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Westrop, Jeffrey; Snow, Daniel D.; and Weber, K. A., "Mobilization of Naturally Occurring Uranium in Groundwater Under Intensely Managed Farmland. Food, Energy, and Water Nexus: A Consideration for the 21st Century" (2022). *Papers in Natural Resources*. 1628.

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Chapter 12

Mobilization of Naturally Occurring Uranium in Groundwater Under Intensely Managed Farmland



Jeffrey P. Westrop, Daniel D. Snow, and Karrie A. Weber

Abstract Groundwater has been demonstrated to bear elevated uranium (U) concentrations in excess of regulatory limits in many regions throughout the world. Within some of these regions, direct anthropogenic U contaminant sources do not exist indicating a naturally occurring U source that results in elevated groundwater U concentrations. Naturally occurring U is ubiquitous and is deposited in evaporative sequences and/or organic carbon-rich soils and sediments, which includes the sedimentary matrix within aquifers. Thus one potential source of U in groundwater is dissolution or release from sedimentary deposits. To date two primary mechanisms have been described that can lead to U mobilization in these aquifers: (i) desorption and binding of U by complexing ligands such as carbonate or (ii) oxidative dissolution of reduced U (U(IV)) minerals. While the former has been studied and described, the latter presents a newly described mechanism that should be considered in shallow alluvial aquifers. Uranium is commonly deposited as reduced U(IV) phases that are stable in reduced environments; however, the influx of molecular oxygen (O₂) or nitrate (an agricultural contaminant) can stimulate oxidative dissolution of U(IV) minerals. An influx of O₂ or nitrate as well as other oxidants during groundwater recharge have been linked to groundwater with elevated U concentrations in major US aquifers. These results highlight the instability of naturally deposited subsurface U and highlight a potential risk to water quality from

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mobilization. Controlling influxes of oxidants such as nitrate, however, may help mitigate U contamination of groundwater and drinking water supplies at risk from geogenic uranium.

12.1 Introduction

Uranium (U) is a ubiquitous naturally occurring radionuclide measured in most soils and sediments between 2 and 4 mg/kg (Fayek et al. 2011). Naturally occurring U consists of three long-lived radioactive isotopes: ^{238}U , ^{235}U , and ^{234}U (Fayek et al. 2011). ^{238}U is the most abundant isotope in nature (99.29% abundance) and decays into stable ^{207}Pb with a half-life of 4.6Ga. ^{234}U is produced during the decay of ^{238}U and is the longest lived daughter product in the series with a half-life of 246 ka. Only ^{235}U (0.7% abundance) is capable of nuclear fission, making it the most economically important form of U. While all known isotopes of U are radioactive, the radiation risk posed by uranium in natural soils and sediments is low, owing to its low specific activity (7.1×10^{-7} curies g^{-1}) (Langmuir 1978). The uranyl ion (UO_2^{2+}) with U in the hexavalent state (U(VI)) is relatively soluble in many natural systems but can adsorb to mineral surfaces (Langmuir 1978) or be biotically or abiotically reduced to the relatively insoluble uranous ion (U^{4+}) in the tetravalent state (U(IV)) which rapidly precipitates (Kasting et al. 2006). Within solid matrices of soils and sediments associated with natural waters, U typically is deposited as or with a solid phase. However, in the presence of water, dissolved ions and redox can initiate geochemical reactions that result in the solubilization of U. These reactions can lead to increases in drinking water sources with measure aqueous U concentrations in excess of maximum contaminant levels (30 $\mu\text{g/L}$) set by the World Health Organization (WHO) and United States Environmental Protection Agency (USEPA). Exposure to U above regulatory limits has negative health consequences (ATSDR 2013).

Uranium-contaminated groundwaters are recognized in the context of anthropogenically contaminated sites (mining, milling, and nuclear waste storage legacy sites). However, there are regions where groundwater U concentrations exceed regulatory limits that are not associated with direct U anthropogenic contamination, indicating the potential for geogenic U sources (Burow et al. 2017; Coyte et al. 2018; Nolan and Weber 2015). While U mobility in contaminated systems has been studied, much less is known about the mobility of U from sedimentary deposits bearing U at concentrations below ore grade. It is recognized that a common agricultural contaminant, nitrate, can serve as an oxidant of reduced uranium minerals (Beller 2005; Finneran et al. 2002b; Senko et al. 2002; Weber et al. 2011). Movement of an oxidant into a reduced natural sediments is predicted to result in oxidative mobilization in a manner similar to a redox roll front (van Berk and Fu 2017). Once the uranium is oxidized, increases in carbonate concentrations can also play a role in continued mobility or desorption of surface-bound U(VI) (Burow et al. 2017; Giblin et al. 1981; Stanley and Wilkin 2019; Zhou and Gu 2005). Both oxidative

dissolution and carbonate driving mobility have the potential to alter belowground geochemistry and result in enhanced U mobility in an aquifer. Since U has been demonstrated to bioaccumulate in food crops irrigated with groundwater containing elevated U concentrations (Hakonson-Hayes et al. 2002), this also represents a risk to food security. Here we provide an overview of U chemistry and toxicology, then discuss the occurrence of low-level geogenic U in sedimentary systems, and discuss the geochemical mechanisms in the context of agricultural systems.

