1058–1068.

- 840 <https://doi.org/10.1021/es970547m>
- 841 Ghani, A., Dexter, M., & Perrott, K. W. (2003). Hot-water extractable carbon in soils: A sensitive measurement for
842 determining impacts of fertilisation, grazing and cultivation. *Soil Biology and Biochemistry*, 35(9), 1231–
843 1243. [https://doi.org/10.1016/S0038-0717\(03\)00186-X](https://doi.org/10.1016/S0038-0717(03)00186-X)
- 844 Ghasemi, A., & Zahediasl, S. (2012). Normality tests for statistical analysis: A guide for non-statisticians.
845 *International Journal of Endocrinology and Metabolism*, 10(2), 486–489. <https://doi.org/10.5812/ijem.3505>
- 846 Ginder-Vogel, M., Stewart, B., & Fendorf, S. (2010). Kinetic and mechanistic constraints on the oxidation of
847 biogenic uraninite by ferrihydrite. *Environmental Science and Technology*, 44(1), 163–169.
848 <https://doi.org/10.1021/es902452u>
- 849 Gosselin, D., Klawer, L., & Noe, A. (2004). *Arsenic in Nebraska's groundwater and public water supplies. Papers*
850 *in the Earth and Atmospheric Sciences Earth and Atmospheric Sciences* (Vol. 442). Retrieved from
851 <http://digitalcommons.unl.edu/geosciencefacpubhttp://digitalcommons.unl.edu/geosciencefacpub/442>
- 852 Hall, S. J., & Huang, W. (2017). Iron reduction: a mechanism for dynamic cycling of occluded cations in tropical
853 forest soils? *Biogeochemistry*, 136(1), 91–102. <https://doi.org/10.1007/s10533-017-0383-0>
- 854 Hamkalo, Z., & Bedernichek, T. (2014). Total, cold and hot water extractable organic carbon in soil profile: impact
855 of land-use change. *Zemdirbyste-Agriculture*, 101(2), 125–132. <https://doi.org/10.13080/z-a.2014.101.016>
- 856 Hansen, H. C. B., & Bender Koch, C. (1998). Reduction of nitrate to ammonium by sulphate green rust: activation
857 energy and reaction mechanism. *Clay Minerals*, 33(1), 87–101. <https://doi.org/10.1180/000985598545453>
- 858 Hansen, H. C. B., Koch, C. B., Nancke-Krogh, H., Borggaard, O. K., & Sørensen, J. (1996). Abiotic nitrate
859 reduction to ammonium: Key role of green rust. *Environmental Science and Technology*, 30(6), 2053–2056.
860 <https://doi.org/10.1021/es950844w>
- 861 Herath, I., Vithanage, M., Bundschuh, J., Maity, J. P., & Bhattacharya, P. (2016). Natural arsenic in global
862 groundwaters: Distribution and geochemical triggers for mobilization. *Current Pollution Reports*.
863 <https://doi.org/10.1007/s40726-016-0028-2>
- 864 Jamieson, J., Prommer, H., Kaksonen, A. H., Sun, J., Siade, A. J., Yusov, A., & Bostick, B. (2018). Identifying and
865 quantifying the intermediate processes during nitrate-dependent iron(II) oxidation. *Environmental Science and*
866 *Technology*, 52(10), 5771–5781. <https://doi.org/10.1021/acs.est.8b01122>
- 867 Janot, N., Lezama Pacheco, J. S., Pham, D. Q., O'Brien, T. M., Hausladen, D., Noël, V., et al. (2016). Physico-

