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Characterizing cesium sorption in freshwater settings using fluvial sediments and characteristic water chemistries

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Abstract

Cesium-137 (¹³⁷Cs) is a persistent contaminant that poses a significant risk to human health and the environment. Understanding the fate and transport of ¹³⁷Cs following a contamination incident is necessary for effective containment and remediation. In this study, we performed experiments to investigate how Cs⁺ sorption processes are affected by sediment type and varying water chemistries to better understand how Cs⁺ is transported in freshwater settings. Sediment was collected from various river deposits along the Susquehanna River adjacent to the Safety Light Corporation United States Environmental Protection Agency (US EPA) Superfund site (Bloomsburg, PA) and characterized prior to being used in batch reactor experiments with waters characteristic of different regions in the US (Central US and Northeast US) and with three different cation types (Mg²⁺, Na⁺, and K⁺) over a range of ionic strengths. Greater amounts of Cs⁺ sorption occurred with increasing sediment mud (silt and clay) content, although no major differences in sorption between the Central and Northeast US water types were observed. At an ionic strength (I) of 10 mM, K⁺ inhibited Cs⁺ sorption most effectively, followed by Mg²⁺, with Na⁺ having little effect on Cs⁺ sorption over the range of ionic strengths tested (I = 0.1, 1, and 10 mM). Our findings indicate that for the representative freshwater conditions tested here, sediment type (e.g., clay fraction) has a greater influence on Cs⁺ sorption processes than water chemistry. Additional reactions or processes occurring in relatively fresh water could buffer cation competition for sorption sites. Conducting experiments using site-specific sediment samples and water chemistries is useful for predicting Cs⁺ sorption and mobility in distinct environmental settings, particularly when the level of Cs⁺ contamination is high and if the waste or contaminated (or receiving) waters have a relatively high ionic strength.

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Keywords

cesium; sorption; Superfund; radionuclide transport

1 Introduction

Nuclear weapons testing and reactor accidents [e.g., Chernobyl, Ukraine in 1986 and Fukushima, Japan in 2011 (Song 2018)] have widely dispersed radionuclides (predominantly ^{131}I , ^{134}Cs , and ^{137}Cs) as environmental contaminants. Adversarial generation and detonation of radiological dispersal devices, or “dirty bombs,” containing ^{137}Cs has also been a recent concern (e.g., National Planning Scenario #11, U.S. Department of Health and Human Services). As a high energy gamma emitter, ^{137}Cs is particularly concerning, as it is highly soluble, is persistent in the environment ($t_{1/2} = 30$ years), and is easily assimilated by living organisms (Giannakopoulou et al. 2007). In addition, ^{137}Cs contamination can readily spread through surface and subsurface environments (Cornell 1993, Evrard et al. 2015, Sanial et al. 2017), and because of these properties, it is considered a risk to human health. Understanding and predicting the fate and transport of ^{137}Cs at contaminated sites has proved to be a major environmental challenge (Lee 2015), yet knowledge of these processes is necessary to contain the spread of contamination and for site remediation.

Cesium mobility and bioavailability is primarily mediated by its sorption to clay in soil (Cornell 1993, Giannakopoulou et al. 2007, Zachara et al. 2002). Because Cs^+ has a small hydration energy and clay particles have a large electrostatic attraction for Cs^+ , they are preferentially sorbed over other ions (Hakem et al. 2004). In general, Cs^+ sorption to clay minerals occurs through a charge-compensating cation exchange and therefore correlates strongly with the cation exchange capacity (CEC) (Cornell 1993, Fuller et al. 2014, Giannakopoulou et al. 2007). At low Cs^+ concentrations, the frayed edge sites (FES) of micaceous minerals, which are a wedge-shaped zone between non-expansible and hydrated clay interlayers, are known to preferentially sorb and retain Cs^+ relatively independent of solution chemistry (Fuller et al. 2014, Nakao et al. 2008). At higher Cs^+ concentrations, the FES are quickly saturated, and excess Cs^+ sorbs to non-specific sites where Cs^+ sorption rates and amounts are affected by a variety of environmental factors including pH, ionic strength, temperature, and cation type/concentration (Comans, Haller, and De Preter 1991, Di Toro et al. 1986, Fuller et al. 2014, Giannakopoulou et al. 2007, Missana et al. 2014, Tsai et al. 2009). Experimental work to investigate how Cs^+ sorption to sediment is affected by these environmental variables is commonly done using sediment in batch reactor experiments with ranging Cs^+ concentrations (Giannakopoulou et al. 2007, Tsai et al. 2009). These studies often use reference materials and change single variables in isolation, which is useful for understanding Cs^+ sorption mechanistically, but may not be as informative for predicting ^{137}Cs transport on and beyond contaminated sites, where many environmental factors may be affecting sorption processes interactively.

