SUMMARY REPORT

Literature Review for Surface Water Contaminant Fate and Transport Modeling of Tims Branch

(Subtask 2.2 of the project "Environmental Remediation Technologies")

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Executive Summary

This summary report includes a detailed literature review for the surface water contaminant fate and transport modeling of Tims Branch at Savannah River Site (SRS). FIU-ARC has been performing research at SRS to support their remediation efforts through hydrological modeling of the Tims Branch watershed in order to examine the response of the system to historical contaminant discharges and environmental management remediation actions. The research is intended to provide a better understanding of the fate and transport of inorganic and organic pollutants of concern with a focus on mercury and tin. FIU completed a literature review to support the hydrological modeling framework for the Tims Branch. More than 30 SRS-DOE reports and 100 published journals were reviewed. A total of 10 reports were found to be significant to this study and are included in this summary report. Specific reports by Looney (2010, 2012) and Betancourt (2011) were among the most addressed in this literature review and a total of 40 journal articles were found relevant to the study. An additional literature review was performed to explicitly address previous hydrological modeling efforts conducted for Tims Branch; however, it was determined that are very few studies involving hydrological model development in this watershed.

This literature review was used to develop a data-driven conceptual model specific to the Tims Branch watershed at Savannah River Site, as well as a generalized process-based conceptual model which depicts the various hydrological components being incorporated in the model development. This report will also be utilized as a foundation for surface water modeling in Tims Branch and other areas at SRS.

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Introduction

Mercury (Hg) is an extremely rare element in the Earth's crust and a potent toxin of great concern for aquatic ecosystems because of its tendency to bio-accumulate in fish (Benoit et al., 2003; Ullrich et al., 2001). Mercury concentrations in the atmosphere are elevated two to five fold over pre-industrial levels, mainly as a result of worldwide increases in industrial activities such as the burning of fossil fuels (Munthe et al., 2007; Ullrich et al., 2001). Atmospheric deposition has been identified as a major pathway by which Hg enters aquatic ecosystems, although some soils are naturally rich in Hg, and contamination of downstream ecosystems by areas of past Hg mining activity is particularly worrisome (Evers et al., 2007; Ullrich et al., 2001). In the United States, mercury was largely used to separate ^{6}Li (lithium isotope) for nuclear weapons production in the late 1940s and 1950s. Savannah River Site (SRS) is one of the nuclear sites that have received mercury contamination over the past 50 years. Mercury treatment started in 2007 by injection of stannous (tin) chloride into contaminated groundwater. As a result, mercury was removed as a vapor, and tin dioxide was precipitated in the sediment.

Tin in elemental form is not very toxic to any kind of organism, but the organic form is toxic. Organotin compounds are very persistent and not fairly biodegradable and they may persist in the environment for long periods of time. They are known to be toxic to aquatic ecosystems (Amouroux et al., 2000). Therefore, understanding the fate of tin and its compounds is of primary importance due to their potential impact on the environment (Donard and Weber, 1985; Maguire et al., 1986). Tin methylation is a great environmental concern because of its toxicity to humans and animals. Although tin is primarily deposited as sediment, remobilization may occur during episodic extreme events, such as storms or heavy rainfall. In these cases, sediment can be resuspended in the water column and deposited further downstream. It is therefore important to study the fate and transport of tin during such events, in particular its potential for methylation.

Numerical modeling has proven to be a cost effective tool in studying natural processes such as hydrology and fate and transport of contaminants. Numerical modeling can provide insight into how sediment may become resuspended, transported and redistributed in a waterbody during various extreme weather scenarios. The objective of this report therefore is to summarize the literature that has been reviewed and that will be significant in development of the conceptual model of the Tims Branch watershed, as well as the hydrological modeling work to simulate the fate and transport of mercury and tin in Tims Branch.

Study Area

During the cold war, the US Department of Energy (DOE) built various facilities around the United States to produce nuclear materials including lithium isotopes. Savannah River Site (SRS) is one of the many nuclear facilities owned by DOE. It is located 24 km southeast of Augusta, Georgia, and 16 km south of Aiken, South Carolina (Fig. 1) and covers approximately 800 km^2. SRS includes facilities such as reactors, laboratories, waste disposal sites, cooling towers, incinerators, etc. After several years of nuclear operations at the site, pollutants such as heavy metals, particularly mercury, and solvents such as trichloroethylene (TCE) have entered the environment, contaminating the soil, surface water and groundwater.

