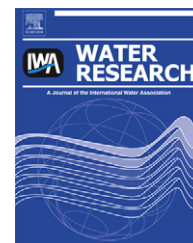


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# Evaluation and application of anion exchange resins to measure groundwater uranium flux at a former uranium mill site

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## ABSTRACT

Laboratory tests and a field validation experiment were performed to evaluate anion exchange resins for uranium sorption and desorption in order to develop a uranium passive flux meter (PFM). The mass of uranium sorbed to the resin and corresponding masses of alcohol tracers eluted over the duration of groundwater installation are then used to determine the groundwater and uranium contaminant fluxes. Laboratory based batch experiments were performed using Purolite A500, Dowex 21K and 21K XLT, Lewatit S6328 A resins and silver impregnated activated carbon to examine uranium sorption and extraction for each material. The Dowex resins had the highest uranium sorption, followed by Lewatit, Purolite and the activated carbon. Recoveries from all ion exchange resins were in the range of 94–99% for aqueous uranium in the environmentally relevant concentration range studied (0.01–200 ppb). Due to the lower price and well-characterized tracer capacity, Lewatit S6328 A was used for field-testing of PFMs at the DOE UMTRA site in Rifle, CO. The effect on the flux measurements of extractant (nitric acid)/resin ratio, and uranium loading were investigated. Higher cumulative uranium fluxes (as seen with concentrations > 1 ug U/gram resin) yielded more homogeneous resin samples versus lower cumulative fluxes (<1 ug U/gram resin), which caused the PFM to have areas of localized concentration of uranium. Resin homogenization and larger volume extractions yield reproducible results for all levels of uranium fluxes. Although PFM design can be improved to measure flux and groundwater flow direction, the current methodology can be applied to uranium transport studies.

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## 1. Introduction

Uranium is a contaminant of concern at many DOE former mining and milling sites. With the passing of the Uranium

Mill Tailings Radiation Control Act (UMTRCA) in 1978, tailings were removed to repositories and the surface soil was remediated from 24 inactive uranium mill sites. In Rifle, Colorado, the site of a former uranium and vanadium mill,

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the contamination remains in the soils and shallow groundwater due to uranium leached from the tailings prior to removal. Monitored natural attenuation (MNA) was the chosen method for remediating the uranium below ground surface (USEPA, 1999). Surface remediation was completed in 1996, but groundwater treatment is ongoing. Uranium, vanadium, and selenium are the main contaminants of concern at this site (DOE, 2008).

The Rifle, CO site is situated directly adjacent to the Colorado River and has a semi-arid climate, receiving on average 300 mm of precipitation. The first 20–30 feet below ground surface is Colorado River alluvium, which covers the sands, silts and clays of the Wasatch Formation. A more complete description of the Rifle mill site geology and hydrology can be found elsewhere (Yabusaki et al., 2007). By natural flushing, soluble uranium discharges under a natural gradient to the Colorado River where it is further diluted to background levels. Initial groundwater modeling predicted this process to take 100 years to reach background levels (DOE, 2008). Decrease in uranium concentration is, however, occurring slower than anticipated and other remediation strategies are being investigated.

Since 2002, biostimulation experiments have been performed at the site to stimulate microbial reduction of uranium (VI), which is the soluble, mobile form, to immobile uranium (IV) using acetate injections (Anderson et al., 2003; Lovley et al., 1991; Ortiz-Bernad et al., 2004; Yabusaki et al., 2007). To determine the effectiveness of the biostimulation, it is necessary to measure the uranium concentrations upgradient and downgradient of the injection wells. It is also valuable to know the rate of groundwater flow. A rapid flow combined with a high soluble contaminant concentration is of greater concern than a slow moving plume of similar contaminant concentration. To be considered successful, bioremediation usually needs to achieve low soluble contaminant concentrations, however a high concentration may be allowed to remain if little or no flow occurs. Examining the concentration alone may lead to an incomplete understanding of the system. Measuring contaminant flux ( $J_c$ ), which is the product of the volumetric water flux, or specific discharge ( $q_0$ ) and the flux-averaged contaminant concentration ( $c$ ) provides better insight into the outcome of remediation efforts (Hatfield et al., 2004).

There are limitations with the current methods for estimating flux. Concentrations are typically measured independently of the specific discharge, possibly at separate sampling times or location, leading to significant variations and errors in flux calculations. Flux estimates generally rely on modeled flow rates or laborious and intrusive hydrologic tests (tracer injections or pump tests). To acquire more reliable information, the passive flux meter (PFM) was developed to provide simultaneous direct measures of the specific discharge ( $q_0$ ) and contaminant mass flux ( $J_c$ ) (Annable et al., 2005; Hatfield et al., 2004). Contaminant measurements made using PFM represent cumulative local fluxes, which can then be used to estimate flux-averaged aqueous concentrations ( $c$ ), according to Equation (1), for comparison to measured aqueous concentrations.

$$J_c = q_0 c \quad (1)$$

PFM schematics and the details of the calculations are provided by Hatfield et al. (2004). The PFMs were initially used to measure the flux of organic contaminants and used silver impregnated (antimicrobial) granulated activated carbon (GAC Ag) as the sorbent material (Annable et al., 2005).

Previously, anion exchange resins such as Dowex 21K and 1-X8, Purolite A500, A600 and A520E, and Lewatit K 6367 have been proven to remove uranium from aqueous solutions (Kolomiets et al., 2005; Phillips et al., 2008) under a large range of pH conditions, from acidic to alkaline, with the most effective sorption observed near neutral pH to alkaline conditions. Chelating resins (Merdivan et al., 2001; Pesavento et al., 2003), such as Chelex 100 and Amberlite XAD-16, and cation exchange resins, such as Dowex-50 (Schumann et al., 1997), have been shown to be most effective at sorbing aqueous uranium in acidic solutions. Due to the near neutral pH at the Rifle site and the expected dominance of anionic uranyl carbonate species, this work focused on anion exchange resins previously shown to be effective.

