54020

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION III
841 Chestnut Building
Philadelphia, Pennsylvania 19107

Mr. Verrill Norwood
President, Environmental Affairs
P.O. Box 248
Lower River Road
Charleston, TN 37310

JAN 18 1990

Dear Mr. Norwood:

The purpose of this letter is twofold. The first purpose of the letter is to issue conditional approval for Operable Unit #2 and #3 Sampling and Analytical Plan for the Saltville Waste Disposal Site. The second purpose is to outline the conditions that were agreed to by Olin and EPA in a teleconference held between these two parties on January 9, 1990.

During this teleconference between Paul Leonard of EPA, Richard Young of Young, Morgan, and Associates, Jim Brown and Keith Roberts of Olin, and David Stillwell of the U.S. Fish and Wildlife Service, several issues were discussed. From this discussion the conditions for approval of the plan were agreed upon by all parties involved. These conditions are listed below:

A. Fish Sampling Plan

1) All parties agreed that sufficient numbers of fish of each species from each station would be collected to determine a size-frequency curve. The fish in the oldest age classes with a sufficient number of fish at each station would be used for the mercury analysis.

2) All parties agreed the generation of a condition factor is appropriate. The four primary species will be used to generate this factor. In addition a smaller stoneroller or darter species will be used, if a sufficient number of these species can be collected.

B. Bentic Macroinvertebrate and Algal Sampling Plan

1) Olin agreed to send David Stillwell a copy of data from the 1980 and 1981 screening of mercury levels in macroinvertebrates. Crayfish and megaloptera were used for this screening.

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2) All parties agreed that crayfish and megaloptera were appropriate for collection if sufficient numbers and biomass at each station could be collected.

3) All parties agreed that every effort would be made to identify both the crayfish and megaloptera to a species level and to use a single species for the analysis at all stations.

C. Mussel Sampling Plan

1) It was agreed that no quantitative data exists to make statistical comparisons between present and historical data for mussel abundancies. The comparisons would be general and illustrate the number of species not the abundance of each species.

D. Ambient Water Toxicity Sampling Plan

1) All parties agreed that chronic (not acute) toxicity tests were appropriate based on the chronic effect of the effluent involved.

2) All parties agreed to use ceriodaphnia as the test organism at least for the first bioassay. The discussion on this matter revolved around the point of whether or not this organism would be adversely impacted by the natural level of salts in the river. If Olin could demonstrate that the organism is intolerant of the natural salt levels, in the river than they could explore the option of using another species of a similar sensitivity. This demonstration could take place only after the first bioassay is completed using ceriodaphinia.

In addition to these conditions EPA will require field filtered surface water samples for those samples taken for water quality analysis if those samples have total suspended solids (TSS) values which are greater than 10 milligrams per liter. If there are any questions on any of these conditions of approval please call me at (215) 597-1286.

Sincerely,

Paul Leonard

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Paul Leonard
Remedial Project Manager

cc: Andrew Levine
Robert L. Collings
Richard Hodgson
Timothy Longe

Olin
Chemicals Group

# Sampling & Analytical Plan

## Remedial Investigation/Feasibility Study

## Volume II
## Field Sampling Plans

Saltville Waste Disposal Site
Saltville, Virginia

October 1989

AR300011

# FIELD SAMPLING PLAN FOR FISH
# FOR THE SALTVILLE WASTE DISPOSAL SITE
# REMEDIAL INVESTIGATION AND FEASIBILITY STUDY
# SALTVILLE, VIRGINIA

OCTOBER 26, 1989

AR300012

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## 1.0 SITE BACKGROUND

### 1.1 Introduction

This Field Sampling Plan for Fish (FSP-Fish) has been prepared for the Remedial Investigation/Feasibility Study (RI/FS) for the Saltville Waste Disposal Site, Saltville, Virginia. This document describes in detail the sampling and data gathering methods which will be used to achieve the fish data quality objectives needed to support decisions regarding remedial response activities. The FSP-Fish was prepared in accordance with the Interim Final EPA document "Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA" (OSWER Directive 9355.3-01), dated October 1988; EPA document "A Compendium of Superfund Field Operations Methods" (OSWER Directive 9355.0-14), dated December 1987; and EPA document "Data Quality Objectives for Remedial Response Activities-Development Process" (OSWER Directive 9355.0-7B), dated March 1987.

### 1.2 Site Description

The Saltville Waste Disposal Site is located along the North Fork of the Holston River (NFHR), between the town of Saltville and the community of Allison Gap in western Smyth County, Virginia, extending partly into Washington County, Virginia (see Figure 1). The NFHR lies adjacent to the southern border of the site at North Fork Holston River Mile (NFHRM) 80.8 - 82.4 and flows southwest. The Saltville Waste Disposal Site includes the former chlorine plant site (FCPS), waste disposal Pond 5 and waste disposal Pond 6. Pond 5 discharges water into the NFHR at Mile 81.7. Pond 6 discharges water into the NFHR at Mile 81.5. Additional description of the Site is given in Section 2.0 of the RI/FS Work Plan.

The NFHR is a fast flowing mountain stream which originates approximately 48 miles above the former chlorine plant site. The stream flows southwest through a rural landscape to the confluence with the South Fork Holston River in Tennessee to form the Holston River. The Holston River flows into Cherokee Reservoir in Tennessee. Figure 2 is a schematic of the Holston-Cherokee system.

Upper watershed areas are primarily hardwood forest on steep slopes while the lower portion is less mountainous and is bordered by pasture and farmlands. Land-use is dominated by agriculture, and little heavy industry is present within the watershed except that located in Saltville, Virginia.

The NFHR is characterized over most of its length by a coarse, rocky substrate with extensive riffle and pool areas. Daily discharge at NFHR Mile 85 range from 23 cfs at low flow (7Q10) to 16,500 cfs at peak storm discharges (USGS data) and averages 290 cfs. Over the course of the study area (NFHRM 98 to NFHRM 53), the river varies in width between 100 and 300 feet. Water depths at normal flow vary between a few inches in the riffle areas to 10 feet in the deeper pools.

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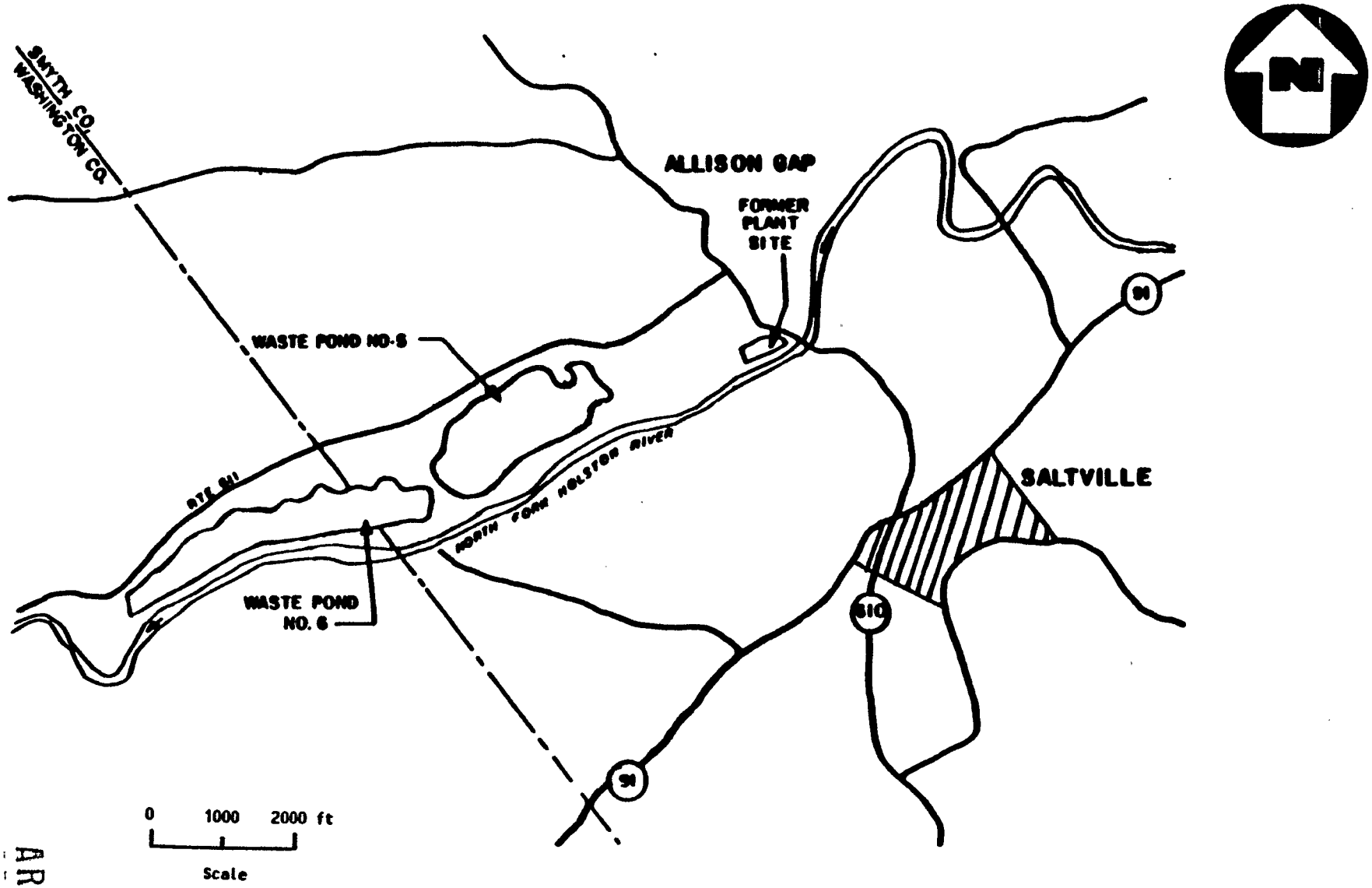


FIGURE 1. Saltville Waste Disposal Site-Area Map

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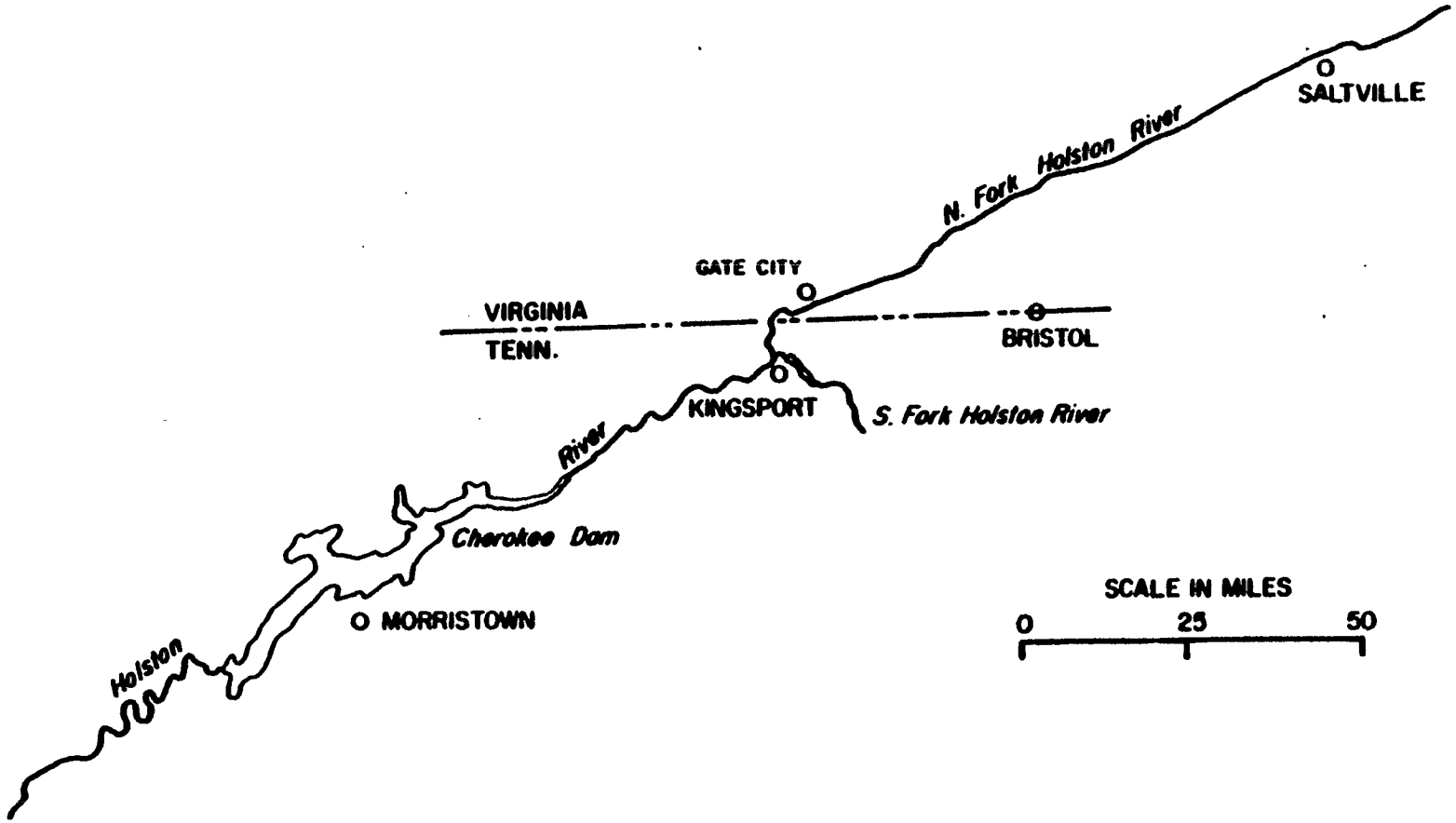


FIGURE 2. Holston River-Cherokee Reservoir System

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## 1.3 Contaminant Sources

The contaminant of concern is mercury (ROD, 1987). Mercury was used in chlor-alkali plant operations (1951 to 1972) and entered the environment via process wastewater streams. Mercury contaminated wastewater initially discharged directly to the NFHR and later to Pond 5.

## 1.4 Transport Pathways

The former chlorine plant site has been remediated with a clay cap. The Pond 5 outfall presently discharges effluent to the NFHR. This discharge can contain up to 120 ppb mercury. The pond 6 outfall also discharges to the NFHR. Pond 6 effluent is generally less than 0.2 ppb (non-detectable). The sediments of the NFHR contain 3 to 9 ppm mercury near the site (report in preparation). Mercury concentrations in the sediments decrease downstream to less than 0.5 ppm at NFHRM 8.

Studies of the fish community have been selected as the focus of the bioassessment program because, as top predators, fish tend to integrate conditions in other biotic components of the stream ecosystem. Thus, difficult-to-quantify changes in primary and secondary producers are reflected by changes in fish growth and community characteristics. Benthic macroinvertebrates have been included because of their prominence in systems where fish populations are greatly reduced or absent, their importance to stream trophic structure, and their importance as a major food source for fish. Also, macroinvertebrates generally respond to environmental changes more rapidly than do fish. Attached algae will be included as one of the biological parameters. Historical data exists on mercury concentrations in attached algae in the study area and attached algae provide a food source for some fish species.

Fish in the NFHR are exposed to mercury through several pathways. The water column downstream of Pond 5 outfall contains low concentrations of mercury (<0.2 ug/l) (Olin, 1986c), suspended sediment contains mercury and food sources (invertebrate, algae, etc.) contain mercury. These are generally the pathways available for uptake. This is not intended to be an in-depth discussion of the mechanism of uptake.

## 1.5 Data Gaps

Fish sampling has been conducted in the NFHR every year since 1970. Collections of fish and mercury analyses of collected fish have been made by several Agencies (including TVA, ORNL, and Virginia) and by Olin Corporation. Since 1983 Olin Corporation has collected fish at seven stations between NFHRM 98 and NFHRM 8 as part of a monitoring program directed by a Special Order with the State of Virginia.

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Historically, there is a good database for mercury concentrations in fish filets. Methylmercury analyses have also been conducted in 1988. There are two data gaps that this sampling program will fulfill. First, information on fish abundance and diversity is limited. TVA conducted an inventory of fish species based on their collection from 1971 to 1983. Second, mercury concentrations in fish need to be determined on a continuing basis to monitor the trend in mercury concentrations in fish filets.

The proposed fish sampling program will address the present data gaps. Fisheries sampling will gather relative abundance information and qualitative data such as life stage or species presence or absence. Such data may be indicative of immigration or emigration, improved survival, or behavioral changes. Evaluation of quantitative indicators of population "health", such as condition factors and incidence of stress indicators, will allow statistical testing of changes in population and community characteristics that may result from discharges from the Saltville Site.

Comparisons of the age-class structure and growth characteristics of fish populations from reference stations with those characteristics from populations in the impact/near field area should indicate changes in growth and survival due to discharges from the waste site. Fish habitat characteristics, particularly the distribution of physical habitat, will be monitored to provide an indication of potential effects on fish of environmental factors related to the waste discharges. Fish will be analyzed for total mercury and methylmercury in the filets. Selected offals will also be analyzed for total mercury and methylmercury to calculate whole body concentrations.