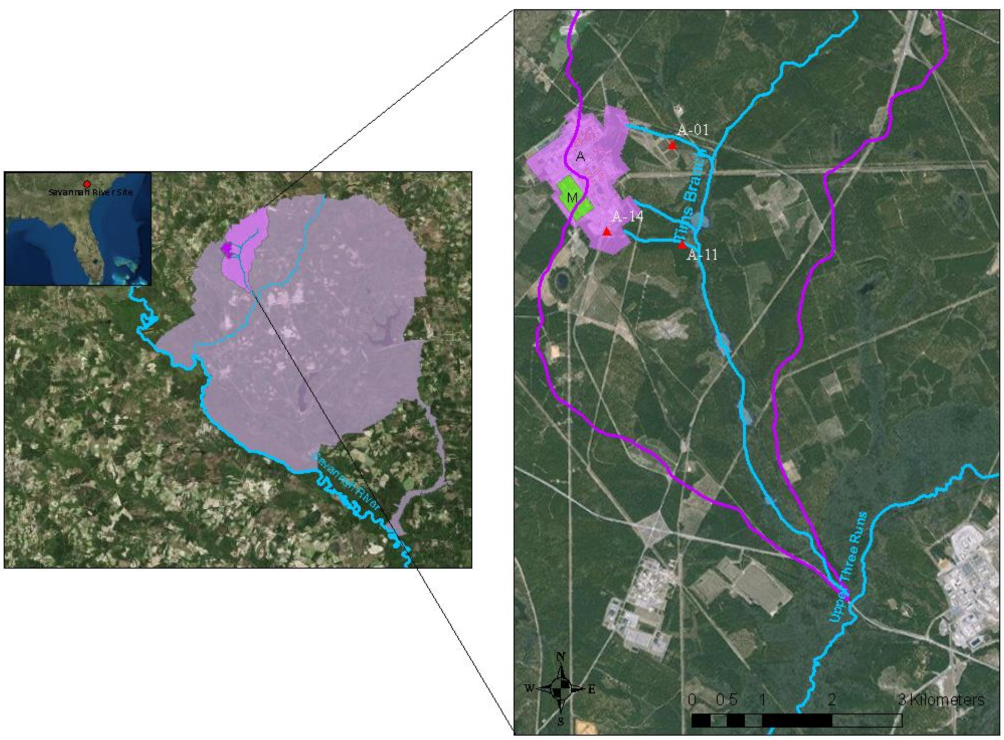

Fig. 1 Location of SRS and Tims Branch, SC

Tims Branch is a small braided, marshy, second-order stream within SRS that starts at the northern portion of SRS and passes through Beaver Ponds 1-5 and Steed Pond, and eventually discharges into Upper Three Runs (Fig. 2). Its drainage area is nearly 16 km^2 (Batson et al., 1996). The length of this stream from outfall A-014 to Upper Three Runs is approximately 8 km. The average width of the stream varies between 2-3 m.

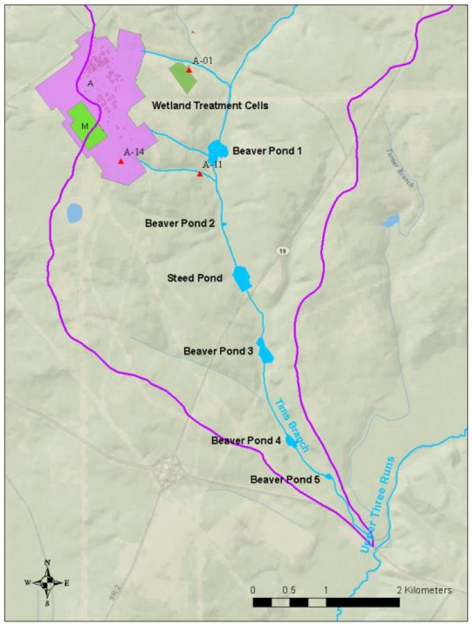

Fig. 2 Tims Branch and Beaver Pond 1-5

Topography and Hydrology of SRS and Tims Branch

SRS is a typical coastal plain watershed that includes a network of rivers and streams that are tributaries to the Savannah River which is the border between South Carolina and Georgia, and a portion of it borders the SRS (Halverson, 2008). Savannah River is formed by the confluence of the Tugaloo and Seneca Rivers in northeast Georgia and flows southeast through the Piedmont and Coastal Plain to the Atlantic Ocean. Major tributaries from SRS to Savannah River include Upper Three Runs, Beaver Dam Creek, Fourmile Branch, Steel Creek, and Lower Three Runs.

