

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

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## Key Points:

- Unsaturated zone serves as a dynamic reservoir for inorganic nitrogen and geogenic contaminants.
- Nitrogen transport and transformation can affect occurrence of geogenic contaminants.
- Irrigation water application can affect nitrogen and geogenic contaminant mobilization and transport.

**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.

## **Plain Language Summary**

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

## 1 Introduction

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

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

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

Contaminants occurring in local groundwater are generally linked to surface soils and subsurface geology. The concentration of arsenic varies widely in soil, and arsenic in Earth's crust is estimated to range from 1 to 40  $\mu\text{g g}^{-1}$  (Chou et al., 2002). Arsenic in soil can also come from previous arsenic-based pesticide use (Reedy et al., 2007). When dissolved in water inorganic arsenic primarily exists as reduced arsenite (As(III)) and oxidized arsenate (As(V)) oxyanions, these species of arsenic can be associated with solid-phase minerals such as iron oxides, and iron oxy(hydroxides) and precipitate in soils (Malakar et al., 2016). However, equilibrium forms and mobilization of arsenic species are sensitive to redox and pH changes of the system. The uranium content in soil ranges from 0.3 – 10.7  $\mu\text{g g}^{-1}$  around the world (Vodyanitskii, 2011). Inorganic uranium exists in soils and groundwater primarily as redox determined complexes of U(IV) and U(VI), while the oxidized U(VI) as  $\text{UO}_2^{2+}$  is considered to be the most mobile and soluble form (Vodyanitskii, 2011). Phosphate fertilizers can also be a source of uranium, (Yamaguchi et al., 2009). However, at the present study site arsenic and

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

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

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

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

## **2 Materials and Methods**

### **2.1 Study Site Description**

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

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

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

#### 2.1.2 Sediment and Groundwater Sampling

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



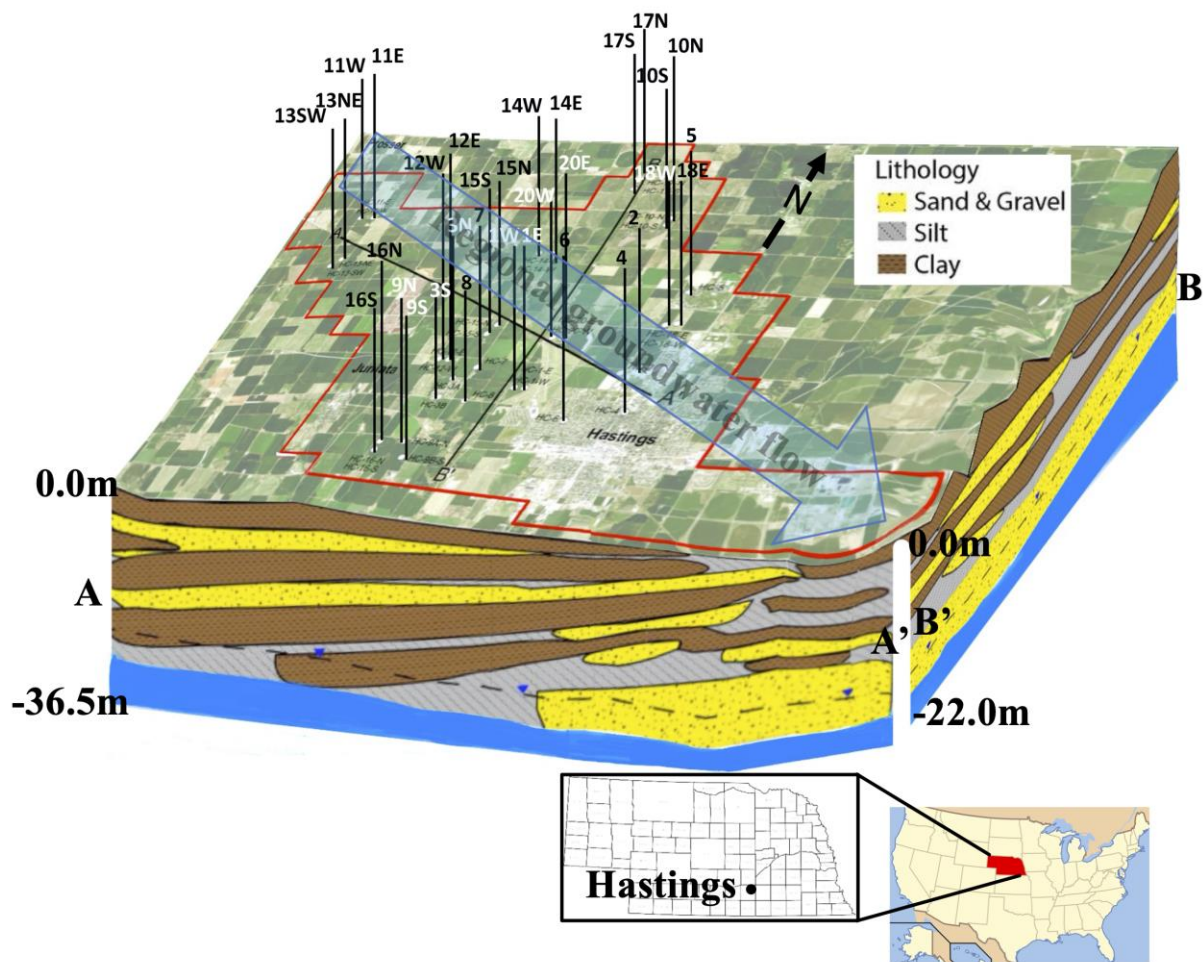
utilizing a Geoprobe Model 66DT (Salina, KS, USA) direct push coring system. A CME (Central Mine Equipment Co, Earth City, MO USA) hollow stem auger with split spoon sampler was used in the remaining sites. Cores (0.053 m diameter by 0.76 m length) were collected in acrylic liners, capped and placed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