- 868 chemical heterogeneity of organic-rich sediments in the rifle aquifer, CO: Impact on uranium
869 biogeochemistry. *Environmental Science & Technology*, 50(1), 46–53. <https://doi.org/10.1021/acs.est.5b03208>
- 870 Juntakut, P., Snow, D. D., Haacker, E. M. K., & Ray, C. (2019). The long term effect of agricultural, vadose zone
871 and climatic factors on nitrate contamination in Nebraska’s groundwater system. *Journal of Contaminant*
872 *Hydrology*, 220, 33–48. <https://doi.org/10.1016/j.jconhyd.2018.11.007>
- 873 Kaiser, K., & Kalbitz, K. (2012). Cycling downwards - dissolved organic matter in soils. *Soil Biology and*
874 *Biochemistry*, 52, 29–32. <https://doi.org/10.1016/j.soilbio.2012.04.002>
- 875 Keech, C. F., & Dreeszen, V. H. (1968). *Availability of Ground Water in Adams County, Nebraska (HA-287)*.
876 Denver, CO.
- 877 Keiluweit, M., Nico, P. S., Kleber, M., & Fendorf, S. (2016). Are oxygen limitations under recognized regulators of
878 organic carbon turnover in upland soils? *Biogeochemistry*, 127(2–3), 157–171.
879 <https://doi.org/10.1007/s10533-015-0180-6>
- 880 Keiluweit, M., Wanzek, T., Kleber, M., Nico, P., & Fendorf, S. (2017). Anaerobic microsites have an unaccounted
881 role in soil carbon stabilization. *Nature Communications*. <https://doi.org/10.1038/s41467-017-01406-6>
- 882 Keiluweit, M., Gee, K., Denney, A., & Fendorf, S. (2018). Anoxic microsites in upland soils dominantly controlled
883 by clay content. *Soil Biology and Biochemistry*, 118, 42–50. <https://doi.org/10.1016/j.soilbio.2017.12.002>
- 884 Kettler, T. A., Doran, J. W., & Gilbert, T. L. (2001). Simplified method for soil particle-size determination to
885 accompany soil-quality analyses. *Soil Science Society of America Journal*, 65(3), 849–852.
886 <https://doi.org/10.2136/sssaj2001.653849x>
- 887 Kim, J. H., Jobbágy, E. G., Richter, D. D., Trumbore, S. E., & Jackson, R. B. (2020). Agricultural acceleration of
888 soil carbonate weathering. *Global Change Biology*, 26(10), 5988–6002. <https://doi.org/10.1111/gcb.15207>
- 889 Küsel, K., Wagner, C., Trinkwalter, T., Göbner, A. S., Bäuml, R., & Drake, H. L. (2002). Microbial reduction of
890 Fe(III) and turnover of acetate in Hawaiian soils. *FEMS Microbiology Ecology*, 40(1), 73–81.
891 [https://doi.org/10.1016/S0168-6496\(02\)00218-0](https://doi.org/10.1016/S0168-6496(02)00218-0)
- 892 Lack, J. G., Chaudhuri, S. K., Kelly, S. D., Kemner, K. M., O’Connor, S. M., & Coates, J. D. (2002).
893 Immobilization of radionuclides and heavy metals through anaerobic bio-oxidation of Fe(II). *Applied and*
894 *Environmental Microbiology*. <https://doi.org/10.1128/AEM.68.6.2704-2710.2002>
- 895 Lambie, S. M., Ghani, A., Mudge, P. L., & Stevenson, B. A. (2019). Decadal changes in soil organic matter due to