Fish surveys will be conducted during low flow periods of the spring and early fall to document the present status of the fish populations of the NFHR. Sampling will be conducted at these times because:

- young-of-year (YOY) of most species will be present and vulnerable to standard collection gear such as seines, minnow traps and electroshockers;
- fish will be concentrated, thus more vulnerable to capture; and
- low water velocities and shallower water will tend to increase the efficiency of collection techniques.

## 2.0 SAMPLING OBJECTIVES

### 2.1 Specific Objectives

A comprehensive bioassessment program for measuring mercury impact on NFHR aquatic communities involves the integrated use of both biological (i.e., benthic and fish surveys) and physio-chemical (i.e., sediment modelling) methods. The NFHR bioassessment program consists of five major tasks which evaluate the effects of present and past mercury discharge from the Site on the biotic integrity of stream communities of NFHR. The five tasks include (I) fish studies, (II) benthic studies, (III) mussel studies, (IV) ambient toxicity studies and (V) mercury fate and transport studies.

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The main objective of the fish studies is to determine the effect of past and present discharges from the Saltville Site on the NFHR fish population. This will be accomplished by determining the following information.

- the relative abundance of fish in the NFHR both upstream and downstream of the Site. This includes a listing of the species present in the NFHR.

- the health of the NFHR fish population using Karr's Index of Integrity, condition factors, age-growth and analyses and success of recruitment.

- the concentration of mercury and methylmercury in filets of four fish species which are potential food sources for the local fishing public.

- the concentration of mercury and methylmercury in the offals of the four fish species to provide an estimate of whole body burden, needed to describe the potential for bioaccumulation.

## 2.2 Uses of Data

Fish Community Structure

Fisheries sampling relies primarily on relative abundance information and qualitative data such as life stage or species presence or absence. Such data may be indicative of immigration or emigration, improved survival, or behavioral changes. Evaluation of quantitative indicators of population "health", such as condition factors and incidence of stress indicators, will allow statistical testing of changes in population and community characteristics that may result from discharges from the Saltville Site.

Fish collected will be identified as to species in the field. Specimens of questionable identification will be frozen and returned to the laboratory for verification. Identification of fish will be based on keys published by Eddy and Underhill (1983) and Pflieger (1975). Species composition and relative abundance will be determined from data collected from each site. Relative abundance will provide species composition in terms of both numbers and biomass. An actual or average weight will be provided for every fish collected. The larger species (i.e., hogsuckers, sunfish, rock bass) will be weighed individually and recorded. The smaller species (i.e., Cyprinids, *Etheostoma* sp.) will be counted and weighed as a group. The average weight per fish will be provided for these species.

Index of Biotic Integrity

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Index of Biotic Integrity (IBI) was designed as a conceptual framework for biological monitoring. IBI includes a range of attributes of fish assemblages. Its twelve measures, or metrics, fall into three broad categories: Species Composition, Trophic Composition, and Fish Abundance and

Condition (Karr, 1986). The 12 metrics are listed in Table 1. Data will be obtained for each metric at each sampling site and evaluated in light of what might be expected at an unimpacted or relatively unimpacted site located in a similar geographical region. The IBI requires that data be available on reference sites within the same region. For this study, the reference site is located upstream of the facility at NFHRM 91.5. Historical information on native species is provided in "Fishes of the North Fork Holston River System, Virginia and Tennessee" (Feeman, 1986). Additional reference data is available for the Clinch and Powell Rivers, if required.

Mercury Concentrations

Smallmouth bass, rock bass, channel catfish and redbreasted sunfish will be collected. Edible muscle tissue (referred to hereafter as filet) of each fish will be analyzed for total and methylmercury. The offal (fish carcass after filet removal) of selected samples will also be analyzed for total and methylmercury to provide data on whole body concentrations. Four randomly selected offal (fish carcass after filet removal) samples of each of 4 species (smallmouth bass, rock bass, channel catfish, and redbreasted sunfish) at each site from the first spring sampling will be analyzed for total and methylmercury. This represents 25 to 50% of the fish collected. These 96 filet and offal mercury analyses will provide sufficient sample size for developing a regression equation which predicts body burden from filet data. The offal samples not analyzed will be stored frozen. The analytical results of the analyzed samples will be evaluated for relationships between filet, offal and re-calculated whole body mercury and methylmercury concentrations. The regression equations will be reviewed with USEPA to determine the need for additional offal analysis. If additional data are needed to define or confirm the relationships, additional samples will be analyzed. Weights of filet and offal will be recorded to allow a calculation of whole body concentrations. The length, weight, and age of each fish will also be determined. Samples of fish (filets and offals) will be stored frozen for other analyses if other contaminants are found at the Saltville Site and are judged to be of sufficient concentration to justify analyses of fish tissues.

Mercury data will be used to determine the present concentration of mercury in fish and the change in mercury concentrations from previous collections. The effect of mercury on the success of recruitment will be established by collection of young-of-year or yearlings. Sampling for young fish will require use of several methods, such as seining, minnow traps, electrofishing, or juvenile traps, deployed in a variety of habitats. Indicators of reproductive activity, such as presence of mature gonads in adults, observation of spawning activity, presence of redds or nests, or presence of eggs and larvae, do not necessarily indicate successful recruitment; but will be noted during sampling trips.

Comparisons of the age-class structure and growth characteristics of fish populations from reference stations with those characteristics from populations in the impact/near field area should indicate changes in growth and survival due to discharges from the waste site. Fish habitat characteristics, particularly the distribution of physical habitat, will be monitored to provide an indication of potential effects on fish of environmental factors related to the waste discharges.

TABLE 1

INDEX OF BIOLOGICAL INTEGRITY

LIST OF METRICS

1. Number of native fish species
2. Number of darter species
3. Number of sunfish species (excluding *Micropterus* sp.)
4. Number of sucker species
5. Number of intolerant species
6. Proportion of individuals as tolerant species
7. Proportion of individuals as omnivores
8. Proportion of individuals as insectivores, minnows and darters
9. Proportion of individuals as piscivores
10. Mean catch per unit effort
11. Proportion of individuals as hybrids
12. Proportion of individuals with disease, parasites or anomaly

Age and growth data will be collected for smallmouth bass, rock bass and redbreasted sunfish. Length and weight and scale samples will be taken from up to 50 individuals of each species in each study segment. Procedures for age and growth analysis are presented Appendix A.

## 3.0 SAMPLE LOCATION AND FREQUENCY

### 3.1 Collection Sites

Data characterizing streamflow and hydrological features of the watershed are essential to proper design and selection of monitoring sites for potential impact areas and reference sites for both biological and water quality sampling. Section 5.0, Task 3.C of the RI/FS Work Plan for OU-3 describes the division of NFHR into segment and reaches. Segments represent sections of the stream with similar characteristics of flow, drainage, width, sinuosity, gradient, and substrate. Segments may be further divided into reaches. Reaches are series of sets of habitat features (e.g., riffle-pool-run-riffle) that occur within a segment. One or more sets of habitat features (roughly 10-14 times the bankfull stream width) comprise a reach. Most reaches within a segment will have similar fish habitat characteristics, and these will be designated "representative" reaches. Some reaches provide special habitat (e.g., deep pools, gravel beds, etc.) that may be important for species which would not otherwise be present or as juvenile nursery areas. These reaches will be identified as "critical" reaches. Careful selection of segments and reaches will allow reasonably accurate description of the entire study area on a focused sampling effort.

Four segments are identified, i.e., A, B, C, and D from the NFHR longitudinal profile. Segment A (NFHRM 88-100) represents the headwaters; B (NFHRM 74-88) includes the waste site (impact area) and represents the segment of greatest stream slope; C (NFHRM 53-74), an area of reduced gradient, represents the downstream limits of this "near field" assessment; D (0-53) represents the lower portion of the watershed which has a decreased stream gradient as compared to Segment C.

Study reaches comprise the sampling units for biological parameters. Two study reaches will be located above the Saltville Site as control reaches and four reaches will be located between the Saltville Site mixing zone and NFHRM 53 (end of Segment C).

Fish surveys will be conducted at six (6) stations sited on the NFHR between Mile 100 and Mile 53. Surveys will be conducted in the spring and early fall. Appendix A of the OU-3 Work Plan contains the schedule for RI/FS activities. Sampling stations are shown in Figure 3 and listed in Table 2. Two stations (Mile 91.5 and Mile 85.6) are located upstream from the former chlorine plant site, Pond 5 and Pond 6. Both of these stations are background stations.

The former chlorine plant site and settling ponds (Pond 5 and Pond 6) are adjacent to NFHR between Mile 82.4 and 80.8. One fish sampling station was chosen along this section. The station at Mile 81.3 was chosen because it was representative of the NFHR adjacent to the Site. Habitat at this station include both pool and riffle areas. The station is located downstream of the outfalls of Pond 5 and Pond 6.

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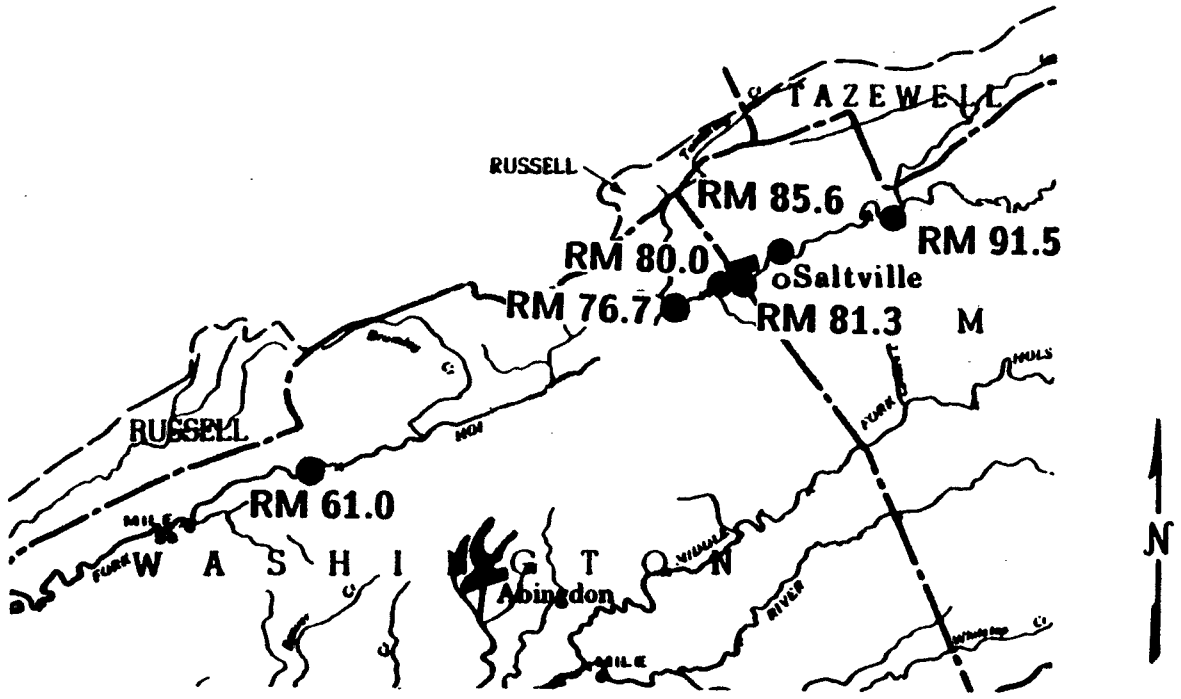


FIGURE 3. Sampling Locations for Fish Monitoring Program

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TABLE 2

COLLECTION SITES FOR THE FISH STUDIES
ON THE NORTH FORK HOLSTON RIVER

| SITE NO. | LOCATION | NFHR RIVER MILE |
|---|---|---|
| 1 | Old Broad Ford | 91.5 |
| 2 | Vicinity of McCready | 85.6 |
| 3 | Downstream of Pond 5 and Pond 6 Outfall | 81.3 |
| 4 | Former Chloride-analyzer site | 80.0 |
| 5 | Downstream of Tumbling Creek - NFHR Confluence | 76.7 |
| 6 | 1.5 mi. east of Route 611 and Route 19 Junction-Mongle Springs | 61.0 |

Three fish sampling stations are sited downstream of the Site. These stations were located at Mile 80.0, Mile 76.7 and Mile 61.0. The habitat of these sites are typical of NFHR in this area. Mile 80.0 is the location of the former chloride monitor which monitored river conditions downstream from the former operating plant. Mile 76.7 has been utilized for fish collections for many years and a good database has been established for this site. The sites at Miles 80.0 and 61.0 have also been utilized occasionally as past fish collection sites.

All sampling sites are representative of the segments of the river where they are located. Each site has a variety of habitats (pool, riffle, etc.). These sites will also be used as macroinvertebrate collection sites.

The NFHR is typically composed of a series of riffle and pools of varying size through the entire length of river. One riffle and one pool area will be sampled at each location. The length of river sampled at each site and the standard time of sampling effort will be sufficient to define species composition and relative abundance of species at each station.

### 3.2 Sample Collection

In order to continue to document the present status of the fish populations of the NFHR, fish surveys will be conducted during low flow periods of the spring and early fall. Sampling will be conducted at these times because:

- Young-of-year (YOY) of most species will be present and vulnerable to standard collection gear such as seines, minnow traps and electroshockers;
- fish will be concentrated, thus more vulnerable to capture; and
- low water velocities and shallower water will tend to increase the efficiency of collection techniques.

Fish collected will be identified and counted in the field. Fish will be inspected for disease, parasites, and anomaly. Fish of questionable identification will be frozen and returned to the laboratory for verification of identity. A reference collection of all species identified in the study will be maintained in the laboratory. The reference collection will be reviewed by a referee ichthyologist as part of the QA/QC program. Data analysis will include species composition, relative abundance and Karr's index of biotic integrity. Determination of species composition will be restricted to fish aged one year (1+) or older.

During the surveys, four species of fish will be selected to characterize total mercury and methylmercury concentrations. The four species are smallmouth bass, rock bass, channel catfish and redbreasted sunfish. These species were selected based on geographic location, available habitat, ease of capture and identification, pollution tolerance, use as a sport fish and non-migrating habits. (A

Compendium of Field Operations Methods, EPA, 1987). These four species represent the different trophic levels found in the NFHR - surface, middle water column and bottom feeders. Northern hogsuckers have been collected and analyzed for mercury in the NFHR for the past five years as part of the Virginia Special Order. Therefore, a substantial database exists for this species. Channel catfish was substituted for hogsuckers at EPA's suggestion and because hogsuckers are a "trash" fish not commonly sought for food. Also, because hogsuckers are known to travel great distances within river systems, it is difficult to relate mercury concentrations in the fish to river reaches of known mercury sediment concentration. Channel catfish will represent bottom feeders. Northern hogsuckers will be collected and archived for retrospective analysis if channel catfish cannot be collected in sufficient numbers to evaluate the effect of site releases on bottom feeders.

Fish of all size ranges will be collected. Olin collections between 1983 and 1987 were required to be within specific size ranges for northern hogsuckers (23.0 - 32.0 cm), sunfish (12.0 - 20.0 cm) and rock bass (15.0 - 23.0 cm). Adequate numbers of these fish species are not always available at every site. Data on fish of all sizes will be valuable. Small fish are often prey for larger fish and wildlife predators and large fish are more likely to be taken by fishermen.

A minimum (if available) of eight (8) and a maximum of sixteen (16) fish of each species from each station will be retained for analysis. Thus, 240 to 480 fish will be collected and retained from each sampling trip for analysis (6 sites x 5 species per site x 8 to 16 fish per species). Evaluation of the mercury concentration data from the 1983 to 1987 Olin fish collections required by the Special Order was conducted to determine the average and variability of the mercury and methylmercury concentrations (report in preparation). Sample sizes were estimated based on the fish data variability. Also, analysis of historical fish data for this system shows no strong statistical relationship between age and mercury concentration.

Dissolved oxygen, temperature, pH, conductivity, alkalinity, and hardness will be measured at each site prior to sampling. All field instruments will be calibrated daily.

### 3.3 Quality Assurance

The Quality Assurance Project Plan for the Saltville Waste Disposal Site Remedial Investigation and Feasibility Study, Saltville, Virginia will be in effect for this project. The goals of the QA program are to insure to the maximum extent possible that sample results are precise, accurate, representative, comparable, and complete.

Field quality assurance is the responsibility of the Field Sampling Coordinator. Frequent checks will be made to insure that all sampling procedures are followed. The analytical quality assurance is described in detail in the Quality Assurance Project Plan (QAPjP).

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The calibration procedures specified by the analytical methods and instrument manuals will be followed. Frequency of calibration specified by the analytical methods or instrument manuals will be considered to be the minimum frequency. More frequency calibration may be required under severe

field conditions (e.g. rain, freezing temperatures). Calibration requirements of the method references will be met. All calibration checks must be documented in log books. At a minimum the following information must be recorded:

- Date of calibration
- Instrument model and serial number
- Identification of standards used
- Personnel performing calibration
- Results of calibration (including raw data and summary statistics)
- Corrective action taken

Field instruments such as pH meters and conductivity meters will be calibrated daily (at a minimum) according to procedures specified by the Field Analytical Procedures and documented in field log books. Calibration must be performed with commercially prepared, certified standards if available, e.g., pH buffers, conductivity standards, etc. Sources of all material used for calibration or for preparing calibration standards will be documented.