The Safety Light Corporation (SLC) in Bloomsburg, Pennsylvania (Figure 1) is an approximately 10 acre U.S. Environmental Protection Agency (EPA) National Priority List

Superfund site that was formerly used to produce luminescent materials such as self-illuminated watches and instrument dials, exit signs, smoke detectors, and other products containing radioactive materials (U.S. EPA). The buildings, their contents, and soils were contaminated with multiple radioactive materials as a result of various production processes. Liquid radioactive waste was dumped into lagoons, and other contaminated materials were buried in dump areas onsite (U.S. Department of Health and Human Services Agency for Toxic Substances and Disease Registry 2009). SLC is adjacent to the Susquehanna River, and many of these contaminated dumps and lagoons lie within the river's 100-year floodplain, where large flooding events could have remobilized and transported radionuclides and contaminated sediment downstream (Tetra Tech NUS Inc. 2006).

In this study, we use the fluvial sediment collected in July 2017 from the Susquehanna River adjacent to, but not in, the SLC site to investigate how different sediment and water quality conditions affect Cs^+ sorption and to better understand how these environmental characteristics could affect the spread of ^{137}Cs contamination. Previous studies have conducted similar batch experiments with changing environmental conditions (e.g., cations present in water or pH), however, this study is unique in that it utilizes different water chemistries representative of two types of water found in different regions of the United States in addition to conducting cation experiments for comparison to existing literature. Previous sorption studies often use reference clay material (Comans, Haller, and De Preter 1991, Missana et al. 2014), but this study uses sediment with a range of characteristics (e.g., varying clay content and percent organic matter) specific to a site of known concern. Many current Superfund sites, as well as sites where contamination could occur (e.g., nuclear power plants), lie within known floodplains or close to sea level (U.S. EPA Office of Land and Emergency Management 2018), and many communities intake downstream river water as their drinking water source. As such, studies utilizing waters and sediment similar to those found in distinct environmental settings will be useful for informing radionuclide fate and transport processes. Knowledge of these transport pathways and environmental processes can be used to help mitigate the spread of contamination and to improve management of water supplies in order to more effectively protect human health.

2 Methods

2.1 Sediment Sample Collection

Field and background samples were collected from four different types of locations in the Susquehanna River adjacent to the SLC field site (Figure 1): the river bed ($n=4$), river bank ($n=4$), and from the upstream ($n=1$) and downstream ($n=1$) banks of an island adjacent to the SLC. Background samples were also collected from the same four location types (one sample per each location type) approximately 5 km upstream. In total, 14 locations (with one duplicate) were sampled. Sampling locations were selected using the R package “spsurvey” (Kincaid et al. 2013), which uses Generalized Random Tessellation Stratified theory (Stevens and Olsen 2004) to identify sample location coordinates. Grab samples were collected from the top 15 cm of sediment deposits and homogenized before storage. Scribe (<https://response.epa.gov/scribe>), a software tool developed by USEPA's Environmental Response Team, was used for managing information related to fieldwork and sampling.

2.2 Sediment Characterization

Sediment from each of the 14 sampling sites was analyzed to determine the percent water content, percent organic content, and grain size distribution. Each sample was homogenized for 30 seconds, and triplicate subsamples (approximately 100 g each) were placed into pre-weighed aluminum pans, weighed, dried at 100°C overnight, and reweighed to determine water content. Samples were then transferred to pre-weighed crucibles and heated in a muffle furnace at 550°C overnight, then reweighed to determine the organic fraction of the sample that was lost on ignition. Next, sediment was disaggregated using a mortar and pestle and sieved through 0.62 mm and 2.0 mm sieves (using a RETSCH analytical sieve shaker) for 10 minutes to determine the gravel, sand, and mud (silt and clay) fractions of each subsample.

