Reactive Transport Modeling to Support Long-Term Monitoring Strategy: Ion Exchange Induced Contaminant Remobilization at Subsurface Contaminated Sites Influenced by Abrupt Changes in Geochemical Conditions

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ABSTRACT

This study presents a long-term monitoring strategy for early risk warning of the remobilization of contaminants, mainly attenuated through an ion exchange reaction, induced by abrupt changes in geochemical conditions. The strategy aims to utilize readily *in-situ* measurable groundwater quality parameters in the prediction of near-future contaminant remobilization caused by cation exchange reactions. The proposed approach was demonstrated using historical monitoring data from the Department of Energy (DOE) Savanna River Site (SRS) F Area, which experienced abrupt geochemical disturbance during the pump-treat-reinjection remedy, and a reactive transport model developed through this study to understand ^{90}Sr migration behavior in the subsurface of the SRS F Area. The historical monitoring data analysis and reactive transport modeling results suggested that *in-situ* specific conductance sensors can be used for an early warning system to detect contaminant remobilization associated with cation exchange species. This strategy is expected to benefit the long-term management of the contaminated site for elements with cation exchange reactions by providing the means to detect the remobilization of contaminants before the remobilization occurs.

KEYWORDS

Early warning, Long-term monitoring, Contaminated sites, Reactive transport modeling, Strontium, Specific conductance

HIGHLIGHTS

- The mechanism of 90Sr remobilization at the Savannah River Site F Area was examined.
- A time lag was observed between increases in background electrolyte and ^{90}Sr levels
- Increased Na^+ concentrations may induce ^{90}Sr remobilization through ion exchange.
- Specific conductance sensor could be used for early detection of ^{90}Sr remobilization.

52 **GRAPHICAL ABSTRACT**

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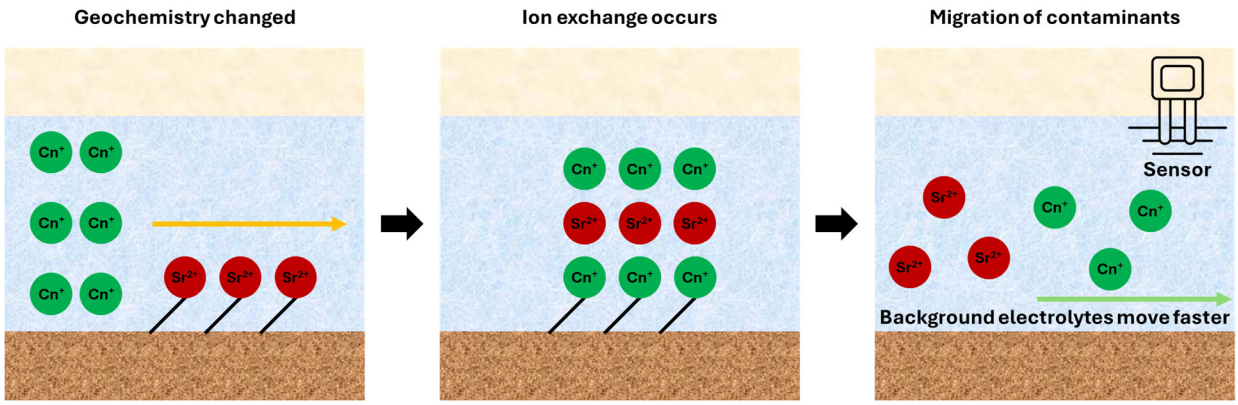

1. INTRODUCTION

Increased anthropogenic activities, including rapid industrialization and urbanization, have left subsurface-contaminated sites across the world.[1] It is estimated that there are more than 5 million of contaminated sites globally, which require remediation and redevelopment to ensure future sustainable land use.[1-3] Common contaminants found at these sites include persistent organic pollutants, heavy metals, petroleum hydrocarbons, pesticides, chlorinated solvents, inorganics, and radionuclides.[4] However, less than 10% of potentially contaminated sites worldwide have been remediated even though site contamination has been recognized already in 1960s.[4] Particularly in the United States, 1340 sites are listed on the National Priorities List (NPL), which classifies sites that warrant cleanup, but remediation goals have been achieved at only 458 sites as of October 01, 2024.[5]

Recent demand and emphasis on sustainable remediation have generated interest in attenuation-based remediation strategies, such as monitored natural attenuation (MNA) and enhanced natural attenuation (ENA), leveraging variety of attenuation processes to immobilize and/or degrade contaminants.[6] Natural attenuation processes occurring in the (sub)surface systems include: (1) partitioning via sorption, accumulation, and volatilization; (2) dispersion and dilution; and (3) abiotic and biotic reactions, degradations, and transformations.[7] Such attenuation-based remedies have been considered cost-effective, less energy-intensive, less intrusive and more sustainable solutions, and are particularly effective for sites where a large volume of soil and groundwater are contaminated with relatively low concentrations and therefore active treatment is no longer feasible.[8] However, attenuation-based remedies inherently accompany a level of uncertainty in assuring remediation performance and regulatory compliance.

At sites where attenuation-based remedies have been deployed, the attenuated contaminants (e.g., metals and radionuclides) may remain in the subsurface for an extended period. However, changes in site conditions (e.g., hydrology and geochemistry) can impact the effectiveness of the remediation and could potentially remobilize some of the attenuated contaminants.[9] In particular, the effect of climate change, such as flooding and groundwater level fluctuations, has become an important and emerging topic at contaminated sites (e.g., Libera, et al. 2019;[10] Cavelan, et al. 2022;[11] Crawford, et al. 2022;[12] Xu, et al. 2022;[13] Hill et al., 2023;[14]). A recent study by Hill et al., 2023 has found that sea level rise would cause groundwater levels to increase, inundating a significant number of coastal contaminated sites in the U.S.[14] The study also warn that an increase in groundwater elevation by only a few centimeters can mobilize soil contaminants and create new exposure pathways, and pumping to prevent floods is expected to elevate the saltwater interface, changing groundwater ionic strength and mobilizing contaminants in soil.[14] Therefore, the sites, where attenuation-based remedies are deployed, often require long-term institutional control and performance monitoring[9, 15, 16] and entail a burden on demonstrating that the contaminants are persistently attenuated and/or immobilized.