12.2 Uranium Toxicology

Human consumption of U has been demonstrated to have negative health consequences causing disease of organs such as the kidneys as well as linked to cancer (ATSDR 2013). Soluble forms of U that would enter the human body ends through ingestion of water would end up in the blood stream. Within the bloodstream, U can bind to ligands, such as citrate, bicarbonate, and proteins. The U is ultimately filtered out of bloodstream by the kidneys (McDiarmid et al. 2018). Around 70% of U that enters the body is excreted in feces and urine (McDiarmid et al. 2018). However, U will accumulate within the kidneys, liver, and bone tissue. Within the kidneys, U accumulates in the renal tubes, similar to other heavy metals like mercury and cadmium (Kurttio et al. 2006) and thus can result in decreased function and renal disease. Of the U that remains in the body, ca. 85% accumulates in bones (Craft et al. 2004; Kurttio et al. 2005). While the exact effect of U on bone health is still debated, studies on human populations exposed to naturally occurring groundwater U, and experiments performed on rats demonstrated that low level U ingestion can lead to decreased bone health and bone repair (Kurttio et al. 2005; McDiarmid et al. 2018; Wade-Gueye et al. 2012). While the primary risk of U at or above the MCL is renal toxicity or osteotoxicity (Craft et al. 2004; Hakonson-Hayes et al. 2002; Kurttio et al. 2006; Kurttio et al. 2005), an increased incidence of cancer has been observed with the consumption of drinking water containing elevated groundwater U concentrations (Wagner et al. 2011). It is noted that U radioactive decay products (notably radon, thorium, and radium) have been linked to cancer (Kurttio et al. 2006) but will not be discussed as they are beyond the scope of this review. As such, it is necessary to develop a thorough understanding of the sources and occurrence of naturally occurring U and the processes that mobilize U in an effort to understand the health risks.

12.3 Uranium Occurrence in the Environment

Geologically, U is considered a large ion lithophile element, meaning that magmatic differentiation processes concentrate it in the continental crust where it occurs as a trace mineral or inclusion in felsic igneous rocks like granites, pegmatites, and

rhyolites. While hundreds of U minerals have been reported to occur in igneous rocks, the most common are uraninite (UO_2), pitchblende ($\text{UO}_{2(\text{am})}$), and coffinite ($\text{U}(\text{SiO})_{1-x}(\text{OH})_{4x}$). Many aquifers contain granitic bedrock, which can leach to become a source of U in local groundwater. For example, Coyte et al. (2018) measured U levels in groundwater from across Northeast India and found that 60% of wells with crystalline bedrock in the state of Rajasthan had U levels above the WHO limit.

Weathering and transport of U in igneous rocks has resulted in the accumulation of U in sedimentary deposits including carbonates, alluvial deposits, and phosphorites (Baturin and Kochenov 2001) (Fig. 12.1). Many of these are important to agricultural production and have served as a source for phosphorus fertilizer or a source of irrigation/drinking water. Carbonate minerals, such as calcite, aragonite, and dolomite, are present in many aquifer systems either as limestone bedrock or as

