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Magnetic iron oxide and manganese-doped iron oxide nanoparticles for the collection of alpha-emitting radionuclides from aqueous solutions

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Abstract

Magnetic nanoparticles are well known to possess chemically active surfaces and large surface areas that can be employed to extract a range of ions from aqueous solutions. Additionally, their superparamagnetic properties provide a convenient means for bulk collection of the material from solution after the targeted ions have been adsorbed. Herein, two nanoscale amphoteric metal oxides, each possessing useful magnetic attributes, were evaluated for their ability to collect trace levels of a chemically diverse range of alpha emitting radioactive isotopes (polonium (Po), radium (Ra), uranium (U), and americium (Am)) from a wide range of aqueous solutions. The nanomaterials include commercially available magnetite (Fe_3O_4) and magnetite modified to incorporate manganese (Mn) into the crystal structure. The chemical stability of these nanomaterials was evaluated in Hanford Site, WA ground water between the natural pH (~8) and pH 1. Whereas the magnetite was observed to have good stability over the pH range, the Mn-doped material was observed to leach Mn at low pH. The materials were evaluated in parallel to characterize their uptake performance of the alpha-emitting radionuclide spikes from ground water across a range of pH (from ~8 down to 2). In addition, radiotracer uptake experiments were performed on Columbia River water, seawater, and human urine at their natural pH and at pH 2. Despite the observed leaching of Mn from the Mn-doped nanomaterial in the lower pH range, it exhibited generally superior analyte extraction performance compared to the magnetite, and analyte uptake was observed across a broader pH range. We show that the uptake behavior of the various radiotracers on these two materials at different pH levels can generally be explained by the amphoteric nature of the nanoparticle surfaces. Finally, the rate of sorption of the radiotracers on the two materials in unacidified ground water was evaluated. The uptake curves generally indicate that equilibrium is obtained within a few minutes, which is attributed to the high surface areas of the nanomaterials and the high level of dispersion in the liquids. Overall, the results indicate that these nanomaterials may have the potential to be employed for a range of applications to extract radionuclides from aqueous solutions.

1 Introduction

Micro- and nanoscale magnetic particles have attracted great interest in the fields of analytical chemistry, waste water treatment, catalysis, biochemistry, and medicine.^{1–6} The combination of chemically active surfaces and magnetic susceptibility facilitates analyte capture and particle collection, respectively. Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) and magnetite (Fe_3O_4) are the most frequently employed magnetic nano-materials, and have the advantages of being widely available and composed of nontoxic elements. They are often surface functionalized or incorporated into other microscopic solids to achieve desired chemical and physical traits, many of which have been recently reviewed.^{1,4–8}

Magnetite, along with other iron oxide minerals, has reactive surfaces and can be used as an extracting agent for a range of ions and molecules in solution.^{3,9–11} Magnetic nanoparticles (MNPs) have the added advantage of possessing very high surface areas. This, combined with their reactivity and ability to be fully suspended in aqueous media, assures fast reaction kinetics and good sorption capacities.³ Magnetite nanoparticles possess superparamagnetic behavior; subsequent to analyte sorption, the MNPs can be efficiently collected from solution *via* the application of an external magnetic field.

Within the past decade, sorbent materials containing MNPs within their cores have been explored. Feraheme®, a magnetite NP coated with polyglucose sorbitol carboxymethylether, is used intravenously to treat anemia. However, recent new applications have been reported in the use of Feraheme® as a carrier for the diagnostic radionuclides ^{64}Cu , ^{89}Zr , and ^{111}In in PET/MRI.^{12,13} MNPs have been functionalized with crown ethers through a silanization process.¹⁴ Using this method, Mesnic *et al.* functionalized 18-crown-6 ether onto MNPs and demonstrated the uptake of ^{226}Ra from solutions of NaCl , NaClO_4 , and picric acid.¹⁵ Additionally, MNPs have been coated with polymers and then treated with 18-crown-6 crown ether to form extraction chromatographic resins with magnetic properties; these materials have been evaluated as a means of collecting ^{90}Sr from various sample matrices.^{16–18} Much work has been conducted in the use of mesoporous silica containing entrained magnetic iron oxide NPs to form nanocomposites that are used in the capture of metals^{19–21} and uranium.^{22,23} Recently, MNPs treated with various chelators for actinide extraction were reviewed.⁷

Another metal oxide, manganese dioxide (MnO_2), has been used to extract a range of toxic elements^{3,24,25} and radionuclides^{26–29} (particularly radium^{30–34}) from aqueous media for decades. Its use spans the fields of analytical chemistry and drinking water, waste water, and mine water treatment. Chemical alteration of the magnetite nanoparticles (Fe_3O_4 NPs) with Mn can have a dramatic effect on the chemical properties of the material, while maintaining the useful magnetic attributes.³⁵ Conversely, Bartos and Bilewicz demonstrated a change in MnO_2 analyte uptake behavior by incorporating Fe into the crystal structure.³⁶

Warner *et al.* reported Mn-doped magnetite nanoparticles (Mn-doped Fe_3O_4 NPs) for purposes of heavy metal extraction from aqueous solutions.²⁴ They found that although the particle size and surface area of the starting Fe_3O_4 nanoparticles did not change considerably following the oxidative Mn doping process, the magnetic properties of the doped material

were altered. This appears to be due to the oxidative doping process removing Fe^{3+} ions from the lattice and incomplete replacement with the larger radius Mn^{2+} ions, resulting in a more disordered structure and subsequent decrease in magnetic strength. This observation was further corroborated by XRD data that showed increasing unit cell constants with increasing Mn^{2+} dopant concentration. However, even at the highest dopant concentration (~14%), the $\text{Mn-Fe}_3\text{O}_4$ was still strongly paramagnetic and easily recovered when placed near an external magnetic field. O'Hara *et al.* explored the use of MNPs (unmodified Fe_3O_4 NPs and the Mn-doped Fe_3O_4 NPs synthesized by Warner *et al.*) in the collection of alpha-emitting radionuclides (^{210}Po , ^{226}Ra , ^{233}U , and ^{241}Am) from human urine at its natural pH and at pH ~2.²⁷ Additionally, they demonstrated a simplified and fast *in vitro* radiobioassay method wherein the MNPs were used to scavenge radionuclides from urine prior to magnetic capture, dissolution of the concentrated MNPs, and subsequent counting source preparation for alpha energy spectroscopy (AES). More recently, members of this research team explored the use of Fe_3O_4 , Mn-doped Fe_3O_4 , and other metal oxide sorbent structures for the collection of U from seawater.³⁷

The Mn-doped Fe_3O_4 NPs described above are distinguished from a prior material, in which micron-sized Fe_3O_4 and MnO_2 were co-mingled to form a composite solid;³⁸ this work by Towler and co-workers represents what is likely the first use of magnetic media in radioanalytical chemistry. This team evaluated the uptake of the naturally occurring radionuclides ^{226}Ra , ^{210}Po , and ^{210}Pb from 1.75 L seawater solutions by evaluation of the percent recovery of the spiked radiotracers ^{133}Ba , ^{208}Po , and stable Pb, respectively. From ~40 L ocean water samples, the authors reported activity concentrations for ^{226}Ra and ^{210}Pb in the range of ~1–2 Bq m^{-3} (^{210}Po activity was not reported).