Recently, numerous monitoring strategies and technologies have emerged for contaminated site applications, yielding considerable progress in the cost-effectiveness of monitoring system operations and facilitating real-time *in-situ* sensing. For example, a machine learning approach was implemented to monitor sensor location optimization, monitoring well data analysis, and contaminant concentration estimation.[16, 17] Denham et al. (2020) proposed a new long-term monitoring concept that focuses on measuring the geochemical and hydrological parameters that control the attenuation and remobilization of contaminants while de-emphasizing direct measurement of contaminant concentration.[9] The benefits of the proposed method include reducing the cumulative cost of long-term monitoring activities and the early detection of changes

in environmental conditions. Schmidt et al. (2018) developed an *in-situ* monitoring technique combined with principal component analysis (PCA) and a Kalman filter to continuously estimate the contaminant concentration based on water quality variables, i.e., specific conductance and pH.[8] This technique enables continuous and real-time estimation of contaminants concentration and cost reduction by decreasing the frequency of contaminant sampling.

Although recent efforts might significantly improve the long-term monitoring strategy in terms of cost-effectiveness and indirect estimation of contaminant concentrations,[8, 16] these approaches are based on site-specific correlations and relationships without physical and predictive understanding. It still emphasizes the estimation of the current status of contaminants without addressing potential time lags between *in-situ* measurable parameters and contaminant concentrations. Furthermore, existing techniques, which rely primarily on measuring contaminant concentration, can only provide alerts once the remobilization has occurred.[9] To the best of the authors' knowledge, however, how monitoring data could be used for early risk warning of contaminant remobilization has not been investigated extensively.

To address the current technical gap, this study aims to demonstrate a monitoring strategy for enabling an early warning of contaminant remobilization induced by abrupt changes in geochemical conditions, utilizing *in-situ* measurable variables combined with reactive transport modeling. A particular focus is placed on employing real-time *in-situ* parameters readily measurable by sensors to predict near-future contaminant remobilization caused by cation exchange reactions. We demonstrate this proposed approach using historical monitoring data from the Department of Energy (DOE) Savannah River Site (SRS) F Area, which experienced an abrupt geochemical disturbance due to the pump-treat-reinjection activities. In particular, an increase in strontium-90 (^{90}Sr) concentrations was observed at the SRS F Area after the reinjection of treated water with high ionic strength, possibly due to the cation exchange reactions. We developed a reactive transport model for strontium migration to understand the attenuation/remobilization mechanism of strontium in the vicinity of the source zones. And the developed model was used to investigate the difference in temporal migration behaviors of strontium and background electrolyte (i.e., Na^+, which is a proxy for ionic strength or specific conductance).

This strategy – although the study was conducted based on the SRS-specific data – is expected to be useful for many other contaminated sites, since ^{90}Sr is one of the important contaminants after nuclear accidents and nuclear waste operations (e.g., Chornobyl,[18] Fukushima,[19] and the Sellafield site[20]). The developed strategy could also be applicable at sites where ion exchange acts as the predominant sorption mechanism and at contaminated sites in the coastal area, where seawater intrusion could increase salinity and change geochemical conditions. Since specific conductance is one of the most commonly available *in-situ* sensors, we aim to increase the use of *in-situ* specific conductance sensors for an early warning application.

2. METHODOLOGY

2.1. Study Site Description

2.1.1. Site Background

The SRS F Area hosted a chemical processing facility for plutonium extraction using the PUREX process, operated between the 1950s and 1980s in South Carolina, United States.[21, 22] In order to dispose of the low-level radioactive acidic liquid waste, three unlined seepage basins were constructed at SRS F Area, and the basins received nearly 7×10^9 L of the waste solutions from 1955 through 1988.[8, 21] The waste solutions contained various radionuclides (e.g., ^{3}H, ^{90}Sr, ^{129}I, $^{137\&139}Cs$, $^{141\&144}Ce$, $^{235\&238}U$, $^{238\&239}Pu$, and ^{241}Am) as well as non-radiological contaminants including Cr, As, Cd, Hg, and Pb.

Since the discharge of the waste to the basins was terminated in 1988, several remediation strategies have been deployed at the site. Remediation began in 1990 with the chemical stabilization of contaminated soils at the bottom of the basins and the installation of a low-permeability cap at the top of the basins to limit infiltration.[8, 9] In addition, a pump-treat-reinjection system, which targeted removing radionuclides and metallic elements, was implemented in 1997. The purpose of the system was to intercept and extract contaminated groundwater downstream from the basins and then treat most of the contaminants (except tritium) using ion exchange, reverse osmosis, and precipitation/flocculation. The treated water would then be reinjected at the upstream of the basins.[21]

After a few years of the operation, the pump-treat-reinjection system was replaced by enhanced natural attenuation using a hybrid funnel-and-gate system, in 2004.[8, 9] This system consists of multiple subsurface low-permeable barriers which are emplaced across the groundwater flow paths, directing the contaminant plume into gates that are gaps between the barriers (Figure 1). Through the gates, alkaline solutions are periodically injected into the groundwater to elevate the pH and therefore to enhance the sequestration of radionuclides. The current ENA is expected to be eventually replaced with MNA which is a promising closure strategy for the SRS.