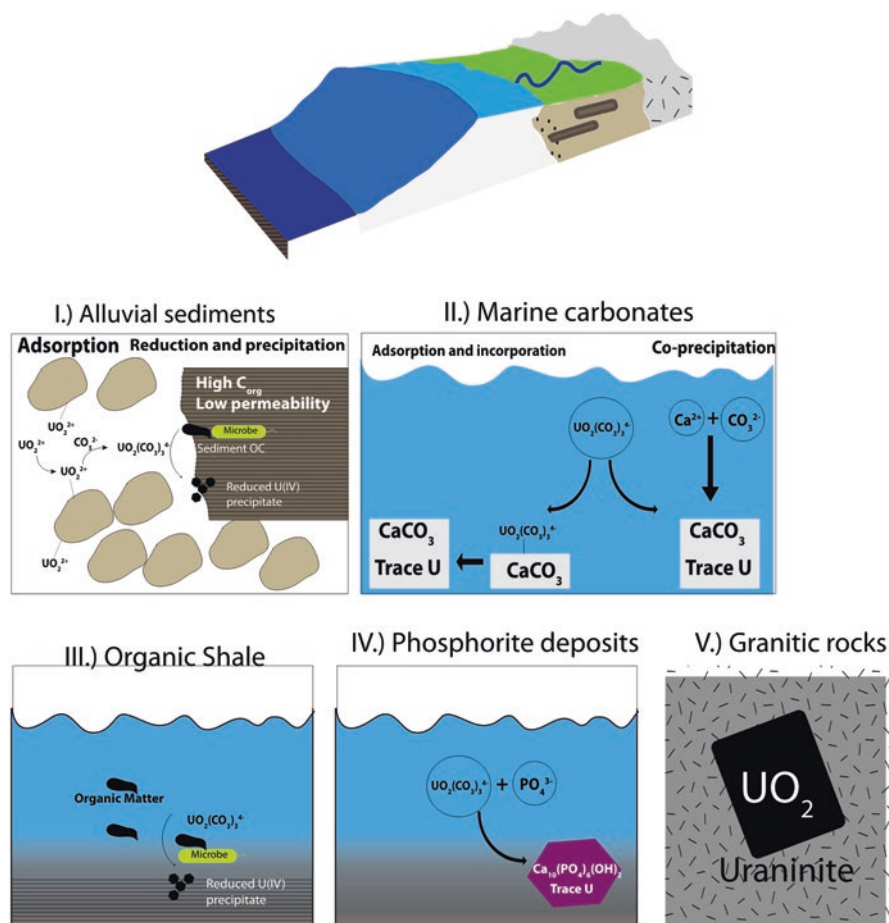


Fig. 12.1 Uranium accumulation processes in different depositional environments

secondary precipitates in clastic aquifers. It has been demonstrated that carbonate minerals, such as calcite, aragonite, and dolomite, may contain U ranging from 0.1 to 10 ppm (Elzinga et al. 2004). U in carbonates exists either directly incorporated in the carbonate crystal structure or as mineral coatings on carbonate surfaces (Elzinga et al. 2004; Reeder et al. 2000). In aquifers a U-bearing carbonate mineral in sediments, aquitard, or bedrock, the dissolution of carbonate minerals may be a significant source of groundwater U (Steffanowski and Banning 2017) or alternatively carbonate precipitation could sequester U (Nolan et al. 2021). Carbonates may also form via the evaporation of permanent, perched, or temporary U-bearing groundwater. In fact, U-bearing carbonates formed by evaporation have been observed in contaminated environments, such as the Riverton Wyoming nuclear legacy site (Dam et al. 2015), where they serve as an input source of groundwater U. In addition, agricultural evaporative carbonates may form when highly saline or alkaline irrigation water is poorly drained, although their role in trace metal and radionuclide cycling has not been thoroughly explored.

Phosphorites are deposits of phosphate minerals, mainly apatite, formed near marine coastal upwelling zones (Crosby and Bailey 2012). These deposits frequently contain high U concentrations, where it substitutes for calcium in the apatite crystal structure (Falck and Wymer 2006). While groundwater in some areas may have been historically impacted by U sourced from phosphorites (Dabous 2003), this is rare due to their scarcity in the rock record (Crosby and Bailey 2012). However, phosphorites are mined as a source of P-based fertilizer, which may become a source of U in agricultural regions where they are applied. Considering that some phosphate fertilizers may contain between 6 and 149 mg/kg U, it could be a significant source of U (Kim et al. 2016). The significance of this source in groundwater is likely variable and depends on surface conditions, phosphate application amounts, and other factors (Liesch et al. 2015). Rock phosphate is rarely used directly today and, depending on the market for uranium, has intermittently been recovered for use as a nuclear fuel (Haneklaus et al. 2017).

The term “alluvial” broadly refers to any sediment deposited by moving water but more generally refers unconsolidated, interlayered sands and gravel deposited in fluvial, deltaic, and mountain-front settings. Shallow, unconfined alluvial aquifers are commonly mined for drinking and agricultural water due to their ease of access and faster recharge times compared to deeper confined aquifer units (although it should be noted that extensive groundwater pumping can put stress on these aquifers). Alluvial aquifers are a major source of agricultural water in the USA (Nolan and Weber 2015), India (Coyte et al. 2018), China (Currell et al. 2012; Wu et al. 2014), and Germany (Liesch et al. 2015), among many others. U concentrations above both the USEPA and WHO recommended levels have been reported in these aquifers. A 2015 metadata analysis by Nolan and Weber (2015) documented elevated U levels in two major US agricultural aquifers: the High Plains Aquifer in the central USA and the Central Valley Aquifer in California. It should also be noted that these regions do not have a history of anthropogenic U contamination from activities such as mining or nuclear waste storage (Jurgens et al. 2010; Nolan and Weber 2015). Similar to the results observed in the USA within unconfined alluvial