Semiquantitative clay speciation X-ray diffraction (XRD) analysis of the river bank sediment, which had the highest mud fraction of the sediment samples collected and was used in the cation reactor experiments, was conducted to determine which clay minerals were present in the sediment sample. Clay minerals were separated from the bulk sample through centrifuging, the addition of ethylene glycol, and high temperature heating. A Bruker AXS D8 Advance Diffractometer was then used to obtain the X-ray diffractogram for the clay fraction of the sediment.

2.3 Radionuclide Analytical Analysis

Sediment samples were analyzed for strontium-90 (^{90}Sr), tritium (^3H), americium-241 (^{241}Am), ^{137}Cs , and radium-226 (^{226}Ra), which are the known contaminants and progenies stemming from SLC processes. ^{90}Sr was measured using a chemical separation process and quantified using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and a low background gas flow proportional counter (GFPC). ^3H was measured by liquid scintillation counting (LSC) as the water exchangeable ^3H utilizing an oven and refrigeration distillation apparatus. ^3H bound to compounds other than water was not measured. ^{241}Am , ^{137}Cs , and ^{226}Ra were measured using gamma spectroscopy. For ^{226}Ra , the samples were sealed in steel cans for at least 21 days to allow radon-222 (^{222}Rn) to approach secular equilibrium with its parent, ^{226}Ra . Except for ^3H , results were reported on a dry weight basis. Due to limited fines in some samples, none of the samples were sieved prior to radionuclide analysis. The gamma spectroscopy measurements included a deionized water method blank, a laboratory control sample, and a duplicate sample. The LSC measurements included three calibration blanks consisting of tritium-free water and liquid scintillation cocktail prepared in the same proportions as the samples and a method blank consisting of tritium-free deionized water.

2.4 Batch Reactor Experiments

Batch reactor experiments were conducted to investigate the conditions that promote radionuclide sorption in different water compositions. Because ^{137}Cs Cesium has a long half-life and is environmentally mobile, we focus on this radionuclide from the SLC site in our experiments. We use Cesium 133 (Cs-133), the only stable isotope of cesium, because the chemical properties of radioactive and non-radioactive cesium are the same (Lee et al. 2017). Each reactor type was performed in triplicate using Corning™ Falcon 50 mL conical

tubes containing 45 mL of water and approximately 4.5 g of sediment (or no sediment). Sediment used in the reactors was dried at 100°C overnight and disaggregated using a mortar and pestle. Reactors with sediment were soaked in their respective water types overnight prior to experiment initiation, when each reactor was spiked with Cs-133 (1,000 ppm NIST-traceable standard solution, High-Purity Standards, Charleston, SC) at a concentration of 10 mg/L (7.5×10^{-5} mol/L). This represents a Cs^+ concentration that is on the order of contaminated onsite storage pond waste at the Sellafield site near Cumbria, England (Fuller et al. 2014). Following the Fukushima Dai-ichi nuclear power plant accident, ^{137}Cs in surface ocean waters close to the plant reached concentrations of approximately 2×10^{-5} mg/L (Bailly du Bois et al. 2012). Therefore, the Cs^+ concentrations used in the experiments presented here are more representative of waste storage ponds with relatively concentrated levels of radionuclides rather than the more dilute Cs^+ concentrations in surface or groundwaters. Conducting experiments at this relatively high concentration also allows us to explore sorption processes at the non-specific cation exchange sites (Type II/Planar sites) rather than just the FES, which become quickly saturated at lower Cs^+ concentrations (Fuller et al. 2014). All reactors were agitated for 14 days on an orbital shaker at 150 rpm at room temperature (21 ± 1 °C). Each reactor experimental condition was performed with and without sediment. At the specified sampling time points, 2 mL aliquots of water were collected and syringe filtered (0.2 μm Corning SFCA-PF membrane), and 985 μL of filtered sample was acidified with 1.5% HNO_3 and stored at 4°C until preparation for Cs-133 analysis. All water recipes were prepared using ultrapure 18.2 MOhm-cm water and ACS grade or higher purity chemicals. For each water type condition, corresponding reactors were set up with and without sediment, such that the difference in adsorption efficiencies between the two is reported here in order to account for any Cs^+ sorption to the reactor containers.