The goal of the overall project was to develop a PFM to quantify aqueous uranium fluxes at the Rifle site that can be used to evaluate the effectiveness of biostimulation by comparing upgradient and downgradient uranium fluxes. To have an effective PFM, the material must quantitatively sorb all of the uranium passing through it, be capable of releasing the sorbed uranium upon extraction, and predictably retain and release the chosen tracers, preferably without microbial growth occurring on the resin. Because the PFM will be used to evaluate the effectiveness of biostimulation an additional constraint for this application was that elution of resident tracers must not affect results of the other experiments being performed simultaneously at the site. To keep total remediation and monitoring costs at a minimum, resin cost is also a factor for making the final choice. Therefore resins will be evaluated for uranium sorbed and desorbed, tracer capacity and finally, cost. In this specific study uranium speciation and water chemistry conditions (pH, alkalinity, major ions, etc.) were investigated to find the best sorbent material for use in the PFMs at Rifle, CO.

## 2. Methods

A sample of background Rifle groundwater was analyzed for speciation. Modeling tests were performed to determine the aqueous uranium (VI) speciation using Visual MINTEQ, Version 3.0, over a pH range of 3–10 using the Multi-problem/Sweep function. Only aqueous species were included and sorption and precipitation were ignored. Data on metal and ligand concentrations were obtained from inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Perkin Elmer 3000 for cation metals, ion chromatography (IC) using a Dionex ICS-90 system for major anions, a Shimadzu TOC analyzer for dissolved organic carbon (DOC) and carbonate was determined by alkalinity titration. The concentrations of these major components in Rifle groundwater can be found in Table 1. These concentration values were used as input for the model and updated constants for the calcium and magnesium species provided by Dong and Brooks (2006) were used to update the database.

**Table 1 – Concentrations of components used to model uranium speciation. Only major components affecting uranium species are included.**

Component	Concentration
U(VI)	226 ug/L
Ca <sup>2+</sup>	262 mg/L
Na <sup>+</sup>	202 mg/L
Mg <sup>2+</sup>	128 mg/L
SO <sub>4</sub> <sup>2-</sup>	795 mg/L
CO <sub>3</sub> <sup>2-</sup>	168 mg/L
Cl <sup>-</sup>	192 mg/L
NO <sub>3</sub> <sup>-</sup>	12 mg/L
DOC	4.5 mg/L

## 2.1. Materials

Numerous sorbents have been developed and used for the removal of uranium from water at near neutral pHs. Organic resins with quaternary amine sites, strong anion-exchange resins, bind uranyl complexes strongly and are available from several manufacturers, for example the Dowex 21K and Purolite A series. (Barton et al., 2004; Chanda and Rempel, 1992a,b; Jelinek and Sorg, 1988; Kolomiets et al., 2004; Vaaramaa et al., 2000) Purolite A500, Dowex 21K and 21K XLT, Lewatit S6328 A and silver impregnated granular activated carbon (GAC Ag) were investigated as possible sorbent materials in the PFMs. The Lewatit resin has been previously used for anion capture in PFMs (Cho et al., 2007). These resins were expected to have good sorption for the uranyl carbonate anion complexes predicted in the Rifle groundwater. Each resin was examined for uranium sorption and desorption and tracer elution properties relative to price. Table 2 shows a comparison of the resin properties and prices at the time of the experiment (fall 2008). Resins were used in the chloride form and rinsed thoroughly five times with deionized water and allowed to air dry. No cleaning procedure was necessary for the GAC Ag.

Adsorption studies were initially done in new, sterile 15 mL polypropylene centrifuge tubes (BD, Franklin Lakes, NJ, PN 352196) using water with added sodium bicarbonate (1 mM) to simulate Rifle alkalinity and pH. Some wall-sorption of uranium was observed using these tubes. After 24 h, polypropylene had sorbed 8% of the uranium present, and 25%

after 72 h. Polystyrene tubes (BD, PN 352095) were then used for comparison. Polystyrene tubes showed less uranium sorption to the walls than did the polypropylene tubes with 17% sorbed after 72 h. Uranium sorption to the tubes increased over time for both materials; however, based on the near complete uranium recovery and mass balance from the resin after material transfer, we concluded that uranium preferentially sorbed to the resin regardless of time or tube material and the tube sorption seen earlier in the blanks was deemed negligible in actual samples. Remaining experiments were done using polystyrene as a precaution to ensure most uranium was sorbing to the resin. Cleaning with nitric acid (3% v/v) was effective in removing all uranium from tubes.

All uranium solutions were made by diluting a 1000 ± 3 ppm U (in 2% nitric acid) ICP standard (High-Purity Standards, Charleston, SC). Dilutions were done using Nano-Pure deionized water for neutral pH, and trace metal grade nitric or hydrochloric acids (Fisher Scientific) for the lower pH standards. Sodium bicarbonate, used to create the groundwater simulant, and the silver nitrate used to impregnate the GAC were ACS grade.