Building on previous work, this research team reports the sorption behavior of a suite of natural (Po(IV) , Ra(II) , U(VI)) and man-made (Am(III)) alpha-emitting radionuclides on Fe_3O_4 and Mn-doped Fe_3O_4 NPs across a range of naturally occurring aqueous matrices (river water, ground water, seawater) and human urine. Urine was selected as a complex biological fluid with relevance to routine or emergency *in vitro* radiobioassay applications.^{39–41} The four alpha-emitting radionuclides chosen for this study possess an array of different valence states and chemical complex formation across the different aqueous solutions and varied pH.

This research effort provides new information on Fe_3O_4 NPs and Mn-doped Fe_3O_4 NPs by exploring the performance of these materials for radionuclide collection from a range of aquatic matrices. This study correlates analyte sorbent performance with the surface chemistry of the nanoparticles and the chemical speciation of the radionuclides. Specifically, we report on (1) the chemical stability of the nanomaterials at different solution acidities, (2) the amphoteric nature of the nano-materials as solution pH is varied, (3) the rate of uptake of the radionuclides onto the nanomaterial suspensions, and (4) the degree of sorption of select trace level radionuclides across a pH range. The results indicate sometimes dramatic differences in the chemical and analyte sorption behavior between the two nanomaterials. In all experiments, the magnetic properties inherent to these MNPs were employed to perform good separation of the solid phase from the solution. In general, it was observed that the degree of analyte sorption could be explained by the surface charge of the nanomaterials *vs.*

the anticipated analyte speciation at a given pH. The results of this effort show that the MNPs under evaluation can be effective for the collection of alpha emitting radionuclides from aqueous solutions. With the high chemical affinities and rapid sorption rates demonstrated herein, these MNPs could be used in a wide range of applications, including analytical or forensic chemistry, waste water treatment, environmental remediation, solution phase mineral recovery, *in vitro* bioassay, and therapeutic or diagnostic medical treatments.

2 Experimental

2.1 Reagents and materials

All reagents used in this study were reagent grade unless otherwise specified. Hydrochloric acid (37%, Fisher Scientific) and sodium hydroxide (pellets, Fisher Scientific) working stock solutions were prepared as dilutions into deionized water (18MΩ cm) using a Barnstead E-Pure water purification system (Dubuque, IA). Iron(II,III) oxide nanoparticles (Fe₃O₄ NPs) were purchased from Sigma-Aldrich (St. Louis, MO). Manganese doped Fe₃O₄ NPs were prepared from this stock material by the method described by Warner *et al.*²⁴ Scintillation cocktail was Ultima Gold AB (PerkinElmer, Waltham, MA). Radiotracers were obtained by the following suppliers: ²¹⁰Po and ²⁴¹Am from Eckert & Ziegler Isotope Products (Valencia, CA); ²²⁶Ra from an in-house supply; ²³³U from the National Institute of Standards and Technology (Gaithersburg, MD).

2.2 Chemical and physical characterization of MNPs

Chemical composition: the Fe fraction of the Fe₃O₄ NPs was determined by first dissolving a known mass in hydrochloric acid followed by analysis of Fe by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using a PerkinElmer Optima 5300. The ratio between the dissolved Fe mass and the mass of Fe₃O₄ initially dissolved in HCl was calculated as the Fe mass fraction (g Fe/g Fe₃O₄). The Fe and Mn fractions within the Mn-doped NPs were determined using the same approach.

Surface area: nitrogen adsorption-desorption isotherms were measured at −196 °C on an AUTOSORB-IQ₂ (Quantach-rome Instruments, Boynton Beach, FL) gas sorption analyzer. Prior to measurements, the samples were degassed at 280 °C for 5h under high vacuum. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method and the pore size distributions were estimated by the Barrett-Joyner-Halenda (BJH) method using the desorption branch.

Particle size distribution: particle size distribution (PSD) of the particles was determined by scanning transmission electron microscopy (STEM) using a FEI Titan 80–300 (Hillsboro, OR) operating at 300 keV. Initially, a suspension of MNPs was formed in water and drop-cast onto carbon and Formvar coated copper grids prior to imaging. Transmission electron microscope (TEM) and scanning transmission electron microscope (STEM) images of the materials used in this study were presented by O'Hara *et al.*²⁷ and Warner *et al.*,²⁴ respectively.

Magnetic susceptibility: magnetometry of the MNPs was carried out on a vibrating sample magnetometer (Model 7404, Lake Shore Cryotronics, Inc., Westerville, OH). Samples were

sealed in Kapton® tubes, and measurements were performed at room temperature with a field strength of 1 T.

Surface polarization: the surface charge of the two amphoteric MNP materials in Hanford ground water (HGW) between natural pH (~8) and pH 2.5 was revealed by potentiometric titration. In order to obtain a reference titration curve for the HGW sample, several titrations ($n = 6$) were performed on 40 mL aliquots *via* sequential 10 μ L additions of 0.096 M HCl (acid additions were spaced 60 s apart) performed using an autotitrator (950 Titrando, Metrohm, Riverview, FL) until pH 2.5 was obtained. Additionally, two masses (21.0 and 39.6 mg) of Fe₃O₄ NP and two masses (24.1 and 40.5 mg) of Mn-doped Fe₃O₄ NP stocks were added to 40 mL HGW volumes, and additional titrations were performed. The MNP + HGW solution titrations were interspersed between the HGW only solution titrations. Solution mixing *via* the titrator's impellor assured good suspension of the MNPs during the titration. In order to visualize the proton interactions with the MNPs, the pH_{MNP+HGW} titration data was plotted against the mean pH_{HGW} data.