- 896 microaggregate and hot water extractable pools. *Soil Science Society of America Journal*, 83(1), 78–85.
897 <https://doi.org/10.2136/sssaj2018.04.0133>
- 898 Li, H. M., Wei, J. B., Ge, Y. C., Wang, Z. Q., Wang, Y., & Li, Y. L. (2016). The influence of Na⁺ and Ca²⁺ on the
899 migration of colloids or/and ammonia nitrogen in an unsaturated zone medium. *Journal of Contaminant*
900 *Hydrology*, 194, 24–29. <https://doi.org/10.1016/j.jconhyd.2016.10.002>
- 901 Lopez, A. M., Wells, A., & Fendorf, S. (2021). Soil and Aquifer Properties Combine as Predictors of Groundwater
902 Uranium Concentrations within the Central Valley, California. *Environmental Science & Technology*, 55(1),
903 352–361. <https://doi.org/10.1021/acs.est.0c05591>
- 904 Luan, F., Gorski, C. A., & Burgos, W. D. (2014). Thermodynamic controls on the microbial reduction of iron-
905 bearing nontronite and uranium. *Environmental Science & Technology*, 48(5), 2750–2758.
906 <https://doi.org/10.1021/es404885e>
- 907 Luo, W., & Gu, B. (2011). Dissolution of uranium-bearing minerals and mobilization of uranium by organic ligands
908 in a biologically reduced sediment. *Environmental Science & Technology*, 45(7), 2994–2999.
909 <https://doi.org/10.1021/es103073u>
- 910 Malakar, A., Islam, S., Ali, M. A., & Ray, S. (2016). Rapid decadal evolution in the groundwater arsenic content of
911 Kolkata, India and its correlation with the practices of her dwellers. *Environmental Monitoring and*
912 *Assessment*, 188(10), 1–22. <https://doi.org/10.1007/s10661-016-5592-9>
- 913 Malakar, A., Kaiser, M., Snow, D. D., Walia, H., Panda, B., & Ray, C. (2020). Ferrihydrite reduction increases
914 arsenic and uranium bioavailability in unsaturated soil. *Environmental Science & Technology*, 54(21), 13839–
915 13848. <https://doi.org/10.1021/acs.est.0c02670>
- 916 McMahon, P. B., Dennehy, K. F., Bruce, B. W., Böhlke, J. K., Michel, R. L., Gurdak, J. J., & Hurlbut, D. B. (2006).
917 Storage and transit time of chemicals in thick unsaturated zones under rangeland and irrigated cropland, High
918 Plains, United States. *Water Resources Research*, 42(3). <https://doi.org/10.1029/2005WR004417>
- 919 Mejia, J., Roden, E. E., & Ginder-Vogel, M. (2016). Influence of oxygen and nitrate on Fe (hydr)oxide mineral
920 transformation and soil microbial communities during redox cycling. *Environmental Science and Technology*,
921 50(7), 3580–3588. <https://doi.org/10.1021/acs.est.5b05519>
- 922 Mladenov, N., Zheng, Y., Miller, M. P., Nemergut, D. R., Legg, T., Simone, B., et al. (2010). Dissolved organic
923 matter sources and consequences for iron and arsenic mobilization in Bangladesh aquifers. *Environmental*

- 924 *Science & Technology*, 44(1), 123–128. <https://doi.org/10.1021/es901472g>
- 925 Nebraska Department of Environmental Quality (NDEQ). (2018). *2018 Water Quality Integrated Report*.
- 926 Neil, C. W., Yang, Y. J., Schupp, D., & Jun, Y. S. (2014). Water chemistry impacts on arsenic mobilization from
927 arsenopyrite dissolution and secondary mineral precipitation: Implications for managed aquifer recharge.
928 *Environmental Science and Technology*, 48(8), 4395–4405. <https://doi.org/10.1021/es405119q>
- 929 Nimmo, J. R. (2009). Vadose Water. In *Encyclopedia of Inland Waters* Ed. Likens, G. E. (pp. 766–777). Academic
930 Press. <https://doi.org/10.1016/B978-012370626-3.00014-4>
- 931 Nolan, B. T., & Hitt, K. J. (2006). Vulnerability of Shallow Groundwater and Drinking-Water Wells to Nitrate in the
932 United States. *Environmental Science & Technology*, 40(24), 7834–7840. <https://doi.org/10.1021/es060911u>
- 933 Nolan, J., & Weber, K. A. (2015). Natural uranium contamination in major U.S. Aquifers linked to nitrate.
934 *Environmental Science and Technology Letters*, 2(8), 215–220. <https://doi.org/10.1021/acs.estlett.5b00174>
- 935 Nolan, J. P. (2016). *Mobilization of naturally occurring uranium in sediment into groundwater*. Ph.D. Thesis
936 University of Nebraska-Lincoln. Retrieved from
937 http://sfx.scholarsportal.info/guelph/docview/1823259445?accountid=11233%5Cnhttp://sfx.scholarsportal.info/guelph?url_ver=Z39.88-2004&rft_val_fmt=info:ofi/fmt:kev:mtx:dissertation&genre=dissertations+%26+theses&sid=ProQ:ProQuest+Dissertations+%26+Theses+A
- 939
940
- 941 Oppong-Anane, A. B., Deliz Quiñones, K. Y., Harris, W., Townsend, T., & Bonzongo, J.-C. J. (2018). Iron
942 reductive dissolution in vadose zone soils: Implication for groundwater pollution in landfill impacted sites.
943 *Applied Geochemistry*, 94(7), 21–27. <https://doi.org/10.1016/j.apgeochem.2018.05.001>
- 944 Pennino, M. J., Compton, J. E., & Leibowitz, S. G. (2017). Trends in drinking water nitrate violations across the
945 United States. *Environmental Science & Technology*, 51(22), 13450–13460.
946 <https://doi.org/10.1021/acs.est.7b04269>
- 947 Rawson, J., Prommer, H., Siade, A., Carr, J., Berg, M., Davis, J. A., & Fendorf, S. (2016). Numerical modeling of
948 arsenic mobility during reductive iron-mineral transformations. *Environmental Science and Technology*,
949 50(5), 2459–2467. <https://doi.org/10.1021/acs.est.5b05956>
- 950 Reedy, R. C., Scanlon, B. R., Nicot, J. P., & Tachovsky, J. A. (2007). Unsaturated zone arsenic distribution and
951 implications for groundwater contamination. *Environmental Science and Technology*, 41(20), 6914–6919.