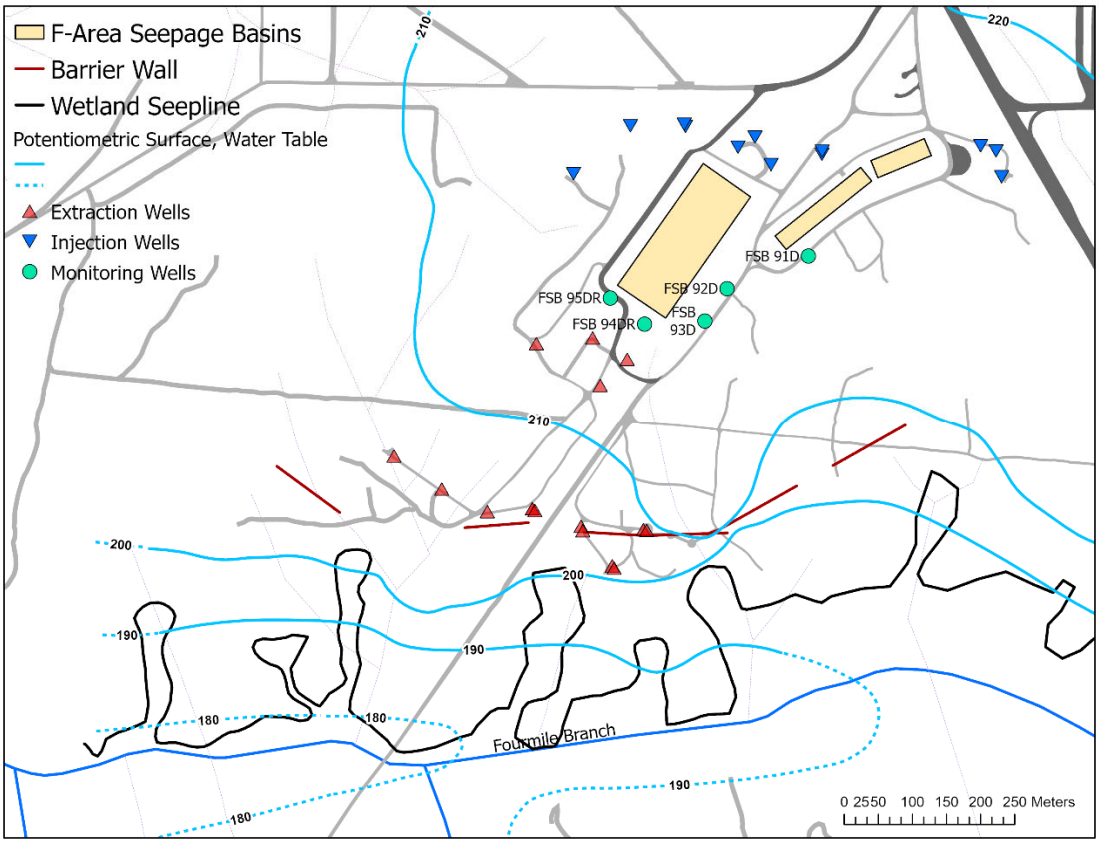

Figure 1. Schematic site description of the SRS F-Area. The circles shown in the figure represent the monitoring wells (FSB 91D, FSB 93D, and FSB 95DR) investigated in this study.

2.1.2. Monitoring of Contaminant Migration at SRS

Monitoring of radioactive constituents started in 1955 at the beginning of the basins' operation. Over the years, various types and number of wells, seepline monitoring points, and surface water locations have been installed at the SRS F-Area. Currently, more than 100 groundwater and surface water monitoring stations are in operation.[23] On one hand, the periodic groundwater sampling for monitoring nonradioactive contaminants began in 1982.[8, 24] Monitoring activities for the SRS F-Area have revealed that around 1 km^2 of subsurface (groundwater) was contaminated and the acidic contaminant plume was extended to approximately 600 m downgradient from the basins.[8, 25]

In this study, about 30 years of monitoring data obtained from the monitoring wells near the SRS F-Area basins was used. We demonstrate the capabilities of the proposed early risk warning strategy with a subset of the F-Area data, including specific conductance and ^{90}Sr concentration. ^{90}Sr is the contaminant of concern whose remobilization was observed near the basins during the pump-treat-reinjection system operation. Specific conductance is considered to be a critical parameter for predicting the remobilization of ^{90}Sr since it can be used as a proxy for measuring changes in cations concentration that could cause the remobilization. Under the monitoring plan expected to be applied for SRS, specific conductance can be continuously and easily measurable using *in-situ* sensors.

2.2. Reactive Transport Modeling Approach

We have developed a reactive transport model using the numerical code, CrunchTope (Steefel et al 2015)[26] to understand the attenuation and remobilization processes of strontium in the SRS F-Area aquifer sediments. Briefly, this code solves the advection-dispersion equation coupled to a range of geochemical reactions. Details in fundamental theories and governing equations can be found in the software manual.[27]

2.2.1. Conceptual Model

The general framework of our conceptual model follows other studies for SRS, including Bea et al. (2013)[28], Arora et al. (2018)[29], and Libera et al. (2019)[10]. As depicted in Figure 2a, previous studies showed that the waste solution disposed of in the basin expected to be moved down into the subsurface through the vadose zone and reached the upper aquifer zone (UAZ). The contaminated plume is introduced to the UAZ through a broad area in the upper part of the UAZ and could be mixed with the upstream groundwater.