General topography of SRS includes upper and lower coastal plains. Lanier (1997) explained that the upper Coastal Plain consists of rounded hills with gradual slopes, areas of highly irregular terrain, and some elevations exceed 200 m above sea level. The highest elevation at SRS is approximately 130 m above sea level, near Tims Branch and the northwest boundary of SRS. The land surface elevation at the boundary of the upper and lower Coastal Plains, located southeast of the SRS, is usually less than 60 m above sea level. Upper Coastal Plain stream slopes range from 1.0 to 4 m/km (Lanier, 1997).

Tims branch is one of the small streams within SRS which receives water from rainfall, groundwater, and discharges from the A/M area. Two major tributaries of Tims branch are A014 and A011 outfalls which are approximately 230 m apart. They combine with the main stream of Tims Branch 1,400 m from the A014 outfall (Hayes, 1984). Flow in Tims Branch is strongly influenced by groundwater discharge (Mast and Turk, 1999). Because of water table elevation and Tims branch bed elevation, it is considered to be a losing stream (surface water discharge into the groundwater) near A/M outfalls and a gaining stream (groundwater discharge into the stream) further south toward the confluence with Upper Three Runs (Looney et al., 2010; Varlik, 2013).

Source of Contaminants in Tims Branch

SRS wastewater including cooling water, steam condensate, groundwater treated by air strippers, storm water runoff, steam and air-conditioning condensates, laboratory drain wastewater, well flushing water, and other industrial and sanitary wastewater are discharged into nearby streams through several outfalls and flows toward Upper Three Runs and eventually discharge into the Savannah River (Halverson, 2008).

Since 1950s, Tims Branch has received contaminated wastewater from the A/M area at outfalls A-1A, A-01, A-11, and A-014. The groundwater treatment process was started in 1985. The treatment process consisted of removal of chlorinated solvents using air strippers. Treated groundwater was discharged into Tims Branch. In November 2007, as part of mercury removal efforts, tin chloride ($SnCl_2$) was injected into groundwater right before entering the air stripping system in order to convert mercury (II) to volatile mercury (0) form which can be removed through the air stripper. Dissolved mercury (II) reacts with tin chloride and produces tin dioxide (SnO_2) that precipitates as sediment at the bottom of Tims Branch:

$$Hg^{2+} + SnCl_2 + 2H_2O \rightarrow Hg_{(g)} + SnO_{2\,(s)} + 4H^+ + 2Cl^-$$

The initial concentration of mercury in the groundwater is approximately 250 ng/L. After treatment with tin chloride, mercury concentration has significantly reduced to approximately 10 ng/L (Looney et al., 2010). At the same time, the tin (IV) concentration, primarily as inorganic solid deposit, has increased substantially. Therefore, the sediment deposits at Tims branch are high in tin (IV). Based on field observations and results of the present study, the best estimate of the theoretical average tin (IV) concentration in the sediment in Tims Branch from the A014 outfall downstream to the confluence of Tims Branch with Upper Three Runs Creek is approximately 28 μg/g. The depth of sediments in which tin has accumulated in significant amounts, due to the tin chloride treatment system, is between 1.5 and 3.5 inches. The estimated total tin released in Tims Branch from November 2007 to August 2011 is approximately 43 kg. Although tin (IV) appears to be less toxic than mercury, it is essential to understand tin behavior and the impacts of the treatment system (both negative and positive) in Tims Branch. The literature suggest the possibility of generation of organotin through a methylation process (Amouroux et al., 2000; Hallas and Cooney, 1981).

