

SCIENCE IN SUPPORT OF ASSESSING ECOLOGICAL RISK AND IMPLEMENTING NOVEL REMEDIATION STRATEGIES AT THE SAVANNAH RIVER SITE, SC

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ABSTRACT

There is a need for credible risk assessments and science-based solutions when dealing with moderate to low levels of environmental contamination occurring over large land areas. Credible risk assessments are needed to define and manage the underlying human health and ecological risk, and scientific understanding is needed to develop and implement novel remediation strategies, as well as to gain regulator and stakeholder acceptance of these approaches. Experience at the Department of Energy's Savannah River Site (SRS) near Aiken, South Carolina has demonstrated that a strong scientific program can have significant consequences in terms of providing input to the remediation process.

INTRODUCTION

Significant challenges remain concerning the remediation and restoration of contaminated environments at DOE facilities nationwide. At the Savannah River Site, near Aiken, SC, DOE and its contractors have made considerable progress in addressing a variety of problems related to waste management that have also resulted in significant cost savings and avoidance [1]. As emphasis shifts from engineered solutions focused on defined contamination problems to those involving moderate-to-low levels of contamination over large land areas, the need for credible risk assessments and science-based solutions will grow. Scientific understanding is needed to develop and implement novel remediation strategies, including *in situ* chemical stabilization, phytoremediation, bioremediation, and monitored natural attenuation, as well as to gain regulator and stakeholder acceptance of these approaches. Decisions regarding cleanup actions on these sites will be driven by human and ecological risks, but risk analysis is inadequate without a strong scientific underpinning. This is especially true for ecological risks where uncertainties remain about how to determine appropriate endpoints and risks that contaminants pose to *ecosystems* as opposed to *individuals*, who are the focus of concern when estimating human health risk [2]. Without adequate scientific understanding, managers may be surprised to find that ecological risks based on effects to individual test organisms result in more conservative soil or water screening levels for certain contaminants, such as Cu and U, than for human health risk determinations. Experience at the Department of Energy's Savannah River Site has demonstrated that a strong scientific program can have significant consequences in terms of remedial action decisions. This paper will focus on examples from the SRS where science has been, and will continue to be, an important component in providing the information needed to make sound decisions regarding remediation and restoration.

EXAMPLES AND CASE STUDIES

A number of examples and case studies from the SRS could have been chosen to illustrate the role and importance of scientific understanding in the overall environmental remediation process. The following were chosen because they focus on radiocesium, one of the most widespread contaminants on the SRS, and because they illustrate the diversity of issues and expertise that come into play.

Par Pond

Par Pond, a 1,069 hectare cooling reservoir on the SRS that received thermal effluents from SRS reactors, was contaminated with low levels of ^{137}Cs , ^{90}Sr , and transuranics between 1954 and 1964. The dominant radionuclide in the reservoir is ^{137}Cs , and the total inventory of ^{137}Cs in the reservoir has been estimated at about 44 curies [3]. After problems with the dam were discovered in 1991, the water level was lowered about 5.8 meters, which exposed about 525 hectares of contaminated sediments. One option under consideration was to drain the reservoir and remediate the site by removing the contaminated sediments. However, site-specific data from ecological research done at the SRS, along with estimated sediment removal costs, argued against this approach. Instead, the dam was repaired and the reservoir was returned to full pool as an interim action, thereby avoiding an estimated \$1 billion or more in remediation costs and significant environmental damage from displacing the contaminated sediments [3].

One of the lessons learned from the Par Pond example is the importance of having sufficient site-specific information to adequately characterize a site and credibly assess ecological and human health risks. Par Pond is certainly a well-characterized site; about 300 publications and dissertations dealing with almost every environmental aspect of the reservoir exist in the scientific literature. Thus, a wealth of information from previous and ongoing research was available to characterize the natural resources in the system, and assess the risks posed by contaminants in the exposed sediments following draw down. Incorporating mostly site-specific data into very conservative models for a self-sufficient, on-site resident and site worker showed cancer risks from radiation in the exposed sediments to be above the regulatory limit [3]. Simply refilling the reservoir, however, provided enough shielding to reduce radiation levels below background.

Two other contaminated reservoirs on the SRS, L-Lake and Pond B, will likely face similar issues some time in the near future.

Monitored Natural Attenuation and Ecological Half-Life

Monitored Natural Attenuation (MNA) refers to the use of natural physical, chemical and biological processes, such as microbial degradation, sorption, radioactive decay, and chemical transformations to remediate contaminants. For radioactive contaminants, such as ^{137}Cs , this can be ideal, as radionuclides naturally disappear over time through physical decay at a known rate. For ^{137}Cs , its half-life is about 30 years, meaning that half of the radiocesium present in a location will disappear in about 30 years through natural physical decay. During that time and subsequent intervals, however, ^{137}Cs can still be mobilized and transported in the environment. Determining when, where and under what circumstances this occurs is an important function of

research. In fact, much is already known about the behavior of radiocesium from studies done at various DOE sites over many years.