Our model uses a simplified horizontal one-dimensional (1D) domain (Figure 2b), following Arora et al. (2018)[29]. This 1D domain represents a part of the saturated UAZ beneath the F Area considered as one of major contaminant plume pathways. The domain length is 227 m and discretized using 227 cells with a uniform grid spacing of 1 m. Multiple observation points were set in the model to understand strontium remobilization behavior according to distance between monitoring wells and source zones (refer to Figure 1). Our model assumed constant Darcy velocity with groundwater flowing along the horizontal axis (Figure 2).

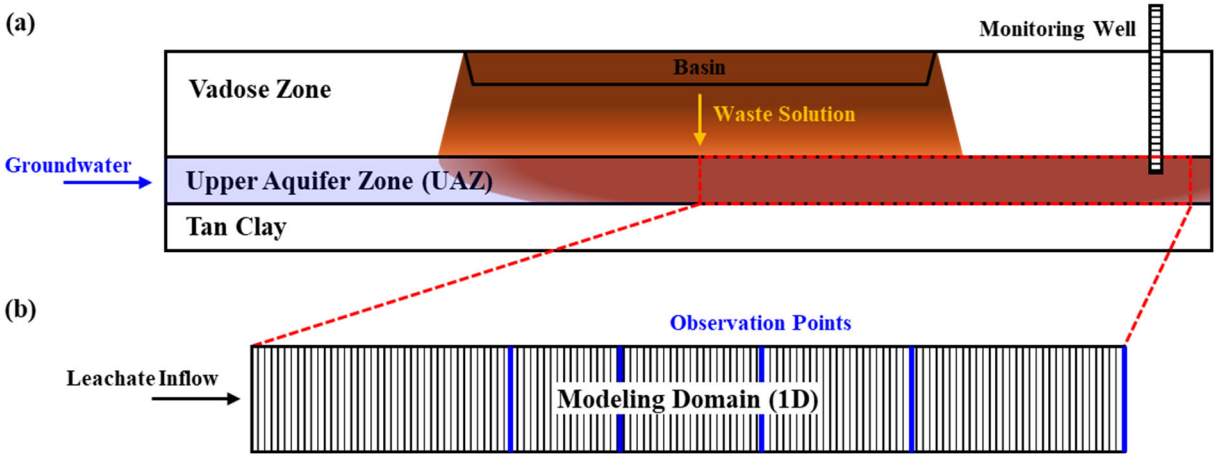

Figure 2. Schematic diagram of (a) geological description of the SRS F-Area and expected plume flow in the subsurface and (b) domain of conceptual model

2.2.2. Hydrogeological and Geochemical Initial Conditions

Homogeneous hydrogeological and geochemical properties were applied to the entire domain. Table 1 summarizes parameters for hydraulic and solute transport simulation used in this study. The longitudinal dispersivity was calculated for the 227 m long sediment 1D column based on the equation proposed by Schulze-Makuch.[30]

Table 1. Input parameters used for hydraulic and solute transport simulation

Parameter	Value	Reference
Porosity (-)	0.39	[29]
Darcy flux (m/year)	48.36	[21]
Molecular diffusion coefficient (m^2/s)	1.80×10^{-9}	[29]
Longitudinal dispersivity (m)	2.18	[30]

Table 2 summarizes the initial mineralogical composition of the sediment compiled from SRS sediment analysis report[31] and the properties of the corresponding minerals. In the SRS report, XRD analysis was conducted for three Upper Aquifer sediment samples obtained from different depths. The analysis results showed that abundance of minerals varies with depth and major constituents were quartz, kaolinite, illite, and goethite. For simplicity, it was presumed that mineral dissolution and precipitation kinetic is very low, i.e., it was treated as like inert phases. Previous studies that considered mineral dissolution and precipitation showed that pH remained under acidic conditions.[28, 29]

Table 2. Initial mineralogical composition of the 1D domain and properties of minerals considered in the simulations

Minerals	Average volume fraction	SSA (m^2/g)	CEC (meq/100g)[d]
Quartz	0.4335	0.14[a]	1
Kaolinite	0.1044	20.6[b]	10
Illite	0.0470	112[c]	25
Goethite	0.0250	16.2[b]	3

[a]Arora et al. (2018)[29]; [b]Dong et al. (2012)[32]; [c]Macht et al. (2011)[33]; [d]VerMeulen and Gonzales-Raymat (2023)[31]

Denham (2021) investigated the contributions of single mineral phases present at SFS F-Area sediments to strontium sorption, and found that silica (quartz) and goethite have small sorption capacity for strontium in acidic conditions.[34] In this study, therefore, the sorption of Sr to only illite and kaolinite was modeled (Table 3). We only consider cation exchange reactions without surface complexation reactions, because previous studies reported that in acidic to neutral pH conditions, the contribution of surface complexation to Sr sorption onto illite was nearly negligible compared to ion exchange.[35, 36] In addition, isotopic effects related to strontium sorption were not considered, as they are generally regarded as insignificant and radioactive decay was not considered as well.