## 2.2. Adsorption batch studies

Sorbent materials were weighed (100 ± 5 mg) into centrifuge tubes. Uranium standard solutions at concentrations of 5, 10, 50, 100 and 300 ppb were prepared in 1 mM sodium bicarbonate (pH 7.3 ± 0.1) to simulate Rifle groundwater. Uranium concentrations in Rifle groundwater average around 200 ppb. The effects of pH, which will influence the aqueous uranium speciation, were tested by lowering the pH with nitric and hydrochloric acid to pH 3.8. 10 mL of uranium solution were added to each tube containing resin. Each concentration was examined in triplicate at both pHs. The samples were placed on a shaker for 24 h to allow mixing and ion exchange. After the 24-h equilibration period, the resins were allowed to settle and the overlying solutions were decanted into new centrifuge tubes, leaving the resins for the next extraction step. In some cases this procedure was repeated with a 72 h equilibration time to verify that complete ion exchange had been achieved over the shorter time period. Since the PFMs will be in place in the aquifer for weeks at a time, testing the sorption for shorter times was deemed unnecessary based on estimated residence times (of groundwater passing through PFM) that were greater

**Table 2 – Comparison of sorbent materials tested using data provided by manufacturer fact sheets. \*Prices listed are values given for educational groups and may not reflect current industry prices.**

Resin	Type	Functional Group	Exchange Capacity (min.eq/L)	Ionic Form (as shipped)	Water Content (%)	Specific Gravity	Price* \$/ft <sup>3</sup>
Purolite A500	Type 1 strong base anion	quaternary amine	1.15	chloride	53–58	1.08	163.00
Dowex 21K 1630	Type 1 strong base anion	quaternary amine	1.2	chloride	50–58	1.06	449.50
Dowex 21K XLT	Type 1 strong base anion	quaternary amine	1.4	chloride	50–60	1.08	384.50
Lewatit S6328 A	Type 1 strong base anion	quaternary amine	1.0	chloride	58–63	1.06	150.00
GAC Ag	activated carbon	carbon	unknown	none	5		266.00

than 24 h. The solutions were analyzed for uranium by inductively coupled plasma-mass spectrometry (ICP-MS).

### 2.3. Extraction

A 1% nitric acid solution (10 mL) was added to all tubes with resins and shaken overnight. By lowering the pH to less than 1, the uranyl,  $\text{UO}_2^{2+}$  cation, becomes the dominant form and should be extracted from the anion exchange resin. Furthermore, the high level of nitrate should also cause desorption through competition for anion exchange sites. After 24 h, the acidic solution was decanted, verified to still be acidic ( $\text{pH} < 2$ ) by indicator paper, and analyzed by ICP-MS. The same extraction procedure was used for field PFMs, using larger volumes as described later. A uranium mass balance was computed using the values of desorbed uranium and the uranium remaining in solution following the sorption experiments.

### 2.4. ICP-MS analysis

A Perkin Elmer Elan 6100 ICP-MS was used for all analyses. All samples were acidified with nitric acid prior to analysis and introduced simultaneously into the argon plasma with a 40 ppb In internal standard using a Gilson peristaltic pump. A check standard was used every ten samples to verify instrument performance to be within 10% of the true value. Instrument calibration was done using uranium standards made in 1% nitric acid (Fisher Optima grade). Running conditions complied with manufacturer recommendations and standard quality controls were practiced.

### 2.5. Resin selection

The ideal resin should have a high uranium sorption capacity that is linear over the concentration range of interest. Linearity allows for predictability in performance and ease in calculations. Linear partition sorption isotherms were developed from the results of each resin batch experiment. The linear partition equation is given as:

$$C_a = K_d C_s \quad (2)$$

where  $C_a$  is the concentration of uranium adsorbed to the resin (ug/kg).  $K_d$  is the sorption equilibrium coefficient (kg/kg) and  $C_s$  is the concentration of uranium remaining in solution (ug/kg).

Sorption (determined from  $K_d$  and average percentage sorbed over linear range) and desorption properties (determined by percentage of sorbed uranium extracted with acid), were evaluated. The data was also analyzed using Langmuir and Freundlich isotherms to investigate non-linearity. Fitting the data to the Freundlich isotherm:

$$C_a = KC_s^n \quad (3)$$

provided a better fit than the Langmuir isotherm. If the exponential term,  $n$ , is equal to one, this equation reduces to the linear isotherm equation. This linear form was found to be sufficient to describe resin sorption with the exception of the Purolite resin.

Along with the use of ion exchange resin for uranium sorption, a second media consisting of granular activated carbon (GAC) pretreated with a suite of short chain alcohol tracers is used to measure volumetric water flux as presented in Hatfield et al. (2004) and Annable et al., 2005. Additional details of device construction and sampling is provided in Section 3.4 Field Application of this paper.

Flow through experiments were performed in a bench-scale three-dimensional aquifer model using similar methods as presented in Hatfield et al. (2004) and Cho et al., 2007. These tests were used to confirm performance of the resin and estimate the requisite flow convergence terms as presented in Hatfield et al. (2004).

### 2.6. Field studies

Resins were tested for microbial growth to ensure minimal interference with uranium sorption and desorption. As a precaution for field samples, resins were pretreated with silver nitrate solution to add ionic silver to the resin for anti-bacterial properties. The solutions were then analyzed by ICP-AES for residual silver (the difference assumed to be sorbed to the resin). Silver was added to the resin to be comparable to the silver concentration ( $\sim 0.03\%$  by weight Ag:resin) on the GAC-Ag used in the initial PFM studies reported by Hatfield et al. (2004).

PFMs were installed in Rifle over a three week period in the summer and the late fall of 2009. The meters were removed from the wells, and a number of vertical segments were separated and homogenized by complete mixing of each sample before being split for uranium, tracer, and microbial analyses. For the data presented in this paper PFM were deployed in 4-inch wells, and each PFM was constructed with six alternating segments of granular activated carbon (GAC) and Lewatit resin (three segments of GAC and three segments of Lewatit). The bottom segment of each PFM was composed of GAC. The PFM were retrieved and sampled with a deployment length of 23 days. Tracer analysis from the GAC segments were used for groundwater flux estimates, and the Lewatit segments were used for uranium flux estimates.