## 4.0 SAMPLE DESIGNATION

Each fish sample collected will be assigned a unique sample identification number. The sample numbering system will be:

Sxx - yyyyyA-zzz or Sxx-yyyyyF-zzz

where

Sxx is the site number shown on Table 2
yyyyy is a five digit number (starting with 00001 with the first fish caught and assigned sequentially)
A is for offal samples
F is for filet samples
zzz is the month/year collected (589 for May 1989)

## 5.0 SAMPLING PROCEDURES AND EQUIPMENT

### 5.1 Pre-Sampling Activities

Sampling and analytical personnel will be properly trained and experienced in the collection and analysis of fishery data. Personnel employed in field sampling will be familiar with all equipment required to collect samples of fish that will accurately represent the true fish assemblage of the NFHR. A minimum of two years of technical training or field experience in fishery science or other similar discipline emphasizing proper scientific methods is required.

Preparation for the sampling event can be divided into three primary areas:

1) Logistics of the event, including site access
2) Equipment preparation
3) Coordination with the analytical laboratory

The sampling coordinating team is responsible for all three areas. Olin will obtain site access for sampling points not on Olin property. The sampling contractor is responsible for obtaining collection permits from the Virginia Department of Game and Inland Fisheries.

### 5.1.1 Logistics

The sampling team will insure that samples can be collected from all sampling points before an event is scheduled. At a minimum the team will contact the Olin Project Manager before mobilizing. Olin will try to arrange for all contacts with property owners for permission to enter their property where necessary to collect samples. The sampling team should check with property owners of any fenced or posted property.

### 5.1.2 Equipment Preparation and Calibration

All equipment to be used in the sampling effort will be checked for service before mobilizing. Any instruments used in water quality monitoring will be calibrated per manufacturer's specifications prior to field measurements. Back-up meters will also be taken into the field. Any maintenance or cleaning will be completed prior to moving into the field for sampling.

### 5.1.3 Coordination with Laboratory

The Field Sampling Coordinators will insure that the laboratory is prepared to receive samples on the required schedule before collecting any samples. The laboratory will be notified of each sample shipment so that samples can be expeditiously unpacked, inspected, and entered into the analytical flow at the laboratory.

## 5.2 Field Procedures

Fish sampling will employ electro-shocking and seining techniques at selected pool and riffle sites at each station. Sampling effort will be distributed over all types of habitat types in each reach to provide a reasonable opportunity to collect all species present. Electrofishing basically involves using a power source (generator or battery) and electrodes to send an AC or DC electric current into the water. A control box allows the operator to vary the output for maximum efficiency in waters of varying conductivity. When output amperage is correctly matched to the conductivity of the water, fish are

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temporarily stunned for collection with a seine or dip net. Electrofishing is a long-established and highly efficient technique for the collection of fisheries data. For the present study, boat-mounted and backpack shocking units will be employed.

Seines and backpack electrofishing units will be used in riffle and shallow pool areas. There are two basic techniques for sampling fish with a seine. Seines can be pulled through the water to trap fish or fish in streams can be driven into a seine held stationary in the river. Fish can be driven by personnel either kicking the substrate, driving with another seine, or backpack electrofishing downstream to "drive" fish to the seine. Two backpack units will be employed during each electrofishing pass. Passes with electrofishing units will continue until three consecutive passes result in no new species. Fish stunned will be collected with dip nets and retained. Seines will be utilized independent of electrofishing, and in addition may be employed as an accessory to electrofishing.

Boat-mounted electrofishing unit will be used in the deeper pools. Electrofishing will be conducted along the banks of the pool and the mid channel area of the pools. The boat-mounted unit will also be used along the upstream edge at the pool where the riffle section ends and the pool section begins. This is an area where many species of fish congregate.

Sampling for young fish will require use of several methods, such as seining, minnow traps, electrofishing, or juvenile traps, deployed in a variety of habitats. Indicators of reproductive activity, such as presence of mature gonads in adults, observation of spawning activity, presence of redds or nests, or presence of eggs and larvae, do not necessarily indicate successful recruitment; but will be noted during sampling trips.

All fish shocked will be collected, if possible. If all fish cannot be collected, an estimate of their number, species and size will be made. The collected fish will be identified, inspected for parasites, disease, anomalies and glochida, and counted. Fish of questionable identification will be preserved (frozen) and returned to the laboratory for verification of identity. A reference collection of all species identified in the study will be maintained in the laboratory.

During the surveys, four species of fish will be selected to characterize total mercury and methylmercury concentrations in muscle tissues. Tentatively, these four species include smallmouth bass, rock bass, channel catfish and redbreasted sunfish. Northern hogsuckers will be collected and stored for further analysis as required. A minimum of eight (8) and a maximum of sixteen (16) fish of each species will be analyzed at each station. Age and growth data will be collected for smallmouth bass, rock bass, and redbreasted sunfish. Length, weight and scale samples will be taken from up to 50 individuals of each species in each study segment. Procedures for age and growth analysis will be presented in Appendix A.

It is the responsibility of Field Sampling Coordinator to insure that field activities and observations are documented. A field log book will be maintained to record the following information:

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- General description of work
- Samples collected and their identification numbers
- Date, time of sampling, weather conditions
- Sample location
- Field measurements and observations
- Field sampling personnel
- SOPs employed
- Written discussion of any deviations from SOPs
- Chain-of-custody references for each sample

### 5.3 Equipment Required

Table 3 is a checklist of the equipment required for conducting a fish collection.

## 6.0 SAMPLE HANDLING AND ANALYSIS

### 6.1 Sample Preparation

Fish retained for analysis will be processed in the field or laboratory using the procedure described in Appendix A. Sample homogenization will be conducted in the analytical laboratory prior to analysis. The length and weight of the fish will be determined. Scales or fins for aging will be removed from each fish. The filets of each fish will be removed, the filet will be skinned, and the skin added to the remaining offal. The weight of filet and offal will be measured. Vertebrate or fins will then be removed from fish which do not have scales for aging. The filet, offal and scales/fins/vertebrate will be packaged separately in zip-lock plastic bags. Each sample will be tagged with the following information:

- Sample Number
- Species
- Sample Type (Filet, Offal, Scales, etc.)
- Location
- Date Collected
- Weight (of Filet or Offal)
- Length (Total)

### 6.2 Equipment Cleanup

All sample preparation equipment which contacts the fish filet or offal will be thoroughly cleaned to prevent cross contamination of samples. This includes fileting knives, forceps, processing pans, etc. The cleaning procedure is as follows:

## TABLE 3

## EQUIPMENT REQUIRED FOR FISH COLLECTION

Electrofishing boat
AC/DC control box
Backpack electrofishing unit
Gasoline can with proper fuel mixture
Funnel
Spare fuses for electrofishing units
Electrodes
Repair tools
Clipboard, data forms, and pencils
Formalin
Reference collection containers
Scales
Measuring board
Buckets
Life jackets
Fire extinguisher
Scale envelopes
Identification keys
Marker ribbon
Stop watch
Camera and film
Field log book
Copies of Standard Operating Procedures
Waterproof labels
Adhesive labels
Dip nets
Seines
Waders and rubber gloves for each crew member
Conductivity meter
pH meter
Thermometer
First aid kit

1) Wash with Saltville tap water and laboratory detergent using a brush if necessary to remove particulate matter and surface films. (Note: Saltville tap water has been demonstrated to be mercury free.)

2) Rinse thoroughly with tap water.

3) Rinse with nitric acid solution.

4) Rinse three times with tap water and allow to air dry as long as possible.

Equipment blanks which consist of final tap water rinse will be collected periodically during processing.

## 6.3 Shipping Requirements

Samples will be shipped on ice (preferably dry ice) to the laboratory in insulated coolers. Arrangements will be made to insure that the samples arrive at the laboratory in an expeditious manner.

A chain-of-custody form will be completed for each cooler, itemizing each fish contained therein. The completed chain-of-custody forms and fish samples will remain under custody until delivery to the analytical laboratory. Copies of the chain-of-custody forms will be included in the final report.

## 6.4 Chain-of-Custody Record

Once a sample is collected, custody must be maintained. A sample is under custody if:

- It is in the sampler's possession.
- It is in the sampler's view, after being in the sampler's possession.
- It is in the sampler's possession and then is placed in a secure area.
- It is in a designated secure area.

Chain-of-custody forms will be prepared for the sample prior to transporting samples from field sites. Each sample will be listed on the form. A chain-of-custody form is shown in Figure 4.

The following sample custody procedures will be utilized:

1) Each sample collected for the project will be entered on the chain-of-custody record. Field personnel will retain a copy of the chain-of-custody record.

2) The original chain-of-custody record plus one copy will accompany the sample containers during transport to document controlled custody.

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# FIGURE 4

## OLIN CORPORATION

### CHAIN OF CUSTODY RECORD

| PROJ. NO. | PROJECT NAME |
|---|---|
| SAMPLERS: *(Signature)* | |

ANALYSES REQUIRED

Instructions: List samples individually. Write time in military time. Record sample type as water, soil, etc. and as grab or composite. Record special handling instructions or precautions in remarks section. Record method of shipment in comments section.

| Station or Sample No. | Date | Time | Sample Type | Number Of Containers | | | | | | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
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| Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* | Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* |
|---|---|---|---|---|---|
| Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* | Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* |
| Relinquished by: *(Signature)* | Date/Time | Received for Laboratory by: *(Signature)* | Date/Time | Comments | |

DISTRIBUTION: Original and Pink copies accompany sample shipment to laboratory. Pink copy retained by laboratory. Yellow copy retained by samplers.

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3) If custody is relinquished through a common parcel carrier for delivery to the laboratory, the following protocol will be followed:

- The method of sample shipment will be noted in the comment section on the chain-of-custody form.

- The original chain-of-custody record plus one copy will be placed inside the shipping package.

- The shipping package will then be sealed with a custody seal. The seal will be placed on the package in such a manner that the package cannot be opened without breaking the seal. The seal will serve to document that the samples remained unaltered during shipment through the common parcel carrier.

4) If the sample is shipped by air freight or express shipment, the air bill will become part of the chain-of-custody procedures.

5) The laboratory will assume custody of the samples upon receipt. A designated Sample Custodian will be charged with sample care and receipt and verification of custody seal condition. These observations will be noted by the Sample Custodian on the chain-of-custody form upon receipt. All sample damage and abnormalities will be noted on the forms. The Sample Custodian will sign the chain-of-custody form, retain the copy for the Laboratory's record, and forward the original to the Field Project Officer.

6) Sample preparation and analysis custody will be tracked by laboratory work sheets.

7) The laboratory will retain custody of the samples in a secure area until such time as the samples are ordered destroyed.

8) A copy of the chain-of-custody record will be retained.

9) If samples are transferred to another laboratory, either as a whole or as a split sample, a new chain-of-custody form will be initiated.

## 6.5 Holding Times

Fish will be analyzed for total mercury and methylmercury. There are no holding times for fish prior to analysis. However, samples should be analyzed in a timely manner. Fish will be kept frozen until analyzed. Samples of fish (filets and offals) will be stored frozen for other analyses if other

contaminants are found at the Saltville Site and are judged to be of sufficient concentration to justify analyses of fish tissues.

Analysis of surface water for dissolved oxygen, temperature, pH, conductivity, alkalinity and hardness will be conducted within the time frame (holding time) specified by Table 4 of the QAPjP. Analytical procedures are given in the QAPjP.

### 6.6 Record Keeping

All records will be maintained in bound books. A master log will be established which will contain the appropriate identity and traceability of each sample. The same code number will be used from sample acquisition through final data tabulation. Detailed notebooks will be maintained by laboratory personnel for samples, instruments and calibration standards.

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## 8.0 APPENDIX

Appendix A Fish Sampling Program Procedures

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# APPENDIX A

# FISH SAMPLING PROGRAM PROCEDURES

FISH AGING PROCEDURE - SCALE METHOD

1. Remove scale sample from envelope

2. Make scale impressions

   a. Place several scale sculptured side down on cellulose acetate.

   b. Run slide through press

   c. Remove scales from slide

   d. Place impression in already properly labeled envelope

3. Aging scales (Microprojector)

   a. Select a magnification that will accommodate all scales of a sample.

   b. Orient impressions with the sculptured surface toward the light source.

   c. Circuli are growth rings laid down in a circular pattern around the focus (scale center). Circuli are formed more closely together during the slow growth period of Winter. The outer edge of a group of closely spaced circuli is considered to be the end of that year's growth, and is referred to as an annulus.

   d. Age of each fish is determined by counting the number of annuli.

# FISH REFERENCE COLLECTION PROTOCOL

## FIELD PROCEDURES

### EQUIPMENT AND MATERIALS

Sample Containers - Assorted sizes, 100-4000 ml. Polypropylene, Nalgene[R], or glass.

Fixative - 10 percent buffered formalin for field use.

Scalpel or Sharp knife

Camera, color film and ruler - For photographic record of rare specimens

Anesthetic - For short-term anesthesia (MS-222) of specimens being photographed.

Fish Holding Containers

### METHOD

Representative fish specimens will be collected during fisheries field surveys. Fish not surviving collection and handling will be selected over living specimens. Several individuals of representative size ranges will be collected.

Specimens less than 150 mm total length will be preserved by direct immersion in 10 percent buffered formalin. Individuals greater than or equal to 150 mm in length will be slit along the right side to allow formalin to enter the abdominal cavity or preservative will be injected into the abdominal cavity.

Sample containers will be labelled inside and outside with the following: Species Name (if known, Stream Name, Date, Time, Sample Location (including reach identifier), Depth, Type of Habitat, Collection Method, and Collector's Initials. Identical information will be recorded on a reference collection field sheet.

Samples will be returned to the laboratory under chain of custody for positive identification.

### MODIFICATION

If rare specimens are collected, photographs will be taken. Photographs will be taken of several specimens representative of the species' size range when available. A clearly marked ruler will be placed in the photo. Frame numbers will be recorded on the reference collection field sheet, along with similar information recorded for sample containers.

## SAMPLE RECEIPT AT LABORATORY

### MATERIALS

Permanent Preservative - 40-50 percent isopropyl alcohol or 70 percent ethyl alcohol.

### METHOD

Samples will be checked in upon arrival from the field. Sample containers will be compared to the reference collection field sheet. Discrepancies will be noted and resolved. Sample containers will be examined for proper preservation.

Samples will be stored in a cool, dark place until identification has been verified. Efforts will be taken to maintain specimens in original condition. Curling of specimens will be avoided.

After several days in formalin fixative, specimens will be soaked in water, and transferred to permanent preservative - either 70 percent ethyl alcohol or 40-50 percent isopropyl alcohol. Specimen handling will be as described by Haedrich (1983).

## LABORATORY PROCEDURE - IDENTIFICATION

Unknown specimens will be identified using keys such as Scott and Crossman (1973), Eddy (1969), and Hubbs and Lagler (1958). Taxonomic nomenclature will conform to that of Robins et al. (1980).

Specimens will be preserved in containers labelled with Species, Water Body Name, Collection Date and Time, Depth, Type of Habitat, Gear Type, and Collector's Name.

## QUALITY CONTROL

Field and laboratory identifications will confirmed with other personnel and verified by an independent expert ichthyologist.

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FISH PREPARATION PROCEDURE (Field or Laboratory)

1. Take fish from freezer or insulated cooler.

2. Record the basic information pertaining to the fish.

   a. Sample number
   b. Species
   c. Date of capture
   d. Location

3. Record the weight and length of the whole fish.

4. Take the aging information according to species. An aging information envelope is prepared which contains:

   a. Sample number
   b. Species
   c. Date of capture
   d. Weight
   e. Length
   f. Sex

   Scales, vertebra, or fins will be placed in the envelope for age determination.

5. Now the processing operation begins. Start the filet by making a cut just behind the pectoral finds of the fish, then make a cut at the base of the tail. Start at the tail and make a lateral cut along the belly. One more cut along the back of the fish and than you can start parting the filet from the offal completing the removal of filet. The other side of the fish is done in the same manner. The filet and offal are placed into separate pans.

6. At this time the offal can be inspected to determine the sex of the fish.

7. The filet is skinned making sure that no skin or scales are contained in the filet pan. The skin is placed in the offal pan.

8. Weigh the filet and record the weight.

9. Weigh the offal and record the weight.

10. The filet and offal are packaged separately in zip-lock plastic bags and are packed with ice for shipment to laboratory. Dry ice is preferred but wet ice or blue ice may be used.

11. Chain-of-custody forms are prepared according to QAPjP.

12. Clean equipment as follows:

a. Wash fileting board, processing pans and knives with local water supply (river, lake, etc.). Distilled water may be used.

b. Wash fileting board, processing pans and knives with alconox and water.

c. Rinse fileting board, processing pans, and knives with dilute (5%) nitric acid.

d. Rinse fileting board, processing pans, and knives with distilled or Saltville tap* water.

* Saltville tap water has been shown to have less than 0.025 ppb Hg.