2.3 Aqueous sample matrices

Various natural water solutions, as well as human urine, were utilized as matrices for batch uptake experiments. Columbia River water (CRW) was collected north of Richland, WA. Uncontaminated Hanford, WA ground water (HGW), originating from an unconfined aquifer, was pumped from well 699–49-100C at the Hanford Site, WA. Seawater (SW) was collected from Sequim Bay, WA. Human urine was provided within 48 h of experimental use.[‡] Some properties of each aqueous matrix are listed in Table 1. Water conductivity was determined using a General Electric Conductivity Monitor (Pittsburgh, PA), which was calibrated with certified KCl solutions. Solution pH was determined using an Accumet Excel XL15 pH meter (Fisher Scientific, Pittsburgh, PA), calibrated with certified pH buffer standards. Solution alkalinity of unpreserved samples was determined as CaCO₃ equivalent *via* a Metrohm Titrando titrator.

Prior to use, room temperature water samples (water was not chemically preserved, and was in equilibrium with the atmosphere) were filtered to 0.45 μ m using a 47 mm diameter Type HA membrane filter (Millipore, Billerica, MA). Filtration eliminated biota and the majority of suspended organic and inorganic solids that could complicate the sorbent/analyte interactions. Urine was not filtered. Samples were spiked with radiotracers, allowed to equilibrate for ~1 h, and then pH adjusted with HCl. See Section 2.6 for more experimental detail. Final radiotracer spike concentrations are shown in Table 2.

2.4 Chemical stability of MNPs

The chemical stability of the two MNP materials was evaluated as a function of pH for three contact time intervals: 1, 4, and 24 h. Along with chemically unmodified HGW (pH ~8), solutions of HGW were pH adjusted between pH 1 and 7 with HCl. Fe₃O₄ and Mn-doped

[‡]The samples were obtained from anonymous sources, having originally been supplied to the laboratory's dosimetry department for use in routine radiological worker bioassays. Sample volumes in excess of that required for worker monitoring were provided for this study. As such, specific consent and ethical approval from the donors was not required, as use of the samples did not fall under the PNNL Human Research Protection Program.

Fe₃O₄ NP suspensions of 10 mg mL⁻¹ were freshly prepared in DI water, then 0.25 mL of each suspension was spiked into 2 dram contact vials that each contained 4.75 mL of the pH-adjusted ground water solution; the resulting suspensions had a MNP concentration of 0.5 mg mL⁻¹. Samples were placed on an orbital shaker (150 rpm) for the appropriate time interval. Following the contact interval, the MNPs were magnetically separated from the solution (see Section 2.6 for magnetic separation details), and the resulting clear solutions were sampled and analyzed by ICP-OES (PerkinElmer Optima 5300) for determination of dissolved Fe and Mn concentrations. From these dissolved metal concentrations, the dissolved mass fraction for each metal was determined as the ratio of dissolved metal mass vs. the total metal content in the MNPs present in each experiment.

2.5 Sorption rate determination

The sorption rates of the radiotracers were determined in chemically unmodified HGW. The experimental conditions were identical to those described in Section 2.6, except that the contact times were varied between 30 s and 8 h, instead of being fixed at 4 h. Each data point is the result of an individual contact experiment performed for that specific contact duration.

2.6 Measuring the affinity of α -emitting radionuclides onto Fe₃O₄ nanoparticles

The affinities of several α -emitting radionuclides were evaluated in two sets of experiments: first, the uptake of the radiotracers was evaluated across a range of HGW samples that were pH adjusted between ~1 and natural (pH ~ 8). This provided an uptake curve of each radionuclide in HGW as a function of pH. Next, the following matrices were evaluated only at pH ~ 2 and natural pH: CRW, SW, and urine.

Measured volumes of the various aqueous matrices (sufficient volume to utilize in all batch contact experiments) were delivered into polyethylene bottles and were then placed into a radiological zone. Each bottle was then spiked with the appropriate radiotracer and allowed to equilibrate in the aqueous matrix for ~1 h on an orbital shaker (~150 rpm). Radiotracer concentrations were below the solubility limits of oxide/hydroxide species (Table 2). After the equilibration period, the samples that required it were pH adjusted with HCl, and the samples were allowed to equilibrate for 1–2 h.

Following the pH adjustment, the spiked matrix was sampled and analyzed for verification of starting activity concentration (see Table 2). Outside of the radiological zone, a series of 2 dram vials (borosilicate or polypropylene) were loaded with a known volume of a concentrated MNP suspension (10 mg mL⁻¹) that was freshly prepared in DI water, briefly sonicated, and then vigorously shaken. Complete dispersion of the MNPs into the solution was observed. No stabilizing ligands or surfactants were used. The vials were then transferred into the radiological zone, where the spiked and pH-adjusted aqueous solutions were dispensed into the vials. Final solid/liquid (S/L) ratios for MNPs in solution were either 0.1 or 0.5 mg mL⁻¹. Contact samples were prepared in triplicate. In addition, control experiments (sans MNPs), run in triplicate, were prepared for each experimental condition. Each sample vial was capped, immediately shaken, and then placed on an orbital shaker (~150 rpm) for approximately 4 h. At the end of the contact interval, the samples were

unloaded from the shaker and placed on top of rare earth magnets (cubic NdFeB, 1.27 cm per side, ~4600 surface Gauss) for approximately 5 min. During this time, the suspended MNPs were observed to be pulled to the bottom of the vessels, resulting in clear solutions (see TOC image for an example of a MNP suspension in ground water and an identical solution following magnetic removal of the MNPs).

After magnetic draw-down of the MNPs from the bulk contact solutions, 2 mL of each contact solution was analyzed to determine the degree of uptake of tracers onto the MNPs. For ^{210}Po and ^{233}U , 2 mL of solution was delivered to plastic 20 mL LSC vials containing 15 mL of Ultima Gold AB. These solutions were homogenized and then counted on a liquid scintillation analyzer (Tri-Carb 3100TR, PerkinElmer). For ^{241}Am and ^{226}Ra , 2 mL of solution was transferred to polypropylene test tubes and analyzed using a Wizard 1470 automatic gamma counter (PerkinElmer, Waltham, MA) that contains a well-type NaI(Tl) scintillation detector. Americium-241 count rates were monitored using the 59.5 keV (35.9%) gamma emission; ^{226}Ra was monitored by its 189.2 keV (3.64%) emission.⁴² Because ^{226}Ra progeny was likewise present in the post-contacted solutions, the 189.2 keV peak needed to be deconvolved from gamma emissions of similar energies.

Distribution coefficient (K_d) and percent sorption ($S\%$) values were calculated from the analyzed post-contact solution and reference solution activity values using the following equations,

$$K_d = \frac{(C_i - C_f) V}{C_f M} \quad (1)$$

$$S\% = \frac{C_i - C_f}{C_i} \times 100 \quad (2)$$

where C_i and C_f are the radiotracer concentrations measured in solution before and after MNP sorbent addition, respectively. V is the contacted volume and M is the mass of MNPs.