aquifers, U levels in groundwater from Northeast India revealed that 39% of wells sampled within the state of Rajasthan had groundwater U levels above the WHO limit of 30 $\mu\text{g/L}$ (Coyte et al. 2018). In contrast, only 1% of wells within a confined alluvial aquifer in the state of Gujarat were measured to exceed the drinking water U WHO limit (Coyte et al. 2018). This highlights the importance of hydrostratigraphic setting when considering U mobilization in groundwater as unconfined alluvial aquifers are prone to contamination. In addition concentrations of groundwater U up to 10 times the WHO limit have been reported in the Datong Basin in the northern China Plains aquifer (Wu et al. 2014), although the authors noted that U could be mobilized from shale in a local coal seam.

While elevated U concentrations in groundwater of many unconfined alluvial aquifers has been documented, the origin and forms available to be mobilized in the aquifer sediment remains uncertain with mechanisms such as ligand associated to oxidative dissolution. It is often assumed that solid-phase U in these systems exists as either crystalline minerals in more anoxic to suboxic systems or oxidized UO_2^{2+} complexes adsorbed to iron, sediment, or organic matter surfaces in oxic systems. However, recent research documented a non-uraninite U(IV) phase in anoxic, organic-rich alluvial aquifers (Campbell et al. 2012; Noel et al. 2017). Additional laboratory experiments have documented that this U(IV) phase is formed when U comes into contact with phosphate (Bernier-Latmani et al. 2010; Fletcher et al. 2010). These studies have demonstrated that this non-uraninite form of U is more susceptible to mobilization in groundwater. Thus, these forms of U in alluvial deposits are likely to be more sensitive to oxidative dissolution.

12.4 Geochemistry of Naturally Occurring Uranium in Aquifers

In most alluvial aquifer sediments, U likely occurs as either oxidized U(VI) or reduced U(IV) (Maher et al. 2013). While U(V) in solids has been observed in laboratory studies, it does not accumulate in significant amounts in the environment because it rapidly disproportionates into U(IV) and U(VI) (Andersen et al. 2017). In general, U(VI) minerals are more soluble and more mobile than those consisting primarily reduced U(IV) (Langmuir 1978). Depending on solution pH, complexing ions, and ionic strength, U(VI) may precipitate as a solid-phase mineral or adsorb to mineral surfaces (Langmuir 1978). Incorporation of uranium with ferrihydrite precipitation under variable redox conditions has also been observed in laboratory experiments and may also determine the form and mobility of uranium (Stewart et al. 2009). Reduced U(IV) is insoluble under circumneutral pH conditions and will readily form solid-phase precipitates including minerals (such as uraninite (UO_2) and coffinite (USiO_4)), amorphous compounds, or adsorbed complexes.

Two general mechanisms have been identified to control U mobility in groundwater: (i) redox transformations between oxidized and reduced U and (ii) ligand

binding and desorption from the solid mineral surface. Several oxidants, including dissolved molecular oxygen (Begg et al. 2011; Campbell et al. 2011b; N'Guessan et al. 2010), nitrate and denitrification intermediates (Beller 2005; Finneran et al. 2002b; Moon et al. 2007, 2009; Senko et al. 2005; Weber et al. 2011), ferrous iron (Jeon et al. 2005), ferric iron oxides (Ginder-Vogel et al. 2006; Ginder-Vogel et al. 2010), and manganese oxides (Wang et al. 2014), may catalyze the oxidative dissolution of reduced U phases under both oxic and anoxic conditions. The oxidation reactions may occur as a complex series of abiotic and biotically catalyzed reactions. Once oxidized, U(VI) (as the UO_2^{2+} ion) may adsorb to many solid-phase constituents of aquifer sediments including Fe(III)-(hydr)oxides (Fox et al. 2006; Waite et al. 1994), quartz sand (Rosentreter et al. 1996), and phyllosilicate clay minerals (Wang et al. 2011). However, U(VI) will readily form aqueous complexes with ligands such as carbonate and divalent cations such as calcium which leads to the formation of stable ternary Ca uranyl carbonate complexes (Dong et al. 2005; Dong and Brooks 2006). These complexes render adsorption behavior insignificant and also decreases the availability of U(VI) for biological reduction (Belli et al. 2015; Brooks et al. 2003; Stewart et al. 2007), thus maintaining dissolved U in natural groundwaters.