- 952 <https://doi.org/10.1021/es070281b>
- 953 Rivett, M. O., Buss, S. R., Morgan, P., Smith, J. W. N., & Bemment, C. D. (2008). Nitrate attenuation in
954 groundwater: A review of biogeochemical controlling processes. *Water Research*, 42(16), 4215–4232.
955 <https://doi.org/10.1016/j.watres.2008.07.020>
- 956 Roberts, H. E., Morris, K., Law, G. T. W., Mosselmans, J. F. W., Bots, P., Kvashnina, K., & Shaw, S. (2017).
957 Uranium(v) incorporation mechanisms and stability in Fe(II)/Fe(III) (oxyhydr)oxides. *Environmental Science
958 and Technology Letters*, 4(10), 421–426. <https://doi.org/10.1021/acs.estlett.7b00348>
- 959 Romanchuk, A. Y., Vlasova, I. E., & Kalmykov, S. N. (2020). Speciation of uranium and plutonium from nuclear
960 legacy sites to the environment: A mini review. *Frontiers in Chemistry*, 8.
961 <https://doi.org/10.3389/fchem.2020.00630>
- 962 Sani, R. K., Peyton, B. M., Dohnalkova, A., & Amonette, J. E. (2005). Reoxidation of reduced uranium with
963 iron(III) (Hydr)oxides under sulfate-reducing conditions. *Environmental Science and Technology*.
964 <https://doi.org/10.1021/es0494297>
- 965 Sato, S., Morgan, K. T., Ozores-Hampton, M., & Simonne, E. H. (2009). Spatial and temporal distributions in sandy
966 soils with seepage irrigation: I. ammonium and nitrate. *Soil Science Society of America Journal*, 73(3), 1044–
967 1052. <https://doi.org/10.2136/sssaj2008.0206>
- 968 Scanlon, B. R., Reedy, R. C., Stonestrom, D. A., Prudic, D. E., & Dennehy, K. F. (2005). Impact of land use and
969 land cover change on groundwater recharge and quality in the southwestern US. *Global Change Biology*,
970 11(10), 1577–1593. <https://doi.org/10.1111/j.1365-2486.2005.01026.x>
- 971 Senko, J. M., Mohamed, Y., Dewers, T. A., & Krumholz, L. R. (2005). Role for Fe(III) minerals in nitrate-
972 dependent microbial U(IV) oxidation. *Environmental Science & Technology*, 39(8), 2529–2536.
973 <https://doi.org/10.1021/es048906i>
- 974 Šeremešić, S., Milošev, D., Sekulić, P., Nešić, L., & Ćirić, V. (2013). Total and hot-water extractable carbon
975 relationship in chernozem soil under different cropping systems and land use. *Journal of Central European
976 Agriculture*, 14(4), 1479–1487. <https://doi.org/10.5513/JCEA01/14.4.1382>
- 977 Shan, J., Zhao, X., Sheng, R., Xia, Y., Ti, C., Quan, X., et al. (2016). Dissimilatory nitrate reduction processes in
978 typical chinese paddy soils: rates, relative contributions, and influencing factors. *Environmental Science &
979 Technology*, 50(18), 9972–9980. <https://doi.org/10.1021/acs.est.6b01765>