3 Results and discussion

3.1 Physical and chemical properties of the MNPs

3.1.1 Physical properties and chemical composition.—Some physical and chemical properties of the two MNP materials were evaluated, and are reported in Table 3. Surface areas for the two MNPs were measured at $42 \text{ m}^2 \text{ g}^{-1}$, while the mean particle sizes were measured at $\sim 30 \text{ nm}$. The magnetic susceptibility of the chemically treated Mn-doped Fe_3O_4 particles were measured at 46 emu g^{-1} , a value roughly half that of the unmodified Fe_3O_4 . This $\sim 2\times$ reduction in magnetic susceptibility was likewise observed with other Mn-substituted iron oxide nanoparticles.^{24,35} Despite the lower magnetic susceptibility, Mn-doped Fe_3O_4 suspensions were quickly cleared from solution with the use of a small rare earth magnet possessing ~ 4600 Gauss at the surface.

3.1.2 Surface polarization.—The interaction of H^+ ions between the MNPs and the HGW solution matrix was observed by evaluating the differences in potentiometric titration curves between a series of reference titrations (HGW) and titrations whereby each MNP was suspended in the HGW immediately prior to initiation of the acid titration. Fig. 1 shows MNP + HGW pH curves plotted against the pH curve of the reference HGW solution for Fe_3O_4 (A) and Mn-doped Fe_3O_4 (B) NPs, respectively.

Surface polarization of amphoteric metal oxides with acidic and basic solutions can be represented as the following, where the point of zero charge (pzc) is obtained by potentiometric titration of the solid/liquid suspension vs. the liquid,^{6,11,43–45}

where $\equiv MeOH_{ave}$ represents a distribution of the three species such that the overall gross charge of the material in solution is neutral. The pzc, or isoelectric point (iep), for Fe_3O_4 is around pH 6.25–7.1,^{10,46–48} while that for MnO_2 is significantly lower, between pH 2.3–5.9,^{44,45,47–50} depending on its crystallographic structure.⁵¹ Mixed metal oxides, as in the case of the Mn-doped Fe_3O_4 , would generally be expected to have an iep between that of the two pure crystalline species. Determination of the pzc is, however, almost always performed using a simple, non-buffering and non-complexing salt solution (*e.g.*, alkali salts of nitrate, chloride, or perchlorate).⁴⁷ Of interest here was the surface interaction of the MNPs in the complex HGW matrix across a pH range.

The Fe_3O_4 trace ($\square$) indicates that virtually no proton interaction occurs with the solids until the pH drops below 7. Above this point, the titrant neutralizes the alkaline ions in the HGW at the same rate as the reference solution. Presumably, surface hydroxyl groups are predominant in this region, as the presence of MNPs has no effect on pH. Between pH 7 and ~3.5, the titration curve for the MNP + HGW mixture deviates to the positive side (*i.e.*, higher pH) of the reference HGW titration. A shallow slope is observed between a pH_{HGW} range of ~7–4.4; the NP surfaces are absorbing protons in this region, creating a transition to $\equiv MeOH_{ave}$ surface sites. Below the coordinate (4.4, 5.8) [mixed MNP-HGW:HGW], the surface hydroxyl groups of the Fe_3O_4 become predominantly protonated.

In contrast, the MNP + HGW titration plot for the Mn-doped Fe_3O_4 is markedly different ($\circ$). The curve indicates a low slope region between the coordinates (6.7, 5.8) and (3.7, 4.9), and a pzc at pH 5.4. Between pH ~8 and the upper coordinate, the pH drops more rapidly in the MNP + HGW mixture than with the HGW alone. It is postulated that the negatively-charged Mn-doped Fe_3O_4 sorbed a measurable amount of the native cations from the HGW solution, thus facilitating $H^+/(HCO_3^-/CO_3^{2-})$ interactions and causing the pH curve to drop more rapidly compared to the reference HGW solution. Between the two coordinates, pH is minimal. As more protons are delivered to the system, sorbed cations are desorbed and the surface hydroxyl groups start to become $MeOH^0$ and $MeOH_2^+$ forms. Below the lower coordinate, the Mn-doped Fe_3O_4 MNP surface hydroxyl groups become increasingly protonated $MeOH_2^+$.

3.1.3 MNP chemical stabilities.—The chemical stability of the MNPs was evaluated in HGW between pH ~ 1 and ~8. Contact times for each solution/MNP combination were for 1, 4, and 24 h. Fig. 2A shows the Fe concentrations resulting from the Fe₃O₄ contacts. Leaching of Fe into the acidified HGW solutions was evident at pH ~ 1 and, to a limited extent, at pH ~ 2. No measurable Fe leaching was evident at and above pH 3. Fig. 2B and C show the chemical leaching data for the Mn-doped Fe₃O₄. Surprisingly, this material exhibited approximately 10 times less leaching of Fe at pH ~ 1 when compared to the unmodified Fe₃O₄, with no observed Fe in solution at pH ~ 2. In comparison, Mn exhibited much higher solubility in the pH ~ 1 and ~2 solutions. Mn also showed a definite solubility trend that decreased as the pH rose to the natural HGW level of ~8. Additionally, the acid leaching data provided dissolution rates. The Fe₃O₄ dissolution rate at pH ~ 1 was 0.86 ppm h⁻¹ ($R^2 = 1.000$); the Mn-doped Fe₃O₄ dissolution rates for Fe and Mn at pH ~ 1 were 0.066 ($R^2 = 1.000$) and 0.49 ($R^2 = 0.996$) ppm h⁻¹, respectively.

The dissolved Fe and Mn concentrations shown in Fig. 2 are expressed as the percent of total dissolved Fe and Mn present in the MNP additions in Table 4. Here, it is shown that the percentage of dissolved Fe in Fe₃O₄ has a maximum at pH ~ 1 and 24 h contact time (6.3%). For the Mn-doped Fe₃O₄, dissolved Fe under all conditions is <1%. However, the percentage of solubilized Mn is substantially higher, and approaches 20% to 30% at pH ~ 1 between a 1–24 h contact time, respectively. Leaching of Mn was almost as severe at pH ~ 2, but dropped off significantly at pH ~ 3.

3.2 Radiotracer sorption rate and pH dependence for Hanford ground water

The rate of uptake of α -emitting radionuclides was evaluated in chemically unmodified HGW for each of the two MNP compositions (Fig. 3). The MNP solid/liquid (S/L) ratio was 0.5 mg mL⁻¹. Uptake of Po and Am on Fe₃O₄ NPs was rapid, with Po and Am equilibrating with the MNPs within ~5 min and ~30 s, respectively. Radium uptake was measurably slower, demonstrating an immediate uptake of ~50%, followed by gradually increasing uptake over the next several hours. Uranium appeared to have virtually no affinity for Fe₃O₄ NPs. Ra, U, and Am, however, had rapid and nearly complete uptake onto Mn-doped Fe₃O₄ NPs within just a few minutes of contact; Po uptake was quantitative within ~2 min. U uptake by Mn-doped Fe₃O₄ NP was >80% from spiked HGW at all contact times.