12.4.1 U Redox Biogeochemistry

The insolubility of U(IV)-bearing minerals retards mobilization under anoxic conditions. However, the influx of oxidants into the reduced system has the potential to increase the redox potential and mobilize U via mechanisms of oxidative dissolution. The oxidation of U(IV) by dissolved molecular oxygen (DO) has been investigated mainly in the context of anthropogenically contaminated sites (legacy U mining, milling, or disposal sites) or in laboratory experiments investigating the stability of bioreduced U in environmental systems. Initial laboratory experiments indicate that DO is an effective oxidant in terms of both rate and extent of U oxidation. Microcosm experiments performed on bioreduced sediments demonstrated that oxidation by air was rapid and complete oxidation of U(IV) occurred in 24 hours (Begg et al. 2011). Similar results were obtained in a series of column experiments containing bioreduced U(IV) amended with air-sparged medium (Komlos et al. 2008). However, the extent of U oxidation was more limited when oxygenated groundwater was used. Limited U mobilization was observed in long-term column experiments performed on bioreduced sediments from Rifle, Colorado (USA) (N'Guessan et al. 2010), and U-bearing sediments from the Hanford site in Washington state (USA) (Ahmed et al. 2012) amended with oxygenated water from the respective field site. Similarly, Campbell and others (2011a) examined oxidation of synthetic biogenic uraninite immersed in monitoring wells on the Rifle Mtn Legacy site (Campbell et al. 2011b) and found that the oxidation rate in the field was 50–100 times slower than the rate observed in laboratory experiments. The authors attributed the difference in rates to the passivation of the uraninite surface by the adsorption of divalent cations and organics (Campbell et al. 2011a). These results emphasize the influence of other

geochemical parameters on the oxidation of U. In addition to solution chemistry, the presence of reduced phases in the sediments, such as Fe(II) sulfide minerals (Janot et al. 2016) or organic matter (Pan et al. 2018), may impact U oxidation. These phases act as a redox buffer that must be overcome in order for U mobilization to take place.

Similarly, the oxidative dissolution of reduced U may be catalyzed by dissolved nitrate. Uranium oxidation by nitrate is complex and may proceed through several different mechanisms including (1) direct oxidation by nitrate, (2) abiotic oxidation by denitrification intermediates, and (3) the production of biogenic Fe(III)-oxides through microbially catalyzed nitrate-dependent Fe(II) oxidation. A series of column experiments containing bioreduced sediments demonstrated that U mobilization occurred more rapidly in nitrate amended columns than DO amended columns (Moon et al. 2007). Although abiotic nitrate oxidation is thermodynamically favorable, multiple studies have demonstrated microbial catalysis enhances the rate and extent of oxidation (Beller 2005; Finneran et al. 2002b; Senko et al. 2005; Weber et al. 2011). Microbially catalyzed U mobilization by nitrate at circumneutral pH has been demonstrated by numerous organisms isolated from soils and sediments including *Acidovorax ebreus* TPSY (Weber et al. 2011), *Pseudogulbenkiania* sp. (Weber et al. 2011), *Geothrix fermentans* (Weber et al. 2011), *Pseudomonas* sp. (Weber et al. 2011), *Thiobacillus denitrificans* (Beller 2005), *Geobacter metallireducens* (Finneran et al. 2002b), and *Klebsiella* sp. (Senko et al. 2005). Finneran and others (2002a, b) tested for the ability of *G. metallireducens* initially grown in batch cultures under nitrate-reducing and Fe(III)-reducing conditions to oxidize U(IV) (as aqueous UBr_4). Only the nitrate grown cells were able to oxidize U(IV) (Finneran et al. 2002a). Beller (2005) demonstrated that *T. denitrificans* was capable of autotrophic U(IV) oxidation coupled to nitrate reduction. However, the authors concluded that U oxidation proceeded primarily through the production of nitrite (Beller 2005). To date, none of these reactions has demonstrated cell growth with U(IV) as the sole energy source (Weber et al. 2011).