Uranium was extracted from the resins using additions of 10 mL of 1% nitric acid, which were replicated until no additional uranium removal was observed as determined by ICP-MS. Initially, small amounts of resin were used for the extracts to minimize waste produced and mirror the lab experiments. Samples of 100–150 mg and 1–1.5 g of resin were extracted for uranium and concentration values were compared between the different resin sample masses. For the 100 mg resin samples, this took one acid extraction with a second to verify complete uranium removal. Poor reproducibility was observed at lower concentrations ( $< 1$  ug U/g resin). Three acid extractions were necessary for the 1 g resin samples, but this larger resin amount had better reproducibility, regardless of uranium concentration or flux. In extractions performed later in the project, 4 g resin samples were extracted in 40 mL of 1% nitric acid, which provided sufficient acid extractant for multiple analyses for uranium and other groundwater anions, while also giving a more representative sample size for improved reproducibility at low

fluxes. The uranium concentration data presented here will be used to calculate the uranium flux through the PFM.

### 3. Results

#### 3.1. Speciation

Visual MINTEQ computations suggest that over the environmentally relevant pH range (7–8), most of the uranium is present as uranyl carbonate anions or uranyl calcium tris-carbonato neutral species (d in Fig. 1). In fact, across the pH range, all of the dominant species are neutral (b,c, and d) as uranyl sulfate,  $\text{UO}_2\text{SO}_4$ , at lower pHs, uranyl carbonate,  $\text{UO}_2\text{CO}_3$ , at the mid range, and uranyl calcium tris-carbonato above pH 5.5. The uranyl cation,  $\text{UO}_2^{2+}$ , becomes more important at the lower pHs (see a in Fig. 1), and this is the basis for removal of uranium from the anion exchange resins using nitric acid. Despite the speciation being predominantly neutral aqueous species, the resins still show strong uranium sorption, demonstrating that anion speciation is not necessarily needed for sorption to an anion exchange resin. More complete geochemical modeling of this system, including sensitivity and error analyses on these samples, can be found in Leavitt et al. 2010 (in review).

#### 3.2. Adsorption

All of the sorbent materials tested showed nearly complete uranium adsorption at the near neutral pH in the artificial groundwater sodium bicarbonate solutions. The GAC Ag, which had the lowest sorption at the higher concentrations as seen in Fig. 2, still sorbed an average of 89% of the uranium in solution.

Both of the Dowex resins showed very good linear sorption across the range of concentrations investigated. These resins sorbed an average of 99% of the uranium in solution. The only

difference between the resins is the mesh size, from 16 to 30 for the 21K, and around 30 (but with more uniform size) for the 21K XLT. At the examined range of uranium concentrations, there is no advantage to the smaller resin beads. Lewatit S6328 A also had a linear sorption isotherm, but with a slightly lower sorption percentage, averaging 95% with a  $K_d$  of 2000 (kg/kg) for aqueous uranium. These linear sorption isotherms are desirable over the concentration range, so the amount sorbed can easily be used to calculate mass flux.

Purolite A500 shows increased uranium sorption at higher concentrations, a pattern that is different from the other resins. Repeating the procedure for Purolite over 72 h rather than 24 h showed the same trend, with a slight increase in sorption at higher concentrations. While equilibrium had been reached for the other resins after 24 h, the Purolite resin was still sorbing uranium; an average of 94% of the uranium sorbed in 24 h, and 97% had sorbed over 72 h. This same trend was seen in sulfuric acid solutions used by Kolomiets et al. (2005). The other resins tested by this group had reached equilibrium within 25 h, while the Purolite A500 had not (Kolomiets et al., 2005). While the linear isotherm has a good  $R^2$  value (0.91), it was not a linear trend, evidenced by a trend in the residuals, which was not seen with the other resins. Using the Freundlich isotherm equation, this was confirmed with an exponent statistically greater than 1 ( $1.6 \pm 0.1$ ). Currently, we do not have a clear explanation for this phenomenon. One possibility is a surface precipitation process that could be tested using infrared or Raman spectroscopy, but this was not done in this experiment since there were other resins with simpler adsorption trends to use in the PFM.

An overview of the sorption calculations is shown in Table 3. While there could be some improvement in the  $R$  squared values and the errors on the slope for our sorption data, the errors were deemed unimportant relative to instrumental errors. With the exception of Purolite A500, each of the other sorbent materials produced Freundlich exponents near one, with only minor statistical differences. The residuals from the

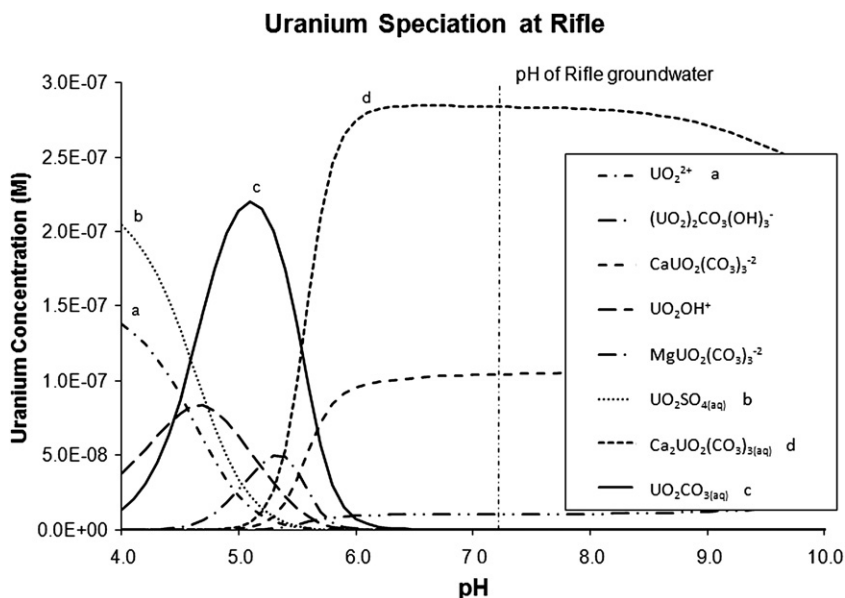


Fig. 1 – Rifle speciation modeled using Visual MINTEQ.