Tin Deposition in Tims Branch

There are seven potential areas on Tims Branch that tin (IV) can be deposited: weir site, Beaver Ponds (2-5), and Steed Pond (Fig. 2). The weir site and Beaver Pond 2 are the only two sites that show actual accumulation of tin (IV) due to the treatment process in their sediment (Looney et al., 2010). The results of data collection of tin (IV) concentration indicate that tin accumulation in the sediment along Tims Branch is more non-uniform with some sites showing elevated concentration while the others report less tin accumulation. This non-uniform concentration distribution may be the result of an increase in bed erosion due to a higher discharge rate (450 gpm = 0.028 m^3/s) into Tims Branch after installation of the air stripper (Looney et al., 2010; Looney et al., 2012).

Although tin is primarily deposited as sediment along Tims Branch, mainly at the weir site and Beaver Pond 2, remobilization may occur during episodic extreme events such as storms or heavy rainfall. Sediment can be resuspended, enter the water body, and be deposited further downstream. Batson et al. (1996) investigated the remobilization of the uranium (U) rich sediment during rainfall events at SRS. Their findings show that a single storm event can effectively erode the sediment and transport it downstream towards Upper Tree Runs. They reported a 15 to 28 fold increase in U transport out of the Tims Branch system during storm events due to sediment erosion. They showed that as little as 16 mm of rainfall was needed to cause significant increase in stream turbidity and resuspension of sediment. This condition may apply to tin sediment erosion when an extreme event occurs.

Looney (2001) has identified three main uncertainties related to mercury treatment using stannous chloride: tin methylation through aerobic and anaerobic processes, tin mediated mercury methylation, and deposition and accumulation of tin in sediments. While the fraction of tin that was observed to be methylated by natural processes in many environments was relatively low and the conditions that maximize methylation (e.g., high salinity) are not present in typical freshwater streams, the potential exists for tin methylation in freshwater streams and riparian systems receiving long term discharges from outfalls being treated using stannous chloride and air stripping.

Modeling Hydrological Processes and Sediment Transport

Hydrology of surface water is proven to be one of the key factors controlling erosion and deposition mechanisms in sediment transport process in streams and rivers. Therefore understanding the hydrology of Tims Branch is vital in determining environmental conditions and what may cause enhancing sediment erosion and deposition in this stream. Developing a conceptual model and numerical simulations provide an improved understanding of how an extreme rainfall or flooding episode may affect the tin (IV) transport in Tims Branch.

A conceptual model describes the general physical framework of the relationship between physical processes that are part of an environment. The hydrologic conceptual model developed for SRS will address processes and features such as discharge points, groundwater/surface water interaction, geological formation, atmospheric characterization, infiltration, sediment erosion /deposition, etc. Very limited studies have addressed the hydrology and sediment transport mechanisms of Tims Branch and SRS. These studies are primarily based on experimental work and field data collections rather than numerical modeling approaches. Modeling hydrological processes and sediment transport mechanisms require a detailed understanding of soil and sediment characteristics, geologic formation, topography, climate, and hydraulic properties.

Most of previous hydrological modeling efforts were conducted in other areas of Savannah River and South Carolina. No particular hydrological model was found to specifically address the surface flow hydrology in SRS or Tims Branch. Conrads et al. (2006) have developed a three-dimensional model of Savannah River estuary to simulate changes in water levels and salinity conditions in the marsh by coupling 3D hydrodynamic river-estuary model and the marsh-succession empirical model. The coupled model however may not be applicable to SRS and Tims Branch because they only simulate water level in marsh areas. In addition, empirical modeling may not produce valid results when applied in other locations.

In a recent study, Feaster et al. (2012) investigated the relation between hydrological, geochemical, and ecological processes on mercury concentration in fish tissue. They applied two watershed hydrology models to the Mc Tier Creek watershed in South Carolina: a topography-based hydrological model, TOPMODEL (Beven and Kirkby, 1979; Wolock, 1993) to simulate surface flow hydrology, and a grid-based mercury model, GBMM (Dai T. et al., 2005) to simulate the fate and transport of mercury. Because TOPMODEL generates stream flow based on a variable-source-area concept, the model only reflects how rainfall moves through the watershed to become stream flow, so it is not feasible to apply it for an existing stream such as Tims Branch. In a similar study, Feaster et al. (2014), investigated the potential for scaling up the previous application of TOPMODEL for the Mc Tier Creek watershed (small scale) to Edisto River Basin (large scale) in South Carolina.