Table 3. Cation exchange reactions and the corresponding selectivity coefficients for illite and Kaolinite

Ion Exchange Reaction	$\log_{10}K_c$ (Illite)	$\log_{10}K_c$ (Kaolinite)[c]
$Na\text{-}X + H^+ \leftrightarrow H\text{-}X + Na^+$	0.0[a]	0.0
$Na\text{-}X + K^+ \leftrightarrow K\text{-}X + Na^+$	1.11[a]	0.70
$2Na\text{-}X + Mg^{2+} \leftrightarrow Mg\text{-}X_2 + 2Na^+$	1.04[a]	0.60
$2Na\text{-}X + Ca^{2+} \leftrightarrow Ca\text{-}X_2 + 2Na^+$	1.04[a]	0.80
$2Na\text{-}X + Sr^{2+} \leftrightarrow Sr\text{-}X_2 + 2Na^+$	1.00[b]	0.91
$3Na\text{-}X + Al^{3+} \leftrightarrow Al\text{-}X_3 + 3Na^+$	1.00[a]	0.46

[a]Bradbury and Baeyens (2009)[37]; [b]Montoya et al. (2018)[35]; [c]Appelo et al. (2005)[38]

2.2.3. Simulation Sequence and the Corresponding Boundary Conditions

In order to model the abrupt changes in geochemical conditions that occurred at SRS F Area due to the pump-treat-reinjection remediation activities, we developed a scenario that consisted of the

following three sequential phases: (1) First, the 1D domain, which represents the UAZ, was preconditioned by flowing pristine groundwater for 3 years; (2) After preconditioning, seepage effluent (waste solution) was applied for 42 years. This duration reflects the period between the first disposal of acidic waste solution to the basin and the commencement of the pump-treat-reinjection system; (3) In the last phase, the domain was leached with treated water with an elevated Na^+ concentration for seven years, which corresponds to the assumed pump-treat-reinjection system operational period. Table 4 gives the chemical conditions of each solution used in the simulations. They were applied to the left boundary condition for each corresponding phase, and the right boundary condition was pristine groundwater in all phases.

Table 4. Chemical composition of leachates used in the simulations

Component (mol··kg^{-1})	Pristine groundwater (Pre-basin-operation phase)	Seepage effluent (Contaminated water discharging phase)	Treated water (Pump-treat-reinjection system operational phase)
pH	5.40	2.05	5.40
Na^+	2.78×10^{-4}	6.82×10^{-5}	0.30
Cl^-	9.99×10^{-3}	3.39×10^{-5}	9.99×10^{-3}
CO_2(aq)	1.22×10^{-5}	1.07×10^{-5}	1.21×10^{-5}
Al^{3+}	1.46×10^{-8}	1.00×10^{-8}	3.65×10^{-8}
Fe^{3+}	5.77×10^{-16}	5.49×10^{-6}	1.96×10^{-15}
K^+	3.32×10^{-5}	1.72×10^{-6}	3.32×10^{-5}
Ca^{2+}	1.00×10^{-5}	1.00×10^{-5}	1.00×10^{-5}
Mg^{2+}	5.35×10^{-3}	2.47×10^{-6}	5.35×10^{-3}
NO_3^-	1.00×10^{-3}	1.00×10^{-2}	3.01×10^{-1}
SO_4^{2-}	2.25×10^{-5}	4.80×10^{-5}	2.25×10^{-5}
Sr^{2+}	-	1.49×10^{-7}	-
SiO_2(aq)	9.83×10^{-5}	1.18×10^{-4}	9.18×10^{-5}
Duration (years)	3	42	7

3. RESULTS AND DISCUSSION

3.1. Analysis of Monitoring Data: Remobilization of ^{90}Sr Near SRS F-Area Basins

Specific conductance, measured at monitoring wells adjacent to the F-Area basins and located in the upper aquifer zone (UAZ), decreased after basin operations ceased but began to increase again between 1999 and 2001 (Figure 3). This increase was associated with the injection of the treated water upgradient of the basins as part of the pump-treat-reinjection system initiated in 1997. In parallel, the ^{90}Sr concentration in the wells showed a gradual decrease over time; however, it subsequently increased between 1999 and 2003. Because the increases in specific conductance and ^{90}Sr concentration occurred during the same period, these two parameters appear to be correlated.

One hypothesis regarding this phenomenon is that increased groundwater salinity, observed in the form of elevated specific conductance, induced the remobilization of strontium that had already been sorbed onto the sediments. This can be explained in detail in sequential phases as follows: (1) First, ^{90}Sr sorbed onto the exchangeable clays in the sediments during the contaminated plume move through the aquifer; (2) The salinity (specific conductance) of the groundwater increased, in other words, the concentration of cation increased, following the operation of pump-treat-

reinjection system; (3) Due to the increased concentration of the cation in the groundwater, the exchange reaction between aqueous cation and pre-adsorbed ^{90}Sr on the sediments was promoted (see Eq. 1). As a result, ^{90}Sr was remobilized and released to the groundwater.

$$>X_2\text{-}^{90}Sr + 2Cn^{+} \leftrightarrow 2>X\text{-}Cn + {}^{90}Sr^{2+} \quad (1)$$

where >X and Cn^{+} represent an exchange site on sediment and monovalent cation, respectively.