### 2.1.3 Sediment Lithology and Texture

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

Surface soil samples were classified based on the web soil survey (USDA, 2014). In the 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.

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

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

### **2.2.1 Water Content, Particle Size, Nitrate and Ammonium Concentrations**

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

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

#### 2.2.2 Acid Digestion and Measurement of Sediment Arsenic and Uranium

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

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

### 2.2.3 Hot Water Extractable Organic Carbon in Sediments

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

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

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

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

### 2.3 Statistical Analysis

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

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

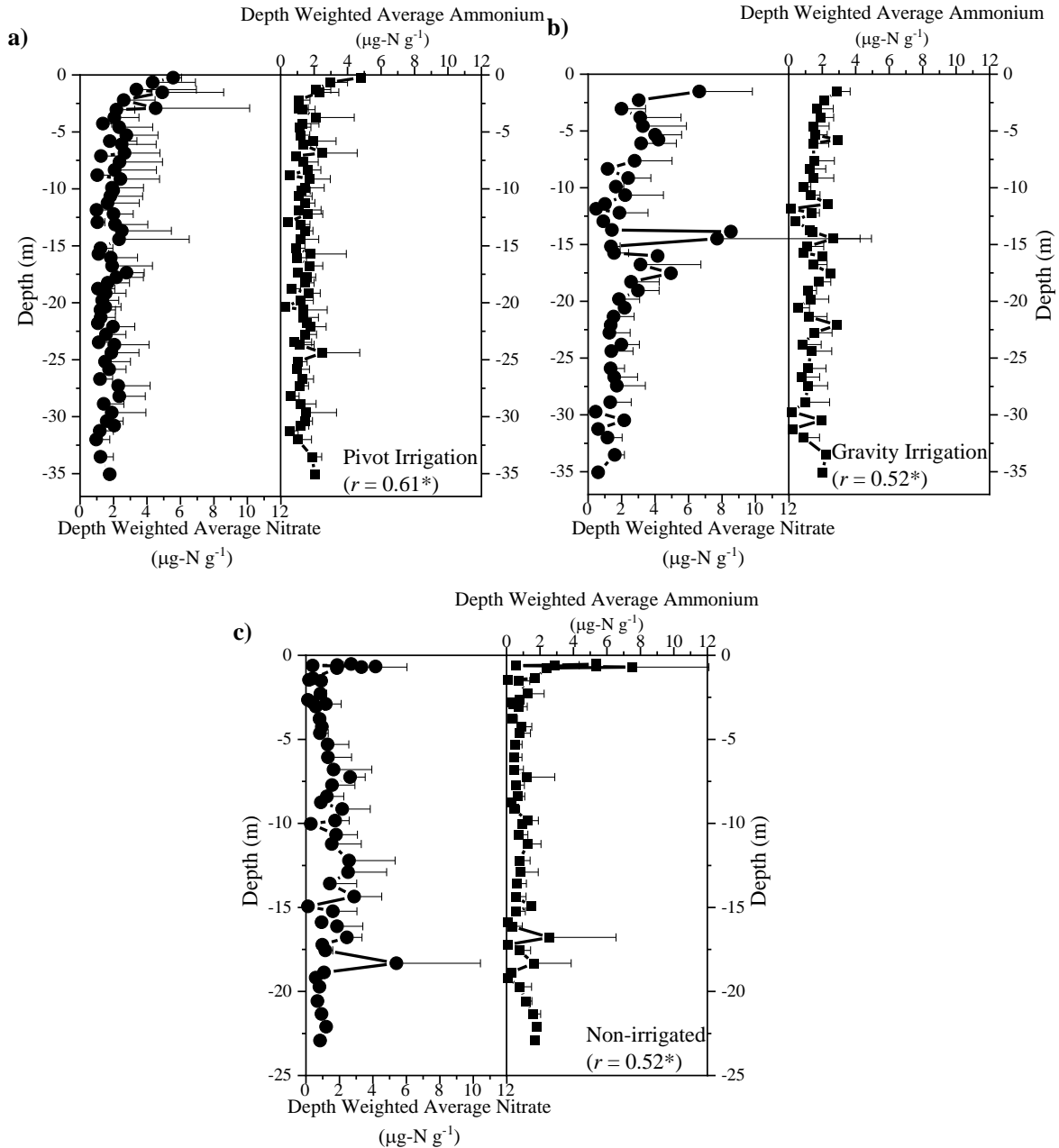
### 3 Results and Discussions

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

##### 3.2.1 Nitrate in the Unsaturated Zone

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

comparable to nitrate. Total nitrate (Figure 2a) amount associated with soils in the sites irrigated 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.



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

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

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

### 3.2.2 Ammonium in the Unsaturated Zone

Sediment associated ammonium concentrations within the unsaturated zone published prior ( $0.4\pm0.6 \mu\text{g-N g}^{-1}$ ) (Spalding & Toavs, 2012) were generally lower than measured in our current study ( $1.8\pm8.4 \mu\text{g-N g}^{-1}$ ). Depth-weighted soil ammonium concentrations were found to have significant ( $p<0.05$ ) correlation with depth-weighted soil nitrate concentration within the unsaturated zone of all three sites (Figure 2), ammonium, with correlation coefficients of  $r=0.61$  for pivot irrigation,  $r=0.52$  under gravity, and non-irrigated sites. These depth-weighted correlations between nitrate and ammonium may indicate co-occurrence of nitrate and ammonium within the sediment profiles of the unsaturated zone in the Hastings WHP area. However, a different picture is presented when mean sediment ammonium concentrations in the unsaturated zone of these three sites are compared to mean sediment nitrate concentrations.