Coupled biotic-abiotic reactions play an important role in nitrate-driven U mobilization. Reactive intermediates produced during denitrification, such as nitrite and nitrous oxide, are capable of abiotic oxidation of reduced U (Senko et al. 2005). In addition, the interactions between iron and nitrogen cycling can influence the mobility of U. Iron is the fourth most abundant element in the Earth's crust and is an integral component of microbial metal and radionuclide cycling. The biogeochemical cycling of U and Fe are closely associated due to the similarity between the U(IV)/U(VI) and Fe(II)/Fe(III) redox couples (Ginder-Vogel et al. 2006; Weber et al. 2011). Fe(III) oxides and Fe(III)-bearing clay minerals have been demonstrated to oxidize and mobilize U in laboratory experiments. The exact rate and extent of U(IV) oxidation depends on the properties of the Fe-oxide including crystallinity and reactive surface area, as well as solution chemistry (Ginder-Vogel et al. 2006; Ginder-Vogel et al. 2010; Senko et al. 2005). Oxidation generally does not occur through direct transfer of electrons between the solid-phase Fe(III) and U(IV). Instead, it occurs in three steps: (1) dissolution of U(IV) (which is sparingly soluble), (2) adsorption of U(IV) on the surface of the Fe(III) oxide, and (3) oxidation of the adsorbed U(IV) to U(VI) with coinciding reduction of Fe(III).

Once U is oxidized to U(VI), there is the potential for biologically catalyzed reduction with U(IV) serving as an electron acceptor. With U(VI) serving as the electron acceptor in microbial respiration, this reaction can be coupled to the oxidation of natural organic carbon or hydrogen (H_2). Biological mechanisms have been identified as significant in alluvial aquifers where dissimilatory metal reducing bacteria are ubiquitous (Kasting et al. 2006). Bacteria capable of U reduction are ubiquitous in sedimentary systems including dissimilatory metal-reducing bacteria (*Geobacter* spp. and *Shewanella* spp.; (Lovley et al. 1991)), sulfate-reducing bacteria (*Desulfovibrio* spp.), and fermentative bacteria (*Clostridium* spp.; (Francis et al. 1994)). The metabolic potential of indigenous microbiota for the reduction of soluble U(VI) to insoluble U(IV) has been intensely studied owing to its potential application as a bioremediation technique for U-contaminated groundwater as aqueous U(VI) complexes can be reduced to a solid-phase U(IV) mineral (Finneran et al. 2002a; Kasting et al. 2006; Suzuki et al. 2005). The mechanism of microbial U reduction varies between species with some pathways able to support cell growth under certain circumstances. Rates of biological reduction are inhibited by carbonate, cations such as Ca^{2+} and Mg^{2+} (Belli et al. 2015; Brooks et al. 2003; Stewart et al. 2010). Despite rate limitations, it has been demonstrated that carbon amendments as well as carbon-rich deposits in the subsurface can drive microbial reduction and lead to sequestration of U (Campbell et al. 2012; Qafoku et al. 2014). Abiotic reductants, such as H_2 , sulfide minerals, and Fe(II), may also reduce U(VI) in these reduced environments (Gallegos et al. 2013) and contribute to geochemical traps in the subsurface sequestering U as U(IV) minerals.

12.4.2 Uranium Adsorption Reactions

Sorption reactions between dissolved U and sediment surfaces are a major factor controlling the mobility of U. The tendency for U to adsorb to these surfaces depends on the aqueous U species present, which is a function of solution chemistry, specifically, pH, presence of carbonate ions, and the presence of divalent cations such as Ca^{2+} and Mg^{2+} (Dong et al. 2005; Dong and Brooks 2006). U adsorption is maximized at low pH (<4) where the dominant species present is UO_2^{2+} . At circum-neutral to basic pH and in the presence of carbonate ions, oxidized U will form various U-carbonate anions or neutral-charged Ca-U-carbonate species that adsorb poorly to sediment surfaces and will remain mobile in the groundwater (Fox et al. 2006). Therefore, reactions that increase pH or generate carbonate alkalinity promote U desorption and mobilize U into groundwater. These include common reactions that occur as groundwaters naturally evolve including carbonate dissolution, the oxidation of organic matter, and weathering of silicate minerals. In addition, certain microbially driven redox reactions may generate alkalinity (Wan et al. 2005) and increase pH such as denitrification and sulfate reduction.

Globally, the relative importance of oxidation and desorption is difficult to evaluate. Recent studies in heavily irrigated and semi-arid areas suggests that spatial and

temporal changes in groundwater uranium concentrations positively correlate with alkalinity (Burow et al. 2017; Jurgens et al. 2010). Because increased irrigation and leaching under intensively fertilized areas in the western USA can contribute to increased dissolved solids, bicarbonate, and nitrate leaching to groundwater, it continues to be difficult prioritizing the primary mechanism for U mobilization in shallow alluvial aquifers.