- 980 Smith, R. L., Kent, D. B., Repert, D. A., & Böhlke, J. K. (2017). Anoxic nitrate reduction coupled with iron
 981 oxidation and attenuation of dissolved arsenic and phosphate in a sand and gravel aquifer. *Geochimica et*
 982 *Cosmochimica Acta*, 196, 102–120. <https://doi.org/10.1016/j.gca.2016.09.025>
- 983 Snow, D. D., & Spalding, R. F. (1994). Uranium isotopes in the platte river drainage basin of the North American
 984 High Plains region. *Applied Geochemistry*, 9(3), 271–278. [https://doi.org/10.1016/0883-2927\(94\)90037-X](https://doi.org/10.1016/0883-2927(94)90037-X)
- 985 Snow, D. D., Malakar, A., Jahangeer, F., Adams, C., & Ray, C. (2020). *Vadose Zone Nitrate-N Study: Final Report*
 986 *Hastings Wellhead Protection Area: City of Hastings*. Lincoln, NE. Retrieved from
 987 <https://digitalcommons.unl.edu/watercenterpubs/52/>
- 988 Sopilniak, A., Elkayam, R., & Lev, O. (2017). Nitrification in a soil-aquifer treatment system: Comparison of
 989 potential nitrification and concentration profiles in the vadose zone. *Environmental Science: Processes and*
 990 *Impacts*, 19(12), 1571–1582. <https://doi.org/10.1039/c7em00402h>
- 991 Sopilniak, A., Elkayam, R., & Lev, O. (2017). Quantification of dissolved organic matter in pore water of the vadose
 992 zone using a new ex-situ positive displacement extraction. *Chemical Geology*, 466, 263–273.
 993 <https://doi.org/10.1016/j.chemgeo.2017.06.017>
- 994 Spalding, R. F., & Kitchen, L. A. (1988). Nitrate in the intermediate vadose zone beneath irrigated cropland.
 995 *Groundwater Monitoring & Remediation*, 8(2), 89–95. <https://doi.org/10.1111/j.1745-6592.1988.tb00994.x>
- 996 Spalding, R. F., & Toavs, M. (2012). *2011 Vadose Zone Nitrate at Hastings, NE (Revised)*. Lincoln. Retrieved from
 997 <https://digitalcommons.unl.edu/agronomyfacpub/996/>
- 998 Spalding, R. F., Watts, D. G., Schepers, J. S., Burbach, M. E., Exner, M. E., Poreda, R. J., & Martin, G. E. (2001).
 999 Controlling nitrate leaching in irrigated agriculture. *Journal of Environment Quality*, 30(4), 1184.
 1000 <https://doi.org/10.2134/jeq2001.3041184x>
- 1001 Spalding, R. F., Hirsh, A. J., Exner, M. E., Stange, M., & Aravena, R. (2019). Integrated deep soil n and
 1002 groundwater isotope investigation of N sources captured by municipal wells. *Groundwater Monitoring &*
 1003 *Remediation*, 39(2), 22–31. <https://doi.org/10.1111/gwmr.12311>
- 1004 Stagnitti, F., Allinson, G., Sherwood, J., Graymore, M., Allinson, M., Turoczy, N., et al. (1999). Preferential
 1005 leaching of nitrate, chloride and phosphate in an Australian clay soil. *Toxicological & Environmental*
 1006 *Chemistry*, 70(3–4), 415–425. <https://doi.org/10.1080/02772249909358766>
- 1007 Stanley, D. M., & Wilkin, R. T. (2019). Solution equilibria of uranyl minerals: Role of the common groundwater