Next, the radiotracer-spiked HGW matrix was pH adjusted with HCl to a range from natural pH (~8) down to pH ~ 1, with samples prepared at each integer value in this range. Batch contacts were performed at each pH for each radiotracer at a S/L ratio of 0.5 mg mL⁻¹. The contact time for all experiments was fixed at 4 h to accommodate for the slow uptake of ²²⁶Ra observed with Fe₃O₄. Fig. 4 shows the uptake curves for Fe₃O₄ and Mn-doped Fe₃O₄ NPs, expressed as S%; each curve is discussed below.

3.2.1 Polonium.—Polonium exhibited high affinity for both Fe₃O₄ and Mn-doped Fe₃O₄ over the entire pH range evaluated. In ground and seawater, Po(IV) is found as a soluble species and is bound onto particulate matter.^{52,53} Wei and Murray have suggested that colloidal phases in water are important in scavenging Po.⁵⁴ Waters high in Fe, Mn, and humic substances are known to drive Po onto particulate matter.^{53,55,56} Towler *et al.* showed

quantitative uptake of Po onto manganese dioxide coated magnetite in spiked seawater.³⁸ Polonium(IV) forms a suite of hydrolysis products, even under acidic conditions.^{57–59} Suganuma and Hataye have defined Po hydrolysis products at pH 0, 1, 2, 3, and 6 in 1.0 M (H, Na)Cl solutions.⁵⁸ They have identified several negatively charged tetraivalent $\text{Po}(\text{OH})_x\text{Cl}_y^{z-}$ species between pH 0 and 3, and the fully hydrolyzed $\text{Po}(\text{OH})_4^0$ at (and presumably above) pH 6. Given the presence of protonated metal hydroxyl surfaces on both Fe_3O_4 and Mn-doped Fe_3O_4 under low pH conditions, and the net negative charge of the Po hydrolysis species, sorption is expected to occur in this range, as was observed. With increasing pH, the complete hydrolysis of Po lends itself to adsorption onto the MNPs, possibly *via* incorporation of $\text{Po}(\text{OH})_4^0$ onto hydroxyl sites on the MNP surface or alternatively co-precipitation onto the solid phase.

3.2.2 Radium.—Radium displayed strong sorption on Fe_3O_4 above pH ~ 3. As an alkaline earth element, Ra^{2+} has little tendency to form hydrolysis species. Therefore, its sorption onto Fe_3O_4 is likely determined by the surface charge of the MNP. Indeed, the transition between $\equiv\text{MeOH}_2^+$ and $\equiv\text{MeOH}_{\text{ave}}$ occurs around pH 4.4 (Fig. 1A). Below this point, the net surface charge of the MNP is positive, and thus sorption does not occur; above this point, anionic $\equiv\text{MeO}^-$ binding sites begin to form which attract cations such as Ra^{2+} .

In comparison, Mn-doped Fe_3O_4 exhibited significantly higher Ra uptake across the pH range ~4–8, and the uptake did not drop to near zero at pH 3, as was observed with Fe_3O_4 NPs. Rather, high Ra binding was observed down to pH ~ 1. Based on the acid titration curve for the Mn-doped Fe_3O_4 (Fig. 1B), it was anticipated that the Ra sorption curve would be shifted to the left due to the lower pH at which the $\equiv\text{MeOH}_2^+$ species appears to dominate. However, the binding model based on the metal hydroxyl species distribution presented in eqn (3) does not seem to explain the mechanism for Ra^{2+} binding at pH ~ 2.5 (the point at which the MNP + HGW and HGW pH curves intersect in Fig. 1B).

Nevertheless, Bartos and Bilewicz observed high binding affinities for Ra onto α - MnO_2 and metal modified α - MnO_2 based mineral phases for alkaline earth elements at acid concentrations as high as 1 mol L⁻¹.³⁶ Interestingly, the alkaline earth binding affinities showed a positive correlation with ionic radii, such that $\text{Ra} > \text{Ba} \gg \text{Sr}$. This phenomenon was attributed to tunnel structures within the α - MnO_2 crystal structure,⁵¹ with the ionic radius for Ra expected to be closest in size to the tunnel diameter. Furthermore, these researchers observed that Fe incorporated into the MnO_2 structure provided greater Ra sorption than pure α - MnO_2 . Although the Mn-doped Fe_3O_4 NPs used in this study were confirmed by X-ray diffraction analysis to have Mn incorporated into the iron oxide structure (*vs.* MnO_2 crystals condensed on the NP surface),²⁴ the possibility of Ra ion sorption through a similar tunneling mechanism cannot be discounted. Although evidence of appropriately-sized tunnel structures in the Mn-doped MNP material is lacking, it was observed that the incorporation of Mn into the Fe_3O_4 NPs caused a significant increase in the surface area of the modified material (Table 3), which could indicate the presence of tunnels within the crystal structure.

3.2.3 Uranium.—On Fe_3O_4 NPs, U had very low uptake between pH 1–3 and 7–8, with a pH zone of uptake between pH ~ 3–7. Between pH ~ 1–5, the uranium sorption curve is in good agreement with that observed on ferrihydrite,⁶⁰ iron(III) hydroxide, goethite, and hematite.⁶¹ In the absence of carbonate in the aqueous solution (0.1 M NaNO_3), these minerals generally sorb the uranyl (UO_2^{2+}) ion strongly at pH ~ 4, as cationic uranyl hydroxo species are formed. However, the addition of carbonate in the system causes suppression in uranyl binding above pH~5; increased carbonate concentration results in greater binding suppression as pH increases. This is due to neutral and anionic uranyl carbonate and uranyl hydroxo aqueous species formation.^{61,62} The addition of alkaline earth elements (especially Ca) into the aqueous system further affects uranyl speciation, but generally at pH ~ 7.^{63–65} Between pH ~ 6.25–7.25, the anionic $(\text{UO}_2)_2\text{CO}_3(\text{OH})_3^-$ is predominant. Using a $\text{Ca}^{2+}/\text{UO}_2^{2+}/\text{CO}_3^{2-}$ system, Dong and Brooks modeled a speciation diagram wherein uranyl ions achieved a 50 : 50 distribution between cationic and anionic uranyl complexes at pH ~ 6.25.⁶⁴ Zachara *et al.* modeled the neutral complex $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ (aq) in simulated Hanford, WA ground water, which they reported as dominant between pH 7–8 (above pH 8, U is complexed as $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$),⁶⁵ which generally agreed with the modeling by Dong and Brooks. This neutral uranyl species $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ (aq) has drawn interest in the last decade, and its molecular dynamics has recently been simulated.⁶⁶