# FIELD SAMPLING PLAN FOR BENTHIC MACROINVERTEBRATES AND ALGAE FOR THE SALTVILLE WASTE DISPOSAL SITE REMEDIAL INVESTIGATION AND FEASIBILITY STUDY SALTVILLE, VIRGINIA

OCTOBER 26, 1989

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## 1.0 SITE BACKGROUND

### 1.1 Introduction

This Field Sampling Plan for Benthic Macroinvertebrates and Algae (FSP-Benthos) has been prepared for the Remedial Investigation/Feasibility Study (RI/FS) for the Saltville Waste Disposal Site, Saltville, Virginia. This document describes in detail the sampling and data gathering methods which will be used to achieve the benthic macroinvertebrates and algae data quality objectives needed to support decisions regarding remedial response activities. The FSP-Benthos was prepared in accordance with the Interim Final EPA document "Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA" (OSWER Directive 9355.3-01) dated October 1988; EPA document "A Compendium of Superfund Field Operations Methods" (OSWER Directive 9355.0-14), dated December 1987; and EPA document "Data Quality Objectives for Remedial Response Activities-Development Process" (OSWER Directive 9355.0-7B), dated March 1987.

### 1.2 Site Description

The Saltville Waste Disposal Site is located along the North Fork of the Holston River (NFHR), between the town of Saltville and the community of Allison Gap in western Smyth County, Virginia, extending partly into Washington County, Virginia (see Figure 1). The NFHR lies adjacent to the southern border of the site at North Fork Holston River Mile (NFHRM) 80.8 - 82.4 and flows southwest. The Saltville Waste Disposal Site includes the former chlorine plant site (FCPS), waste disposal Pond 5 and waste disposal Pond 6. Pond 5 discharges water into the NFHR at Mile 81.7. Pond 6 discharges water into the NFHR at Mile 81.5. Additional description of the site is given in Section 2.0 of the RI/FS Work Plan.

The NFHR is a fast flowing mountain stream which originates approximately 48 miles above the former chlorine plant site. The stream flows southwest for 130 miles through a rural landscape to the confluence with the South Fork Holston River in Tennessee to form the Holston River. The Holston river flows into Cherokee Reservoir in Tennessee. Figure 2 is a schematic of the Holston-Cherokee system.

Upper watershed areas are primarily hardwood forest on steep slopes while the lower portion is less mountainous and is bordered by pasture and farmlands. Land-use is dominated by agriculture, and little heavy industry is present within the watershed except that located in Saltville, Virginia.

The NFHR is characterized over most of its length by a coarse rocky substrate with extensive riffle and pool areas. Daily discharge at NFHR Mile 85 range from 23 cfs at low flow (7Q10) to 16,500 cfs at peak storm discharges and averages 290 cfs. Over the course of the study area (NFHRM 100 to NFHRM 53), the river varies in width between 100 and 300 feet. Water depths at normal flow vary between a few inches in the riffle areas to 10 feet in the deeper pools.

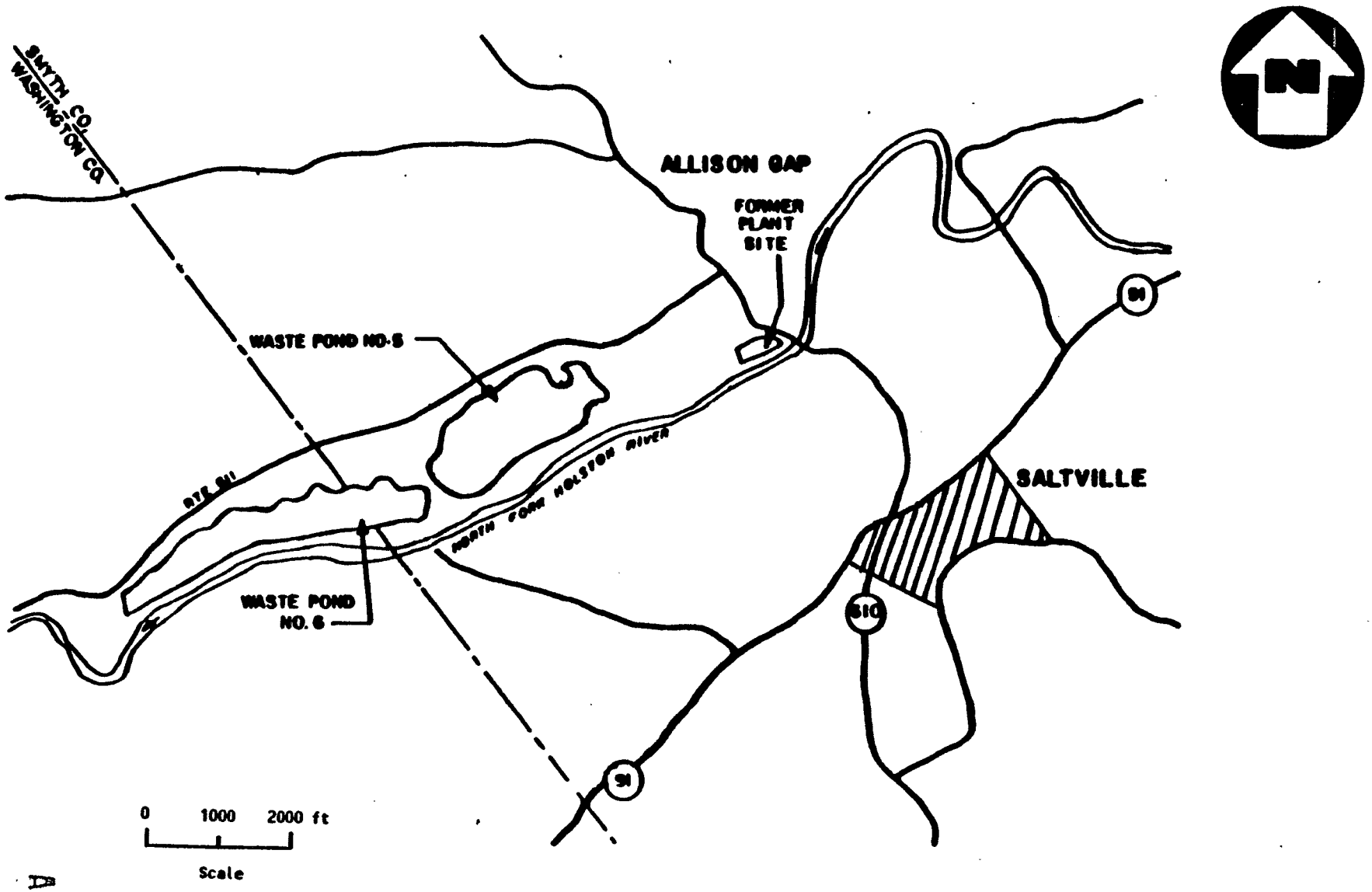


FIGURE 1. Saltville Waste Disposal Site-Area Map

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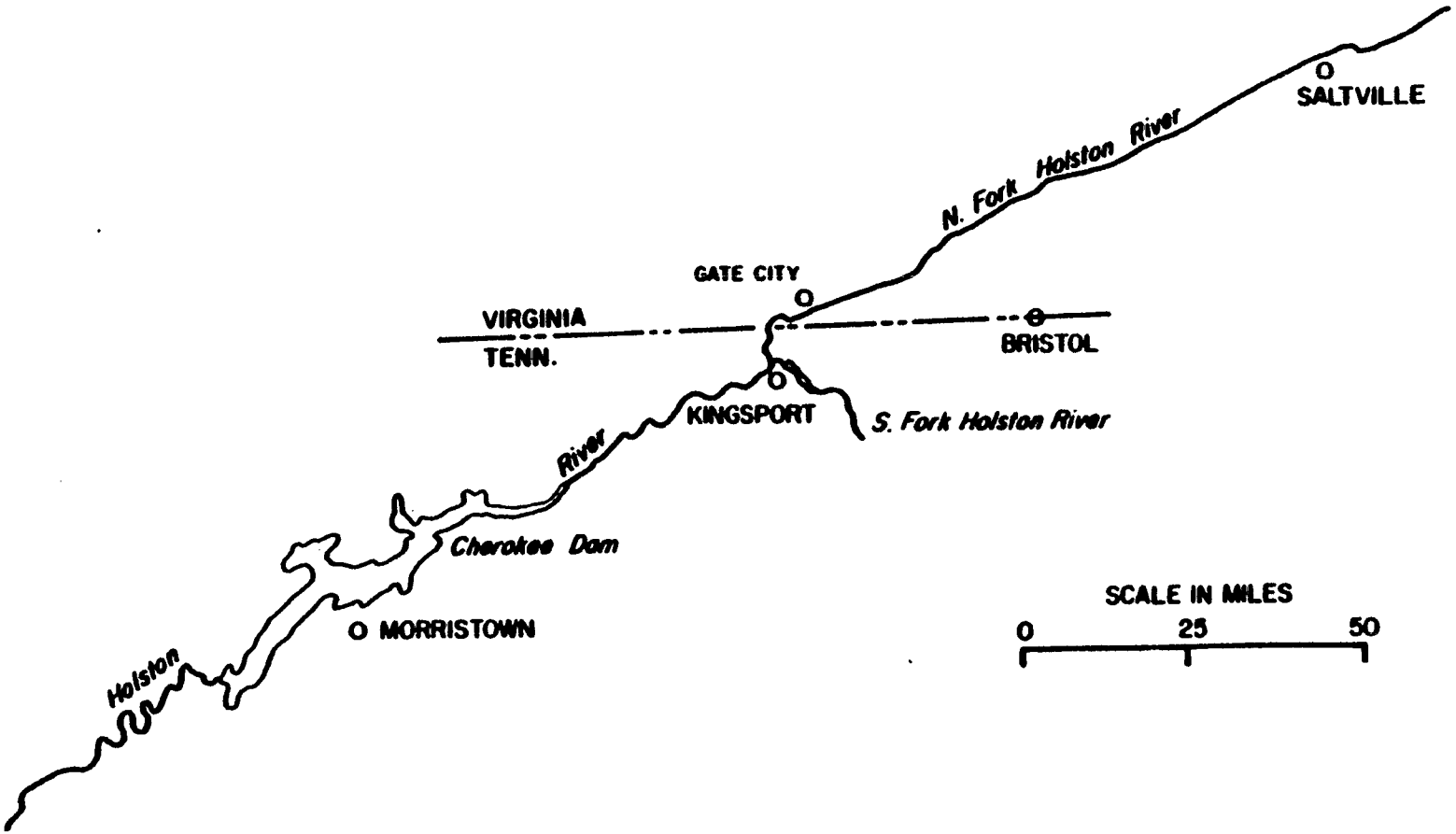


FIGURE 2. Holston River-Cherokee Reservoir System

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## 1.3 Contaminant Sources

The contaminant of concern is mercury (ROD, 1987). Mercury was used in chlor-alkali plant operations (1951 to 1972) and entered the environment via process wastewater streams. Mercury contaminated wastewater initially discharged directly to the NFHR and later to Pond 5.

## 1.4 Transport Pathways

The former chlorine plant site has been remediated with a clay cap. The Pond 5 outfall presently discharges effluent to the NFHR. This discharge contains up to 120 ppb mercury. The Pond 6 outfall also discharges to the NFHR. Pond 6 effluent is generally less than 0.2 ppb (non-detectable). The sediments of the NFHR contain 3 to 9 ppm mercury near the site (report in preparation). Mercury concentrations in the sediments decrease downstream to less than 0.5 ppm at NFHRM 8.

Benthic macroinvertebrates and algae in the NFHR are exposed to mercury through two pathways: sediment in the NFHR contains mercury concentrations up to 9 ppm and the water column downstream of Pond 5 outfall contains low concentrations of mercury (<0.2 ug/l) (Olin, 1986). These are generally the pathways available for uptake. This is not intended to be an in-depth discussion of the mechanism of uptake.

## 1.5 Data Gaps

Benthic macroinvertebrates were collected by Oak Ridge National Laboratories (ORNL) in 1975. These were collected by disturbing river substrate upstream from a collection net. Samples were collected at four locations (NFHRM 85.9, 80.6, 69.5 and 0). Macroinvertebrate from each site were separated by taxa and analyzed for mercury and methylmercury. Total mercury concentrations ranged from 16 to 88 ng/g (ppb) above the former chlorine plant site and 560 to 1120 ng/g (ppb) downstream of the site. Approximately 50% of the mercury in the benthic macroinvertebrates was in the methylated form.

TVA collected benthic macroinvertebrates between NFHR Mile 91.5 and Mile 6.3 during the period of 1971 through 1977. Diversity, number of taxa and standing crop were determined. Their conclusion was "although there are still some apparently measurable differences between aquatic faunal communities above and below Saltville, Virginia, the fauna in all three reaches would be recognized as a healthy and diverse one" (TVA, 1980).

Olin Corporation collected benthic macroinvertebrates and algae in 1980, 1981 and 1988. Samples were collected between NFHR Mile 91.5 and Mile 8.8. Mercury concentrations in benthic macroinvertebrate ranged from <0.0002 to 11.6 ppm. Mercury concentrations in algae ranged from <0.0002 to 11.87 ppm. Mercury concentrations were generally the highest adjacent to the former chlorine plant site.

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Current information about benthic macroinvertebrates diversity and community structure is not available. Data on present mercury concentrations in benthic macroinvertebrate and algae are limited. The proposed sampling program will address these data gaps. This new data, when compared to previous studies, will be used for trend analysis.

## 2.0 SAMPLING OBJECTIVES

### 2.1 Specific Objectives

A comprehensive bioassessment program for measuring mercury impact on NFHR aquatic communities involves the integrated use of both biological (i.e., benthic and fish surveys) and physio-chemical (i.e., sediment modelling) methods. The NFHR bioassessment program consists of five major tasks which will evaluate the effects of present and past mercury discharges from the Site on the biotic integrity of stream communities of NFHR. The five tasks include (I) fish studies, (II) benthic studies, (III) mussel studies, (IV) ambient toxicity studies and (V) mercury fate and transport studies.

The main objective of the benthic studies is to determine the effect of past and present discharges from the Saltville Site on the NFHR benthic community. This will be accomplished by determining the following information:

- the relative abundance, diversity and species composition of benthic macroinvertebrate in the NFHR both upstream and downstream of the Site.
- the species composition and diversity of the algae community in the NFHR both upstream and downstream of the Site.
- the concentration of mercury and methylmercury in the benthic macroinvertebrate, adult insect and algae communities which are a part of the biological food chain.

### 2.2 Uses of Data

Monitoring of benthic macroinvertebrate provides data on short-term system responses to waste discharges and may help explain any observed changes in the fish community. Qualitative sampling of macroinvertebrates is designed to detect changes in species presence and gross changes in relative abundance. Quantitative macroinvertebrate sampling will allow application of more powerful statistical methods to address questions concerning the effects of site discharge on the NFHR ecosystem.

Benthic Algal Community Structure

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The taxonomic composition of the algal community at each site for each sampling period will be evaluated among sites using numerical taxonomic procedures. Information concerning the taxonomic composition of each site and relative abundance of each taxon will be maintained both in computer

database files and in printed archival records. Total mercury and methylmercury will be measured on total periphyton scrapings samples (three per station) at each station. Periphyton scrapings will be normalized by effort. Five minutes of effort wil be dedicated to each major habitat type at each site. Samples will be collected that provide the required 10 grams of material. Statistical methods used to compare data between stations will be based on the type of probability distribution encountered (i.e., normal, lognormal).

Benthic Macroinvertebrate Community Structure

Data analysis will include species composition, diversity, biomass and relative abundance. These analyses will include measures of diversity, redundancy, etc,, cluster analysis and indices such as those by Hilsenhoff (1982) and others. The individual genus (species if possible) present at each site will be determined. The presence or absence of pollution sensitive genus (species if possible) generally found in this type of habitat will be noted. Diversity indices will be calculated using a computer program which calculates indices based on several well known equations, Shannon-Weiver, Broullion, etc. General statistical procedures will include determination of data probability distribution type (i.e. normal, lognormal, Poisson, etc.), calculation of the Minimum Variance Unbiased Estimators (MVUE) of the mean and variance for each dataset, comparisons between means (i.e., Student's T-test, Mann-Whitney test) and interpretation of statistical results. The degree of confidence with which all interpretations are made (i.e., confidence level, Type I and Type II Error) will be provided with the results of the calculations.

The taxonomic composition of the benthic macroinvertebrate community at each site for each sampling period will be evaluated among sites and between years for each site using numerical taxonomic procedures. Qualitative data will be treated on a presence/absence basis. Quantitative data will be treated on a Euclidean distance basis. Quantitative data collected during this sampling program will be compared with data collected before and during the remediation effort to assess any subsequent changes. Information concerning each site's taxonomic composition and the abundance of each taxon will be maintained both in computer database files and in printed archival records.

Biotic Index

The Biotic Index (Hilsenhoff, 1982) was designed as a conceptual framework for biological monitoring. Data at each site will be evaluated in light of what might be expected at an unimpacted or relatively unimpacted site located in a similar geographical region.

Mercury Concentrations

Selected taxonomic groups of benthic macroinvertebrates and algae from each site will be analyzed for total mercury and methylmercury. Crayfish and megalopterans will be the macroinvertebrates analyzed. *Cladophora glomerate* will be the algae analyzed. Adult insects, such as mayflies, stoneflies, and caddisflies, will be collected at each site in the spring and fall for mercury analysis. Analytical methods are detailed in the Quality Assurance Project (QAPjP) Plan. Mercury

data will be used to determine the present concentration of mercury in benthic macroinvertebrates and algae. Appropriate statistical analyses will be used to compare mercury concentrations, species composition, abundance, and diversity between control and downstream sites (i.e., parametric and/or non-parametric statistical methods). Mercury concentrations will be compared to data from previous collections to determine the change in concentrations from previous collections.