At the SRS, several recent studies have reported on natural attenuation of radiocesium and its relationship to ecological half-life [4-7]. Ecological half-life (T_e) is the time required for a contaminant in an ecosystem, or one of its components, to decline by half as a result of all combined physical, chemical and biological processes that remove the contaminant or otherwise make it unavailable. Brisbin et al. [4] summarized the historical development of this concept and its application to MNA. Paller et al. [5] estimated the ecological half-life of ^{137}Cs in fish collected from SRS streams and reservoirs over a 24-year period. The ecological half-life estimates ranged from 3.2-16.7 years, considerably shorter than the 30-year half-life that would be expected based on radioactive decay. The shorter estimates were for streams; the longer estimates were for reservoirs. Although no attempt was made to identify the specific reasons for the differences, presumably they were the combined result of sediment erosion and deposition, plant uptake, stream flow, and similar processes that removed ^{137}Cs from those ecosystems. Having this understanding then allowed the researchers to predict that, if current trends continue, ^{137}Cs concentrations in fish from contaminated streams and reservoirs on the SRS will likely decline to levels acceptable for consumption in not more than 50 years. Peles et al. [6] estimated T_e for ^{137}Cs in fish from one of the same SRS streams (Steel Creek) and found similar results. T_e estimates for aquatic plants in this same stream, however, were somewhat higher than for fish [7]. The authors hypothesized that over time in such a system uncontaminated sediments might be deposited over contaminated sediments, thereby limiting ^{137}Cs uptake in fish while leaving plant roots exposed to underlying contaminated sediments.

Trophic Transfer

The transfer of contaminants from one environmental compartment to another and across trophic levels has been the subject of many studies in the scientific literature in recent decades. Some of the earliest environmental research conducted at DOE sites concerned the transfer of radionuclides through the environment. The main reason for this emphasis has been an obvious concern about the movement of contaminants from soils and sediments, the main repository for most contaminants, to ecological and human receptors via the food chain and other pathways.

In spite of the wealth of information that exists about trophic transfer of contaminants, there is still an important role for scientific research in providing a better understanding of the mechanisms involved in contaminant transport and bioavailability. For example, on the SRS transfer factors for ^{137}Cs from soils to plants are considerably higher than at other DOE sites (Table I).

Table I Transfer factors for ^{137}Cs from a variety of soil types to plant species. Compiled from various literature sources.

DOE Site	Transfer Factors
Hanford	0.053 – 0.15
INEEL	0.04 – 0.50
Oak Ridge	0.03 – 0.10
SRS	3.1 – 43.0

Explanations for this observation typically involve differences in clay mineralogy among the sites and the fact that soils on the SRS and throughout the Southeast are low in potassium, a chemical analog of cesium. Subsequent sections will discuss this topic in more detail and present hypotheses that might explain the mechanisms underlying these observations.

It is often useful to know the source of contaminants and the pathways by which they are transferred to various receptors. This can be difficult to determine, however, particularly in the case of animals that move and feed over large areas, and perhaps have a variety of food sources. In a recent study involving a novel approach, Gaines et al. [8] used stable isotopes to assess trophic transfer of metal contaminants in raccoons, a common receptor species in ecological risk assessments. They concluded that trace element burdens in raccoons were related to trophic position within a contaminated environment, and that the raccoons probably fed over a range of three trophic levels. Having such site-specific knowledge can be important for generating realistic risk assessments.

Mineralogical Controls on ^{137}Cs Mobility

Nearly all (99%) of the ^{137}Cs inventory in these contaminated environments exists in soils and sediments [2, 9]. Underlying the transport and bioavailability of cesium in this situation are the molecular-scale physicochemical interactions that occur between cesium and the soils and sediments, particularly the clay mineral fraction.

A common explanation for the relatively high mobility of ^{137}Cs in SRS environments is the predominance of kaolinite, gibbsite, and goethite in the clay mineral fraction. Several studies, however, have demonstrated that the majority of sediment-bound ^{137}Cs behaves consistently with the presence of mica minerals, i.e., ^{137}Cs remains nonexchangeable, even when extracted with concentrated solutions containing large monovalent cations, such as K^+ or NH_4^+ [10-12]. A smaller fraction (5-10%) of ^{137}Cs has been shown to be readily exchanged by moderate to low concentrations of monovalent cation competitors, such as NH_4^+ [10, 11].

A recent study [13] examining ^{137}Cs distributions among particle size fractions in contaminated floodplain sediments at the SRS revealed that >70 % of the cumulative radiocesium activity resided in the 50-300 μm fraction. The evidence suggests that nanophase micaceous zones exist as occlusions within 2:1 phyllosilicate hydroxy interlayered mineral (HIM) grains and it is this low abundance phase that controls ^{137}Cs dynamics in SRS soils and sediments [13]. These intragrain micaceous mineral occlusions are not detectable by x-ray diffraction but have been

identified by HRTEM in larger particle fractions, as coatings on quartz grains, consistent with previous observations of highly weathered soils [14]. While in low abundance from a bulk mineralogical standpoint, there exist sufficient quantities of these micaceous relic phases to dominate ^{137}Cs dynamics in these systems.