- 1008 ions calcium and carbonate. *Journal of Hazardous Materials*, 377, 315–320.
1009 <https://doi.org/10.1016/j.jhazmat.2019.05.101>
- 1010 Summers, D. P., & Chang, S. (1993). Prebiotic ammonia from reduction of nitrite by iron (II) on the early Earth.
1011 *Nature*, 365(6447), 630–633. <https://doi.org/10.1038/365630a0>
- 1012 Tesoriero, A. J., Burow, K. R., Frans, L. M., Haynes, J. V., Hobza, C. M., Lindsey, B. D., & Solder, J. E. (2019).
1013 Using age tracers and decadal sampling to discern trends in nitrate, arsenic, and uranium in groundwater
1014 beneath irrigated cropland. *Environmental Science & Technology*, 53(24), 14152–14164.
1015 <https://doi.org/10.1021/acs.est.9b03459>
- 1016 U.S. EPA. (2007). Method 3051A (SW-846): Microwave assisted acid digestion of sediments, sludges, and oils.
1017 Washington, DC. Retrieved from <https://www.epa.gov/sites/production/files/2015-12/documents/3051a.pdf>
- 1018 USDA. (2014). *Soil Survey Field and Laboratory Methods Manual. Soil Survey Investigations Report No. 51*
1019 *Version 2.0*. Retrieved from
1020 https://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/ref/?cid=nrcs142p2_054247
- 1021 USDA. (2019). USDA ERS - Irrigation water use. Retrieved October 7, 2019, from
1022 <https://www.ers.usda.gov/topics/farm-practices-management/irrigation-water-use/background.aspx>
- 1023 Vitousek, P. M., Aber, J. D., Howarth, R. W., Likens, G. E., Matson, P. A., Schindler, D. W., et al. (1997). Human
1024 alteration of the global nitrogen cycle: Sources and consequences. *Ecological Applications*, 7(3), 737–750.
1025 [https://doi.org/10.1890/1051-0761\(1997\)007\[0737:HAOTGN\]2.0.CO;2](https://doi.org/10.1890/1051-0761(1997)007[0737:HAOTGN]2.0.CO;2)
- 1026 Vodyanitskii, Y. N. (2011). Chemical aspects of uranium behavior in soils: A review. *Eurasian Soil Science*, 44(8),
1027 862–873. <https://doi.org/10.1134/S1064229311080163>
- 1028 Wan, J., Tokunaga, T. K., Brodie, E., Wang, Z., Zheng, Z., Herman, D., et al. (2005). Reoxidation of bioreduced
1029 uranium under reducing conditions. *Environmental Science & Technology*, 39(16), 6162–6169.
1030 <https://doi.org/10.1021/es048236g>
- 1031 Wang, F. L., & Alva, A. K. (2000). Ammonium adsorption and desorption in sandy soils. *Soil Science Society of*
1032 *America Journal*, 64(5), 1669–1674. <https://doi.org/10.2136/sssaj2000.6451669x>
- 1033 Wang, S., Wei, S., Liang, H., Zheng, W., Li, X., Hu, C., et al. (2019). Nitrogen stock and leaching rates in a thick
1034 vadose zone below areas of long-term nitrogen fertilizer application in the North China Plain: A future
1035 groundwater quality threat. *Journal of Hydrology*, 576, 28–40. <https://doi.org/10.1016/j.jhydrol.2019.06.012>