## 3.0 SAMPLE LOCATION AND FREQUENCY

### 3.1 Collection Sites

Qualitative and quantitative benthic macroinvertebrate and qualitative algae surveys will be conducted during the winter, spring and fall to evaluate the status of the invertebrate and aquatic plant communities from NFHRM 100 to NFHRM 53. Summer sampling was not included in the program because macroinvertebrate populations are less diverse and population numbers are reduced during the summer. By summer many species of macroinvertebrates have emerged and only eggs or early instars are present. Therefore, sampling is more difficult in the summer and consequently, data less amenable to statistical analysis. Sampling will be conducted for two years to estimate seasonal and annual variability. Two years of sampling may not be sufficient for statistical analysis. The project time frame for the RI/FS limits the overall length of the macroinvertebrate program. However, data will be compared to previous studies by TVA to develop estimates of annual variability and the usefulness of macroinvertebrate sampling. If the macroinvertebrate sampling program is providing data which can be linked to the fate or impact of mercury in the system, additional sampling will be considered.

Benthic macroinvertebrates and algae surveys will be conducted at six (6) stations sited on the NFHR between Mile 100 and Mile 53. Sampling stations are shown in Figure 3 and listed in Table 1. Two stations (Mile 91.5 and Mile 85.6) are located upstream from the former chlorine plant site, Pond 5 and Pond 6. These stations are background stations. The station at Mile 91.5 has been utilized for previous benthos collections. The stream at this point is typical of the upper reaches of NFHR. The station at Mile 85.6 is located near Saltville, McCready and North Holston.

The plant site and settling ponds (Pond 5 and Pond 6) are adjacent to NFHR between Miles 82.4 and 80.8. One sampling stations was chosen along this section. The station at Mile 81.3 was chosen because it was representative of the NFHR adjacent to the site. The site has a relatively diverse habitat (island, riffle, pool) and is located downstream of the outfalls of Pond 5 and Pond 6.

Three benthic macroinvertebrates and algae sampling stations were sited in the downstream vicinity of the site. These stations are located at Mile 80.0, Mile 76.6 and Mile 61.0. The habitat of these sites is typical of NFHR in this area. Mile 80.0 is the location of the former chloride monitor which monitored river conditions downstream from the former operating plant. Mile 80.0 was a sample site used in earlier collections. The sampling site at Mile 76.7 is representative of this reach of NFHR and located in the vicinity of past fish collection sites. The last downstream station is located at Mile 61.0. This station is representative of the downstream area of the river.

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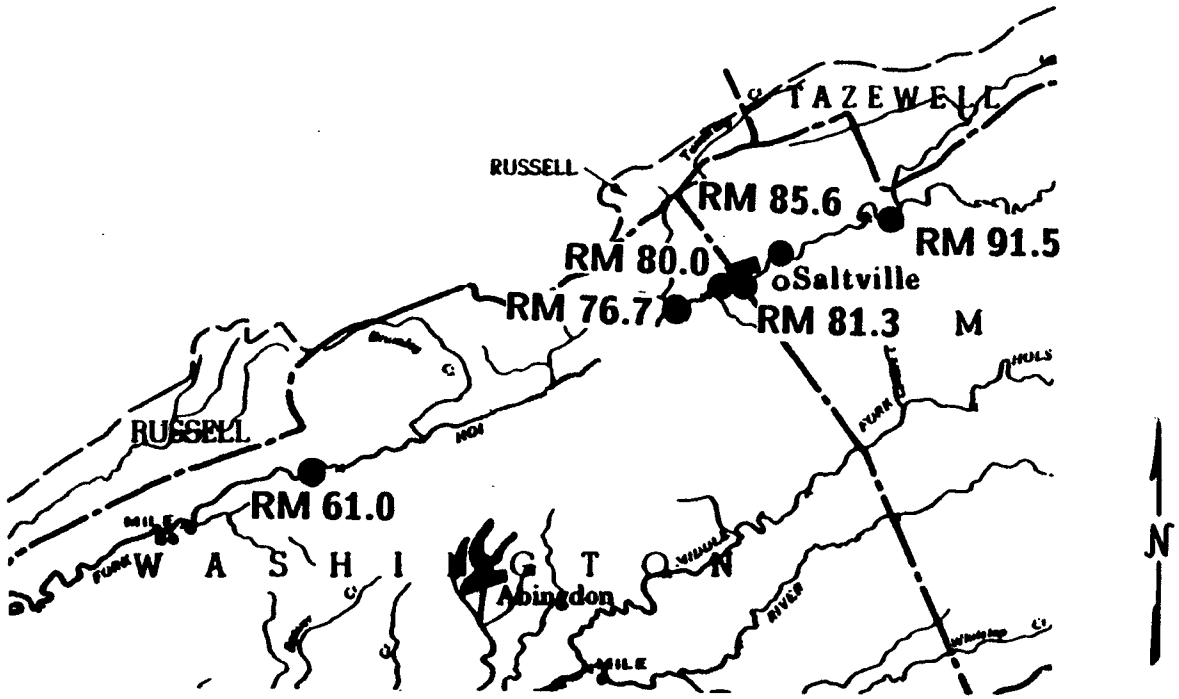


FIGURE 3. Sampling Locations for Benthic and Algae Monitoring Program

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TABLE 1

COLLECTION SITES FOR THE BENTHIC AND ALGAE STUDIES ON THE NORTH FORK HOLSTON RIVER

| SITE NO. | LOCATION | RIVER MILE |
|---|---|---|
| 1 | Old Broad Ford | 91.5 |
| 2 | Vicinity of McCready | 85.6 |
| 3 | Downstream of Pond 5 - left side of island | 81.3 |
| 4 | Former Chloride analyzer site | 80.0 |
| 5 | Downstream of Tumbling Creek-NFHR Confluence | 76.6 |
| 6 | 1.5 miles east of Route 611 & Route 19 Junction (Mongle Springs) | 61.0 |

All sites provide a relative diverse habitat (riffle, pool, etc.) and are typical at stream segment they represent. They should provide adequate macroinvertebrate for analysis. These sites will also be used for fish collections. Thus, fish data and macroinvertebrate data can be compared and evaluated.

### 3.2 Sample Collection

Several types of benthic macroinvertebrate samples will be collected from the major and minor habitats at each site. These habitats may include riffles, pools, depositional areas, log jams, exposed tree roots, undercut banks, etc. Samples for quantitative analysis (abundance, community structure and diversity) will be collected from the riffle areas using a Hess sampler.

To assess the variability of macroinvertebrate data within the North Fork Holston River system, historical data reported by TVA were examined. Variances reported by Hill et al (TVA, 1980) were utilized to estimate statistically valid sample sizes. Sample size calculations were based on techniques published by Gilbert (1987). Results of the statistical calculations revealed that samples size requirements to represent the benthic fauna of the North Fork Holston River would vary considerably on a site-to-site basis. Based on statistical parameters of historical data, the required number of quantitative samples ranged from less than 10 to several hundred samples per site. Obviously, collection and analysis of several hundred samples is cost prohibitive.

EPA (1983) states that a minimum of three replicate Surber samples are required to describe bottom fauna of a particular station. Collection of six quantitative Hess samples and one qualitative "kick" sample per site is more than a reasonable compromise between good data sets and reasonable costs. The data collected by this sampling is also compatible with the statistical protocols which will be employed to analyze the data and is consistent with the procedures given by EPA (1983).

Six Hess samples will be taken from the riffle areas at each site. Four samples will be used for quantitative analyses and two will be used as QA/QC samples. Composite samples for qualitative analyses will be collected from the major and minor habitats at each site. These will be used to further determine community structure. Three samples of crayfish and megalopterans if present will be collected from each site for mercury and methylmercury analyses.

In addition, adult insect sampling will be conducted during the spring and fall surveys employing light trap and tangle-foot techniques. Adult insect sampling will be conducted at each sampling site. Mayflies, stoneflies, and caddisflies will be collected for mercury analysis.

Composite samples of algae at each of the 6 sites will be collected from the major and minor habitats at each site. These samples of algae will be used for species identification. Samples of fixed filamentous algae *Cladophora glomerata* will be collected from each site if present. These samples will be used for mercury and methylmercury analysis. A field duplicate sample for mercury analysis will be collected from one site.

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## 3.3 Quality Assurance

The Quality Assurance Project Plan for the Saltville Waste Disposal Site Remedial Investigation and Feasibility Study, Saltville, Virginia will be in effect for this project. The goals of the QA program are to insure to the extent possible that samples results are precise, accurate, representative, comparable and complete.

Field quality assurance is the responsibility of the Field Sampling Coordinator. Frequent checks will be made to insure that all sampling procedures are followed. The analytical quality assurance is described in detail in the Quality Assurance Project Plan (QAPjP).

The calibration procedures specified by the analytical methods and instrument manuals will be followed. Frequency of calibration specified by the analytical methods or instrument manuals will be considered to be the minimum frequency. More frequency calibration maybe required under severe field conditions (e.g. rain, freezing temperatures). Calibration requirements of the method references will be met. All calibration checks must be documented in log books. At a minimum the following information must be recorded:

- Date of calibration
- Instrument model and serial number
- Identification of standards used
- Personnel performing calibration
- Results of calibration (including raw data and summary statistics)
- Corrective action taken

Field instruments such as pH meters and velocity meters will be calibrated daily (at a minimum) according to procedures specified by the Field Analytical Procedures and documented in field logbooks. Calibration must be performed with commercially prepared, certified standards if available, e.g., pH buffers, etc. Sources of all material use for calibration or for preparing calibration standards will be documented.

## 4.0 SAMPLE DESIGNATION

Each benthic macroinvertebrate and algae sample collected will be assigned a unique sample identification number. The sample numbering system will be:

Sxx - yyyyyB-zzz or Sxx-yyyyyP-zzz

where

xx is the site number shown on Table 1

yyyyy is a five digit number (starting with 00001 with the first sample) and assigned sequentially

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B is for benthic macroinvertebrate samples
P is for algae samples
zzz is the month/year collected (589 for May 1989)

## 5.0 SAMPLING PROCEDURES AND EQUIPMENT

### 5.1 Pre-Sampling Activities

Sampling and analytical personnel will be properly trained and experienced in the collection and analysis of benthic macroinvertebrate and algal data. Personnel employed in field sampling will be familiar with all equipment, procedures, and techniques required to collect samples of benthos that will accurately represent the true benthic assemblage of the NFHR. A minimum of two years of technical training or field experience in liminology science or other similar discipline emphasizing proper scientific methods is required.

Preparation for the sampling event can be divided into three primary areas:

1) Logistics of the event, including site access
2) Equipment preparation
3) Coordination with the analytical laboratory

The sampling coordinating team is responsible for all three areas. Olin will obtain site access for sampling points not on Olin property.

#### 5.1.1 Logistics

The sampling team will insure that samples can be collected from all sampling points before an event is scheduled. At a minimum the team will contact the Olin Project Manager before mobilizing. Olin will try to arrange for all contacts with property owners for permission to enter their property where necessary to collect samples. The sampling team should check with property owners of any fenced or posted property.

#### 5.1.2 Equipment Preparation and Calibration

All equipment to be used in the sampling effort will be checked for service before mobilizing. Any instruments used in water quality monitoring will be calibrated per manufacturers specifications prior to field measurements. Backup meters will also be taken into the field. Any maintenance or cleaning will be completed prior to moving into the field for sampling.

### 5.1.3 Coordination with Laboratory

The Field Sampling Coordinator will insure that the laboratory is prepared to receive samples on the required schedule before collecting any samples. The laboratory will be notified of each sample shipment so that samples can be expeditiously unpacked, inspected, and entered into the analytical flow at the laboratory.

## 5.2 Field Procedures

Qualitative sampling of the benthic macroinvertebrates will be conducted in each of the major and minor habitats at each site (riffles, pools, lateral depositional areas, log-jams, exposed tree roots, under-cut banks, etc.) Qualitative sampling of benthic macroinvertebrates will involve use of kick-nets, screens, and visual examination of substrates. A minimum of 2-3 square meters of habitat will be qualitatively sampled at each site. The size of area samples will be the same at each site. Kick-nets are most useful in flowing waters having a pebble to cobble substrate size. The substrate is disturbed by vigorous kicking action upstream of the net. The water current carries the dislodged organisms into the net. Screens are often used in lateral stream microhabitats having a muck, silt, sand, or gravel substrate. The screen allows passage of much of the substrate, and the organisms are then picked off the screen and preserved. Kick-nets, screens, and visual observation methodology will be employed. Adults will be collected whenever possible to facilitate identification to the species level. Visual examination involves the physical examination of larger rock substrates, logs, leaf packs, and aquatic plant parts for colonizing macroinvertebrates. Sometimes a shallow, white pan is used to facilitate this examination.

During the spring and fall sampling trips, adult aquatic insects will be collected at night using an ultra-violet light to attract them onto a white sheet. The light traps will be placed at each of the sampling sites. The traps will be operated for a minimum of one hour at each site.

Quantitative sampling of benthic macroinvertebrates will be conducted in the riffle area of each sample site. Stratified random sampling techniques will be employed during each sampling. Using a Hess sampler, the benthic macroinvertebrates are brushed or otherwise dislodged from the substrate in a contained area and are then carried by stream flow into a collection net. Assuming that the samples locations were selected randomly and the area of the Hess sampler was known, then a quantitative estimate of density per unit area can be obtained. Six (6) Hess samples will be taken at each of the sites, with at least 4 samples used for density estimates and the remainder serving as QA/QC samples.

Qualitative sampling for periphytic algae will be conducted in all the major and minor habitats at each site. Three composite collections of scrapings from rocks and other substrates will be obtained.

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Samples of benthic macroinvertebrates and algae will be collected for analyses. Crayfish and megalopterans will be collected from each site for mercury and methylmercury analyses. If available, three ten-gram samples will be collected from each site. The sample from one site will be split for field duplicate analysis. A sample of fixed filamentous algae (*Cladophora glomerata*) will be collected

from each site for mercury and methylmercury analysis. Mayflies, stoneflies and caddisflies are probable candidates for insects. These were selected for analysis because they are generally available at all sites, historical data concerning mercury concentrations are available and they are a major part of the biological food chain. One sample will be split for field duplicate analysis.

Each site will be characterized according to substrate type (silt-sand-clay, gravel, cobble, sheet rock, etc.) during the sampling. Sediment samples for grain size analysis and TOC will be collected at each sampling site. Water depth, water temperature, alkalinity, hardness, pH and velocity will also be measured.

Sediment samples will be collected with a decontaminated shovel, scoop or spoon. Special effort will be taken to minimize the loss of fine sediment during the sampling process. Larger rocks, debris and vegetation will be removed by hand from each sample. The sample will be homogenized by hand mixing, screened through a No. 10 sieve (2.00 mm) and a 4 oz. sample bottle filled with sediment and labeled.

Identification tags used in the collections described above will include the following information:

1) sampling location
2) collector
3) sampling date and time
4) identification number

It is the responsibility of Field Sampling Coordinator to insure that field activities and observations are documented. A field log book will be maintained to record the following information:

- General description of work
- Samples collected and their identification numbers
- Date, time of sampling, weather conditions
- Sample location
- Field measurements and observations
- Field sampling personnel
- SOPs employed
- Written discussion of any deviations from SOPs
- Chain-of-custody references for each sample

## 5.3 Equipment Required

Table 2 is a checklist of the equipment required for conducting the benthic macroinvertebrate and algae collections.

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TABLE 2

MACROINVERTEBRATE SAMPLING EQUIPMENT CHECKLIST

Hess Samplers
D-frame net
Hand-held screen or sweep net
Ethyl alcohol, 80%
White enamel dissection pan
Scrub brush
Tape measure
Repair tools
Clipboard, data forms, and pencils
Collection containers
Identification keys
Marker ribbon
Camera and film
Field log book
Copies of Standard Operating Procedures
Waterproof labels
Adhesive labels
Dip nets
First aid kit
Light traps
Killing jars
Ethyl acetate
White sheets
Flow meter
pH meter with buffers

## 6.0 SAMPLING HANDLING AND ANALYSIS

### 6.1 Sampling Preparation

Benthic macroinvertebrate and algae samples collected for mercury and methylmercury analysis will be packaged in zip-lock plastic bags, plastic containers or glass jars and stored in an insulated cooler with wet or dry ice. Dry ice will be used whenever available.

Benthic macroinvertebrate samples collected for qualitative analysis will be preserved in 80% ethanol, labeled and stored in glass or plastic bottles. The bottles will be stored in boxes or insulated coolers to prevent breakage.

Algae samples collected for qualitative sampling will be placed in zip-lock plastic bags and stored on ice in an insulated cooler.

A portion of the organisms collected by light trap will be preserved in 80% ethanol for subsequent identification. A second portion will be collected dry, placed in a killing jar where they are exposed to vapors of ethyl acetate, and retained for total and methylmercury analysis.

### 6.2 Shipping Requirements

Samples will be shipped on ice (preferably dry ice) to the laboratory in insulated coolers. Arrangements will be made to insure that the samples arrive at the laboratory in an expeditious manner.