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

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

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

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

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

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

#### **3.2.1 Major Elemental Composition of Unsaturated Zone Sediments**

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

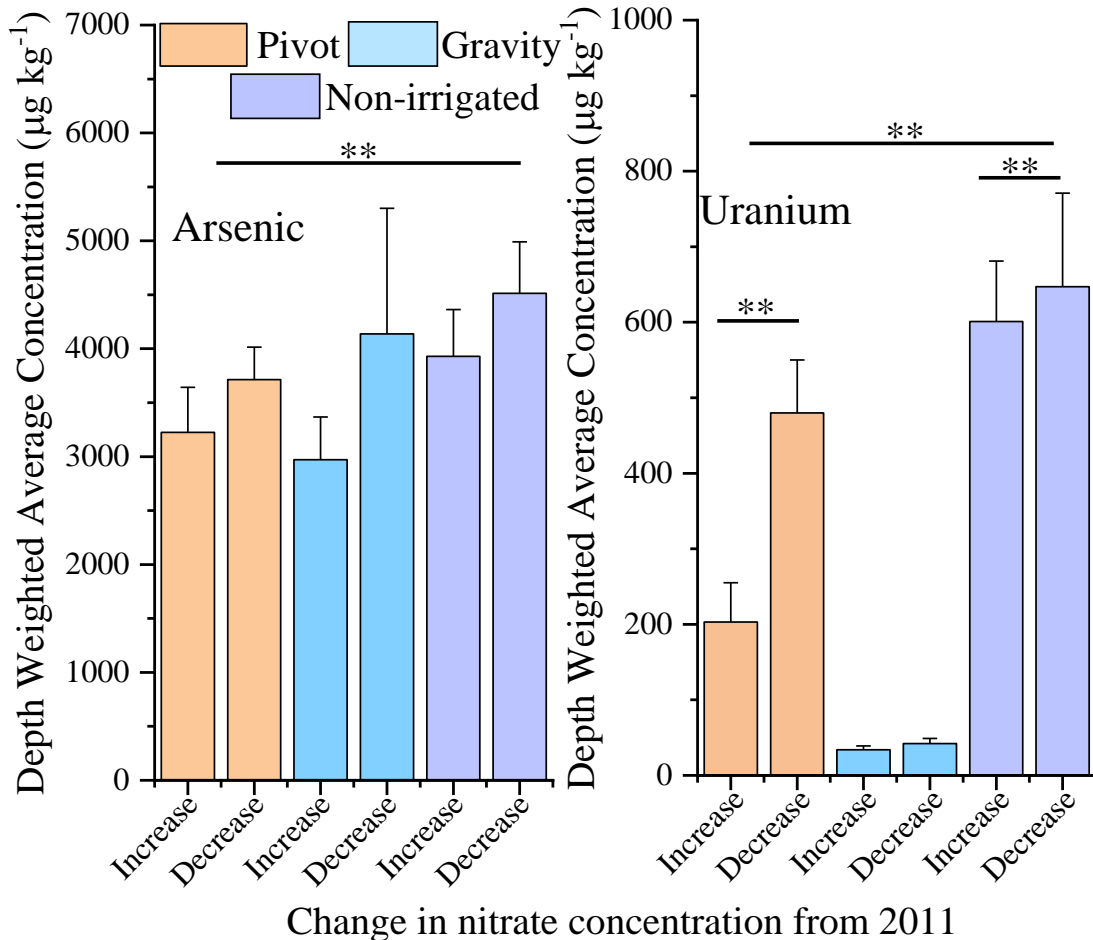
clay and ammonium among the samples analyzed by XRF are shown in Figure S1 of supplementary information.

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

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

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

Figure 3 are sub-categorized, within the water application volume, by an increase or decrease in total unsaturated zone nitrate storage in the top 18.2 m over a period of five years. The vinculum above the bar graph with ‘\*\*’ sign indicates that the interaction between the factors is significantly different. Concentrations were analyzed utilizing Two-way ANOVA, considering water application, and change in nitrate storage in last five years (Table S1). Arsenic concentration in the unsaturated zone was found to be significantly different (at 0.05 level) among water application type. However, within the same water application type, change in 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.

