Life Cycle Management of Onsite Wastewater Treatment
Contaminants of Concern: A Case Study Review

M. T. T. Retallack *, W. Hart ** and G. Gagnon **

* Pollution Probe, 63 Sparks Street, Suite 101, Ottawa, Ontario, K1P 5A6, Canada
(E-mail: mretallack@pollutionprobe.org)

** Centre for Water Resources Studies, Dalhousie University, 1360 Barrington Street, Office D-514, P.O. Box 1000, Halifax, Nova Scotia, B3J 2X4, Canada
(E-mail: William.Hart@Dal.Ca; Graham.Gagnon@Dal.Ca)

Abstract: Contaminant fate and behaviour during wastewater treatment is becoming of concern to onsite wastewater treatment systems as they increase in use through suburban growth. In the septic tank component of an onsite wastewater treatment system, the fate of a given contaminant will depend on its interaction with the biological and chemical constituents of the tank. Through bringing onsite wastewater treatment residuals from numerous individual sites to a central facility, environmental implications can arise from contaminant sequestration in the sludge fraction of the tanks contents. In Nova Scotia, Canada, naturally occurring uranium can be present in domestic well water supplies. A literature review of relevant fate and transport mechanisms for uranium within a septic tank is used as an analogue to illustrate unidentified waste management dimensions of onsite wastewater treatment. Through discussion of key chemical and biological mechanisms, the environmental behaviour of uranium is linked with expected bio-chemical conditions of a septic tank giving insight into expected partitioning behaviour of uranium within a septic tank. Localised ecotoxicological concerns and associated waste management implications are also discussed.

Keywords: biosolids; onsite wastewater; partitioning; septic tank; uranium; waste management

INTRODUCTION

Significant levels of naturally occurring uranium are known to be regionally present in Nova Scotian groundwater. One investigation sampled 784 wells and found that 195 had uranium concentrations in excess of the Canadian Drinking Water Guidelines, with the average concentration in wells being 70 mg/L, and a maximum concentration of 700 mg/L (Grantham, 1986).

Though groundwater uranium concentrations are typically quite small, the large volumes of water drawn for domestic purposes compound these small concentrations into considerable amounts, in terms of mass. As domestic well water supplies are typically associated with onsite wastewater treatment, and with approximately 400,000 people in Nova Scotia using onsite wastewater treatment systems (Province of Nova Scotia, 2007), substantial amounts of naturally occurring uranium will enter Nova Scotian septic tanks.

Proper maintenance of a septic tank requires that accumulated sludge and supernatant be removed periodically. Environmental legislation in Nova Scotia requires that this material be properly handled and treated to reduce potential adverse effects to the environment. This is normally done through storage and treatment of the material in lagoon systems (Province of Nova Scotia, 2007). Where waste residuals from numerous tanks are brought to the same treatment facility, this process can serve to concentrate otherwise distributed amounts of uranium, thereby magnifying the potential for environmental effects and escalating the need for greater understanding of the waste management implications of naturally occurring uranium.

Results compiled from various ecotoxicological studies indicate a predicted no-effect concentration of 0.005 mg uranium L⁻¹ water for freshwater plants; 0.005 mg uranium L⁻¹ water for freshwater invertebrates; 100 mg uranium kg⁻¹ dry sediment for freshwater benthos; 250 mg uranium kg⁻¹ dry soil for terrestrial plants; and 100 mg uranium kg⁻¹ dry soil for other soil biota (Sheppard et al., 2005). One particular study using Eisenia fetida,
the common earthworm, *Corbicula fluminea*, a bivalve mollusc, and the fish, *Brachydanio rerio*, determined uranium to be relatively very toxic to both *Eisenia fetida* and *Brachydanio rerio* but relatively non-toxic to *Corbicula* (Labrot et al., 1999).

While the exact extent of uranium contamination of groundwater is not clear, it is known to exist and has been shown to be an environmental toxin of significant potency. In light of potential ecological impacts, the bringing together of septic tank sludge from numerous tanks can be seen as introducing a level of risk through the amassing of a known environmental contaminant. It also presents a clear opportunity to intervene and remove uranium from produced biosolids through additional treatment, thereby improving the sustainability of the process and the marketability of the product. To better manage this potential environmental risk, the partitioning behaviour of uranium within a septic tank becomes of central interest. Similar concerns can be expected to arise from the sequestration of other contaminants of concern.