A chain-of-custody form will be completed for each cooler, itemizing each benthos and algae sample contained therein. The completed chain-of-custody forms and benthos and algae samples will remain under custody until delivery to the analytical laboratory. Copies of the chain-of-custody forms will be included in the final report.

### 6.3 Chain-of-Custody Record

Once a sample is collected, custody must be maintained. A sample is under custody if:

- It is in your possession.
- It is in your view, after being in your possession.
- It is in your possession and you placed it in a secure area.
- It is in a designated secure area.

Chain-of-custody forms will be prepared for the sample prior to transporting samples from field sites. Each sample will be listed on the form. A chain-of-custody form is shown in Figure 4. The following sample custody procedures will be utilized:

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# FIGURE 4

## OLIN CORPORATION

### CHAIN OF CUSTODY RECORD

| PROJ. NO. | PROJECT NAME |
|---|---|
| SAMPLERS: *(Signature)* | |

ANALYSES REQUIRED

Instructions: List samples individually. Write time in military time. Record sample type as water, soil, etc. and as grab or composite. Record special handling instructions or precautions in remarks section. Record method of shipment in comments section.

| Station or Sample No. | Date | Time | Sample Type | Number Of Containers | | | | | | | Remarks |
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| Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* | Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* |
|---|---|---|---|---|---|
| Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* | Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* |
| Relinquished by: *(Signature)* | Date/Time | Received for Laboratory by: *(Signature)* | Date/Time | Comments | |

DISTRIBUTION: Original and Pink copies accompany sample shipment to laboratory. Pink copy retained by laboratory. Yellow copy retained by samplers.

1) Each sample collected for the project will be entered on the chain-of-custody record. Field personnel will retain a copy of the chain-of-custody record.

2) The original chain-of-custody record plus one copy will accompany the sample containers during transport to document controlled custody.

3) If custody is relinquished through a common parcel carrier for delivery to the laboratory, the following protocol will be followed:

   - The method of sample shipment will be noted in the comment section on the chain-of-custody form.

   - The original chain-of-custody record plus one copy will be placed inside the shipping package.

   - The shipping package will then be sealed with a custody seal. The seal will be placed on the package in such a manner that the package cannot be opened without breaking the seal. The seal will serve to document that the samples remained unaltered during shipment through the common parcel carrier.

4) If the sample is shipped by air freight or express shipment, the air bill will become part of the chain-of-custody procedures.

5) The laboratory will assume custody of the samples upon receipt. A designated Sample Custodian will be charged with sample care and receipt and verification of custody seal condition. These observations will be noted by the Sample Custodian on the chain-of-custody form upon receipt. All sample damage and abnormalities will be noted on the forms. The Sample Custodian will sign the chain-of-custody form, retain the copy for the Laboratory's record, and forward the original to the Field Project Officer.

6) Sample preparation and analysis custody will be tracked by laboratory worksheets.

7) The laboratory will retain custody of the samples in a secure area until such time as the samples are ordered destroyed.

8) A copy of the chain-of-custody record will be retained.

9) If samples are transferred to another laboratory, either as a whole or as a split sample, a new chain-of-custody form will be initiated.

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## 6.4 Holding Times

There are no holding times for benthic macroinvertebrate, algae and sediment prior to analysis. However, samples should be analyzed in a timely manner.

Analysis of surface water for dissolved oxygen, temperature, pH and conductivity will be conducted at the time of sampling using field meters. Analytical procedures are given in the QAPjP.

## 6.5 Record Keeping

All records will be maintained in bound books. A master log will be established which will contain the appropriate identity and traceability of each sample. The same code number will be used from sample acquisition through final data tabulation. Detailed notebooks will be maintained by laboratory personnel for samples, instruments and calibration standards.

## 6.6 Laboratory Identification Procedures

Qualitative algal and benthic macroinvertebrate samples will be returned to the laboratory for further processing. The algal samples will be examined using a standard compound microscope, with identification to the lowest practical taxonomic level. Identification will be to the genus level at a minimum and to the species level wherever possible. A relative abundance (rare, common, dominant) ranking will be assigned to each of the algal taxa.

The benthic samples will be separated from associated detritus and substrate, sorted according to taxonomic order or class, and examined using a stereo binocular microscope, with identification to the lowest practical taxonomic level. Identification will be to the genus level at a minimum.

Ten percent of the samples will be picked a second time by a different technician as part of project QA/QC procedures. After picking, the sample will be identified to the lowest practical taxonomic level. The total number of organisms per sample and the total number of per taxa will be recorded. A reference collection of each taxa identified during the study will be archived. Ten percent of the samples will be identified a second time by an independent invertebrate zoologist for QA/QC purposes.

Adults collected either during daytime sampling or during nighttime light-trapping will be examined in the same manner as the benthic samples above. Quantitative benthic macroinvertebrate samples will be treated in the same manner as the qualitative samples discussed above. However, each taxon will be quantified.

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# FIELD SAMPLING PLAN FOR MUSSELS
# FOR THE SALTVILLE WASTE DISPOSAL SITE
# REMEDIAL INVESTIGATION AND FEASIBILITY STUDY
# SALTVILLE, VIRGINIA

OCTOBER 26, 1989

AR300071

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| 3 | Asiatic Clam and Mussel Sample Site NFHR |
| 4 | Schematic Design of Quantitation Mussel Sampling Plan |
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## 1.0 SITE BACKGROUND

### 1.1 Introduction

This Field Sampling Plan for Mussels (FSP-Mussels) has been prepared for the Remedial Investigation/Feasibility Study (RI/FS) for the Saltville Waste Disposal Site, Saltville, Virginia. This document describes in detail the sampling and data gathering methods which will be used to achieve the data quality objectives needed to support decisions regarding remedial response activities. The FSP-Mussel was prepared in accordance with the Interim Final EPA document "Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA" (OSWER Directive 9355.3-01), dated October 1988; EPA document "A Compendium of Superfund Field Operations Methods" (OSWER Directive 9355.0-14), dated December 1987; and EPA document "Data Quality Objectives for Remedial Response Activities-Development Process: (OSWER Directive 9355.0-7B), dated March 1987.

### 1.2 Site Description

The Saltville Waste Disposal Site is located along the North Fork of the Holston River (NFHR), between the town of Saltville and the community of Allison Gap in western Smyth County, Virginia, extending partly into Washington County, Virginia (see Figure 1). The NFHR lies adjacent to the southern border of the site at North Fork Holston River Mile (NFHRM) 80.8 - 82.4 and flows southwest. The Saltville Waste Disposal Site includes the former chlorine plant site (FCPS), waste disposal Pond 5 and waste disposal Pond 6. Pond 5 discharges water into the NFHR at Mile 81.7. Pond 6 discharges water into the NFHR at Mile 81.5. Additional description of the Site is given in Section 2.0 of the RI/FS Work Plan.

The NFHR is a fast flowing mountain stream which originates approximately 48 miles above the former chlorine plant site. The stream flows southwest through a rural landscape to the confluence with the South Fork Holston River in Tennessee to form the Holston River. The Holston River flows into Cherokee Reservoir in Tennessee. Figure 2 is a schematic of the Holston-Cherokee system. Upper watershed areas are primarily hardwood forest on steep slopes while the lower portion is less mountainous and is bordered by pasture and farmlands. Land-use is dominated by agriculture, and little heavy industry is present within the watershed except that located in Saltville, Virginia.

The NFHR is characterized over most of its length by a coarse rocky substrate with extensive riffle and pool areas. Daily discharge at NFHR Mile 85 range from 23 cfs at low flow (7Q10) to 16,500 cfs at peak storm discharges (USGS data) and averages 290 cfs. Over the course of the study area (NFHRM 92 to NFHRM 53), the river varies in width between 100 and 300 feet. Water depths at normal flow vary between a few inches in the riffle areas to 10 feet in the deeper pools.

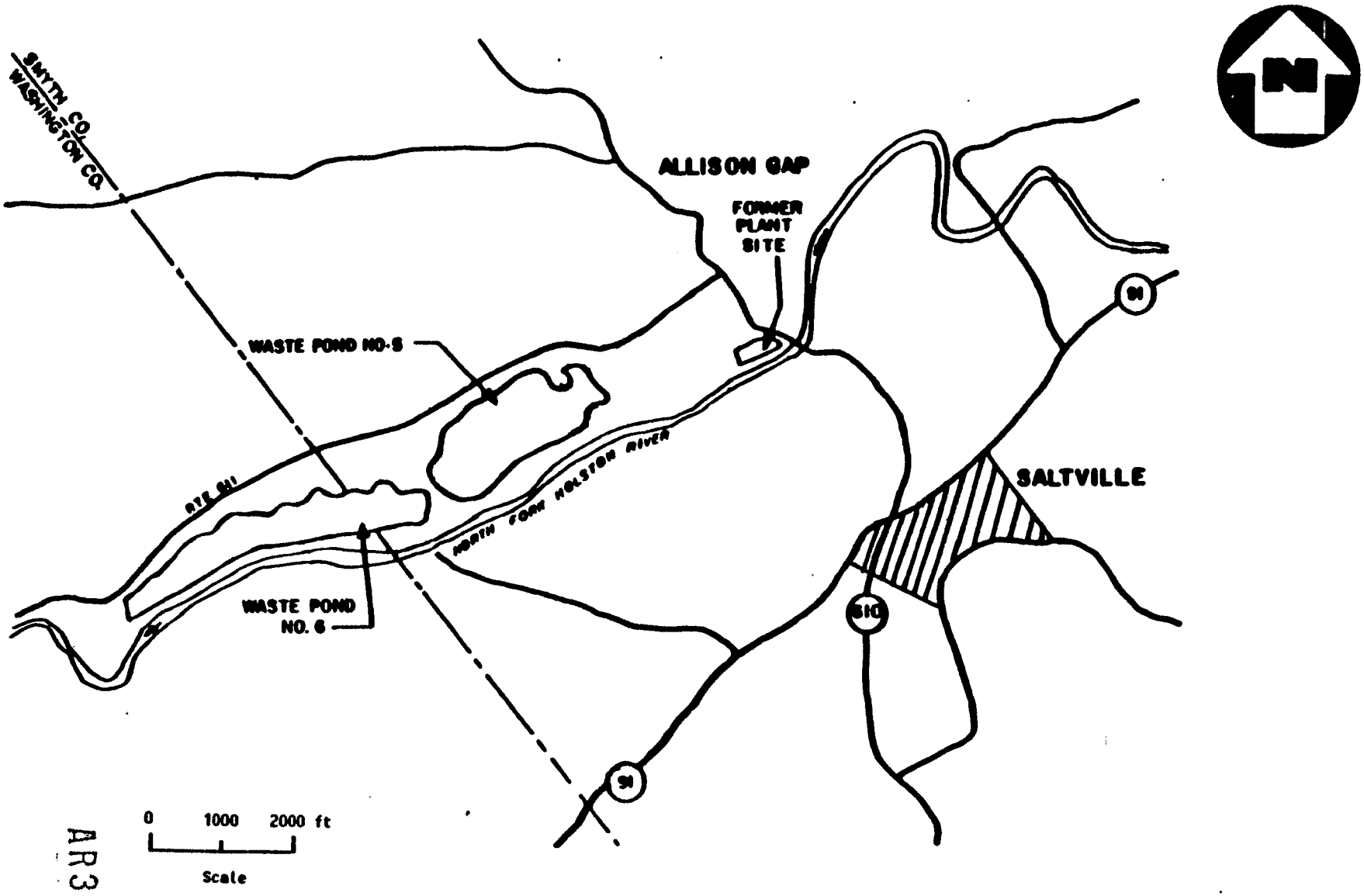


FIGURE 1. Saltville Waste Disposal Site-Area Map

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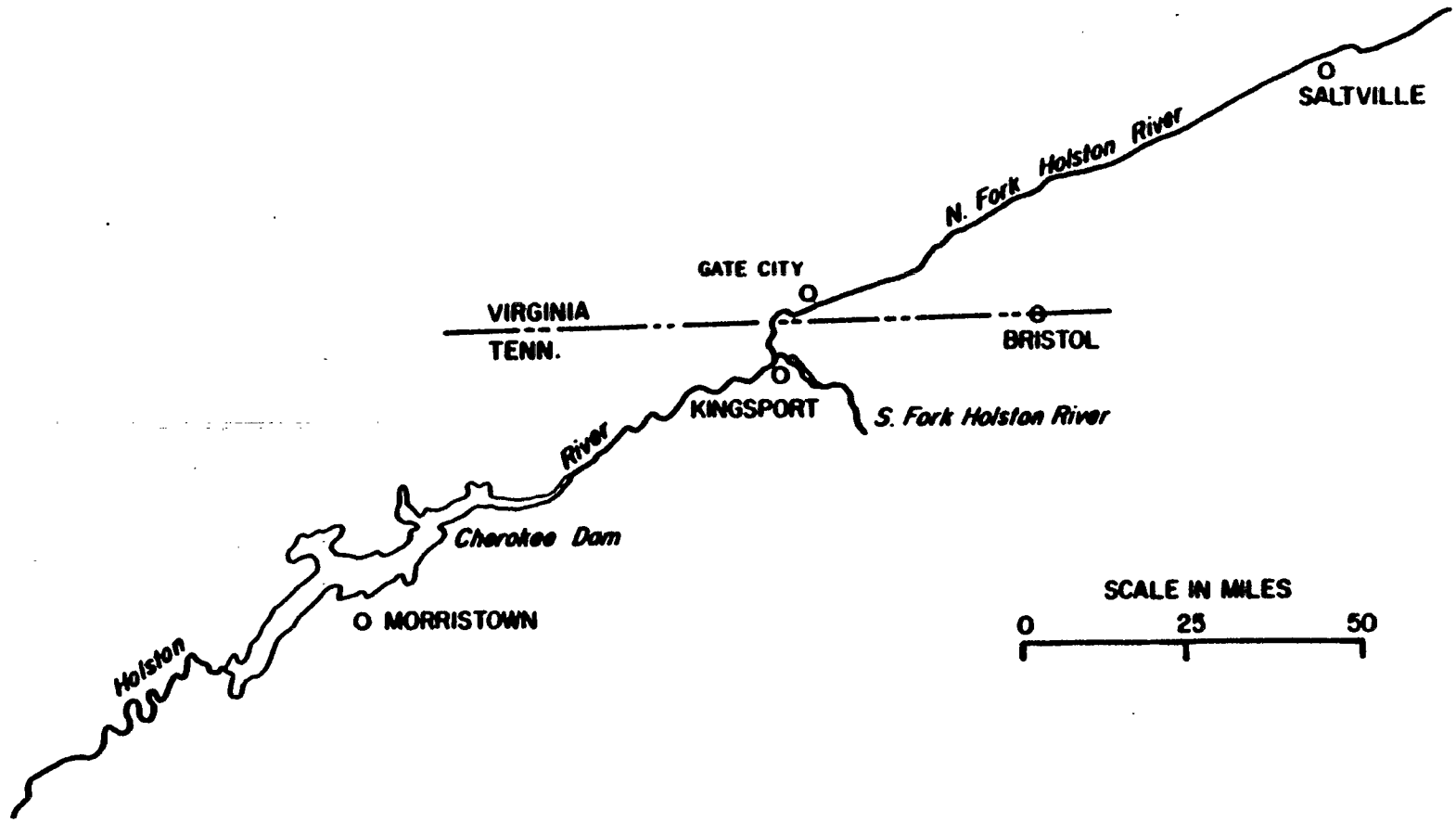


FIGURE 2. Holston River-Cherokee Reservoir System

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## 1.3 Contaminant Sources

The contaminant of concern is mercury (ROD, 1987). Mercury was used in chlor-alkali plant operations (1951 to 1972) and entered the environment via process wastewater streams. Mercury contaminated wastewater initially discharged directly to the NFHR and later to Pond 5.

Total dissolved salts (mainly calcium chloride and calcium sulfate) are a secondary source of concern for mussel populations due to possible effect on reproduction. There are two sources of dissolved salts - 1) the Ponds on the Olin Site and 2) the natural "old salt ponds" located in Saltville. Water from the natural brine ponds discharge to the NFHR near the old chlorine plant site. Salt concentrations from both sources vary as a function of rainfall. Concentrations generally range from 10,000 to 20,000 mg/l.

## 1.4 Transport Pathways

The former chlorine plant site has been remediated with a clay cap. The Pond 5 outfall presently discharges effluent to the NFHR. This discharge can contain up to 120 ppb mercury. The Pond 6 outfall also discharges to the NFHR. Pond 6 effluent is generally less than 0.2 ppb (non-detectable). The sediments of the NFHR contain 3 to 9 ppm mercury near the site (report in preparation). Mercury concentrations in the sediments decrease downstream to less than 0.5 ppm at NFHRM 8.

Mussels in the NFHR are exposed to mercury through several pathways. The water column outside Pond 5 outfall mixing zone contains low concentrations of mercury (<0.2 ppb), suspended sediment contains mercury and food sources (plankton, etc.) contain mercury. These are generally the pathways available for uptake. This is not intended to be an in-depth discussion of the mechanisms of uptake.

## 1.5 Data Gaps

Over the past 100 years various mussel population studies have been reported for portions of the river and certain tributaries. Historical surveys focused on the qualitative presence of unionid species above and below the plant during the period of early plant operations (prior to 1920) and following the closing of the chlorine operations in 1972.