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

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

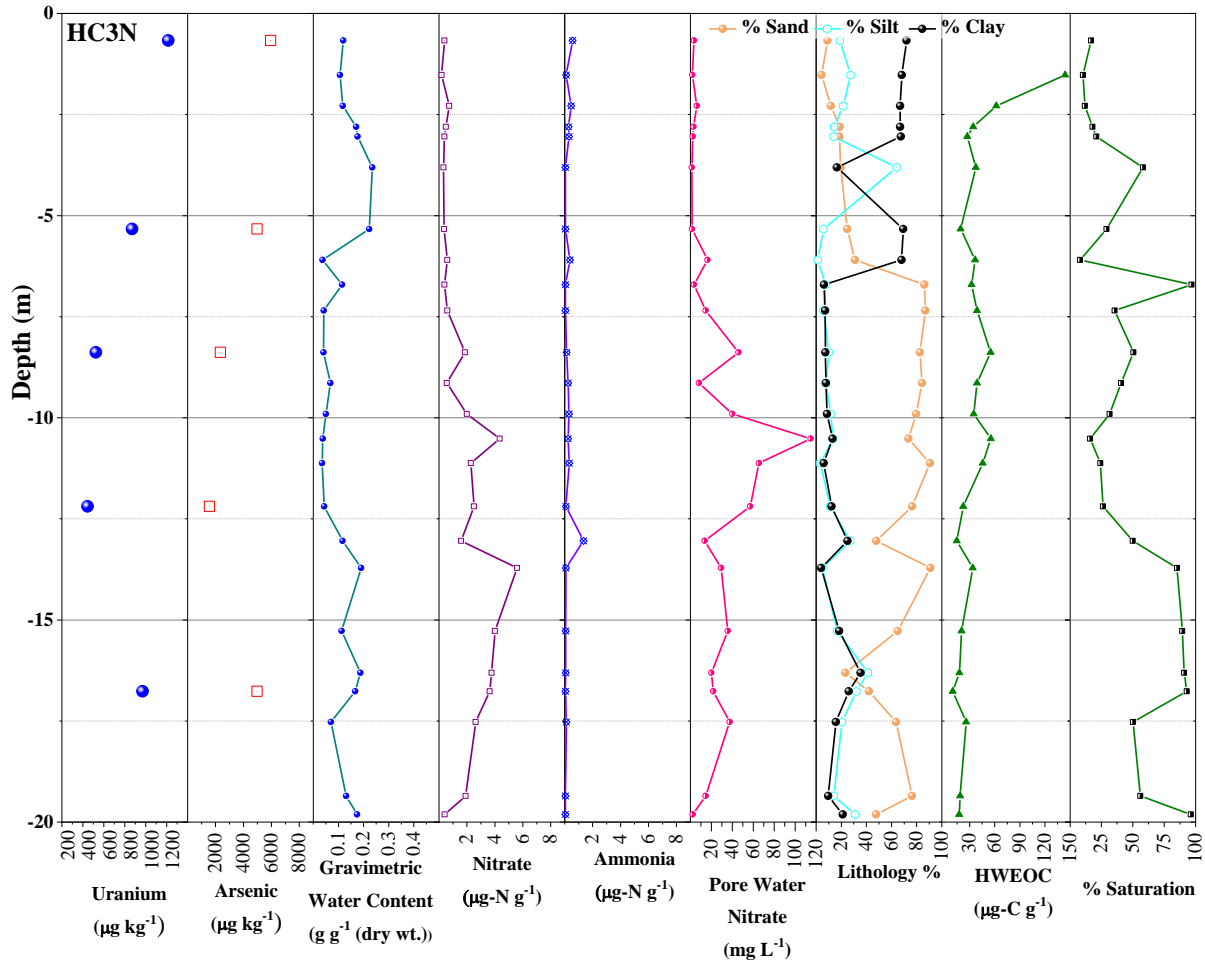


Hastings WHP area was found to be related to water application volume and change in stored nitrate in the unsaturated zone.