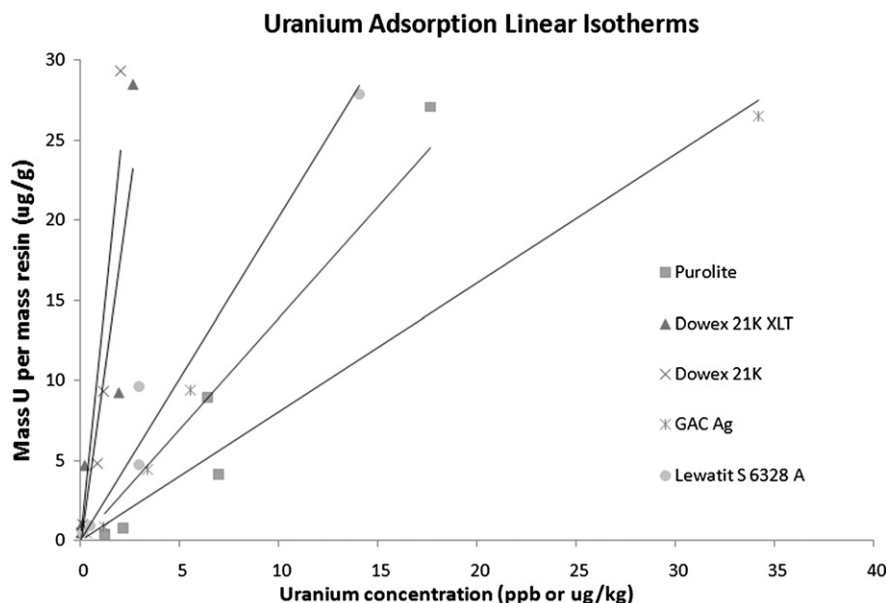


Fig. 2 – Sorption isotherms for all materials tested comparing mass uranium sorbed to the resin ( $\mu\text{g U/g resin}$ ) versus to mass uranium remaining in solution ( $\mu\text{g/kg}$ ). Each point represents an average of the three replicates with error bars omitted for clarity (values given in text). Lines indicate the linear sorption isotherm from which  $K_d$  values were calculated.

linear partition isotherms were also investigated to verify linearity and showed no trend that would indicate a deviation from linearity. Thus, the linear isotherms were presented.

When resins were tested using groundwater collected from the Rifle, CO field site, all of the anion exchange resins performed in a similar manner as in the lab experiments with quantitative sorption at 99% sorbed. This matched the sorption performance seen with Dowex resins in laboratory studies, suggesting improved sorption with all resins in natural waters. Each of the resins maintained the original groundwater pH of 7.2, with only a minor drop to 7.1 for the Dowex resins. The activated carbon did not follow the same pattern of uranium sorption in Rifle groundwater. The pH increased slightly to 7.4. It sorbed around 33% of the calcium in the water, but it removed only 5% of the uranium. This result ruled out the GAC as a sorbent choice for the field PFMs, but it could still be considered in the use of tracers for groundwater flux measurements. This work focused on U(VI) sorption since the solubility of U(IV) is so low and was not expected to influence the results. It has been suggested that

U(IV) complexation to organic ligands can increase solubility, but since the groundwater samples showed complete sorption and we are only interested in total uranium quantification, U(IV) vs U(VI) speciation was not investigated further.

At a lower pH (3.8), uranium cations dominate speciation, and so little uranium adsorption would be expected to sorb to the resins. This was not the case for the Purolite and Lewatit resins when pH was adjusted using nitric acid. With each of the other resins, much lower masses of uranium were sorbed at pH 3.8 than at neutral pH with the same bicarbonate concentrations. Purolite A500 and Lewatit S6328 A both showed the same 94–95% sorption at the lower pH. Gu et al. (2004) had examined Purolite resins and suggested that this phenomenon may be due to the concentration of nitrate on the resin surface allowing for aided uranium adsorption since the resin, has a very high affinity for nitrate anions. All of the resins have quaternary amine groups, but they suggest that the triethylamine groups have a higher affinity for nitrate than the trimethylamine groups present in the Dowex resins. In another experiment pH was lowered using HCl to test if concentrated nitrate aided uranium sorption, and very different results were obtained. As was expected with the acidic pH, there was very little uranium sorption to the resins. As an additional test to confirm this nitrate-aided sorption, we exchanged the chloride ions already present on the resins with nitrate ions by rinsing the resins in excess sodium nitrate before testing the resins for uranium sorption at the lower pH. Uranium sorption was at 12% for Lewatit and 20% for Purolite; these lower sorption results do not suggest a nitrate aided sorption. One possibility is that there might be a uranyl–nitrate complex in solution that is sorbing to the resin rather than the uranyl species sorbing to concentrated nitrates on the resin. More work is necessary to fully understand these results.