2.4.1 Kinetic Experiments—The kinetic experiments utilized two different synthetic water types, which are representative of different water compositions characteristic of the United States, and sediment from the four different Susquehanna River sampling locations (riverbed, river bank, upstream and downstream island banks) plus a control (with no sediment) for a total of 10 different reactor types. One water type represents relatively hard water, which is common in the central U.S. (herein called ‘Central U.S.’ water), and it has a hardness (added as magnesium nitrate salt) of approximately 200 mg/L as CaCO_3 (4 mM Na^+ and 2 mM Mg^{2+} concentrations), alkalinity of approximately 200 mg/L as CaCO_3 (added as NaHCO_3), and a pH of 8.3 (adjusted using NaOH and an Oakton® pH 150 probe and meter). The other is representative of water from the northeast U.S. (‘Northeast U.S.’ water), and it has no added hardness but an ionic strength of 10 mM (added as NaNO_3), an alkalinity of approximately 50 mg/L as CaCO_3 (added as NaHCO_3), and a pH of 6.5 (adjusted using concentrated HNO_3) for a total Na^+ concentration of 10 mM. Aliquots from each reactor were collected at specified sampling times (1 hr, 2 hr, 4 hr, 8 hr, 1 day, 7 days, and 14 days), filtered, acidified and stored as described in section 2.4.

2.4.2 Cation Experiments—Additional reactor experiments were performed to determine the effect of ionic strength and three cation types on Cs-133 sorption behavior. Sediment from the river bank was used in these experiments because it has the highest mud-

sized sediment fraction. Three different cations (Mg^{2+} , Na^+ , and K^+) were each tested at three different ionic strengths (0.1, 1, and 10 mM) with and without the river bank sediment for a total of 18 different reactor types (plus an ultrapure water control). Aliquots from each reactor were taken at the end of 14 days, filtered, acidified and stored as described in section 2.4 until Cs-133 analysis.

2.5 ICP-MS Analysis—Water samples ($n=267$) were gravimetrically diluted and analyzed for Cs-133 concentrations using Inductively Coupled Plasma Mass Spectrometry (ICP-MS) according to the quality control measures outlined in EPA Method 200.8 (U.S. EPA 1994).

3 Results and Discussion

3.1 Sediment Characterization

Table 1 summarizes the grain size distributions of the field samples. The river bank and downstream island bank samples were mostly composed of sand (83% and 81%, respectively) and had the highest mud fractions (14.4% and 7.6%), whereas the upstream island bank and riverbed were comprised mostly of gravel. The organic content of the field samples ranged from 7.6% to 11.4%, with the downstream island bank having the highest fraction and the river bank having the lowest average percent organic content (Table 1). The average water content in the sediment samples ranged from 10% to 33%, with the river bank sediment having the highest average water content (31%).

The textural characteristics of the sediment are suggestive of two different types of fluvial settings. The first setting (at the riverbed and upstream island bank) is more erosive, where the sediment is composed mostly of gravel, and mud is present at relatively low levels (~1%). The second condition, which has approximately an order of magnitude higher mud content (~10%), is composed mostly of sand and is indicative of lower energy flow conditions. Relatively high flow velocities would be expected along the riverbed and the upstream island bank, and the grain size distributions and relatively low mud content suggest that these two locations are generally more erosive environments. Conversely, obstructed flow at the downstream side of the island and relatively low velocities along the river bank (where flow velocities for relatively shallow flows are decreased by friction along the stream bed) are relatively less erosive and more conducive for finer-grained sediment deposition, which is reflected in the grain size distributions.

Results from the XRD analysis of the clay fraction of the river bank sediment showed that the major (>30% weight) clay mineral present was illite, with chlorite present at 10–30% (by weight), and kaolinite as a minor mineral (2–10% weight) (See Figure S2 for XRD diffractogram). Illites are a non-expandable 2:1 aluminosilicate clay mineral in which the permanent negative charge is typically balanced by K^+ ions in the planar surfaces and in the clay interlayers. Because the K^+ ions cause the clay interlayers to collapse, these ions typically aren't available for cation exchange. Only the surface K^+ ions and those at the FES are exchangeable, resulting in a lower CEC than clay minerals with expandable interlayers (Cornell 1993, Missana et al. 2014). Illite has been generally described to have three different Cs^+ sorption sites: the high-affinity FES, which selectively sorb Cs^+ , and two

different non-specific sites (Type II and Planar), where other cations (e.g., Na^+ , H^+) can more effectively compete for cation exchange and therefore more effectively reduce Cs^+ sorption (Fuller et al. 2014, Missana et al. 2014).

