Ecological Risk Assessment of Metals in Savannah River Tributaries on the Savannah River Site

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Abstract. Department of Energy (DOE) operations at the Savannah River Site (SRS) near Aiken, South Carolina have resulted in the release of metals into several Savannah River (SR) tributaries. To investigate the effects of these contaminants, the SRS has developed an ecological risk assessment (ERA) program that incorporates multiple lines of evidence including comparisons of contaminant levels between reference (R) and potentially impacted (PI) sites, the use of contaminant exposure models (CEMs) to estimate effects on selected ecological receptors, and bioassessments of fish and benthic macroinvertebrate (BMI) assemblages. The CEMs estimate doses of metals in food and water ingested by the river otter *Lontra Canadensis* and belted kingfisher *Ceryle alcyon* and compare them with chronic toxicity reference values. The bioassessments provide empirical information concerning the cumulative impacts of contaminants on lower trophic level organisms. To facilitate these analyses, the SRS has been partitioned into Integrator Operable Units (IOUs) that correspond to the watersheds of the SR tributaries that drain the SRS.

Concentrations of metals in sediments, fish, and water are elevated in streams affected by SRS operations, but CEM results indicate that toxicological reference values are exceeded only by Al for the otter and Hg for both the otter and the kingfisher. Al exceedances occurred in reference IOUs without waste sites or industrial facilities as well as potentially impacted IOUs and were likely the result of natural Al levels in sediments and soils. Hg exceedances were restricted to the middle and lower reaches of SRS streams where environmental conditions favor methylation. Some of the Hg in SRS streams is the result of atmospheric deposition from offsite sources. However, SRS streams that formerly received SR water for reactor cooling exhibit elevated Hg levels as a possible result of Hg contamination in the SR. BMI assemblage structure was unrelated to sediment metal concentrations indicating an absence of measurable cumulative effects, but fish assemblage data were inconclusive. The SRS is continuing to refine the IOU database and identify factors that contribute to uncertainty in the ERA process as part of an ongoing effort to protect SR tributaries.

INTRODUCTION

Industrial operations at the 780 km^2 SRS near Aiken SC have resulted in the release of metals and other contaminants into SRS streams that flow into the SR. Many of the industrial areas and waste disposal sites on the SRS have been evaluated and are being remediated. However, there are streams that have received and may still receive contaminants through surface and subsurface transport mechanisms that are not fully evaluated. The SRS has developed an ERA process that incorporates multiple lines of evidence to investigate the effects of these contaminants, This paper will describe the results of this process to date to help provide perspective on the effects of more than 50 years of industrial operations at the SRS. The results will be of interest to those concerned with the ecological health of aquatic ecosystems potentially affected by the SRS.

BACKGROUND

Site-specific approaches for assessing risks posed by contaminants in SRS streams are inadequate because multiple drainages of large size are involved, levels and types of contamination vary, and there are multiple sources of contaminantion To deal with these issues, SRS streams have been partitioned into Integrator Operable Units (IOUs) and IOU subunits that, respectively, correspond to entire streams and portions of streams. The streams are “integrators” because they have the potential to receive contaminants that can be transported by water from any source within their watersheds. Organisms associated with the streams are exposed to these contaminants, and their health is potentially affected by the extent of contamination.

Several lines-of-evidence are needed to assess the potential ecological effects of contaminants in SRS streams because these streams may be affected by multiple impacts. This evidence includes comparisons of contaminant levels in various media between reference and potentially impacted sites, the use of CEMs to estimate effects on selected ecological receptors, and bioassessments of aquatic macroinvertebates and fish. The CEMs provide estimates of potential contaminant doses and effects on trophic apex predators based on the consumption of fish, crayfish, sediment (incidentally ingested) and water from SRS streams. Bioassessments provide information on the cumulative impacts of contaminants on lower trophic level organisms. Both fish and BMI assemblages are assessed because they may respond differently to the same stressors. Habitat data are collected concurrently with biotic data to provide a basis for separating physical factors affecting biotic assemblages from the effects of contaminants. A watershed approach was used to organize the contaminant distribution data, accommodate the size and complexity of the SRS, and characterize the effects of multiple potential impacts acting within the same watershed.

EXPERIMENTAL DESIGN AND METHODS

There are five major stream drainages on the SRS: Upper Three Runs, Fourmile Branch, Pen Branch, Steel Creek, and Lower Three Runs. Each constitutes an IOU, and each IOU is divided into subunits representing ecologically distinct stream reaches. Six subunits had no waste sites or industries in their drainages and were considered R subunits that represented ambient conditions. The remaining 10 subunits were considered potentially impacted (PI) because they received discharges and/or had waste sites within their drainages. Former reactor cooling reservoirs constitute additional subunits that are not covered in this report.