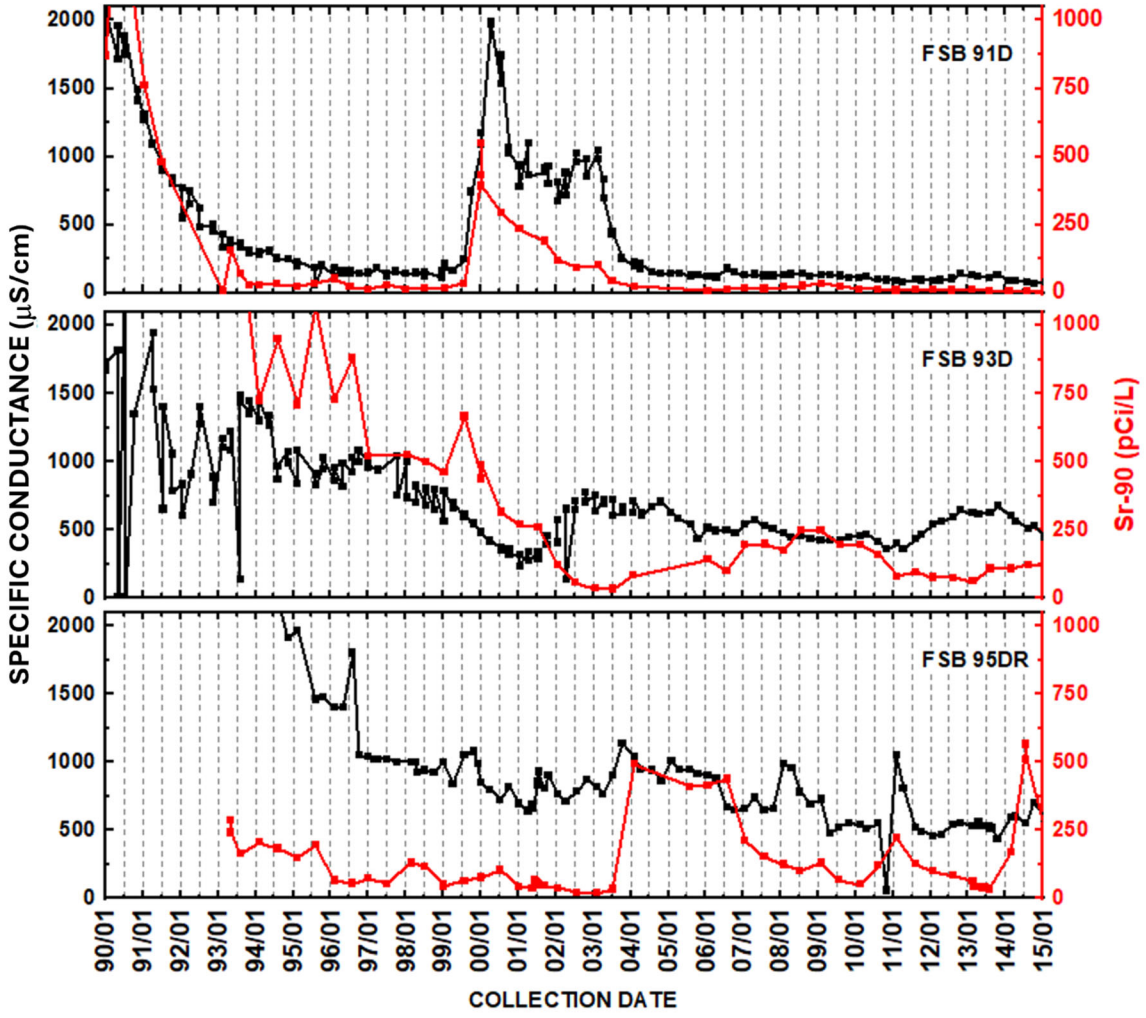

Figure 3. Monitoring data of specific conductance and ^{90}Sr from monitoring wells (FSB 91D, 93D, and 95DR) located at upper aquifer zone (UAZ)

3.2. Mechanism Behind the Remobilization of Strontium at the SRS F-Area

The breakthrough curves of Sr at the multiple observation points obtained from the simulation are shown in Figure 4a. In the figure, the red area represents a phase when the contaminated water was discharged into the subsurface (the second column in Table 4). During this period, no strontium was detected at any observation points, while a non-reactive tracer was observed with a breakthrough curve, which implies that Sr sorbed onto the sediments. When the treated water (higher sodium concentration) is injected, increases in both sodium and strontium concentrations were observed at every observation point (Figure 4a and 4b). The peak Sr concentrations detected at the observation points were tens of times greater than those in the seepage effluent, which

implies that this Sr did not originate only from the contaminated plume. The modeling results capture the trend observed in the monitoring data from the F-Area wells (Figure 3), which supports the hypothesis that abrupt changes in ionic strength caused the ^{90}Sr remobilization by promoting an ion exchange reaction between aqueous cations and strontium originally built-up onto sediments.