Fig. 1A shows that the hydroxyl groups on the surface of the Fe_3O_4 NPs in HGW are largely protonated at pH < 3 and fully deprotonated at pH > 7 (per eqn (3)). In the range pH 1–5, the uranyl cation, followed by the uranyl hydroxo cation ($\text{UO}_2(\text{OH})^+$) dominate.^{64,65,67} Sorption of these cations on the Fe_3O_4 NPs begins to occur above pH ~3 as the protonated Fe_3O_4 surface hydroxyl sites ($\equiv\text{MeOH}_2^+$) start to deviate from a fully protonated state. Up to pH ~ 7, a continuum of cationic and anionic uranyl species interacts with the surface hydroxyl groups, which are concurrently becoming decreasingly protonated. At and above pH ~ 7, the dominant uranyl species are either neutral or anionic, and subsequently demonstrate no interaction with the Fe_3O_4 NPs.

Interaction of the Mn-doped Fe_3O_4 with uranyl species begins to occur above pH ~ 2, a slight shift below that of the unmodified Fe_3O_4 . In the region above pH ~ 3, these MNPs are expected to be transitioning from the fully protonated $\equiv\text{MeOH}_2^+$ form, thereby providing some binding sites for the predominantly cationic uranyl species. The sorption curve does not, however, show a major drop in U species sorption at higher pH, as was observed with the Fe_3O_4 NPs. Instead, only a shallow drop in sorption is observed above pH ~ 6. Once again correlating the sorption curve to Fig. 1B, the Mn-doped Fe_3O_4 is anticipated to have a predominant surface distribution of $\equiv\text{MeOH}_{\text{ave}}$ between pH 3.7 and 6.7, thus providing binding sites for both cationic and anionic uranyl species. Above pH 6.7, transition to $\equiv\text{MeO}^-$ begins to occur, and at pH 8, the metal hydroxyl surfaces should be largely deprotonated. Interestingly, this is the same general region where the neutral $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ (aq) species is modeled to exist. So between the net negative MNP surface charge and the absence of cationic uranyl species present in solution, the sorption fraction would be expected to drop in the zone between pH ~ 7–8 (as with Fe_3O_4 NPs). Thus, an alternative sorption mechanism(s) may be required to account for the U sorption observed in the higher pH range HGW.⁴³ For example, it is plausible that a partial positive charge on the Ca^{2+} cations

in the polynuclear $\text{Ca-UO}_2\text{-CO}_3$ aqueous species could be attracted to the $\equiv\text{MeO}^-$ surface charges.

3.2.4 Americium.—Americium is known to form hydroxo and carbonate complexes in low organic content ground water. The pH and carbonate concentration of the water are major drivers in Am aqueous species formation.^{68–70} In carbonate rich waters, Am speciation extends from $\text{Am}^{3+} \rightarrow \text{AmCO}_3^+ \rightarrow \text{Am}(\text{CO}_3)_2^- \rightarrow \text{Am}(\text{OH})_2^+$ at pH levels between pH ~ 5.5 to above pH ~ 9.⁶² Americium has a strong tendency to sorb onto colloids, sediments, and minerals,^{68,71,72} including iron oxides.^{70,73,74} Indeed, Am exhibited nearly quantitative uptake on Fe_3O_4 between pH 5–8. Below this pH, its affinity toward the MNPs dropped, as increasing acidification would lead to the formation of free Am^{3+} and possibly AmSO_4^+ .⁶⁹ This is in agreement with other observations made with Am(III), and its homologue Lu(III), on iron oxides.^{73,75} Within the region pH 3–6, the $S\%$ of Am had a high degree of scatter among the replicate batch contact experiments (Fig. 4). Therefore, the sorption/non-sorption pH boundary was difficult to ascertain. Nevertheless, decreasing Am sorption is apparent when the pH drops below pH 5, when $\equiv\text{MeOH}_2^+$ formation begins to dominate the metal oxide surfaces.

Sorption of Am(III) onto Mn-doped Fe_3O_4 was similar to that of Fe_3O_4 , but the range of sorption was once again shifted to the lower pH range. Whereas Am(III) sorption began to drop below pH 5 for Fe_3O_4 , its affinity for the Mn-doped Fe_3O_4 did not begin to fall until below pH 3. Again, this shift may be explained by the Mn-doped Fe_3O_4 NP's conversion to predominantly $\equiv\text{MeOH}_2^+$ at a lower solution pH relative to Fe_3O_4 .

3.3 Radionuclide uptake from a suite of aqueous matrices

The distribution coefficient (K_d) and sorption percent ($S\%$) values for the two MNPs for Po, Ra, U, and Am has been explored in the following aqueous matrices: Columbia River water (CRW), Hanford ground water (HGW), Sequim Bay seawater (SW), and human urine (urine). K_d is a direct measurement of sorbent affinity for an analyte for the conditions under which it is measured. For trace levels of analytes (Table 2), where sorbent performance is limited by chemical affinity and/or competing ions, the K_d value provides a more meaningful measure of the performance of a sorbent than other parameters, such as a material's ion exchange capacity (which demonstrates performance under saturated conditions). Whereas K_d is theoretically independent of S/L ratio in the contact experiment (as long as the contact conditions are within the linear portion of the adsorption isotherm), the $S\%$ value is dependent on this ratio, and can therefore not be averaged across different experimental S/L ratio conditions.

Each aqueous matrix was evaluated at its natural pH and also at a pH of ~2, adjusted with hydrochloric acid (Table 5). The results are for a S/L ratio of 0.5 mg mL^{-1} . Table SI 1 in the ESI[†] addendum provides equivalent sorption data for a S/L ratio of 0.1 mg mL^{-1} . It is important to note that the chemical composition of urine is variable between specimens from

[†]Electronic supplementary information (ESI) available: Table of $\log K_d$ and $S\%$ values for Po, Ra, U, and Am on Fe_3O_4 and Mn-doped Fe_3O_4 NPs in Columbia River water, Hanford ground water, Sequim Bay seawater, and urine at S/L ratios of 0.1 mg mL^{-1} . See DOI:10.1039/c6ra22262e

one subject, and between subjects. The K_d and $S\%$ values for the radiotracers on MNPs in urine reported here are from a few specimens taken from a single source that were homogenized before use, unless otherwise specified. Therefore, the reported values in Table 5 may or may not be consistent with other urine specimens.

A brief summary of each of the adsorption behaviors for each of the radiotracers used in this experimental set is provided below.