Metal concentrations

Al, Sb, As, Ba, Be, Cd, Cr, Cu, Pb, Mn, Hg, Ni, V, and Zn concentrations were measured in surface wetland sediments, fish, and crayfish. These metals were identified as possible problems in preliminary studies. Data were collected between 1990 and 2005 by numerous organizations and organized in a geographic information system data base. The data base included nearly 49,000 individual metal measurements.

Exposure point concentrations (EPCs) were calculated for the metal concentrations in each medium in each subunit. Three types of EPCs (listed below in decreasing order of preference) were used based on sample size and the amount of data censoring:

1) The upper 95% confidence limit (UCL) - computed with ProUCL 4.0 software (Singh and Singh 2007), which identifies an appropriate UCL based on the data distribution and prevalence of censoring.
2) The maximum concentration - used when the number of detects were insufficient to compute UCLs.
3) One half of the maximum detection limit - used when all data were below the detection limit(s).

Differences in metal concentrations between PI and R subunits were tested with Mann-Whitney Wilcoxin or Gehan tests depending upon sample size and amount of censoring.

Contaminant Exposure Models

Risks to biota posed by metals were evaluated with CEMs for the river otter and the belted kingfisher, two locally common apex predators that feed on aquatic organisms. Exposure pathways were ingestion of food, surface water, and soil. Estimated diets of these organisms were taken from EPA (1993). Concentration rations were used to estimate EPCs for some pathways in subunits with insufficient data (see Paller et al. 2008).

The contaminant exposure models were similar to those in EPA (1993). Ingestion rates for all pathways were summed:

$$ED_{total} = \sum_{i=1}^{n} ED_{food\ i} + ED_{water} + ED_{soil}, \text{ where:}$$

ED_{total} = total exposure dose from all sources (mg/kg/d)
$ED_{food\ i}$ = exposure dose from ingestion of food source i
ED_{water} = exposure dose from ingestion of water
ED_{soil} = exposure dose from ingestion of soil.

ED_{total} was compared with lowest observed adverse effect levels (LOAELs); i.e., lowest metal concentrations that caused adverse chronic effects (ERD 1999). The contaminant exposure models were used to compute probabilistic and deterministic risk estimates. The former were based on Monte Carlo methods in which metal concentrations were represented as probability distributions rather than point estimates. All PI stream subunits were combined and all R stream subunits were combined for the probabilistic evaluations. Deterministic evaluations were conducted for individual PI and R subunits. More details can be found in Paller et al. (2008).

Bioassessment

BMIs were collected with Hester-Dendy multiplate artificial samplers and a timed natural substrate sampling protocol. Five Hester-Dendy samplers were deployed at one to four sites in each subunit. The natural substrate sampling protocol was similar to SCDHEC (1998): organisms were collected using three man-hours of effort at each site using multiple methods. Habitat quality was assessed using methods similar to SCDHEC (1998). Fish assemblage data were collected by electrofishing 150 m stream segments at one to three locations in each subunit.

Multivariate differences in biotic metrics among sample sites were analyzed with Redundancy Analysis (RA), which permitted testing relationships among biotic metrics, habitat, and environmental metal concentrations (indicated by EPCs in sediment). Partialling techniques with habitat quality and stream size as covariables were used to assess the independent effects of sediment metal concentrations on biotic metrics (Lepš and Šmilauer 2007).

RESULTS

Metal Concentrations

Metal concentrations varied among media but were usually highest in sediment and lowest in water, except for highly bioaccumulative Hg, which was highest in fish (Table 1). Statistical tests of the sediment data showed that concentrations of most metals were significantly ($P \leq 0.05$) higher in the PI subunits than the R subunits (Table 1). Tests of the fish tissue data showed that Al, Cr, Cu, Mn, Hg, Ni, and Zn were higher in the PI subunits, and tests of the water data showed that Al, Cd, Cr, and Zn were higher in the PI subunits.

Contaminant Exposure Models

The exposure doses for most metals were higher in the PI than the R subunits. However, few (0 to1%) doses exceeded the LOAEL indicating a lack of significant risk for all metals except Hg and Al. In the probabilistic otter model, the percentages of estimated Hg doses that exceeded the LOAEL were 88 in the PI subunits and 19 in the R subunits (Figure 1). Most (78%) of the Hg dose resulted from fish consumption. The kingfisher model produced similar results for Hg (79% in the PI subunits and 13% in the R subunits). The spatial pattern of Hg exposure (based on EPCs for individual subunits) indicated that exposure doses exceeded the LOAEL in one R subunit and seven PI subunits. The highest doses were in the Steel Creek and Lower Three Runs drainages.