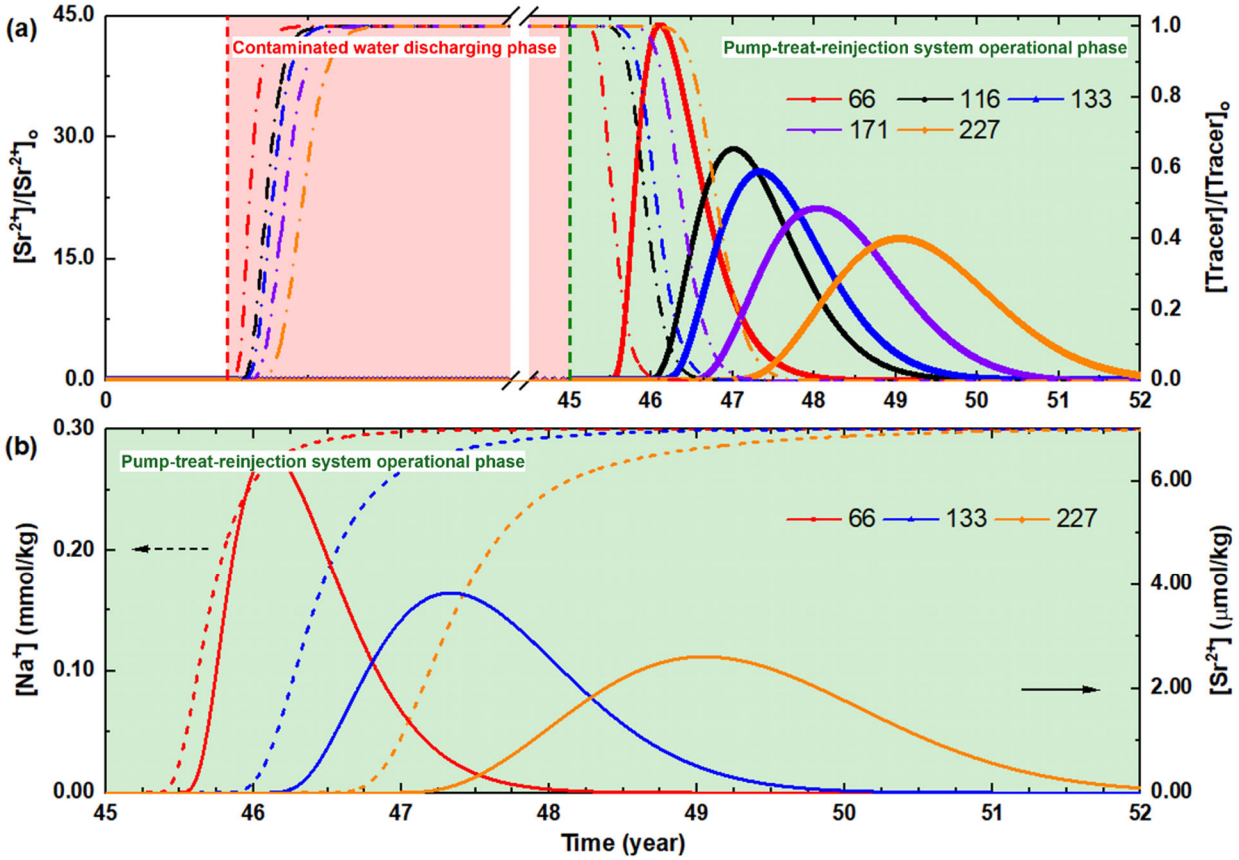

Figure 4. Breakthrough curve of (a) Sr^{2+} (solid line) and tracer (dash-dotted line) at various observation points (left and right y-axes represent a ratio of Sr^{2+} and tracer concentration in porewater to initial Sr^{2+} and tracer concentration in seepage effluent, respectively) and (b) Na^+ (dashed line) and Sr^{2+} (solid line): shows the pump-treat-reinjection system operational period only

3.3. Early Risk Warning Strategy for Remobilization of Strontium

As shown in Figure 3, the increase in specific conductance was observed first, prior to the increase in ^{90}Sr concentration (FSB 93D and 95DR), and a similar trend was observed in our simulations. Regardless of observation points, an increase of Na^+ (indicative of specific conductance), was detected first after the injection of the treated water, and an increase in Sr^{2+} concentration arrived later (Figure 4b). This phenomenon is expected to be due to the fact that Na^+ and Sr^{2+} have different sorption affinity onto clays. In general, Na^+ has lower sorption affinity compared to Sr^{2+} and therefore, moves faster than Sr^{2+}. Even though desorption of Sr^{2+} occurred near the upstream end of the domain due to increased Na^+ concentration, it can be sorbed onto sediment again as it moves downstream, i.e., retardation in Sr^{2+} migration can occur. For these reasons, an increase in specific conductance can be detected prior to increase in ^{90}Sr concentration.

The lag between changes in specific conductance and strontium concentration depends on the path length of the contaminant plume. As can be seen from Figure 4b, the time difference between increase in Na^+ concentration and Sr^{2+} concentration becomes more apparent downstream. Consistent trends are also seen in the monitoring data when comparing FSB 91D and FSB 93D data in Figure 3 (refer to Figure 1 for comparing the locations of the wells).

Based on this difference in temporal behavior of specific conductance and strontium, specific conductance could be used as an indicator of remobilization of ^{90}Sr. For example, if a sudden increase in specific conductance was detected, then one can expect there might be an increase in ^{90}Sr in the near future. During that period, additional remediation can be applied to the site to mitigate the expected remobilization. Furthermore, if the lag between such indicators (e.g., specific conductance) and contaminant migration is understood sufficiently, even the extent and occurrence time of the contaminant remobilization would be predictable.

3.4. Sensitivity Analysis: The Effect of Cation Concentration and Flow Rate on Remobilization of Strontium

To understand how the degree of change in specific conductance affects the remobilization characteristics of strontium, sensitivity analysis was conducted. Three different types of treated water with different sodium ion concentrations (0.25 mol/kg, 0.3 mol/kg, and 0.4 mol/kg) were used in the simulations. As shown in Figure 5a, the remobilization of strontium is significantly affected by the sodium concentration in the treated water. Higher sodium concentrations were associated with a higher and narrower Sr^{2+} peak, implying that a higher cation concentration causes more intensive remobilization.

In addition, this analysis shows the time lag between the *in-situ* measurable parameters and contaminant concentration depends not only on the observation locations but also on the sodium concentrations. A shorter time difference between Na^+ and Sr^{2+} concentration increase was observed with higher sodium concentration. The simulation results also showed that changing groundwater velocity has a similar effect. We compared the temporal behavior of Sr^{2+} remobilization with different groundwater velocity (Figure 5b). If the groundwater velocity increased, accelerated remobilization was observed with an increased and narrowed Sr^{2+} peak, and the opposite phenomenon was observed when it decreased. Consistent with these observations, the time difference between Na^+ and Sr^{2+} concentration increase becomes intensified with a reduced groundwater velocity.