Po(IV): polonium expressed exceptionally high affinity for both MNPs for all aqueous matrices at both pH ~ 2 and the natural pH. However, obtaining a consistent K_d measurement for Po in urine was challenging, as its affinity for the MNPs in urine was observed to vary by specimen. In specimens from the original source, the uptake of Po on Fe_3O_4 in unfiltered human urine was moderate for natural pH and pH 2 (log K_d 2.9 and log K_d 3.2, respectively), while uptake of Po on Mn-doped Fe_3O_4 was improved at natural pH (log K_d 3.6), but moderate at pH 2 (log K_d 3.0). However, urine specimens provided by another source resulted in nearly quantitative Po uptake for Mn-doped Fe_3O_4 NPs at pH 2 (log K_d 5.1), while similar log K_d values were observed for Fe_3O_4 and Mn-doped Fe_3O_4 at the natural pH.[§]

Ra(II): on Fe_3O_4 , radium uptake in fresh water solutions was good under neutral pH conditions, but was low for the same solutions under reduced pH (~ 2) conditions. The highly saline SW exhibited moderate Ra uptake and no measurable uptake for both neutral and pH ~ 2 conditions, respectively. Radium sorption results for urine were similar to those found for SW. On Mn-doped Fe_3O_4 , Ra sorption was greater for all aqueous matrices, with substantial increases in uptake at pH 2 relative to Fe_3O_4 . Mn-doped Fe_3O_4 NPs provided nearly quantitative uptake in urine, but no uptake in acidified urine.

U(VI): uptake of U(VI) was marginal in unacidified CRW, but decreased with increasing ionic strengths of HGW and SW for Fe_3O_4 . Acidified aqueous solutions provided even less U(VI) sorption. Moderate improvement in uptake was found in urine at both pH conditions. Uptake of U(VI) onto Mn-doped Fe_3O_4 was significantly improved for all unacidified solutions, with low uptake under acidified conditions.

Am(III): americium affinity for Fe_3O_4 exhibited a strong pH dependence, with high affinity for all neutral aqueous matrices (including urine), and virtually no uptake under pH ~ 2 conditions. Mn-doped Fe_3O_4 provided nearly quantitative uptake of Am(III) under natural pH conditions, and moderate uptake at pH 2, except for urine, where Am(III) uptake did not occur.

4 Conclusions

Magnetic iron oxide nanoparticles, as Fe_3O_4 and Mn-doped Fe_3O_4 , were evaluated for their ability to sorb several alpha-emitting radionuclides from naturally occurring aqueous matrices. These radionuclides included a metalloid (Po), alkaline earth (Ra), and naturally occurring actinide (U), along with the man-made transuranic actinide, Am. The

[§]Po K_d and $S\%$ values reported in the ESI[†] table are from this second urine source.

radionuclides evaluated here possess considerably different chemical behavior and form a range of species in natural water systems across the pH ranges tested. The reactive surfaces and high surface areas of solution-dispersed MNPs facilitate rapid uptake rates under conditions wherein the radiotracers exhibit affinity for the materials. Furthermore, the superparamagnetic property of the MNPs enables a simple means to concentrate the sorbed analytes from a sample volume without the need for traditional wet chemical concentration methods such as bulk precipitations or liquid-liquid or column-based extractions.

Potentiometric titrations were performed on Hanford ground water and suspensions of the MNPs in the ground water. The pH curves of the MNP + ground water mixture titration as a function of the reference ground water titration provided some insight into the pH-dependent charge of the surface sites on the metal hydroxyl groups in the complex aqueous matrix as the solutions were taken from the natural state (pH ~ 8) to pH 2.5. In many cases, the sorption behavior of the radiotracers could be explained by the observed titration profiles; in other cases, it was necessary to suggest that alternative sorption mechanisms were involved.

The Fe₃O₄ nanoparticles were surprisingly stable in acidified ground water, with a Fe solubilization rate measured at 0.86 ppm h⁻¹ at pH ~ 1; vastly lower solubilization rates observed at pH ~ 2. The Mn-doped Fe₃O₄ demonstrated approximately 10 times lower Fe solubilization rate at pH 1, and no measurable Fe solubilization was observed as pH increased. However, Mn was solubilized from the material at a rate of 0.49 ppm h⁻¹ at pH 1, and its solubility in acidified HGW continued, albeit to a lower extent, through pH ~6. Despite significant losses of Mn observed at lower pH, the Mn-doped Fe₃O₄ NPs demonstrated superior sorption of radionuclides across the pH range ~2–8 in comparison to that of the pure Fe₃O₄ NPs. Furthermore, even under pH conditions wherein Fe or Mn were leached from the NPs, the solids maintained adequate magnetic susceptibility to be cleanly removed from the aqueous suspensions when an external magnetic field was applied.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Fig. 1. Differentials in the titration curves between MNP + HGW mixtures and HGW for Fe_3O_4 (a) and Mn-doped Fe_3O_4 NPs (b). MNP suspension concentrations are indicated. Arrows indicate direction of the titrations.

Fig. 2.

(a) Dissolution of Fe from Fe₃O₄. Dissolution of Fe (b) and Mn (c) from Mn-doped Fe₃O₄ NPs as a function of HGW solution pH at 1 (), 4 (□), and 24 h (○) contact intervals.

Fig. 3. Sorption rates of α -emitting radionuclides onto Fe₃O₄ (□) and Mn-doped Fe₃O₄ (○) NPs from HGW at its natural pH of ~8. Uptake measured between 30 s and 8 h.

Fig. 4. Sorption of α -emitting radionuclides onto Fe_3O_4 (□) and Mn-doped Fe_3O_4 (○) NPs from HGW that was pH adjusted between ~1 and the natural pH of ~8. Contact time was 4 h.