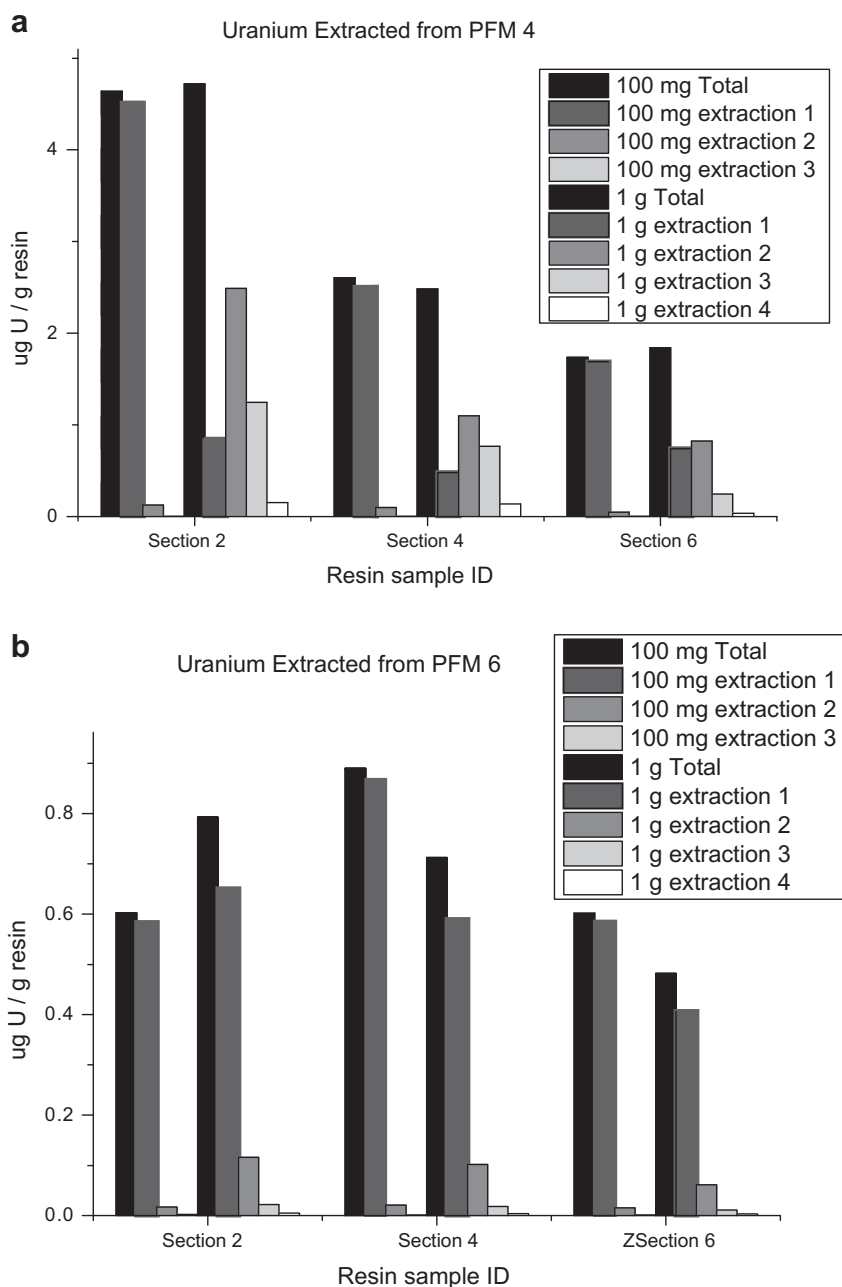
Table 3 – Results of resin sorption studies.  $K_d$  was determined from the linear slopes, and errors on those slopes are shown along with the R squared value of the linear fit.

Resin	$K_d$	Error	R squared	% Sorbed
Purolite A500	1400	160	0.91	94
Dowex 21K 1630	8800	1500	0.82	99
Dowex 21K XLT	12000	1700	0.86	99
Lewatit S6328 A	2000	70	0.97	95
GAC Ag	800	130	0.84	89

A 1% nitric acid solution (pH ~1) was effective at extracting uranium from all resins. Essentially all of the sorbed uranium was desorbed into the acidic solution. This was not the case for the GAC Ag. Repeat acid extractions as well as bicarbonate and carbonate extraction solutions were used, but only a combined, inconsistent 40–70% of the total uranium could be removed from the GAC using the different extraction solutions. This result again confirms the elimination of the GAC Ag as the sorbent of choice for the uranium PFMs since it would be nearly impossible to quantify uranium passing through the meter without a more efficient and reliable extraction method.

### 3.3. Resin choice

Based on sorption capacity, tracer studies and resin price, Lewatit S6328 A was the chosen resin for the field PFMs. GAC had been eliminated due to poor extraction recovery and lower sorption than the other resins, and Purolite was eliminated due to the unexplained sorption phenomenon at higher concentrations. Table 3 presents a summary of the results from the resin sorption tests. While the Dowex resins exhibited better uranium sorption, the price difference for the 3–4% improvement in sorption, given the lower uranium concentrations at Rifle, was deemed unnecessary for this



**Fig. 3 – a) Uranium extracted from PFM#4 and b) from PFM #6. Since Lewatit was alternated with GAC to obtain tracer information, resin samples were 2, 4 and 6 (top) in the depth sequence. The left-most bar (black) in each series represents the total uranium concentration removed from the resin after all extractions using the two different masses.**