3.2 Radionuclide Activity in Sediment

The activities of ^{90}Sr , ^3H , ^{241}Am , ^{137}Cs , and ^{226}Ra were all relatively low, with the majority of activity values for all radionuclides (except for ^{226}Ra) falling below the sample-specific minimum detectable concentration (Table S1, Supplementary Information). The river bank samples showed the most elevated activity (particularly for ^{90}Sr and ^3H) above the average background sample activity (Figure S1). However, at <10 pCi/g above background levels, these values are very low (see bottom rows of Table S1 for Annual Limits on Intake of Radionuclides for Occupational Exposure, U.S. NRC Title 10 CFR Part 20 Appendix B). Slightly elevated activity along the river bank sediments could be due either to proximity to SLC or due to the higher mud content in these samples (since this fraction of the sediment contains clay, which has a high sorption capacity for radionuclides). EPA announced the completion of interim cleanup of contaminated soils at the SLC Superfund Site in May 2019 (U.S. EPA Region 3 2019), and these values all fall below the USEPA soil cleanup guideline values (U.S. Department of Health and Human Services Agency for Toxic Substances and Disease Registry 2009).

3.3 Effects of Sediment Type and Water Quality on Cesium-133 Sorption

During the kinetic experiments, the greatest amount of cesium sorption occurred in the reactors with the river bank sediment, which had the highest mud (silt and clay) content (Figure 2). The downstream island bank, which has the second highest mud fraction, experienced the second-highest amount of cesium sorption. The sediments with the lowest fraction of mud (riverbed and upstream island bank sediments) sorbed the least amount of Cs-133. These results follow previous work in showing that the particle size distribution, particularly the presence of clay, plays a predominant role in determining the amount of cesium sorption (Cornell 1993). Both the river bank and the upstream island bank sediments also contain a relatively large fraction of sand-sized sediment particles, which can also sorb cesium, particularly when the percentage of sand in the sample is relatively high (He and Walling 1996).

For all sediments and both Central and Northeast water types, initial sorption occurs relatively rapidly, followed by a slower continual sorption of cesium. Initial rapid sorption likely involves the saturation of FES, with the subsequent slower sorption of Cs^+ occurring at non-specific cation exchange sites (Fuller et al. 2014). The river bank and downstream island bank sediment cesium uptake occurs more rapidly than that of the sediments with the lower mud and sand-sized fractions. None of the conditions tested appear to have reached equilibrium at the end of the two week experiment period, which is consistent with prior observations (Comans, Haller, and De Preter 1991).

No major differences in sorption behavior are evident between the two different characteristic water types, although the two different sediment types (relatively high vs. low clay content) appear more closely clustered in the harder and more alkaline Central U.S.

water. The difference in pH between the two waters (8.3 for Central U.S. and 6.5 for Northeast U.S.) also does not appear to play a significant role in mediating Cs^+ sorption, and previous studies have found that pH does not substantially affect Cs^+ sorption over the range of pH tested here (Missana et al. 2014, Poinssot, Baeyens, and Bradbury 1999, Fuller et al. 2014). Cs^+ does not hydrolyze or readily form complexes, so it is present as Cs^+ over a wide range of pH. Therefore, the pH of the system is only important in how it affects the substrate, rather than how it affects Cs^+ speciation (Cornell 1993). In more acidic (e.g., $\text{pH} < 4$) or alkaline conditions, the potential for clay dissolution and ion competition will play a more influential role in mediating Cs^+ sorption [particularly at trace concentrations of cesium, e.g., Poinssot, Baeyens, and Bradbury (1999)].

The relatively minor differences in Cs^+ sorption in the two different water types could be due to occurring reactions that buffer the differences between the competing cations (Mg^{2+} and Na^+). Differences in Cs^+ sorption behavior between the two waters may also be more apparent for clay minerals that have a higher CEC. Illite, the major clay mineral present in the Susquehanna River sediment, is non-expandable and generally has a lower CEC than swelling clays because the interlayer is collapsed and not available for cation exchange. With a greater CEC, competition between Cs^+ ions and other cations for a greater number of non-specific sorption sites may result in larger differences in Cs^+ sorption behavior in different water types.