As none of the previous hydrological modeling efforts were specifically applicable to the SRS and Tims Branch, it is critical to develop a site specific flow and transport model to better understand the fate and transport of tin in surface water. FIU-ARC proposes to develop an integrated flow and transport model using the MIKE software package created by the Danish Hydraulic Institute (DHI). The integrated flow and transport model (MIKE-SHE/MIKE-11/ECOLAB) analyses the effect of hydrological events on potential tin erosion, resuspension, and transport in the Tims Branch watershed. The model includes the main components of the hydrological cycle and sediment transport; groundwater flow (saturated and unsaturated), overland flow, precipitation, and evapotranspiration. The objective of the model is to provide a spatiotemporal distribution of tin in the sediment of Tims Branch and forecast the fate and transport of tin and its possible methylation when an extreme event happens.

Available Modeling Tools

MIKE-11 is a 1-D river modeling system developed by DHI. According to EPA, it is one of the most advanced and comprehensive models available. MIKE-11 is routinely used by state regulators for analysis of natural stream flow and flow in canals and rivers in complex water management scenarios, including floodplain calculations, dam breaks, and control structures. MIKE-11 uses an implicit, finite difference scheme to solve the nonlinear equations of open channel flow (Saint-Venant) numerically. In addition to this fully dynamic description, other descriptions are also available to choose from including high-order, fully dynamic, diffusive wave, kinematic wave, quasi-steady state, and kinematic routing.

MIKE-SHE is a fully integrated model for the 3D simulation and linkage of hydrologic systems including overland, subsurface, and river flows. It has been successfully applied at multiple scales, using spatially distributed and continuous climate data to simulate a broad range of integrated hydrologic, hydraulic, and transport problems. MIKE-SHE couples partial differential equations that describe flow in the saturated and unsaturated zones with the overland and river flow. Different numerical solution schemes are then used to solve the different partial differential equations for each process.

ECOLAB is an ecological solver provided by DHI which can be coupled with MIKE-11 for the purpose of ecological modeling. An ECOLAB template can be developed by the user to model the ecological processes such as heavy metal transport, eutrophication, and xenobiotics.

Fig. 3 shows all the processes involved in flow and transport simulation with the MIKE package for Tims Branch. One of the strengths of the MIKE package is the GIS interface that allows the user to prepare input data and output results using GIS tools.

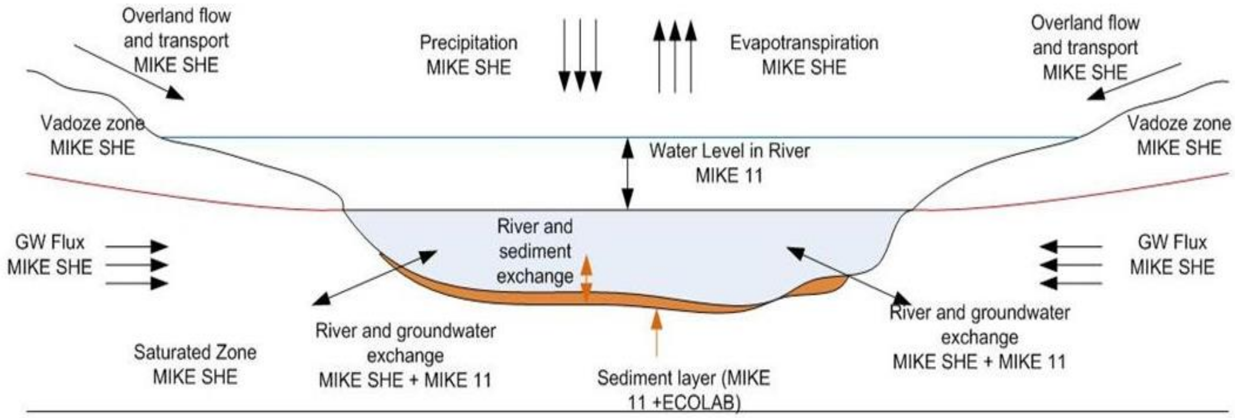

Fig. 3: Flow and transport components included in the model

Roelant et al. (2013) developed an integrated model of flow and transport using MIKE package for East Fork Poplar Creek (EFPC), Tennessee, to evaluate fate and transport of mercury in surface water and groundwater. With that model and through various scenarios, they explained how an extreme event may impact the fate and transport of mercury in surface water and groundwater. Their results confirmed the capability of the MIKE package for further modeling attempts in other areas. In this project, therefore, this software package will be utilized in the same manner to develop the Tims Branch model.