Al exhibited fewer LOAEL exceedances than Hg: 49% in the PI sites and 15% in the R sites, as shown by the otter model (Figure 2) Al intake was associated with invertebrate, sediment, and fish consumption. There were no Al exceedances in the kingfisher model because the avian LOAEL for Al was relatively high (1100 compared with 19.3 for mammals). Al exposure doses exceeded the LOAEL in one R subunit and seven PI subunits and did not show a pattern among drainages.

Table 2. Exposure point concentrations (ppm) for metals in potentially impacted (PI) and reference (R) subunits on the SRS. Asterisks indicate metals with significantly ($P \leq 0.05$) higher concentrations in the PI subunits.

	Sediment		Fish		Water	
Metal	PI	R	PI	R	PI	R
Al	9434.0	7314.0	89.7	49.1*	3.141	2.003*
Sb	11.5	2.1	0.6	0.9	0.004	0.007
As	3.9	1.1*	0.3	1.3	0.005	0.012
Ba	134.1	55.2*	19.5	25.6	0.060	0.061
Be	0.7	0.3*	<0.1	0.25	0.001	0.000
Cd	1.6	0.2*	0.1	0.2	0.063	0.002*
Cr	52.1	7.8	1.7	0.5*	0.007	0.005*
Cu	70.0	16.4	2.5	1.0*	0.019	0.023
Pb	418.5	8.2*	1.4	6.4	0.014	0.019
Mn	633.9	142.9*	94.3	41.6*	0.163	0.190
Hg	0.5	<0.1*	0.9	0.2*	0.001	0.009
Ni	104.1	2.1*	1.7	0.22*	0.008	0.007
V	26.9	17.7*	0.5	0.28	0.002	0.002
Zn	171.4	20.7*	140.5	33.8*	0.034	0.005*

Bioassessments

Six metrics were computed from the BMI data collected from natural substrates: total number, total taxa number, number of Ephemeroptera, Trichoptera and Plecoptera (EPT) taxa, % Ephemeroptera, % clinger and BI (a biotic index based on pollution tolerances). Stream width (a natural determinant of assemblage structure) and habitat quality were covariables in the RA, thereby permitting a test of the independent effects of sediment metal concentrations. The amount of variation in the BMI metrics explained by sediment metal concentrations was 25% compared with 45% by stream width and habitat quality. A Monte Carlo permutation test showed that sediment metal concentrations did not have a significant effect (at $P<0.05$) on the metrics after stream width and habitat quality were statistically controlled.

Similar analyses on the five BMI metrics computed from the Hester-Dendy data indicated that variation in the metrics explained by sediment metal concentrations (39%) was not statistically significant after the effects of habitat quality were removed.

A third set of analyses showed that stream width and habitat quality accounted for only 12% of the variance in the fish assemblage metrics, and that the variance explained by sediment metal concentrations (59%) was significant ($P<0.05$). This was the result of high metal concentrations in two subunits that suffered from environmental degradation not represented in the habitat quality variable. One subunit was located just upstream from a reservoir, which may have reduced the number of fish species because of isolation from downstream sources. The other subunit was affected by the release of anoxic water from upstream beaver ponds.

DISCUSSION

The CEMs showed that most metals in SRS streams were not sufficiently elevated to individually pose significant threats to mammals and birds. An exception

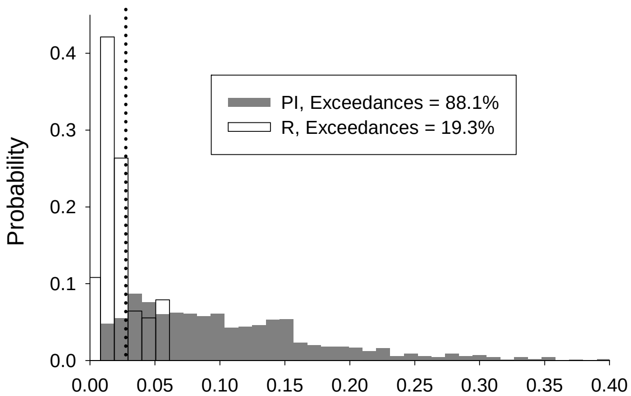

Figure 1. Estimated exposure doses for methyl mercury in potentially impacted (PI) and reference (R) IOU subunits. Also shown is the LOAEL (dotted line) and the percent exceedance of the LOAEL for the PI and R subunits.