12.5 Impacts of Agricultural Activity on the Mobilization of U

Agricultural activity can negatively impact water quality in numerous ways. These include increased inputs of nitrogen and phosphorus from the application of fertilizers and organic livestock waste, application of herbicides and pesticides, and salts from irrigation residues (Fig. 12.2). In addition, activities such as pumping of irrigation water and tillage practices can impact biogeochemical reactions by altering the local hydrology and geochemistry (Burow et al. 2017). The following section will address how agricultural practices could lead to the mobilization of U into the groundwater.

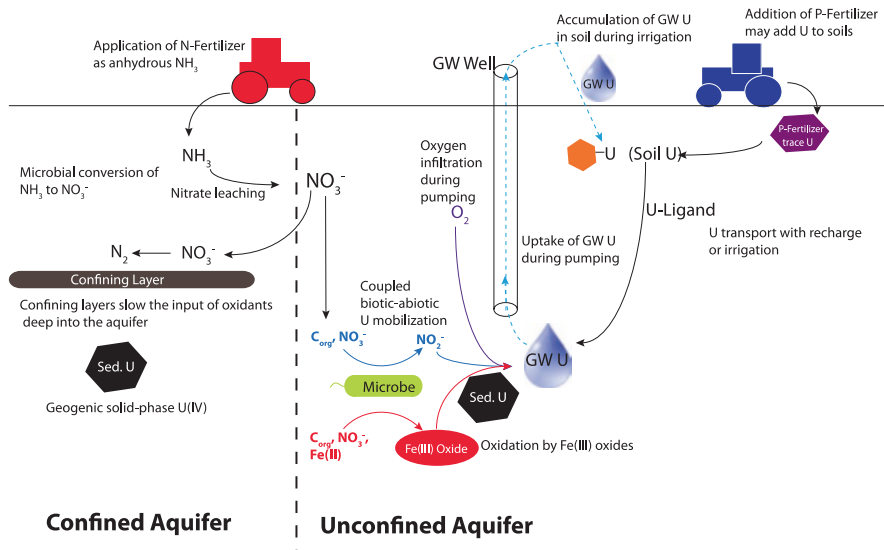


Fig. 12.2 Schematic of agricultural processes that may lead to geogenic U mobilization

12.5.1 Loading of Nitrogen and Phosphorous

Phosphorous and nitrogen species may be introduced into agricultural waters either through the application of fertilizers to enhance crop production or from the runoff of livestock waste. While several types of P-fertilizers are available, all originate through the processing of rock phosphate, which is commonly mined from phosphorite deposits. Due to the environmental conditions which these deposits form, they may contain high levels of U (Crosby and Bailey 2012). Despite this, it should be noted that as U became a valuable commodity (Kim et al. 2016), fertilizer manufacturers developed processes for extracting U during production, thus limiting U content in fertilizers. In addition, a review of groundwater U levels from Germany found that inputs of P-fertilizers had minimal impact of groundwater U levels over a 50 year period and thus were not a likely source of U (Liesch et al. 2015). Additionally, research within the USA has also revealed that the ^{234}U to ^{238}U isotopic activity ratio of U in groundwater and surface waters exceeds 1.4, which exceeds the ratio observed from fertilizers around 1.0 or below (Bohlke et al. 2007; Schnug and Haneklaus 2008; Schnug et al. 2008; Snow and Spalding 1994; Suksi et al. 2006; Verstraeten et al. 2000; Zielinski et al. 1997) and thus suggests uranium originates from a natural source.

Shallow subsurface aquifers are prone to nitrate contamination resulting from agricultural activity (such as N-based fertilizers or animal waste) or from septic systems in more densely populated areas (Burow et al. 2010; Nolan et al. 1997). Application of N-based fertilizers is a major source of groundwater nitrate contamination in the USA (Burow et al. 2010). N-fertilizers are commonly applied as ammonia and converted into nitrate by nitrifying bacteria in the soil. While plants will consume nitrate in the root zone, excess nitrate will leach below the root zone and enter the groundwater during recharge (Bohlke 2002). This leaching leads to increases in groundwater nitrate concentrations. Shallow aquifers have been demonstrated to be the most susceptible to nitrate contamination (Nolan et al. 2002; Nolan and Weber 2015). This was also true for U contamination and is likely the result of nitrate infiltration into the aquifers (Nolan and Weber 2015). As discussed in the previous section, it is well documented from field and laboratory research conducted in systems anthropogenically contaminated with U that inputs of nitrate stimulate the oxidative dissolution of U(IV) minerals, through a series of biotic and abiotic reactions. Once U is mobile, increased carbonate alkalinity can further drive U mobilizing in agricultural systems. A statistically significant correlation between nitrate and U was observed in groundwater metadata, which includes two major US agricultural aquifers (Hudak 2018; Nolan and Weber 2015; Riedel and Kübeck 2018). There are several lines of evidence that support this correlation. While direct abiotic oxidation of U by nitrate is kinetically limited, microbes capable of denitrification (production of reactive intermediates) and nitrate-driven U(IV) oxidation are common in soils and sediments (Beller 2005; Weber et al. 2011). Moreover, Fe is abundant in aquifer sediments, and the influx of nitrate could catalyze the formation of Fe(III)-oxides, which are effective U(IV) oxidants (Ginder-Vogel et al. 2006;