The earliest, most complete description of the mussel fauna on the NFHR Holston was compiled by Ortmann (1918) using data gathered by Adams in 1900 and 1901, himself in 1912, 1913, and 1915, and Peterson in 1917. At that time he listed 16 species of mollusks at Saltville and 37 species below Saltville. He made no collections above Saltville. In 1968, Stansbery (1972) found no species of mussel from below Saltville to the confluence with the South Fork Holston River. During the same year, Stansbery and Clench (1974) found 11 species at Saltville but in 1971 they identified an additional 6 species. They also found the same 17 species above Saltville.

Review of available literature shows that following the Olin Plant closure in 1972, the Tennessee Valley Authority (TVA) initiated a sampling program in the NFHR to monitor the anticipated recovery of both fish, macroinvertebrate, and mussel populations. Between 1975 and 1978, a total of 2,887 mussels representing 16 species were transplanted from the Clinch River and Upper NFHR (upstream of Saltville) to four sites downstream of Saltville (i.e. Click Island (NFHRM 6.3), Highway 33 Bridge (NFHRM 9.3), North Fork Church (NFHRM 52.7), and McKenna Island (NFHRM 78.0))(TVA, personal communication with J.L. Jenkinson). Other transplant/bioaccumulation studies have been conducted by researchers at Virginia Tech since site remediation in 1984 (personal communication, Richard Neves, VPI). No systematic surveys have been conducted in the bioassessment area (NFHRM 92 - 53) in the past few years.

Preliminary mussel surveys conducted by Olin in 1988 downstream of Saltville (i.e., approximately eight miles) found live representatives of *Lampsilis fasciolia* and *Villosa iris*. These species are not believed to have been transplanted (TVA and VPI, personal communication).

The present status of the mussel population in the NFHR is not known. The mercury concentration in the bivalve population of the NFHR is not known.

The proposed mussel sampling program will address the present data gaps. Mussel surveys will document the present status of the mussel fauna upstream and downstream of the Saltville Site between NFHR Mile 92 and Mile 53. Mussel surveys will be conducted in the spring of 1990. Sites where mussel were transplanted by VPI and TVA will be surveyed. Samples of the most abundant bivalve species (*Corbicula fluminea*) will be sampled and analyzed for total mercury and methylmercury.

## 2.0 SAMPLING OBJECTIVES

### 2.1 Specific Objectives

A comprehensive bioassessment program for measuring mercury impact on NFHR aquatic communities involves the integrated use of both biological (i.e., benthic and fish surveys) and physio-chemical (i.e., sediment modelling) methods. The NFHR bioassessment program consists of five major tasks which evaluate the effects of present and past mercury discharge from the Site on the biotic integrity of stream communities of NFHR. The five tasks include (I) fish studies, (II) benthic studies, (III) mussel studies, (IV) ambient toxicity studies and (V) mercury fate and transport studies.

The main objective of the mussel studies is to determine the effect of past and present discharges from the Saltville Site on the NFHR mussel community. This will be accomplished by:

- conducting a mussel survey in the NFHR both upstream and downstream of the Saltville Site.

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- determining the species composition, relative abundance, size and age of the NFHR mussel population.

- collection and analysis of mercury and methylmercury in *Corbicula fluminea* (Asiatic clam).

## 2.2 Uses of Data

Mussel Community Structure

The mussel fauna from NFHRM 92 to NFHRM 53 will be surveyed at regular intervals (approximately every 3 miles) to document the present status of the mussel fauna above and below the Saltville Site. This task will determine species composition and relative abundance and will determine if natural re-colonization has occurred at sites below Saltville in areas known to have been impacted by point source discharges from historical industrial and municipal discharges. During recent years, mussels have been transplanted into the NFHR. These transplant sites will be surveyed.

Mussels collected will be identified as to species in the field. Specimens of questionable identification will be photographed and returned to the river. Identification of mussels will be based on experience and verified reference material previously collected from the NFHR. In areas where mussels are found, qualitative sampling will be conducted to determine species composition, relative abundance, size and age. A map showing species locations will be developed.

The general hypotheses to be tested will be:

1. Relative abundance of mussels is not significantly different below Saltville than above Saltville.

2. The current relative abundance of mussels has not changed significantly from historical data, above and below the site.

The general statistical procedures outlined in the RI/FS Work Plan (Section 5.0, Task 3.B.4) will be utilized to test these hypotheses where data are available. These procedures include determination of data probability distribution type, calculation of the unbiased estimators of the mean and variance for each dataset, comparisons between means and interpretation of statistical results. The degree of confidence with which all interpretations are made will be provided with the results of the calculations.

Mercury Concentrations

Asiatic clams (*Corbicula fluminea*) from each mussel survey site (total of 13 sites) will be analyzed for total and methylmercury. Analytical methods are detailed in the Quality Assurance Project Plan (QAPjP). Mercury data will be used to determine the present concentrations of mercury in Asiatic clams. Appropriate statistical analyses (i.e. parametric and/or non-parametric statistical methods) will be used to compare mercury concentrations among sites.

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## 3.0 SAMPLE LOCATION AND FREQUENCY

### 3.1 Collection Sites

Mussel surveys will be conducted in the spring on the NFHR between Mile 92 and Mile 53. Utilizing random search procedures, this stretch of the NFHR will be preliminarily surveyed to identify habitat types and locations and fauna present. This reconnaissance survey will provide qualitative data and enable the selection of specific sampling locations for quantitative measurement of mussel population structure. The stretch of river to be surveyed includes areas upstream (3 sites), adjacent to (1 site) and downstream (9 sites) of the Saltville Site. The mussel survey will be spaced at three-mile intervals, depending on the availability of suitable mussel habitat. Sites are tentatively located at NFHRM 91.5, 88.5, 85.6, 81.3, 76.7, 74.0, 71.0, 66.3, 63.8, 61.0, 58.2, 56.4 and 53.2 (see Figure 3).

### 3.2 Sample Collection

The stations identified during the reconnaissance survey will be quantitatively sampled to document species composition, age, sex, relative abundance and size. Mussels collected will be identified, weighed, measured and counted in the field. Mussels will be inspected for disease, parasites, and anomaly. Mussels of questionable identification will be photographed and returned to the river. Fresh dead shells will be collected and returned to the laboratory for verification of identity. A reference collection of all species identified in the study will be maintained in the laboratory. The reference collection will be reviewed by a referee malacologist as part of the QA/QC program. Data analysis will include species composition, relative abundance, size, age and sex. A description of each station where mussels are found will be recorded in the field log and will include location, habitat type, water depth and other descriptive notes of observation.

*Corbicula fluminea* will be sampled from each site during the mussel survey to provide baseline data on mercury and methylmercury in present bivalves. Sampling locations will include 3 upstream (background) stations located at NFHRM 91.5, 88.5 and 85.6 and 10 stations adjacent to or downstream of the Saltville Site. These stations are tentatively located at NFHRM 81.3, 76.7, 74.0, 71.0, 66.3, 63.8, 61.0, 58.2, 56.4 and 53.2. Three composite tissue samples will be collected from each site and analyzed for mercury and methylmercury. Any tissue remaining after analysis will be retained (frozen) for potential future analysis of other contaminants which may be found at the Saltville Site.

Dissolved oxygen, temperature, pH, conductivity, alkalinity, and hardness will be measured at each site prior to sampling. All field instruments will be calibrated daily.

### 3.3 Quality Assurance

The Quality Assurance Project Plan for the Saltville Waste Disposal Site Remedial Investigation and Feasibility Study, Saltville, Virginia will be in effect for this project. The goals of the QA

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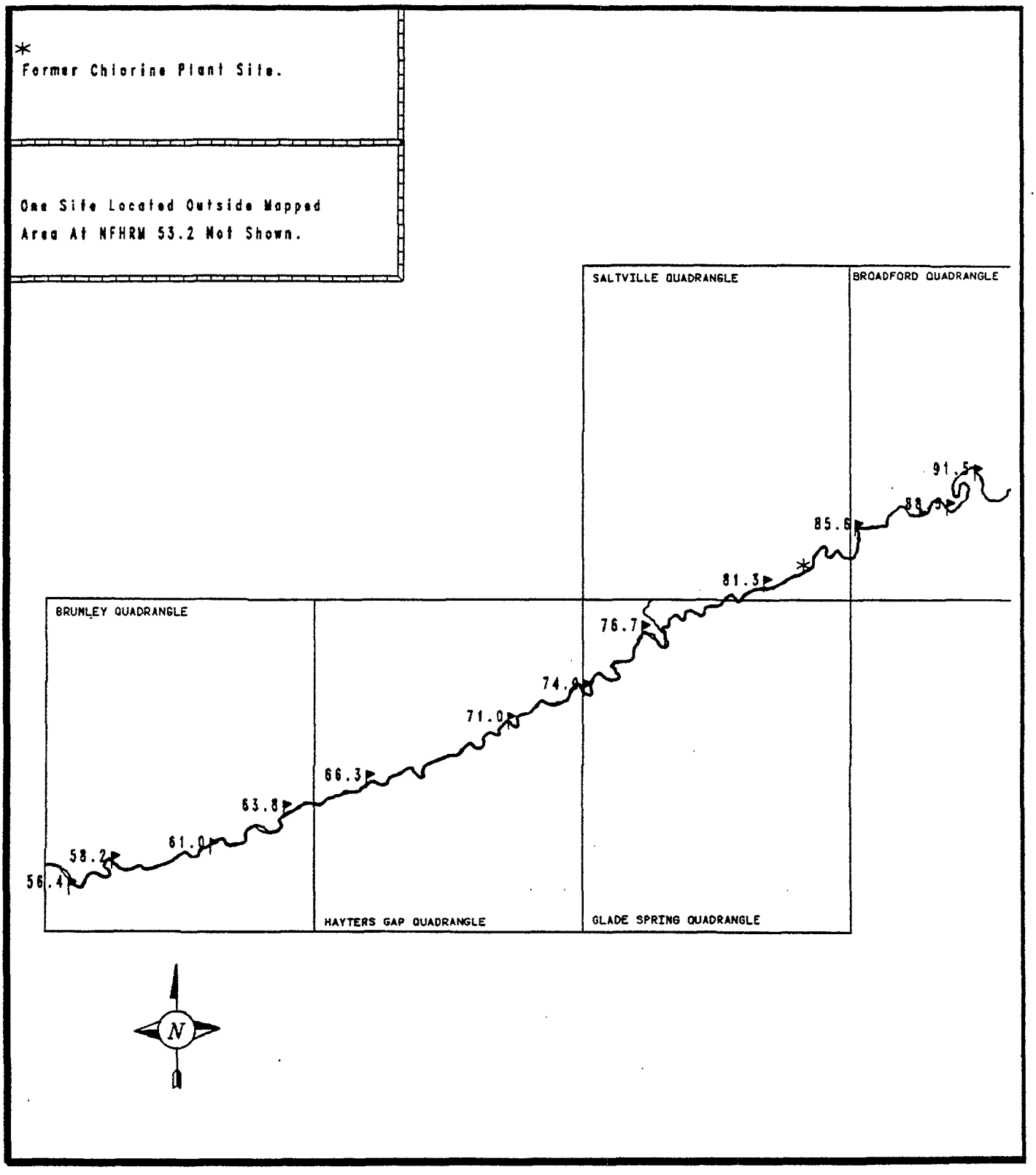


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**FIGURE 3. Asiatic Clam and Mussel Sample Site NFHR**

program are to insure to the maximum extent possible that sample results are precise, accurate, representative, comparable, and complete.

Field quality assurance is the responsibility of the Field Sampling Coordinator. Frequent checks will be made to insure that all sampling procedures are followed. Random audits of field procedures will be conducted by the QA Officer to insure that specified protocols are being followed. The analytical quality assurance is described in detail in the Quality Assurance Project Plan (QAPjP).

The calibration procedures specified by the analytical methods and instrument manuals will be followed. Frequency of calibration specified by the analytical methods or instrument manuals will be considered to be the minimum frequency. More frequent calibration may be required under severe field conditions (e.g. rain, freezing temperatures). Calibration requirements of the method references will be met. All calibration checks must be documented in log books. At a minimum the following information must be recorded:

- Date of calibration
- Identification of standards used
- Instrument model and serial number
- Personnel performing calibration
- Results of calibration (including raw data and summary statistics)
- Corrective action taken

Field instruments such as pH meters and conductivity meters will be calibrated daily (at a minimum) according to procedures specified by the Field Analytical Procedures and documented in field log books. Calibration must be performed with commercially-prepared, certified standards if available, e.g., pH buffers, conductivity standards, etc. Sources of all material used for calibration or for preparing calibration standards will be documented.

## 4.0 SAMPLE DESIGNATION

Each mussel sample collected for the reference collection and each composite sample of Asiatic clams collected for total mercury and methylmercury analysis will be assigned a unique sample identification number. The sample numbering system will be:

Sxx - yyyyyM-zzz or Sxx-yyyyyC-zzz

where

Sxx is the site number
yyyyy is a five digit number (starting with 00001 with the first clam or clam composite collected and assigned sequentially)

M is the designation for mussel sample
C is the designation for Asiatic clam sample
zzz is the month/year collected (589 for May 1989)

## 5.0 SAMPLING PROCEDURES AND EQUIPMENT

### 5.1 Pre-Sampling Activities

Sampling and analytical personnel will be properly trained and experienced in the collection and analysis of field aquatic biological data. Personnel employed in field sampling will be familiar with all equipment required to collect mussel samples for the reference collection. A minimum of two years of technical training or field experience in fishery science or other similar discipline emphasizing proper scientific methods is required.

Preparation for the sampling event can be divided into three primary areas:

1. Logistics of the event, including site access
2. Equipment preparation
3. Coordination with the analytical laboratory

The sampling coordinating team is responsible for all three areas. Olin will obtain site access for sampling points not on Olin property.

#### 5.1.1 Logistics

The sampling team will insure that samples can be collected from all sampling points before an event is scheduled. At a minimum the team will contact the Olin Project Manager before mobilizing. Olin will arrange for all contacts with property owners for permission to enter their property where necessary to collect samples. The sampling team should check with property owners of any fenced or posted property. The sampling contractor is responsible for obtaining collection permits from the U. S. Fish and Wildlife Service and the State of Virginia (Department of Game and Inland Fisheries).

#### 5.1.2 Equipment Preparation and Calibration

All equipment to be used in the sampling effort will be checked for service before mobilizing. Any instruments used in water quality monitoring will be calibrated per manufacturers specifications prior to field measurements. Backup meters will also be taken into the field. Any maintenance or cleaning will be completed prior to moving into the field for sampling.

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### 5.1.3 Coordination with Laboratory

The Field Sampling Coordinators will insure that the laboratory is prepared to receive any samples on the required schedule before collecting any samples. The laboratory will be notified of each sample shipment so that samples can be expeditiously unpacked, inspected, and entered into the analytical flow at the laboratory.

## 5.2 Field Procedures

During the reconnaissance survey, a minimum of three experienced aquatic biologists will travel the NFHR from Mile 53 to Mile 92. A field log will be used to document encountered mussel populations and key habitat areas. Representative transects of key habitat substrates will be identified for quantitative sampling. The purpose of the reconnaissance survey is solely to gather qualitative data to determine specific sampling stations for quantitative surveys.

Once specific sampling locations have been selected, quantitative sampling at each site will be conducted. The preliminary sampling protocol requires identification of a 10-meter X 20 meter area. Each area is traversed by 4 line transects. Each line transect (I, II, III, IV) consists of 40 sampling locations resulting in 160 sequential 0.5 $m^2$ sample points within the grid. A table of random numbers will be utilized to randomly select 40 numbers between 1 and 160 which correspond to sampling points on the line transects. Forty 0.5 $m^2$ samples represents 10 percent of the area within the grid. This procedure will result in less than 5 percent of the total habitat of any selected site (shoal) being disturbed. Figure 4 presents a schematic view of the structured line transect random sampling design. Samples will be collected by hand within the 0.5 $m^2$ frame to a depth of 15 centimeters (where possible). All mussels found in each 0.5 $m^2$ quadrant will be placed in individually marked mesh bags and retained in flowing river water. This sampling protocol will be applied initially to five sampling sites. Results of these surveys will be used to calculate the number of samples required to estimate the mean density of species populations using an alpha value of 0.05 and beta value of 0.10. If less than 40 samples are required, the sampling protocol will be adjusted to collect fewer samples. However, if more than 40 samples are required to meet the stated precision, we will re-evaluate our protocol.

The proposed mussel sampling program will address the present data gaps. Mussel surveys will document the present status of the mussel fauna above and below the Saltville Site. Mussel surveys will be conducted in the spring of 1990.

Each mussel collected will be measured in three dimensions using wooden calipers, weighed using a fish scale, identified by species, sex and age by experienced malacologists. This data will be recorded in the field log by site. A representative of each species encountered will be returned to Young-Morgan & Associates Laboratory in Franklin, Tennessee and preserved in alcohol as part of the reference collection. No live endangered mussels will be removed from the system. Fresh dead or relic shells of endangered mussels will be collected for reference. Any mussels which cannot be identified in the field will be photographed for identification and returned to the river. The reference collection will also be reviewed by a referee malacologist as part of QA/QC protocol.