- 1036 Wang, Y., Le Pape, P., Morin, G., Asta, M. P., King, G., Bártoová, B., et al. (2018). Arsenic speciation in mekong
1037 delta sediments depends on their depositional environment. *Environmental Science and Technology*, 52(6),
1038 3431–3439. <https://doi.org/10.1021/acs.est.7b05177>
- 1039 Warrinnier, R., Bossuyt, S., Resseguier, C., Cambier, P., Houot, S., Gustafsson, J. P., et al. (2020). Anaerobic
1040 respiration in the unsaturated zone of agricultural soil mobilizes phosphorus and manganese. *Environmental*
1041 *Science & Technology*, 54(8), 4922–4931. <https://doi.org/10.1021/acs.est.9b06978>
- 1042 Weber, K. A., Picardal, F. W., & Roden, E. E. (2001). Microbially Catalyzed Nitrate-Dependent Oxidation of
1043 Biogenic Solid-Phase Fe(II) Compounds. *Environmental Science & Technology*, 35(8), 1644–1650.
1044 <https://doi.org/10.1021/es0016598>
- 1045 Weber, K. A., Urrutia, M. M., Churchill, P. F., Kukkadapu, R. K., & Roden, E. E. (2006). Anaerobic redox cycling
1046 of iron by freshwater sediment microorganisms. *Environmental Microbiology*, 8(1), 100–113.
1047 <https://doi.org/10.1111/j.1462-2920.2005.00873.x>
- 1048 Weber, K. A., Achenbach, L. A., & Coates, J. D. (2006). Microorganisms pumping iron: anaerobic microbial iron
1049 oxidation and reduction. *Nature Reviews Microbiology*, 4(10), 752–764. <https://doi.org/10.1038/nrmicro1490>
- 1050 Weber, K. A., Cameron Thrash, J., Ian Van Trump, J., Achenbach, L. A., & Coates, J. D. (2011). Environmental and
1051 taxonomic bacterial diversity of anaerobic uranium(IV) bio-oxidation. *Applied and Environmental*
1052 *Microbiology*, 77(13), 4693–4696. <https://doi.org/10.1128/AEM.02539-10>
- 1053 Wedepohl, K. H. (1991). Chemical composition and fractionation of the continental crust. *Geologische Rundschau*.
1054 <https://doi.org/10.1007/BF01829361>
- 1055 Wells, M., Gilmore, T., Mittelstet, A., Snow, D., & Sibray, S. (2018). Assessing decadal trends of a nitrate-
1056 contaminated shallow aquifer in western nebraska using groundwater isotopes, age-dating, and monitoring.
1057 *Water*, 10(8), 1047. <https://doi.org/10.3390/w10081047>
- 1058 Xiao, C., Ma, T., & Du, Y. (2020). Arsenic releasing mechanisms during clayey sediments compaction: An
1059 experiment study. *Journal of Hydrology*, 125743. <https://doi.org/10.1016/j.jhydrol.2020.125743>
- 1060 Xiao, Z., Xie, X., Pi, K., Yan, Y., Li, J., Chi, Z., et al. (2018). Effects of irrigation-induced water table fluctuation on
1061 arsenic mobilization in the unsaturated zone of the Datong Basin, northern China. *Journal of Hydrology*,
1062 564(July), 256–265. <https://doi.org/10.1016/j.jhydrol.2018.07.018>
- 1063 Yamaguchi, N., Kawasaki, A., & Iiyama, I. (2009). Distribution of uranium in soil components of agricultural fields

1064 after long-term application of phosphate fertilizers. *Science of the Total Environment*, 407(4), 1383–1390.

1065 <https://doi.org/10.1016/j.scitotenv.2008.10.011>

1066 Yitayew, M., Letey, J., Vaux, H. J., & Feinerman, E. (1985). Factors affecting uniformity and optimal water

1067 management with furrow irrigation. *Irrigation Science*, 6(3), 201–210. <https://doi.org/10.1007/BF00572668>

1068 Zhu, I., & Getting, T. (2012). A review of nitrate reduction using inorganic materials. *Environmental Technology*

1069 *Reviews*, 1(1), 46–58. <https://doi.org/10.1080/09593330.2012.706646>

1070