In the cation experiments, Cs^+ sorption was affected by the cation present and the ionic strength (I) of the solution (Figure 3). Differences among cesium sorption behaviors between the different cation solutions were most evident at the highest ionic strength tested ($I = 10$ mM). At this higher ionic strength, K^+ most strongly inhibits cesium sorption of the cations tested. Since Cs^+ adsorption occurs through cation-exchange reactions, cations with a similar hydration energy and radius can compete for sorption sites on the mineral surface more effectively with Cs^+ (Tsai et al. 2009). Our results are consistent with previous work, which has found that K^+ reduces Cs^+ sorption due to the similarities in ionic radius and hydration energy (Cornell 1993, Lee et al. 2017). Because FES are highly selective to Cs^+ and K^+ , a higher concentration of K^+ ions in solution can suppress Cs^+ sorption at these sites (Zachara et al. 2002).

At $I = 10$ mM, Mg^{2+} inhibits Cs^+ sorption more so than Na^+ ions. Divalent ions have been found to compete more strongly with Cs^+ for sorption sites (Cornell 1993). Previous studies (Bouzidi, Souahi, and Hanini 2010, Tsai et al. 2009) have also found that Mg^{2+} is a more effective inhibitor of Cs^+ sorption than Na^+ over the range of ionic strengths tested here. At higher ionic strengths, Na^+ could become more effective than Mg^{2+} at inhibiting Cs^+ sorption, as has been shown in Tsai et al. (2009) for $I \geq 100$ mM. This could in part be due to the fact that when the concentration of monovalent ions (such as Na^+) is sufficiently high, these ions can also access and occupy the FES of micaceous minerals (Missana et al. 2014).

Comparing the results from the two sets of experiments and their cation concentrations highlights the need to consider additional environmental and water quality parameters in predicting sorption rates. For the waters used in the kinetic experiments, the molar concentration of Na^+ is 4 mM and 10 mM in the Central and Northeast waters, respectively,

and their ionic strengths are both 10 mM. Results from the cation experiments indicate that the Na^+ concentration does not significantly affect Cs^+ sorption over the range tested here, which is in line with results from the kinetic experiments. For the Mg^{2+} cation experiments, Cs^+ sorption was impacted at $I = 10$ mM (where the Mg^{2+} concentration is 3.3 mM) but was not significantly affected at $I = 1$ mM (Mg^{2+} concentration 0.33 mM). The Mg^{2+} concentration in the Central US water was 2 mM, whereas the Northeast US water had no Mg^{2+} ions present. Given the role that Mg^{2+} plays in inhibiting Cs^+ sorption in the cation experiments at a concentration of 3.3 mM, it is surprising that it does not play a greater role in mediating Cs^+ sorption in the kinetic experiments with the Central US water. This further suggests that other reactions or processes are buffering the cation competition for sorption sites.

The ionic strength of Na^+ varies over several orders of magnitude in fresh surface water (typically 10^{-4} to 10^0 mM) and is approximately 450 mM in average seawater (Hem 1985). Na^+ concentrations in groundwater can also range from typical surface water concentrations to saltier than seawater, depending on the residence time and surrounding geology. Thus, the results from the Na^+ experiments presented here are most relevant for cation exchange processes related sorption in fresh surface waters or in relatively fresh groundwater ($I = 10$ mM), rather than in seawater or brinier groundwater. Our results also indicate that under these fresh surface water conditions, Mg^{2+} is a more effective inhibitor of Cs^+ sorption than Na^+ . The concentration of K^+ in fresh surface water and groundwater also ranges several orders of magnitude (typically 10^{-4} to 10^{-1} mM), and its ionic strength is close to 10 mM in average seawater (Hem 1985). Therefore, the highest ionic strength K^+ condition tested here is representative of the concentration of K^+ in seawater. Water quality data from a sampling station on the Susquehanna River close to SLC (Station ID: 21PA_WQX-WQN0301, data downloaded from the Water Quality Portal, <https://www.waterqualitydata.us/portal/>) indicate that the average sodium, magnesium, and potassium concentrations in the river are 0.7 mM (2008–2018), 0.2 mM (1998–2018), and 0.05 mM (1998–2018), respectively, over the time periods indicated for each element. Our results and these concentrations suggest that the cation concentrations in the Susquehanna River are not high enough to significantly impact Cs^+ sorption processes for the sediment collected and tested as part of this study.