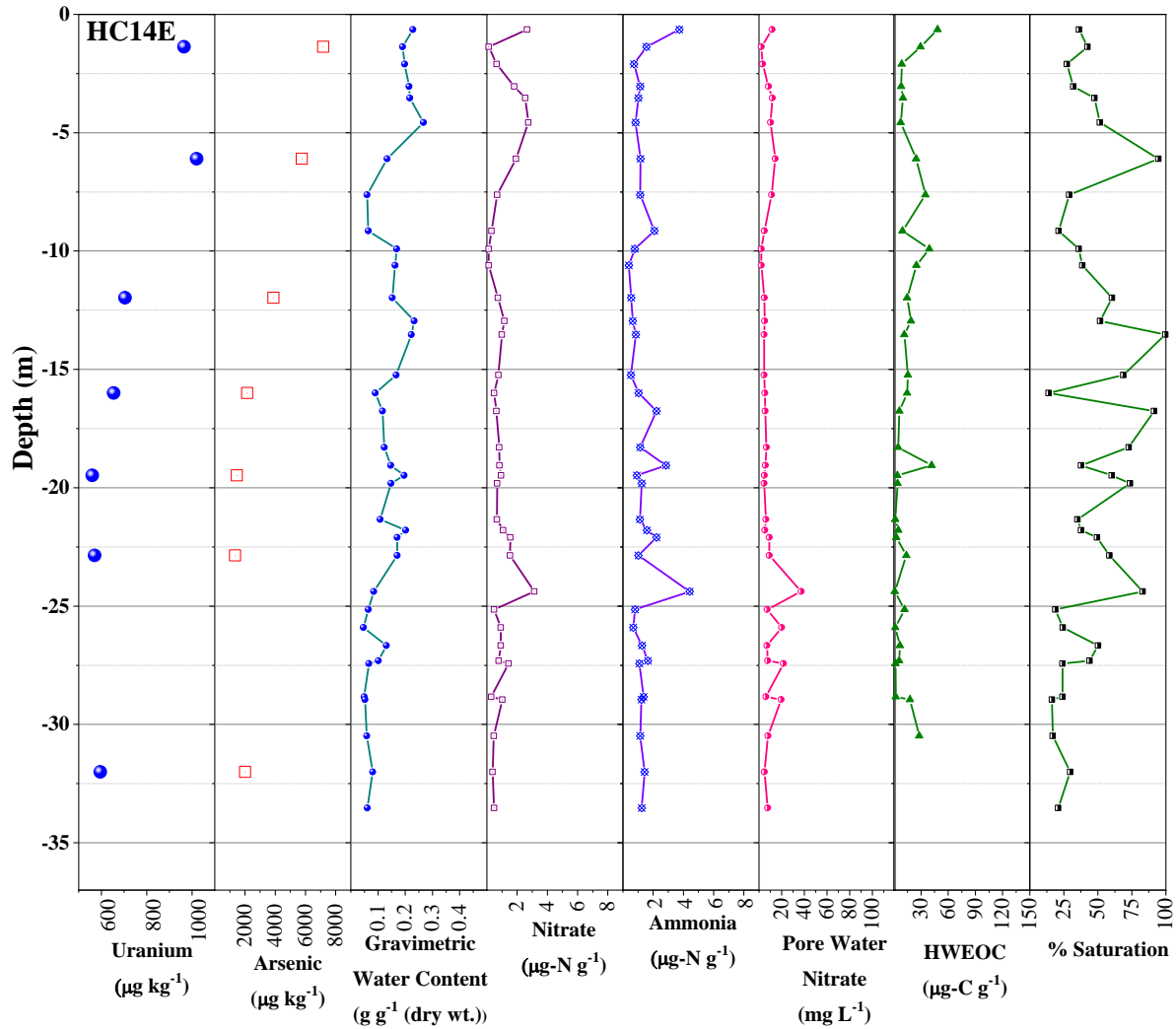
### 3.2.3 Detailed Arsenic and Uranium Sediment Core Profiles

Water application volume was found to be a significant factor for variation in sediment arsenic and uranium concentration within the unsaturated zone. Further, these pivot and non-irrigated sites also presented significant difference for uranium concentration with respect to change in nitrate storage over a period of five years. Therefore, sites HC3N (non-irrigated) and HC14E (pivot), which had measurable amount of arsenic and uranium concentration in the unsaturated zone, were selected for hot water extractable organic carbon measurement and the concentrations are shown together with sediment arsenic, sediment uranium, gravimetric water content, sediment nitrate, sediment ammonium, particle size distribution and percentage (%) saturation in Figure 4 and 5, respectively. HC3N, a non-irrigated site, showed a 95% increase in nitrate input into the unsaturated zone from five years ago, and represents shallow depth to water table. HC14E, a pivot irrigated site, showed decrease in nitrate storage by 9% from the earlier study, and represents a deeper unsaturated zone. Both sites contain higher than average sediment uranium and arsenic concentrations for Hastings WHP area. Core samples from HC3N contained 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 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 highest amount of hot water extractable organic carbon was found in shallow unsaturated zone depth near the topsoil, though substantial concentrations of hot water extractable organic carbon were present throughout the cores. Hot water extractable organic carbon for depth below 9 m 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, respectively. The moisture profile in these two sites was similar to the previous study and most

of the gravimetric moisture content range was within the values observed earlier. The percentage saturation was found to be on the higher side at few depths within the unsaturated zone as seen from Figure 4 and 5. HC14E, the pivot irrigated site, which received added water during irrigation presented multiple depths where the conditions were saturated. If compared to HC3N, within a depth of 20 m bgs, irrigated site HC14E presented two depths where percentage saturation was close to ~100%, representing fully saturated zones. Fully saturated conditions within the unsaturated zone may be transient in nature and dependent on the movement of the 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 ~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.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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