**DISCUSSION**

Uranium chemistry and chemical partitioning mechanisms

The behaviour and mobility of uranium under different environmental conditions is central to its partitioning within a septic tank. Uranium has four valence states, U(III), U(IV), U(V) and U(VI), with U(IV) and U(VI) being the most stable. It has a high affinity for oxygen and readily oxides to form the highly soluble uranyl cation, UO$_2^{2+}$ (Zhang et al., 1994). This is a key factor influencing the mobility of uranium in geological formations. As U(IV), uranium tends to precipitate, however once oxidised the dissolved cation is available for complexation either with surface sites within rock formations, which may tend to retard the transport of uranium, or with dissolved ligands, which may reduce the availability of the uranyl cation to adsorb to surface sites, thereby enhancing its mobility (Langmuir, 1978).

A well studied ore deposit in Kookgarra, Australia, demonstrates the mobilisation and subsequent geologic fixation of uranium. The weathering of a uranium bearing quartz chlorite schist exposed uraninite to oxygen, causing its transformation to the U(VI) valence state and the soluble uranyl cation. It also caused the formation of iron oxides and associated binding sites. The influence of adsorption to mineral surface sites on the mobility of uranium in groundwater systems is demonstrated by iron nodules found at Koongarra, with enriched uranium levels $10^6$ times higher than local groundwater (Sato et al., 1997).

There is a strong association between uranium and phosphate in the natural environment, with fixation of U(VI) by precipitation of minerals such as uranyl phosphates being an important mechanism for the long term sequestration of uranium (Murakami et al., 1997). At Kookgarra, when mobilised uranyl cations encountered phosphate, deposits formed increasing the sequestration of uranium. The potential for precipitation of U(VI) with phosphates as secondary minerals is so dominant that inorganic phosphate solids have been proposed as reactant material for reactive chemical barriers, an in-situ groundwater remediation technology (Barger et al., 1997). In a solution where among five competing ligands the concentration of phosphorous was the lowest, the tendency of the uranyl cation to complex with phosphate ligands was essentially absolute at near neutral pH ranges (Langmuir, 1978). At higher pH values, however, carbonate ligands were dominant.

Uranium exhibits a strong tendency toward complexation with carbonate ligands. With carbonate present almost everywhere in the natural environment, it becomes one of the most important reactive anions involved with the transport of uranium, exacting a significant effect on the mobility of uranium in subsurface systems (Banyai et al., 1995). In single mineral iron oxide solutions, uranyl complexation by carbonate led to a significant decrease in sorption to negatively charged bonding sites (Giammar & Hering, 2001), with the greatest decrease being realised at higher pH values (Waite et al., 1994).

Groundwater entering a septic tank will often maintain much of its original chemistry, at which point it will be exposed to an environment much different from that of its geological origin. This environmental shift can be expected to perturb the original chemical balance established underground, and give rise to changes in how uranium is found in solution. A multi-element titration experiment started with groundwater at an initial pH
of around 3.8, and chemical composition consisting of 453 mg/L Al; 955 mg/L Ca; 2.3 mg/L Co; 13.6 mg/L Fe; 160 mg/L Mg; 129 mg/L Mn; 12.5 mg/L Ni; 93 mg/L K; 24 mg/L Si; 50.5 mg/L U; 1.6 x 10⁻³ mg/L Tc; 7950 mg/L NO₃⁻; 88 mg/L SO₄²⁻; 64 mg/L TOC; 240 mg/L TIC; and 2 – 4 mg/L DO (Gu et al., 2003). Base titrations were performed using NaOH and Na₂CO₃ to observe the precipitation, coprecipitation, sorption, desorption, and dissolution of uranium through a range of pH values.

Both iron and uranium concentrations were found to decrease with the addition of NaOH. At a pH of approximately 4.5 the majority of iron had precipitated out of solution. Observed uranium concentrations decreased as well, with uranium being rapidly removed from solution as further NaOH additions raised the pH to around 5.5. Partly due to naturally present carbonate ligands, about 20% of the uranium had moved back into the aqueous phase by pH 8.6, however the main finding was that more than 90% of the uranium had been removed from solution by pH ~ 5.5, suggesting sorption onto and then coprecipitation with iron oxides in particular. Depending on differences in chemistry and pH between the groundwater and septic tank water, the tendency of iron to remain in, or leave solution, may result in the sorption and coprecipitation of uranium in association with iron oxides.