4 Conclusions

In this study, we characterized sediment from various locations in and along the Susquehanna River adjacent to a U.S. EPA National Priority List Superfund site and presented results from Cs^+ sorption experiments using this sediment. In addition to conducting cation sorption experiments for comparison with previous studies, we also conducted experiments using two different water types characteristic of different geographic locations. Consistent with previous research, we found that K^+ ions significantly inhibited Cs^+ sorption at sufficiently high concentrations ($I = 10$ mM), more so than Mg^{2+} and Na^+ . Greater amounts of Cs^+ sorbed to the sediments with a higher mud content, which is expected given that Cs^+ primarily sorbs to clay particles. No appreciable differences in Cs^+ sorption processes were observed between the Central U.S. water and Northeast U.S. water types, suggesting that additional reactions or processes occurring in the waters can serve to buffer cation competition at the non-specific sorption sites. In waters with higher ionic

strengths (e.g., seawater or saline groundwater), other cations will likely affect Cs^+ sorption processes more so than in the two fresh waters tested here.

5 Implications

The findings reported here further our understanding of how environmental conditions affect radionuclide transport processes and have important implications for developing more effective sampling and remediation efforts for locations contaminated with ^{137}Cs . Focusing sampling activities in areas with a relatively high clay content is practical for characterizing the activity and spread of contamination. For example, in certain settings, sampling efforts may be most economical when focused along depositional environments (e.g., point bars along a river, the bottom of hillslopes, or other accretional landforms) where the landscape is likely to have a relatively higher fraction of clay-sized particles. For a spill with a relatively high Cs^+ concentration, reducing the ionic strength of the contaminated area may help to reduce the spread of contamination. In areas with relatively high salt concentrations (e.g., seawater), Cs^+ sorption could be inhibited by competing cations, causing radionuclides to be transported farther.

Numerous Superfund and other contaminated sites lie within known floodplains or close to sea level, so understanding how radionuclides could be transported during future widespread flooding events is critical. The results presented here indicate that simple experiments aimed at understanding how single cations affect sorption processes in isolation may not be effective for predicting radionuclide sorption and transport processes with more complex sediment mixtures in more complicated water matrices. Conducting experiments using site-specific sediment samples and actual receiving waters (or similar water chemistries) can be an effective way to predict Cs^+ transport, particularly when the Cs^+ concentration in the waste is high, and the waste and/or receiving waters have a relatively high ionic strength.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

- Experiments with site-specific sediment and water types useful for predicting Cs^+ mobility
- Cs^+ sorption higher in sediments with greater mud (silt and clay) content
- Cation experiments showed Cs^+ sorption inhibited by $\text{K}^+ > \text{Mg}^{2+} > \text{Na}^+$
- Freshwater chemistry has relatively minor impact on sorption processes

Figure 1:
Study area map with Safety Light Corporation Superfund site (Bloomsburg, PA) and field and background sample locations (outlined in grey) noted. Flow in the Susquehanna River is from right to left in this map.

Figure 2:
Average amount of Cs-133 sorbed over the course of the kinetic batch reactor experiments with two water types characteristic of different U.S. geographical regions. Error bars represent a standard deviation for n=3 samples.

Figure 3:

Average amount of Cs-133 sorbed at the end of 14 days in the cation batch reactor experiments using the river bank sediment. Error bars represent a standard deviation for $n=3$ samples. Relatively high variability in Mg^{2+} at $I = 10^{-1}$ mM is due to one lower replicate value.

Table 1.

Average grain size distribution and percent organic content (of bulk sample) for sediment samples taken from the Susquehanna River adjacent to the Safety Light Corporation Superfund Site.

Sample Type	% Gravel	% Sand	% Mud	% Organic
Riverbed	50.2	48.7	1.1	7.9
River Bank	2.4	83.2	14.4	7.6
Upstream Island Bank	61.7	37.7	0.6	8.4
Downstream Island Bank	11.2	81.2	7.6	11.4