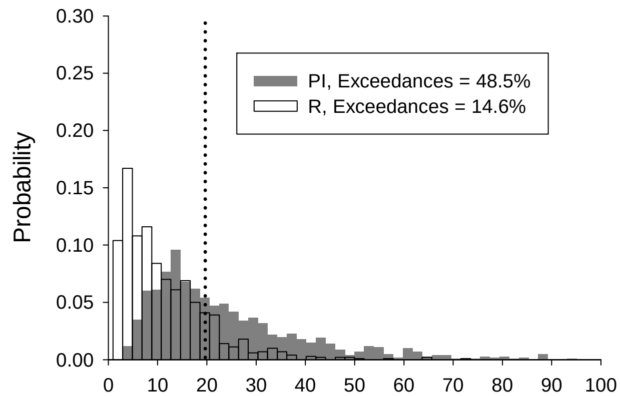

Figure 2. Estimated exposure doses for aluminum in potentially impacted (PI) and reference (R) IOU subunits. Also shown is the LOAEL (dotted line) and the percent exceedance of the LOAEL for the PI and R subunits.

was Hg, which occurs in elevated levels in fish throughout the SR basin as a result of atmospheric deposition (EPA 2000). Although this factor undoubtedly contributed to Hg levels in the SRS subunits, the most and highest exceedances occurred in streams that formerly received reactor cooling water from the SR. This water was contaminated with Hg from industries located upstream of the SRS (Paller and Littrell 2007), and some Hg may remain in the streams as suggested by other studies (Newman and Messier 1994). Thus, while elevated Hg levels may not be a direct result of SRS industrial processes, they could be related to the former use of contaminated SR water by the SRS.

Al was the only other metal that resulted in significant LOAEL exceedances, but the lack of a significant difference in sediment Al concentrations between the PI and R subunits suggests that this was not the result of SRS operations. Al exceedances in the SRS subunits may be related to high Al levels in the soil. Kaolinite [$Al_2Si_2O_5(OH)_4$] is mined in the region and is a component of the SRS geological strata.

The contaminant exposure models were unable to evaluate the cumulative effects of metals on ecological receptors because mechanisms of cumulative metal toxicity are poorly understood. Therefore, alternative lines of evidence were examined including degradation of benthic BMI and fish assemblages, both of which are sensitive to metals. Assessment of metal effects on these organisms was complicated by habitat degradation in streams that were formerly subjected to extreme flow perturbations and other habitat modifications as well as metal contamination. MI metrics were uncorrelated with sediment metal concentrations after these variables were accounted for. In contrast, fish community metrics were related to sediment metal concentrations, although this relationship was strongly influenced by two subunits where unmeasured, co-occurring habitat factors could also have affected fish community structure.

Collectively, these studies suggest that, with the possible exception of Hg, elevated metal levels have not seriously compromised the ecological integrity of SRS streams, although discrimination between habitat and metal related effects on fishes in some streams will require more study. The cumulative effects of multiple stressors including metals, radionuclides, and habitat alterations are still under evaluation, and efforts continue to refine the IOU database and fill data gaps that contribute to uncertainty in the ERA process.

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LITERATURE CITED

EPA (US Environmental Protection Agency), 1993. *Wildlife exposure factors handbook, volume I.* EPA/600/R-93/187. US Environmental Protection Agency, Washington, DC, USA.

ERD (Environmental Restoration Division), 1999. Terrestrial toxicity reference values (TRVs) (including exposure dose (ED) and hazard quotient (HQ) calculations). ERD-AG-003, P.7.3, Revision 0. Savannah River Site, Aiken, SC, USA.

Lepš, J., and P. Šmilauer, 2007. *Multivariate analysis of ecological data using CANOCO*. Cambridge University Press, New York, USA.

Paller, M.H., and J.W. Littrell, 2007. Long-term changes in mercury concentrations in fish from the middle Savannah River. Sci. Total Environ. 382:375–382

Paller, M.H., S.A. Dyer, and D.P. Coughlin, 2008. Exposure of Ecological Receptors to Metals in the Savannah River Site Integrator Operable Units. WSRC-STI-2008-00365. Savannah River National Laboratory, Aiken, SC, USA.

SCDHEC (South Carolina Department of Health and Environmental Control). 1998. Standard operating and quality control procedures for macroinvertebrate sampling. Technical Report No. 004-98. Bureau of Water, Division of Water Monitoring, Assessment and Protection, Aquatic Biology Section.

Sing, A., and A.K. Sing, 2007. ProUCL Version 4.0 Technical Guide. EPA/600/R-07/041. US Environmental Protection Agency Office of Research and Development, Washington, DC, USA.