Although the addition of Na₂CO₃ induced a similar precipitation of iron minerals, approximately 30% of Fe was still in solution at pH 5. Below pH 5.5 more than 90% of the uranium had left solution. This was partly due to the effect of iron and coprecipitation but also possibly due to direct precipitation of UO₂CO₃ species due to its relatively low solubility. With further base addition significant amounts of uranium went back into solution. By pH 7 around 40% had returned to solution and by pH 9 approximately 70% of previously non-aqueous uranium had re-entered the dissolved phase. This illustrated both the dramatic effects that can be brought by a shift in pH, and the difference between a carbonate and non-carbonate system.

Discussion of the titration experiments has been limited to two key factors: the behaviour and influence of iron, and the effects induced by the presence of carbonate ligands. If the study water contained phosphate a different set of behaviours would be expected, especially with respect to the influence of carbonate. The presence of phosphates is expected in domestic wastewaters due to their association with excreta and common use in soaps and detergents. Accordingly, we can expect higher levels of phosphate to be found in the septic tank water above any background levels present in the raw water. This, along with differences in pH, can be expected to drive a change in the uranium concentration of wastewater in the septic tank.

**Biological partitioning mechanisms**

Numerous bacteria have been found to reduce uranium from U(VI) to U(IV) as a part of their metabolic process. One bacteria of particular interest is the sulphate reducer Desulfovibrio desulfuricans. It was found that while D. desulfuricans metabolically reduces sulphate and uranium in anaerobic conditions, its ability to do so is not negatively impacted by exposure to atmospheric oxygen (Lovely & Phillips, 1992). Knowing that a septic tank is not strictly anaerobic (Winneberger, 1984), bacteria may undergo periodic exposure to aerobic conditions due to mixing action in the tank. Furthermore, the sulphate reducer D. desulfuricans is known to be found in the microbiological composition of a septic tank (Kinsey et al., 2005).

Studies have shown both extra and intra-cellular associations between uranium and microorganisms, with microbial cells having been found to act as a biosorbant for the removal of uranium from water (Strandberg et al., 1981), and high levels of enrichment having been found to be associated with suspended river particles (Mann & Fyfe, 1987). A study of the Thames River in Ontario found that the accumulation of uranium associated with suspended particles exhibited a concentration factor of 10⁵ – 10⁶ when compared to background levels in the surrounding river water (Mann & Fyfe, 1987). A relatively constant year-round partition coefficient for uranium associated with microorganisms, with respect to background concentration of uranium in the river water, was determined to be 2 · 10⁻⁴. In absolute terms this was converted to 28.4 g U/g organic (dry cell weight). A batch study that investigated the ability of two microbes to act as bio-sorberts for the removal of uranium from solution found levels of accumulated uranium of up to 10 to 15% of dry cell weight (Strandberg et al., (1981), a difference of five orders of magnitude when compared to the Thames River study. The difference
in accumulated uranium was likely driven by the comparatively very small concentrations of organics and uranium in the river system versus much higher concentrations in the batch system. In both of these studies phosphate played a key role in developing an association between uranium and microbial material.

A study involving the bacteria Citrobacter found that enzymatically liberated phosphate ligands could act first as reactive sites for dissolved uranium, and subsequently serve as points of nucleation for the bio-crystallisation of dissolved uranium (Macaskie et al., 1996).

Solution pH was found to be a determining factor for the removal of uranium in both the batch bio-sorption experiments and the bio-crystallisation experiments, with both processes realising an increase in removal rates when the pH was adjusted to between 5 and 5.5. This adjustment was made from a starting pH of 2.5 in the case of the batch experiments, and from pH 7.0 in the Citrobacter experiments. Some of the batch experiments employed pre-exposure to HgCl₂ and formaldehyde, both lethal compounds to study cells. It was determined that uranium uptake was unaffected by metabolic activity of the cell suspensions.

Central to the partitioning of uranium within onsite systems are the contents and chemistry of the septic tank. A Canadian study provides insight into typical tank chemistries (Brandes, 1977). Generally the pH of the sludge layer was found to be less than that of the supernatant. This is consistent with findings from other studies where tank pH was typically smaller with greater liquid depth (Winneberger, 1984). Greater amounts of total phosphorous, with similar levels of soluble phosphorous, were found in the sludge when compared to the supernatant. This may reflect the much larger concentration of BOD₅ found in the sludge blanket. Conversely, sulphate concentrations were larger in the supernatant than in the sludge, possibly resulting from processes of anaerobic digestion, with sulphate being used by some bacteria as an electron acceptor (Droste, 1997). Iron concentrations were between one and two orders of magnitude larger in the sludge than in the supernatant.