Model Development

The integrated flow and transport model will be developed in four phases:

1. Developing a MIKE-11 model of the river network.
2. Developing an overland and subsurface flow model using MIKE-SHE coupled with MIKE-11.

3. Model boundary conditions and calibration.
4. Developing the transport model using ECOLAB coupled with MIKE-SHE and MIKE-11.

The model will calculate flow velocity and depth in Tims Branch and provide spatiotemporal distribution of tin concentration during an extreme event. By providing detailed spatial information and characteristics including hydrological and transport properties in the four subdomains, Saturated Zone (SZ), Unsaturated Zone (UZ), Overland Flow (OL), and Transport in Streams (OC), the model will provide accurate water and mass balance for the study domain.

The MIKE-SHE model of flow and transport in the overland, saturated and unsaturated zones requires a number of spatial and temporal parameters which will be introduced to the model in the form of standard GIS data. Overland flow requires topography, land use and imperviousness. Some of the input GIS files for the overland module of the model are shown in Fig. 4. Manning's numbers for different regions is estimated from Manning's charts based on land use and vegetation information extracted from the SRS data provided. The original Manning's values, n, range between 0.01 and 0.05 (MIKE-SHE assumes an inverse Manning's number, M = 1 / n in the calculations and values range from 3 to 100).

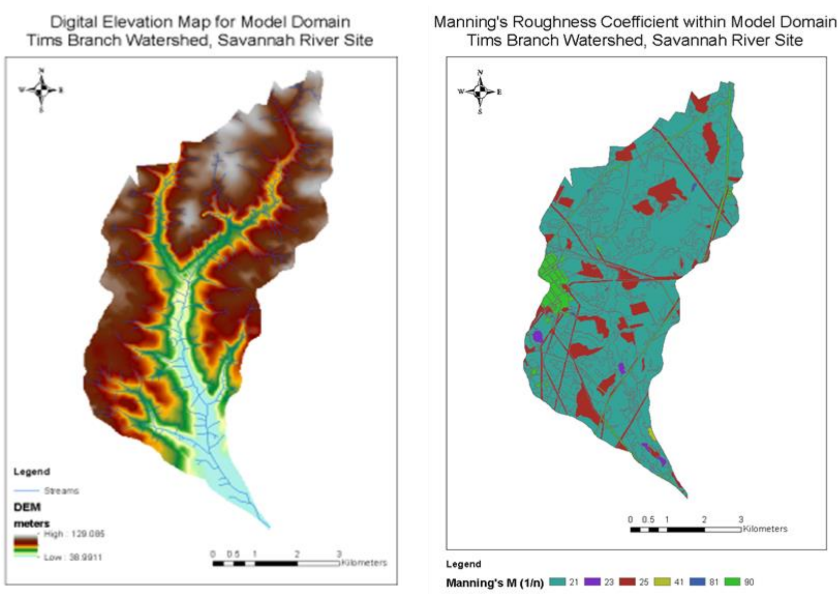

Fig. 4: Digital Elevation Model (DEM) and Manning's roughness coefficient grid files used in MIKE-SHE model

Conclusion

This report summarizes the literature that has been reviewed and that will serve as a foundation for development of the conceptual model of the Tims Branch watershed, as well as the hydrological modeling work to simulate the fate and transport of mercury and tin in Tims Branch. This extensive literature review is necessary to establish a detailed characterization of the site being studied, in this case, the Tims Branch watershed. The detailed information retrieved from the reviewed literature mentioned in this report as well as from online databases from various agencies such as USGS, NRCS, EPA, etc., will serve to improve the accuracy and ability of the hydrological model being developed to simulate contaminant fate and transport in Tims Branch.

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