Table 1Chemical properties of the aqueous matrices utilized in this study^a

Aqueous matrix	Abbrev.	Conductivity, $\mu\text{S cm}^{-1}$	pH	Alkalinity ^b , $\mu\text{g L}^{-1}$
Columbia river	CRW	1.5×10^2	8.1 ± 0.5	7.0×10^4
Hanford ground water	HGW	5.8×10^2	7.9 ± 0.3	2.0×10^5 ^c
Seawater	SW	5.0×10^4	8.1 ± 0.1	1.2×10^5
Urine	—	9.4×10^3	6.3 ± 0.3	$1.1 \times 10^6 \pm 5.4 \times 10^5$

^a All measurements taken on chemically unmodified waters that were filtered to $0.45 \mu\text{m}$.^b Alkalinity as CaCO_3 .^c $[\text{Ca}]$ in HGW is $6.2 \times 10^4 \pm 3.5 \times 10^3 \mu\text{g L}^{-1}$ 76

Table 2

Alpha-emitting radiotracers used in contact experiments, along with corresponding spiked activity concentrations of radiotracers in solution, expressed as activity, mass, and molar concentrations

Radio-tracer	Primary α -emission ^a , MeV (% abundance)	Spiked concentration			Mode of analysis
		Bq mL ⁻¹	$\mu\text{g L}^{-1}$	moles L ⁻¹	
²¹⁰ Po	5.304 (100)	70	4.2×10^{-4}	2.0×10^{-12}	LSA ^b
²²⁶ Ra	4.784 (93.8)	25	6.7×10^{-1}	3.0×10^{-9}	Gamma ^c
²³³ U	4.824 (84.3)	29	8.1×10^1	3.5×10^{-7}	LSA ^b
²⁴¹ Am	5.486 (84.8)	27	2.2×10^{-1}	9.0×10^{-10}	Gamma ^c

^a Obtained from the National Nuclear Data Center, operated by Brookhaven National Laboratory, <http://www.nndc.bnl.gov/> accessed February, 2016.

^b Liquid scintillation analyzer.

^c NaI(Tl) scintillation detector.

Table 3Physical properties of Fe₃O₄ and Mn-doped Fe₃O₄ nanoparticles

Material	[Fe], g g ⁻¹ (mmol g ⁻¹)	[Mn], gg ⁻¹ (mmolg ⁻¹)	Surface area, m ² g ⁻¹	Particle size distribution, nm	Specific magnetization, emu g ⁻¹
Fe ₃ O ₄	0.708 ± 0.006 (12.7 ± 0.1)	—	42 ^a	27 ± 8 ^a	81 ^a
Mn-doped Fe ₃ O ₄	0.491 ± 0.004 (8.79 ± 0.07)	0.188 ± 0.002 (3.42 ± 0.04)	69	36 ± 9	46

^aValue published by Warner *et al.*, *Langmuir*, 28, (2012), 3931–3937.

Table 4

Observed mass percentages of solubilized Fe and Mn following 1, 4, and 24 h contact times in HGW at pH levels between 1 and 8^a

Approx. solution pH	Fe ₃ O ₄ % dissolved Fe ^b			Mn-doped Fe ₃ O ₄ % dissolved Fe Mn ^c					
	Contact time, h			Contact time, h					
	1	4	24	1	4	24	1	4	24
1	0.7	1.5	6.3	0.3	17	0.4	19	1.0	29
2	0.2	0.5	0.6	—	16	—	19	—	25
3	—	—	—	—	10	—	12	—	12
4	—	—	—	—	5.7	—	5.4	—	5.2
5	—	—	—	—	3.6	—	4.0	—	3.8
6	—	—	—	—	2.8	—	2.8	—	3.9
7	—	—	—	—	1.6	—	1.3	—	1.1
8	—	—	—	—	0.6	—	0.3	—	0.2

^aCells with (—) indicate dissolution fractions < 0.1%.

^bTotal mass of Fe in 2.5 mg Fe₃O₄ present in each experiment is 1.77 mg.

^cTotal mass of Fe and Mn in 2.5 mg Mn-doped Fe₃O₄ is 1.23 and 0.47 mg, respectively.

Table 5

Fe₃O₄ and Mn-doped Fe₃O₄ NP distribution coefficient and percent sorption summary for several α -emitting radionuclides in a range of aqueous matrices. S/L ratio was 0.5 mg mL⁻¹

Radio-tracer	Aqueous matrix	Approx. solution pH	Fe ₃ O ₄		Mn-doped Fe ₃ O ₄	
			log <i>K_d</i> , mL g ⁻¹	S %	log <i>K_d</i> , mL g ⁻¹	S %
²¹⁰ Po	CRW	8	5.4	99.3	>6.3	>99.9
		2	5.5	99.4	>6.3	>99.9
	HGW	8	5.9	99.3 ^a	5.6	95.5 ^a
		2	5.4	97.3 ^a	5.5	97.8 ^a
	SW	8	5.8	99.7	>6.2	>99.9
		2	4.3	91.4	6.0	99.8
²²⁶ Ra	Urine	7	2.9 ^b	27.5 ^b	3.6 ^b	68.2 ^b
		2	3.2 ^b	46.3 ^b	3.0 ^{b,c}	31.9 ^{b,c}
	CRW	8	4.1	86.6	>4.5	>94.3
		2	1.8	3.2	4.4	91.8
	HGW	8	4.1	83.8 ^a	5.4	98.4 ^a
		2	2.3	8.6 ^a	4.5	90.7 ^a
²³³ U	SW	8	3.2	45.6	>4.9	>97.3
		2	<2.1	<5.4	3.3	52.4
	Urine	7	3.8 ^b	77.2 ^b	4.9 ^b	>97.6 ^b
		3 ^c				
	CRW	2	2.4 ^b	10.3 ^b	<1.7 ^b	<2.5 ^b
		8	2.8	22.3	4.4	93.1
²³⁵ U	HGW	2	1.9	3.4	2.2	6.5
		8	2.3	8.1 ^a	4.2	88.0 ^a
	SW	2	1.8	3.4 ^a	2.2	7.8 ^a
		8	2.2	7.9	4.0	83.7
		2	<1.0	<0.5	1.4	1.2

Radio-tracer	Aqueous matrix	Approx. solution pH	Fe ₃ O ₄		Mn-doped Fe ₃ O ₄	
			log <i>K_d</i> , mL g ⁻¹	S%	log <i>K_d</i> , mL g ⁻¹	S%
²⁴¹ Am	Urine	7	2.7 ^b	20.1 ^b	4.1 ^b	87.3 ^b
		2	2.5 ^b ₂	13.0 ^b	2.6 ^b	15.7 ^b
	CRW	8	4.7	95.8	5.0	98.0
		2	2.1	5.3	3.3	52.1
	HGW	8	5.0	94.8 ^a	5.2	95.1 ^a
		2	2.7	18.1 ^a	3.7	71.5 ^a
	SW	8	4.8	97.1	5.2	98.6
		2	<1.3	<0.9	2.7	18.6
	Urine	7	5.3 ^b	99.0 ^b	5.3 ^b	99.1 ^b
		2	1.9 ^b	4.0 ^b	1.9 ^b	3.6 ^b

^aValue included in Fig. 4.

^bValue published by O'Hara *et al.*, *Health Phys.*, **101** (2011), 196–208.

^c An alternate urine specimen from a different source resulted in log *K_d* and S% values of 5.1 and 99.6%, respectively, while values for Po on Fe₃O₄ (pH 2 and 7) and Mn-doped Fe₃O₄ (pH 7) were similar.