Limited information about the groundwater chemistry suggests it was unlikely that either total or soluble phosphorous, in either the sludge or the supernatant, originated from the raw water (Brandes, 1977)

**Uranium mobility in septic tanks**

When uranium bearing wastewater of a certain chemistry encounters supernatant of a different chemistry, the equilibrium of the original groundwater will be disturbed, leading to potential partitioning of uranium out of solution. For example, the presence of high levels of phosphates in the supernatant, relative to the incoming wastewater, can be expected to exert a high demand for complexation between uranyl cations and available phosphate ligands. The uranyl phosphate ions are then available for further reaction. Incorporation into biological growth is one possible partitioning mechanism. Alternatively, exposure to higher iron concentrations in the sludge layer and its associated zone of increasingly concentrated suspended solids offer other opportunities for uranium to partition out of solution.

In anaerobic zones UO₂⁺ may be used as an electron acceptor by uranium reducing bacteria such as Desulfovibrio. desulfuricans. The biological reduction of uranium by D. desulfuricans will be limited to anaerobic zones. Though dissolved oxygen (DO) concentrations in a septic tank are highly variable, there is typically a slightly higher concentration near the water surface, likely related to the air space above the supernatant. The lowest DO concentration is found approximately one foot below the water surface, with an increase in DO with increased water depth. The largest suspended solids concentrations are in the upper and lower depths of the tank, with smaller concentrations found in the middle (Winneberger, 1984). Since microorganisms in solution are often associated with suspended solids, uranium-reducing bacteria found suspended in the supernatant would most likely be present in the top or bottom regions. Elevated DO concentrations could be expected in either of these areas. While this would not cause mortality for D. desulfuricans, it would impede metabolism and limit the potential reduction of uranium. While DO levels do vary, the sludge layer and lower parts of the tank have a high likelihood of being anaerobic. As such, reduction of uranium within the lower portion of the tank may be expected, and any organically fixed uranium that settles into the sludge layer may be reduced and sequestered. Biologically driven partitioning not regulated by metabolism, such as sorption
illustrated by the batch experiments (Strandberg et al., 1981), would be expected to be regulated by suspended solids concentrations, regardless of DO concentrations.

An example of elevated uranium concentrations in septic tank sludge comes from the United States. Septic tank samples associated with Area 25, Building 3124, at the U.S. Department of Energy's Nevada Test Site found an average liquid uranium-238 concentration of 0.47 g/L (0.33 +/- 0.08 pCi/L), and an average sludge uranium-238 concentration of 1.7 mg/kg (1.19 +/- 0.22 pCi/g), resulting in an enhanced sludge uranium concentration 10^3 times larger than that of the supernatant (Appenzeller-Wing & Wycoff, 2002).

In Colorado, groundwater from the Lowry Landfill Superfund Site, with a maximum groundwater uranium-238 concentration of 190 pCi/L, or 270 g/L (Dodson, 2002), is mixed with municipal sewage at a ratio of 20,000 gallons of pre-treated groundwater to 160,000,000 gallons of municipal sewage (EPA Region 8, 2001). With partial removal of uranium through pre-treatment, municipal biosolids uranium concentrations of 46 +/- 22 ppm (mg/kg) have been recorded (Yager et al., 2004). After incorporating the dilution factor, uranium concentrations in the municipal biosolids are elevated by a factor of 10^6 relative to the maximum concentrations expected in the blended municipal wastewater and pre-treated Lowry groundwater.

CONCLUSIONS

Known chemical and bacteriological reactions provide evidence that uranium will partition out of solution within a septic tank, and that there will be different governing partitioning regimes depending on location within the septic tank. When wastewater of one composition encounters supernatant of a different chemistry in the upper section of the tank, the disequilibrium that occurs will induce uranium and the uranyl cation to undergo a change of state or association, opening it up to chemical partitioning processes. It is less likely that biological reduction will occur here, however bio-sorption and subsequent settling is a precursor for biological reduction. In the sludge layer and proximate area near the bottom of the tank, the biological reduction of uranium is a key partitioning and sequestration mechanism. Anecdotal evidence of elevated uranium concentrations in sludge and biosolids, relative to wastewater concentrations, lends support to the theory that uranium will partition out of wastewater and be sequestered within sludge residuals.

The geological occurrence of uranium is not uncommon, making this a shared issue, however more important is the perceptual shift toward the identification of the onsite wastewater treatment residuals as a source of potentially unidentified waste management challenges. Globally, total sludge volumes originating from onsite systems are significant. Additional levels of septic tank sludge treatment may be appropriate to ensure an environmentally safe product. By addressing potential problems with more complete and comprehensive analysis, sustainable biosolids management policy can deliver substantial environmental benefits.

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