Other studies [15] have demonstrated that the initial sorption of ^{137}Cs is controlled by the concentration of frayed edge sites (FES). Frayed edge sites are typically found on micaceous minerals and demonstrate very high sorption selectivity for monovalent cations having low hydration energy, i.e., K^+ , Cs^+ , Rb^+ and NH_4^+ compared to di- and trivalent cations. The average FES associated with the $>50\ \mu\text{m}$ fraction of SRS flood plain sediments was found to be $0.76\ \text{cmol (+) kg}^{-1}$, which is in the range of previously reported values for similar soils [13]. While many studies have demonstrated an evolution of initially sorbed ^{137}Cs at FES to ^{137}Cs fixed in interior regions of micas over time, this trend is not observed at the SRS, where the fraction of ^{137}Cs associated FES has remained unchanged over decades of aging [10-13]. This may suggest that the properties of the highly weathered mica minerals in SRS soils and sediments have different properties compared to less highly weathered mica minerals of more temperate regions. Thus, the FES probed via selective ion exchange for SRS soils and sediments may represent what has been termed “wedge sites” [16, 17]. Wedge sites (WS) are a type of FES highly selective for monovalent cations having low hydration energies. They are, however, located more towards crystallite interiors and stabilized by hydroxy-Al interlayers, which prohibit edge layer collapse upon ^{137}Cs sorption thus reducing the cesium selectivity at these sites and enhancing exchange reversibility [16, 17]. This may be one explanation for the observed greater bioavailability of ^{137}Cs at the SRS compared to other environs.

Novel Remediation Strategies

Having a foundation of knowledge about contaminants, as well as habitats and receptors that are being affected, allows one to begin developing novel remediation strategies that may be more appropriate than conventional means—and hopefully more cost effective. It should be emphasized, however, that having better information about a system does not guarantee that a cheaper solution can be developed, but knowledge should lead to better and more appropriate solutions.

Knox et al. [18] thoroughly reviewed a number of *in situ* remediation techniques, all of which depend on a sound scientific foundation to be effective, to gain regulator and stakeholder acceptance, and to understand the limitations of the techniques. These include changing environmental conditions, such as pH and redox status, as well adding a variety of amendments that sequester specific contaminants.

Seaman et al. [12] studied the effectiveness of various soil amendments, such as hydroxyapatite, illite and zeolite, in reducing the migration of ^{137}Cs and uranium in contaminated sediments. As might be expected, the various treatments and combinations differed in their effectiveness, but in general illite > hydroxyapatite > zeolite. Just as important as having results such as these, however, is knowledge about the underlying processes that can explain them.

Another approach being studied at the SRS involves the use of illite clays as an *in situ* method for remediating ^{137}Cs -contaminated wetlands. In aquatic field settings, Hinton et al. [19, 20] showed that an *in situ* method using illite minerals reduced ^{137}Cs concentrations in water 25- to 30-fold, in aquatic plants 3- to 5-fold, and in fish 2- to 3-fold. Analyses of water (the only component sampled again) at the same field sites two years later showed that ^{137}Cs concentrations were still lower than untreated control sites, suggesting some permanence to the treatments.

DISCUSSION

Long-term investigations on ^{137}Cs dynamics in contaminated SRS ecosystems have consistently demonstrated that the ecological half-life of ^{137}Cs is considerably less than the physical half-life. This observation provides phenomenological evidence for MNA processes operating to reduce the bioavailability of ^{137}Cs over time. However, the time-dependent reduction in ^{137}Cs bioavailability at the SRS appears to be considerably less than other environs world wide as revealed by the consistently higher soil to biota transfer factors. Two hypotheses emerge to account for these observations. One is that the highly weathered nature of the low abundance micaceous mineral phases results in a larger fraction of reversibly sorbed ^{137}Cs than for other sites having more abundant illitic clays. Some evidence for this hypothesis is the observation that the addition of illite clays to systems in the SRS has resulted decreased soluble and bioavailable ^{137}Cs in short-term studies.

The highly weathered soils of the southeastern U.S. are depleted in potassium, a nutrient mineral required in significant quantities especially by plants. Thus, another hypothesis for the greater biogeochemical mobility of ^{137}Cs is that K remobilization mechanisms may be acting to enhance the mobility of sorbed ^{137}Cs , which has very similar geochemistry. Some evidence for this hypothesis is the lower ^{137}Cs ecological half-life for animals than for plants. There are known biochelators, produced by fungi, which have very high selectivity for K^+ . It is also possible that both of these mechanisms could operate simultaneously. Additional information on the primary biogeochemical controls on ^{137}Cs mobility will be required to fully implement MNA or *in situ* immobilization remediation strategies on the vast contaminated soils and sediments on the SRS.

SUMMARY

Remediating relatively large land areas on the SRS and elsewhere having moderate or low level contamination (often of mixed wastes) will be a major challenge in the future. Science, along with costs and acceptability to regulators and the public, will be important in determining final remedial actions. Fundamental science on the biogeochemical cycling of contaminants in the environment, factors controlling bioavailability and trophic transfer of contaminants, and methods and models for establishing proper endpoints for evaluating risk of contaminants to ecosystems will be essential for guiding decisions on environmental remediation and restoration.

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