Ginder-Vogel et al. 2010; Senko et al. 2005). In addition, heterotrophic denitrification can generate bicarbonate alkalinity and consume proton acidity. Thus further creating geochemical conditions that would promote U mobilization. In oxic systems, these conditions promote desorption of oxidized U from sediment surfaces into groundwater further enhancing U mobility and maintaining dissolved U in groundwater. However, it should be noted that Nolan and Weber (2015) identified that low nitrate concentrations (below the MCL) likely would not lead to mobilization. This may be a result similar to a recent study that revealed low concentrations of DO influxes into a reduced region of an aquifer resulted in a decrease of groundwater U concentrations (Pan et al. 2018), thus suggesting a tipping point for oxidative dissolution of U.

Other microbial mediated processes that generate proton acidity such as ammonium oxidation could also impact U mobility. Ammonium oxidation produces protons, which could result in the dissolution of carbonate minerals present either naturally in the soil zone or added to buffer soil pH (Bohlke 2002; Semhi et al. 2000). The dissolution of carbonate minerals would increase the levels of carbonate and divalent cations in recharge water, resulting in the formation of neutrally charged aqueous U-Ca/Mg-CO₃ complexes (Dong et al. 2005; Dong and Brooks 2006). Since these complexes do not readily sorb to sediment surfaces due to their neutral charge (Dong et al. 2005), this enhances the mobility of U in groundwater. In addition, since carbonate minerals may accommodate trace amounts of U in their crystal structure(s) (Elzinga et al. 2004; Reeder et al. 2004), carbonate dissolution could potentially directly release U as well.

Hydrological factors that can influence U mobilization must also be considered. It is well understood that irrigation to increase agricultural productivity will also influence hydrology. Irrigation systems tend to increase local recharge rates, which increase nitrate leaching from the soil and vadose zone into the groundwater (Gurdak and Qi 2012; Nolan et al. 2002). Groundwater withdrawal also can change flow paths and alter mass transport, which can also alter microbial activity (Alley et al. 2002). The changes in microbial activity can thus alter both nitrogen and uranium biogeochemistry. However the latter has been poorly studied in the context of uranium mobility in agricultural systems.

12.6 Conclusion

The occurrence of elevated levels of groundwater U represents a public health risk for private and public wells that utilize the groundwater as a drinking water resource. The detrimental health impacts of ingesting U-contaminated water coupled with the potential for bioaccumulation of U in food crops during irrigation represents a risk to water and food security. Studies on naturally occurring U outside of ore deposits are limited. However, significant and notable research has been conducted within environments anthropogenically contaminated with U and details the biogeochemical behavior of this contaminant in both saturated and unsaturated subsurface

systems. In natural systems, adsorption and redox processes are the dominant controls on U mobilization in subsurface systems, although geologic setting has to be accounted for to determine the contributions of these processes. In oxic aquifers, desorption reactions controlled by variations in pH and bicarbonate alkalinity are the major driver of U mobilization. In anoxic settings, the role of redox reactions driven by inputs of oxidants, such as nitrate and dissolved oxygen, must also be considered. While inputs of agricultural chemicals, such as nitrate, may influence the release of geogenic U, published research is limited. Uranium mobilization is a complex process and a single model is likely not applicable to all systems. Since most research on U mobilization has been conducted in anthropogenically contaminated systems, there are still questions on what forms of U are present and how they behave (especially at low sediment U concentrations). Therefore, more research is necessary investigating the forms of U present in different aquifer systems and how they respond to biogeochemical reactions initiated by agricultural activity. While uranium releases from natural sources are a risk to public health that should be addressed, it may not be the only negative impact. Inputs of agricultural chemicals, such as nitrate, could be catalyzing other biogeochemical weathering reactions, and U may not be the only potentially toxic element released. These reactions could enhance the release of ions into groundwater, which when reapplied through irrigation could further decrease soil health.

Acknowledgments This research was supported by the USGS 104 g Program (2014NE265G) to K.A.W and D.D.S and the Robert B. Daugherty Water for Food Global Institute at the University of Nebraska to K.A.W. and J.P.W.

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