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

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

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

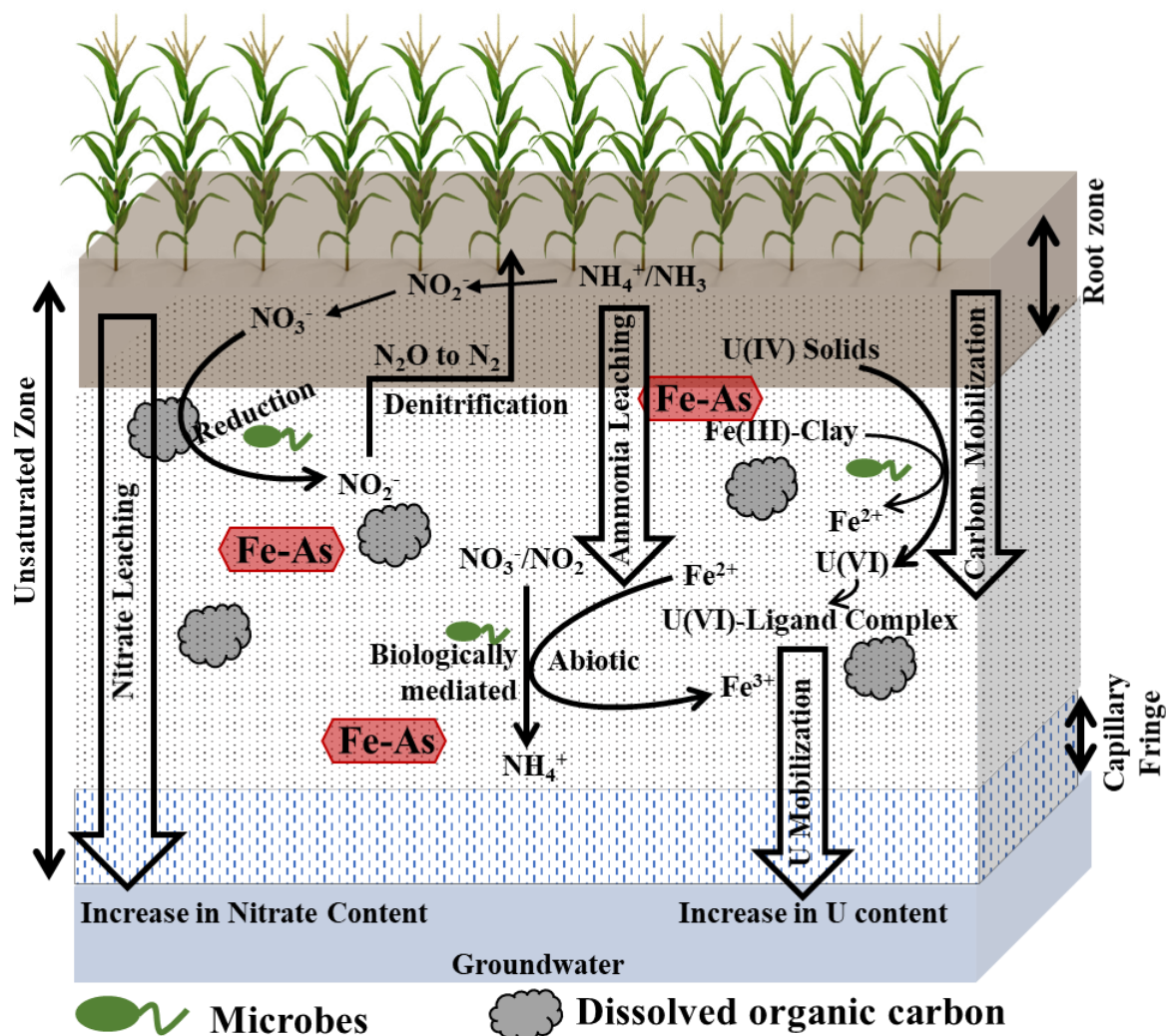
by reductive mineral dissolution but may attenuate uranium by precipitation to mineral forms (Campbell et al., 2012; Hall & Huang, 2017; Janot et al., 2016; Küsel et al., 2002; C. Xiao et al., 2020). However, even under iron reducing conditions prevalent in anoxic microsites, under similar pH, uranium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

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

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

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

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

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

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

#### **4 Conclusions**

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

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

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

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The authors declare no conflict of interest.

## **Data Availability**

Data supporting the conclusions in this paper is available at:

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

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