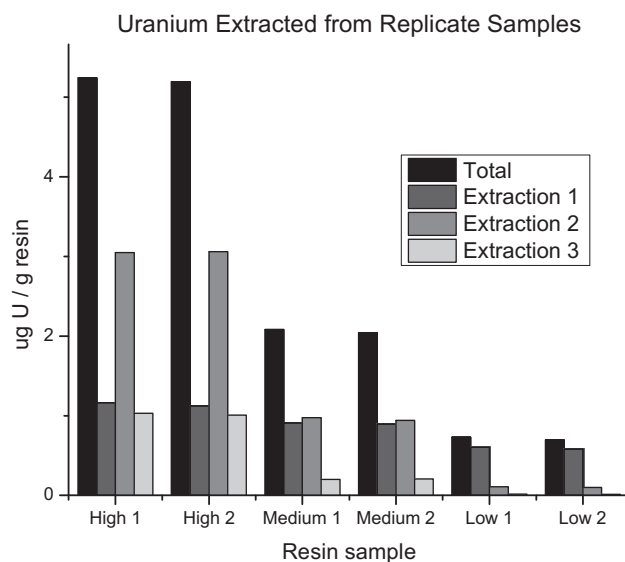
experiment, especially given the improved performance in the actual groundwater samples. If it was necessary to get more accurate flux measurements, without having to make a minor correction for incomplete sorption, either Dowex resin would be a better choice. Using this method, the greatest uncertainty a flux measurement lies in the up to 10% error of the ICP-MS, not the slight loss that may be seen by using the Lewatit resin over one of the Dowex resins. Since the resins did not reach a sorption capacity, it would be difficult to use these results to choose the best resin for use in high uranium flux contaminated sites. One consideration for testing samples is that as the U fills the strongest resin binding sites, the apparent partitioning  $K$  will change (decrease) and the actual U flux would be underestimated. However, based on the levels of U bound to the resin (Fig. 3), we are in fact well within the experimental range (Fig. 2), so this is not a problem for this work.

### 3.4. Field application

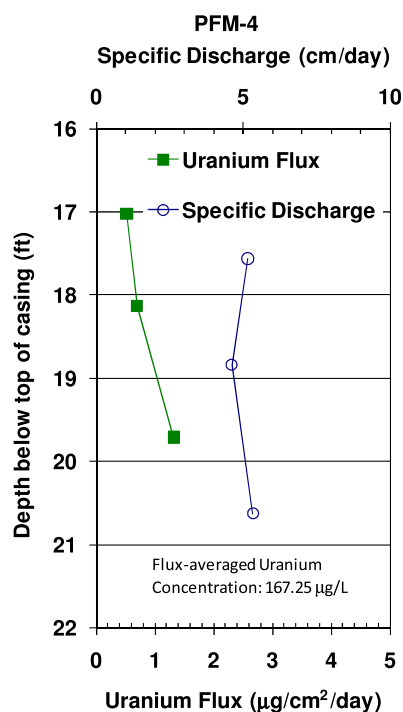
For the initial field test six PFM were deployed in six 4-inch wells. Each PFM was constructed using a new flux pod design having six alternating segments of granular activated carbon (GAC) and Lewatit resin (three pods or segments of GAC and three pods of Lewatit). The bottom segment of each PFM was GAC. The flux pods are self-contained segments of sorbent that can be stacked on a common center tube. The pods can then be retrieved individually for sampling on site or packaged for shipment to an analytical laboratory for remote sampling and analysis. The objective for using individual segments of sorbent was two-fold: to test the individual capability of the Lewatit resin to capture uranium under field conditions while using the GAC to estimate groundwater flux and to test the new modular flux pod design. This was a necessary step to test the efficiency of the Lewatit as a sorbent under field conditions. However, the alternating segment design does not allow for measurement of water flux and uranium flux at the exact same vertical location. One design modification implemented following this experiment was to develop a three-layer prototype which will allow both groundwater and uranium flux measurements at the same vertical location and mixed media sorbents are now also being tested.

The PFM were retrieved and sampled after a deployment of 23 days (approximately three weeks). Tracer analysis from the GAC segments were used for groundwater flux estimates, and the Lewatit segments were used for uranium flux estimates. For comparison and validation of PFM performance, water samples were collected in each well four days prior to PFM deployment.

Silver additions to the Lewatit resin matched the concentrations on the alternating GAC layers. Solutions decanted after silver addition indicated that the Lewatit resin had in fact been coated to 0.03% silver by weight. This prevented microbial growth on the resin while installed at Rifle. After coating with silver (98% of silver sorbed to the resin), lab experiments were conducted to ensure that the silver was not being released from the resin and uranium sorption remained the same as without added silver. Treating Rifle groundwater with the silver coated resin showed release of silver to be 0.3% of



**Fig. 4** – The results of using larger amounts of resin (4 g) and acid (40 mL) for extractions. Samples were chosen for this test based on the initial results so that a range of concentrations would be presented. High, medium and low represent the concentration/flux ranges expected from the first set of tests.



**Fig. 5** – Measured fluxes for PFM 4 showing vertical distribution of uranium mass flux and volumetric water flux (specific discharge or Darcy Velocity). The PFM flux-averaged uranium concentration for this well was 167.25  $\mu\text{g}/\text{L}$  which compares well with the aqueous uranium concentration (180.95  $\mu\text{g}/\text{L}$ ) measured in the well.



**Table 4 – Summary of uranium mass flux, volumetric water flux (specific discharge or Darcy Velocity), flux-averaged concentration for all PFM segments in all wells, and measured aqueous concentrations for all wells.**

	From Passive Flux Meter (PFM)			
	Uranium Mass Flux ( $\mu\text{g}/\text{cm}^2 \text{ day}$ )	Specific discharge (Darcy Velocity) ( $\text{cm}/\text{day}$ )	Flux averaged uranium concentration ( $\mu\text{g}/\text{L}$ )	Measured aqueous uranium concentration ( $\mu\text{g}/\text{L}$ )
Minimum	0.13	2.27	57.62	171.00
Maximum	3.57	6.83	615.31	192.30
Standard Deviation	0.84	1.38	140.31	8.84
Mean	0.13	5.00	188.43	180.63

Sample size (n) for each data set: For PFM: n = 3 PFM segments (samples) per 6 wells = 18, For aqueous samples = n = 1 sample per 6 wells = 6.

the sorbed silver and 99% of aqueous uranium sorbed to the resin, which is unchanged from the sorption to resin with no silver addition, making it suitable for use at the field site. We are unsure of the mechanism by which  $\text{Ag}^+$  sorbs to an anion exchange resin, perhaps it is related to the matrix material. A complete understanding of this was not necessary, however, since we were only interested in just adding it for an antimicrobial purpose that would not interfere with uranium sorption.