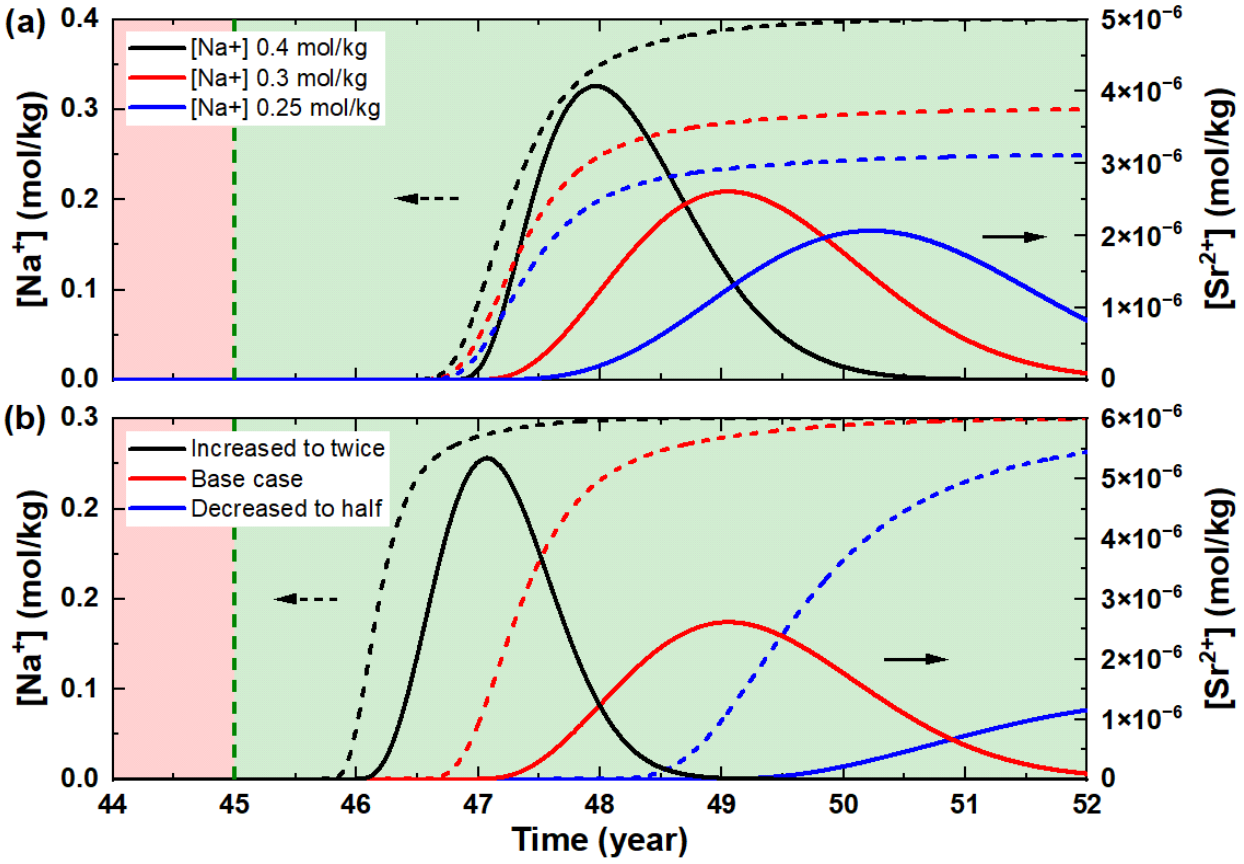

Figure 5. Sensitivity analysis for analyzing the effect of (a) cation (Na^+) concentration and (b) groundwater velocity on the temporal behavior of Sr remobilization. Dash line and solid line represent changes in Na^+ and Sr^{2+} concentration, respectively. The red and green shaded areas in the figures indicate the contaminated water discharging phase and the pump-treat-reinjection system operational phase, respectively.

4. CONCLUSION

In the present study, a reactive transport model was developed to understand the migration characteristics of the contaminant in the subsurface under abrupt changes in geochemical conditions, and to identify the mechanism of ^{90}Sr remobilization observed at the SRS F Area during the operation of the pump-treat-reinjection system. The historical monitoring data from the SRS F Area and our reactive transport modeling results showed that there was a time lag between the migration of a background electrolyte and the remobilized contaminant under abrupt changes in geochemical conditions. In particular, an increase in specific conductance (or Na^+ concentration) was detected first at the monitoring wells before a remobilized contaminant arrived at the well. These findings suggest that the remobilization of contaminants, mainly attenuated through an ion exchange reaction, induced by abrupt changes in geochemical conditions can be predicted by monitoring the specific conductance of the groundwater, which is real-time and readily measurable using *in-situ* sensors.

Our findings also show how changes in the environmental conditions affect the effectiveness of the proposed strategy. For example, the time lag between the migration of a background electrolyte

and the remobilized contaminant, and the peak concentration of the contaminant varied with background cation concentration and groundwater velocity.

We acknowledge the limitations in our study. Because the model employed a simplified one-dimensional (1D) column domain, it may not fully account for variations in water elevation, which could also influence the behavior of ^{90}Sr. This study aimed at improving our system understanding rather than quantitively matching the observation data. In addition, due to limited data availability, the model assumed the chemical composition of the leachates and injected solutions such as sodium concentrations. We addressed such uncertainty using the sensitivity analysis. This modeling approach serves an important step toward the long-term management of contaminated sites where the ion exchange reaction is mostly responsible for the attenuation of the contaminants (e.g., low pH soil contaminated by Pb and Cd[39]) by providing the means to detect the remobilization of contaminants before the remobilization occurs.

CRediT authorship contribution statement

Sol-Chan Han: Conceptualization, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft. **Hansell Gonzalez-Raymat**: Data curation, Investigation, Resources, Visualization, Writing – review and editing. **Miles Denham**: Investigation, Validation, Writing – review and editing. **Toshiyuki Bandai**: Methodology, Software, Writing – review and editing. **Zexuan Xu**: Formal analysis, Methodology, Supervision. **Sergi Molins**: Formal analysis, Investigation, Methodology, Project administration, Supervision, Writing – review and editing. **Haruko Wainwright**: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Writing – original draft

Declaration of Competing Interest

The authors declare no competing financial interest.

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