Uranium was extracted from the resins taken from the Rifle PFMs by the same 1% nitric acid solution used for lab studies. As mentioned before, small quantities of resin were compared to a larger sample to determine homogeneity in sample and method during the first sampling trips. Fig. 3 shows the results of the multiple extractions. If the samples are homogeneous, the final total concentration of uranium extracted from both quantities of resin should be the same. There were some minor discrepancies that can be attributed to either ICP-MS error or sample heterogeneity. PFMs that were exposed to higher water and uranium fluxes were more likely to have a homogeneous composition of uranium on the resin (totals match in Fig. 3a). Lower flows yielded locally concentrated uranium in the PFM on the upgradient side and were more difficult to completely homogenize leading to inconsistent concentration values in samples less than 1 g (see Fig. 3b). Using a large quantity of resin, or the whole sample for the extraction, will improve the accuracy of the uranium masses used for flux calculations. Samples were reanalyzed using the 4 g/40 mL method listed, and replicate samples showed excellent reproducibility with a maximum difference between replicates of 5%, even at the lower concentrations of uranium (Fig. 4). All samples from subsequent trips were analyzed in this manner. Future PFM design may examine water flow direction (which changes with the river water stage) by cross-sectional quartering of samples. This may also be useful for samples with localized concentrated uranium.

### 3.5. Summary of field results

Observed variations and trends in measured fluxes were consistent amongst wells and similar to the results provided for PFM 4 in Fig. 5, which shows the vertical distribution of uranium mass flux and volumetric water flux (specific discharge). It can be observed that vertical trends in uranium

flux tend to agree with water flux, and the resulting flux-averaged concentration for this well (167.25  $\mu\text{g}/\text{L}$ ) compares favorably with the aqueous concentration measured in the well (180.95  $\mu\text{g}/\text{L}$ ).

Table 4 provides a summary of uranium mass flux, volumetric water flux (specific discharge), flux-averaged concentration for all PFM segments, and measured aqueous concentrations. The summary provides a comparison of flux-averaged uranium concentrations estimated from all PFM segments across all wells to aqueous uranium concentrations measured in each well. One key point to observe is the similarity of mean concentrations while noting the larger standard deviation for PFM-based flux-averaged estimates. This is because the aqueous concentrations represent the volumetric average within the entire borehole, while the flux-averaged concentrations show much higher resolution with respect to variation with depth (as shown in Fig. 5). The similar mean values for flux-averaged and measured aqueous uranium concentration provides a positive validation for PFM measurement of uranium flux while also providing additional detail with regard to the vertical variation of flux within the well and surrounding formation.

As seen in Fig. 3a, when larger resin samples were extracted for uranium, the second extraction removed the most uranium, whereas the smaller resin amounts demonstrated expected extraction patterns, with the most uranium removed in the first extraction and less in each subsequent extraction. This pattern was seen only in the first sampling trip in samples with high uranium fluxes. This is possibly due to high concentrations of organics binding to the resin and preventing release of uranium in the first extraction. To determine other anions sorbed to the resin and possible desorption interferences, a larger resin sample and volume of acid were used to have sufficient volume for both ICP-MS and ICP-AES analyses. This larger volume also saw better consistency in low flux samples and was used for all future extractions. It was also observed that significant sulfate was removed, with less in each subsequent extraction. Based on the acid strength and nitrate concentration, there were still enough exchangeable nitrate anions to remove all uranium and sulfate together, even with the 2:1 nitrate:sulfate molar charge ratio, supporting the theory that organics are binding and blocking the sites. However, if the binding strength of sulfate to Lewatit resin is much higher than that of nitrate, an excess of 5 times as many exchangeable ions of nitrate to

sulfate may not have been sufficient, also contributing to the pattern of uranium removal.

#### 4. Conclusions

Anion exchange resins provide an effective material for use in a passive flux meter under the water chemistry conditions at the old mill site in Rifle, CO. The Dowex 21K resins had the highest uranium sorption capacity, but are more costly than some of the other resins (i.e. Lewatit) which have sufficient uranium sorption for this purpose and concentration range. Despite geochemical computations indicating mostly neutral uranium species, anion exchange resins were very useful as uranium sorbents. These resins may be good for anionic and neutral species, but more work is needed to understand the sorption mechanisms and speciation covering a larger pH range. Coating the resins with silver nitrate does not affect uranium sorption, and it prevents microbial growth on the resins which could negatively impact the flux measurements and concentrations obtained. PFM's that were placed in high flux areas at the Rifle field site allowed for simple, reliable flux measurements due to homogeneity in the resin samples removed from the PFM; uranium passed through the whole PFM. At sampling locations where uranium fluxes were low the mass of extracted uranium was much more variable from small resin samples and therefore contributed to the error in the flux calculations. When homogenization was incomplete, some of these small resin samples were taken from the upgradient side with more uranium and others were from the downgradient side with little, if any, uranium. The best extraction method found for good reproducibility with sufficient sample size and minimal waste uses 40 mL of a 1% nitric acid solution and 4 g of resin. This finding will be useful in future PFM applications to quantify uranium mass contaminant fluxes in groundwater.

Results from an initial field experiment demonstrated that calculated flux-averaged uranium concentrations compared well with measured aqueous uranium concentrations under field conditions, which provided positive validation for use of ion exchange resins for quantifying uranium flux. Ultimately, these flux measurements will provide insight into the mobility of uranium and effectiveness of current remediation strategies employed at the contaminated former mill site in Rifle, Colorado.

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