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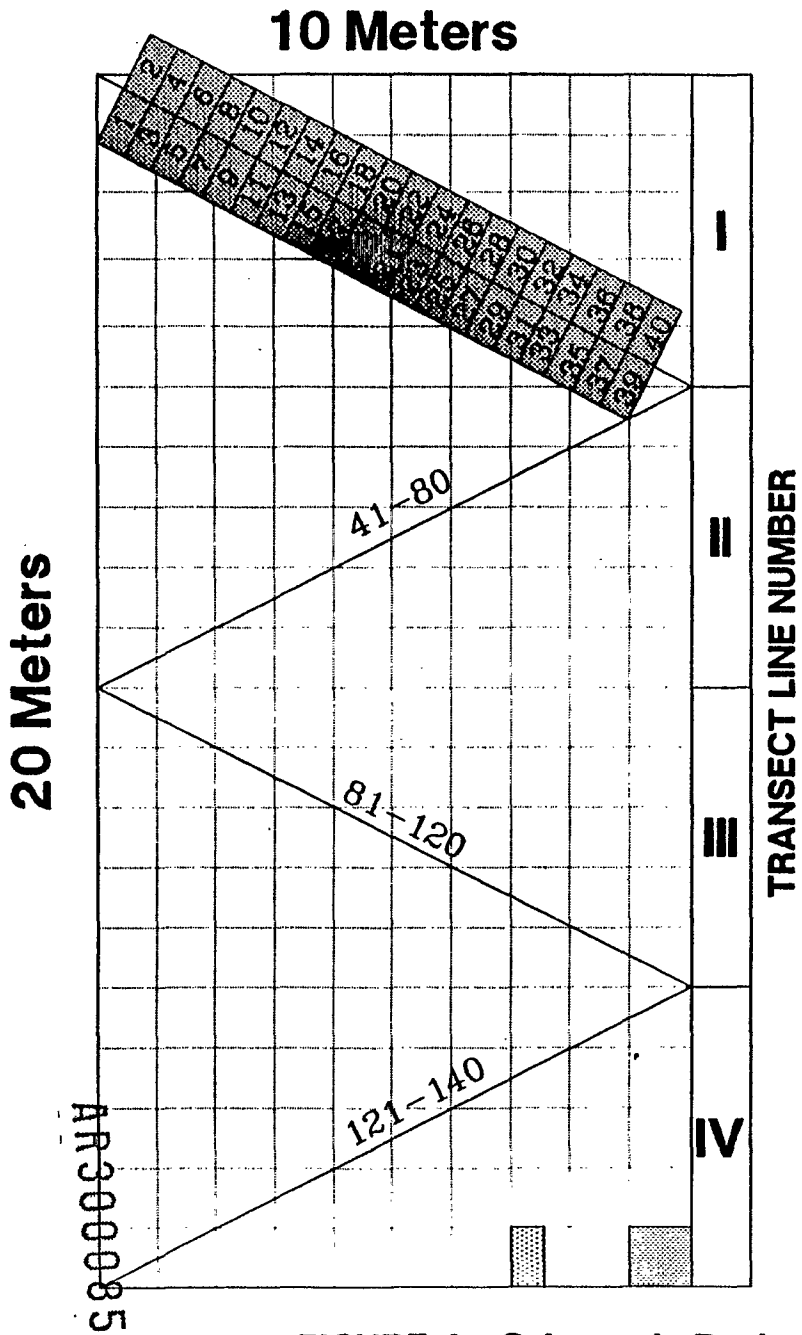


Total Area Per Collection Site = 200 $M^2$

Total Sampled Area = 40 X 0.5 $M^2$ QUADRATS
= 20 $M^2$

Percent of Area Sampled = 10 %

If Overlapping Numbers are Selected,
Numbers will be Redrawn.

0.5 $M^2$

1 $M^2$

FIGURE 4. Schematic Design of Quantitation Mussel Sampling Plan

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In addition, Asiatic clams will be collected for total mercury and methylmercury analysis. Three 10-gram composite tissue samples will be collected from each sampling location for mercury analysis. Clams will be sampled with hand-held nets and clam rakes. Clams will be divided into 3 composite samples and placed in zip-lock plastic bags, labelled, and stored in an insulated cooler with ice or dry ice. The clams will be shipped to the laboratory under chain-of-custody for processing (tissue removal) and analysis. Processing and analytical methods are provided in the Quality Assurance Project Plan (QAPjP).

Dissolved oxygen, temperature, pH, conductivity, alkalinity, and hardness will be measured at each site prior to sampling. All field instruments will be calibrated daily.

It is the responsibility of Field Sampling Coordinator to insure that field activities and observations are documented. A field log book will be maintained to record the following information:

- General description of work
- Samples collected and their identification numbers
- Date, time of sampling, weather conditions
- Sample location
- Field measurements and observations
- Field sampling personnel
- SOPs employed
- Written discussion of any deviations from SOPs
- Chain-of-custody references for each sample

## 5.3 Equipment Required

The following equipment may be required for mussel surveys:

- mask and snorkel
- wet or dry suit
- weight belt
- regulator
- backpack (SCUBA)
- buoyancy compensator
- dive fins, knife and bag
- camera with film
- boat with motor and appropriate safety equipment
- grid sampler
- quadrant sampler
- nylon bags for mussel collection
- gloves

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- waterproof labels
- hand-held nets
- clam rakes
- sample containers (plastic)
- plastic zip-lock bags
- chain of custody forms
- coolers with ice or cold packs
- sample seals
- permanent markers
- utility box
- first aid kit
- flash lights/dive lights
- site map
- field log book
- pH meter with buffer
- conductivity meter with calibration solution
- thermometer

## 6.0 SAMPLE HANDLING AND ANALYSIS

### 6.1 Sample Preparation

Mussels collected for the reference collection or further identification will be placed in a plastic bag, sealed, labelled by site, transect/quadrant number, species (if known), sample number, date, collector, weight, size, and project title and placed in a cooler on ice for return to the laboratory. Asiatic clams collected for total mercury and methylmercury analysis will be placed in zip-lock plastic bags. The bags will be labeled with the following information:

- Project name
- Sample number
- Species
- Location collection
- Date and time collected
- Sampler's name
- Analysis required

The samples will be placed in a cooler with ice (preferably dry ice) for shipment to the laboratory.

All samples collected will be listed on chain of custody forms. A chain-of-custody form will be completed for each cooler, itemizing each mussel or clam sample contained therein. The completed chain-of-custody forms and samples will remain under custody until delivery to the laboratory. Copies of the chain-of-custody forms will be included in the final report.

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## 6.2 Equipment Cleanup

All sampling equipment which contacts the mussels or clams will be thoroughly cleaned. This includes scales, calipers, processing pans, etc. The cleaning procedure is as follows:

1) Wash with river water and laboratory detergent using a brush if necessary to remove particulate matter and surface films

2) Rinse thoroughly with river water.

## 6.3 Shipping Requirements

Samples will be shipped on ice (preferably dry ice) to the laboratory in insulated coolers. Arrangements will be made to insure that the samples arrive at the laboratory in an expeditious manner.

## 6.4 Chain-of-Custody Record

Once a sample is collected, custody must be maintained. A sample is under custody if:

- It is in the sampler's possession.
- It is in the sampler's view, after being in the sampler's possession.
- It is in the sampler's possession and then is placed in a secure area.
- It is in a designated secure area

Chain-of-custody forms will be prepared for the sample prior to transporting samples from field sites. Each sample will be listed on the form. A chain-of-custody form is shown in Figure 5.

The following sample custody procedures will be utilized:

1) Each sample collected for the project will be entered on the chain-of-custody record. Field personnel will retain a copy of the chain-of-custody record.

2) The original chain-of-custody record plus one copy will accompany the sample containers during transport to document controlled custody.

3) If custody is relinquished through a common parcel carrier for delivery to the laboratory, the following protocol will be followed:

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   - The method of sample shipment will be noted in the comment section on the chain-of-custody form.

# FIGURE 5.

## OLIN CORPORATION

### CHAIN OF CUSTODY RECORD

| PROJ. NO. | PROJECT NAME |
|---|---|
| SAMPLERS: *(Signature)* | |

ANALYSES REQUIRED

Instructions: List samples individually. Write time in military time. Record sample type as water, soil, etc. and as grab or composite. Record special handling instructions or precautions in remarks section. Record method of shipment in comments section.

| Station or Sample No. | Date | Time | Sample Type | Number Of Containers | | | | | | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
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| Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* | Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* |
|---|---|---|---|---|---|
| Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* | Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* |
| Relinquished by: *(Signature)* | Date/Time | Received for Laboratory by: *(Signature)* | Date/Time | Comments | |

DISTRIBUTION: Original and Pink copies accompany sample shipment to laboratory. Pink copy retained by laboratory. Yellow copy retained by samplers.

- The original chain-of-custody record plus one copy will be placed inside the shipping package.

- The shipping package will then be sealed with a custody seal. The seal will be placed on the package in such a manner that the package cannot be opened without breaking the seal. The seal will serve to document that the samples remained unaltered during shipment through the common parcel carrier.

4) If the sample is shipped by air freight or express shipment, the air bill will become part of the chain-of-custody procedures.

5) The laboratory will assume custody of the samples upon receipt. A designated Sample Custodian will be charged with sample care and receipt and verification of custody seal condition. These observations will be noted by the Sample Custodian on the chain-of-custody form upon receipt. All sample damage and abnormalities will be noted on the forms. The Sample Custodian will sign the chain-of-custody form, retain the copy for the Laboratory's record, and forward the original to the Field Project Officer.

6) Sample preparation and analysis custody will be tracked by laboratory work sheets.

7) The laboratory will retain custody of the samples in a secure area until such time as the samples are ordered destroyed.

8) A copy of the chain-of-custody record will be retained.

9) If samples are transferred to another laboratory, either as a whole or as a split sample, a new chain-of-custody form will be initiated.

## 6.5 Holding Times

There are no holding times for Asiatic clams prior to analysis. However, samples should be analyzed in a timely manner. The reference collection will be maintained for the duration of the study.

Analysis of surface water for dissolved oxygen, temperature, pH, conductivity, alkalinity and hardness will be conducted at the time of sampling using field meters or test kits. Holding times and analytical procedures are given in the QAPjP.

## 6.6 Record Keeping

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All records will be maintained in bound books. A master log will be established which will contain the appropriate identity and traceability of each sample. The same code number will be used

from sample acquisition through final data tabulation. Detailed notebooks will be maintained by laboratory personnel for samples, instruments and calibration standards.

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# FIELD SAMPLING PLAN FOR AMBIENT WATER TOXICITY FOR THE SALTVILLE WASTE DISPOSAL SITE REMEDIAL INVESTIGATION AND FEASIBILITY STUDY SALTVILLE, VIRGINIA

OCTOBER 26, 1989

AR300093

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## 1.0 SITE BACKGROUND

### 1.1 Introduction

This Field/Laboratory Sampling Plan for ambient water toxicity (F/LSP-TOX) has been prepared for the Remedial Investigation/Feasibility Study (RI/FS) for the Saltville Waste Disposal Site, Saltville, Virginia. This document describes in detail the sampling and data gathering methods which will be used to achieve the data quality objectives needed to support decisions regarding remedial response activities. The F/LSP-TOX was prepared in accordance with the Interim Final EPA document "Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA" (OSWER Directive 9355.3-01), dated October 1988; EPA document "A Compendium of Superfund Field Operations Methods" (OSWER Directive 9355.0-14), dated December 1987; and EPA document "Data Quality Objectives for Remedial Response Activities-Development Process" (OSWER Directive 9355.0-7B), dated March 1987.

### 1.2 Site Description

The Saltville Waste Disposal Site is located along the North Fork of the Holston River (NFHR), between the town of Saltville and the community of Allison Gap in western Smyth County, Virginia, extending partly into Washington County, Virginia (see Figure 1). The NFHR lies adjacent to the southern border of the Site at North Fork Holston River Mile (NFHRM) 80.8 - 82.4 and flows southwest. The Saltville Waste Disposal Site includes the former chlorine plant site (FCPS), waste disposal Pond 5 and waste disposal Pond 6. Pond 5 discharges water into the NFHR at Mile 81.7. Pond 6 discharges water into the NFHR at Mile 81.5. Additional description of the Site is given in Section 2.0 of the RI/FS Work Plan.

The NFHR is a fast flowing mountain stream which originates approximately 48 miles above the former chlorine plant site. The stream flows southwest through a rural landscape to the confluence with the South Fork Holston River in Tennessee to form the Holston River. The Holston River flows in Cherokee Reservoir in Tennessee. Figure 2 is a schematic of the Holston-Cherokee system.

Upper watershed areas are primarily hardwood forest on steep slopes while the lower portion is less mountainous and is bordered by pasture and farmlands. Land-use is dominated by agriculture, and little heavy industry is present within the watershed except that located in Saltville, Virginia.

The NFHR is characterized over most of its length by a coarse, rocky substrate with extensive riffle and pool areas. Daily discharge at NFHR Mile 85 range from 23 cfs at low flow (7Q10) to 16,500 cfs at peak storm discharges (USGS data) and averages 290 cfs. Over the course of the study area (NFHRM 98 to NFHRM 53), the river varies in width between 100 and 300 feet. Water depths at normal flow vary between a few inches in the riffle areas to 10 feet in the deeper pools.

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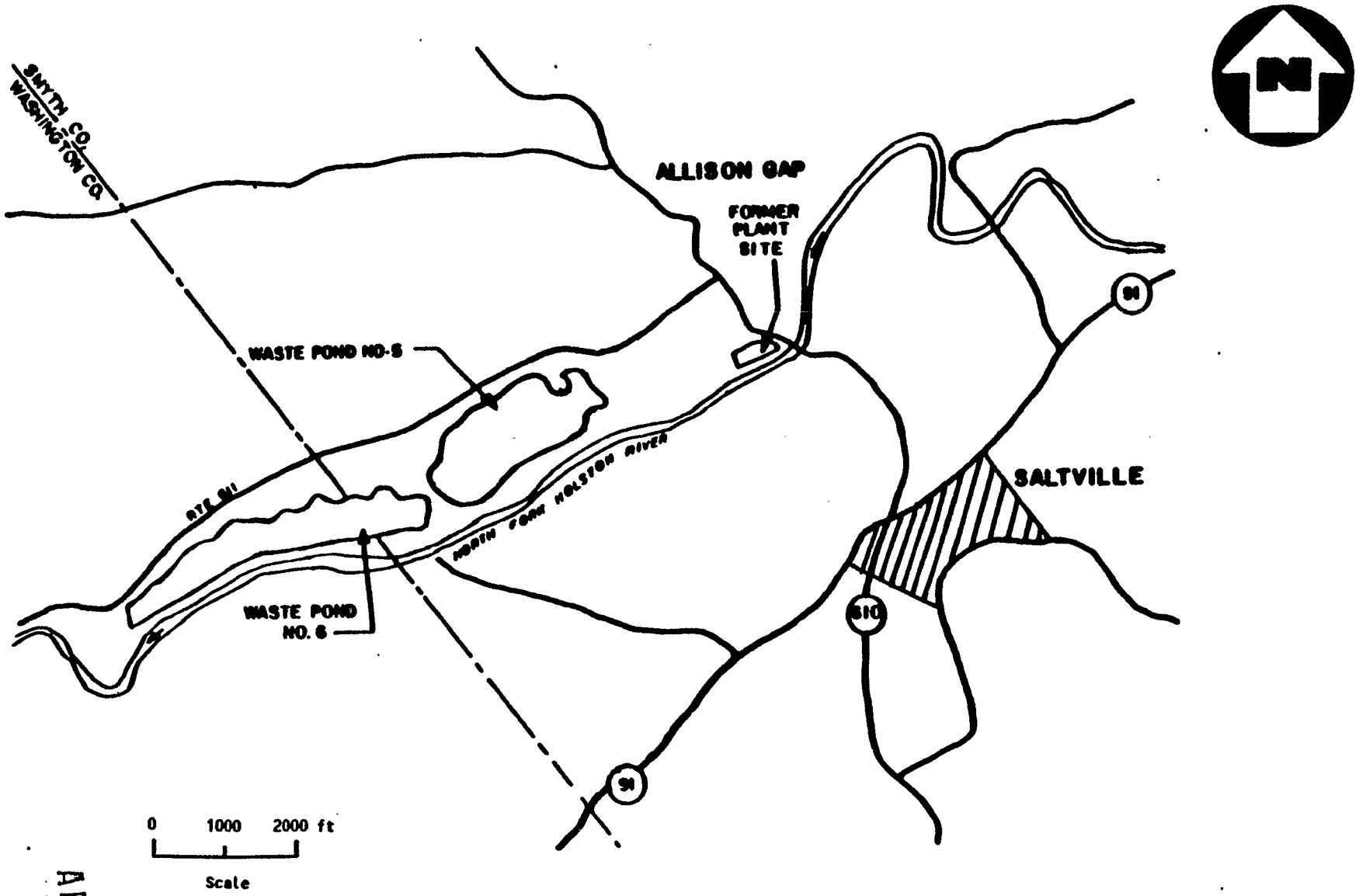


FIGURE 1. Saltville Waste Disposal Site-Area Map

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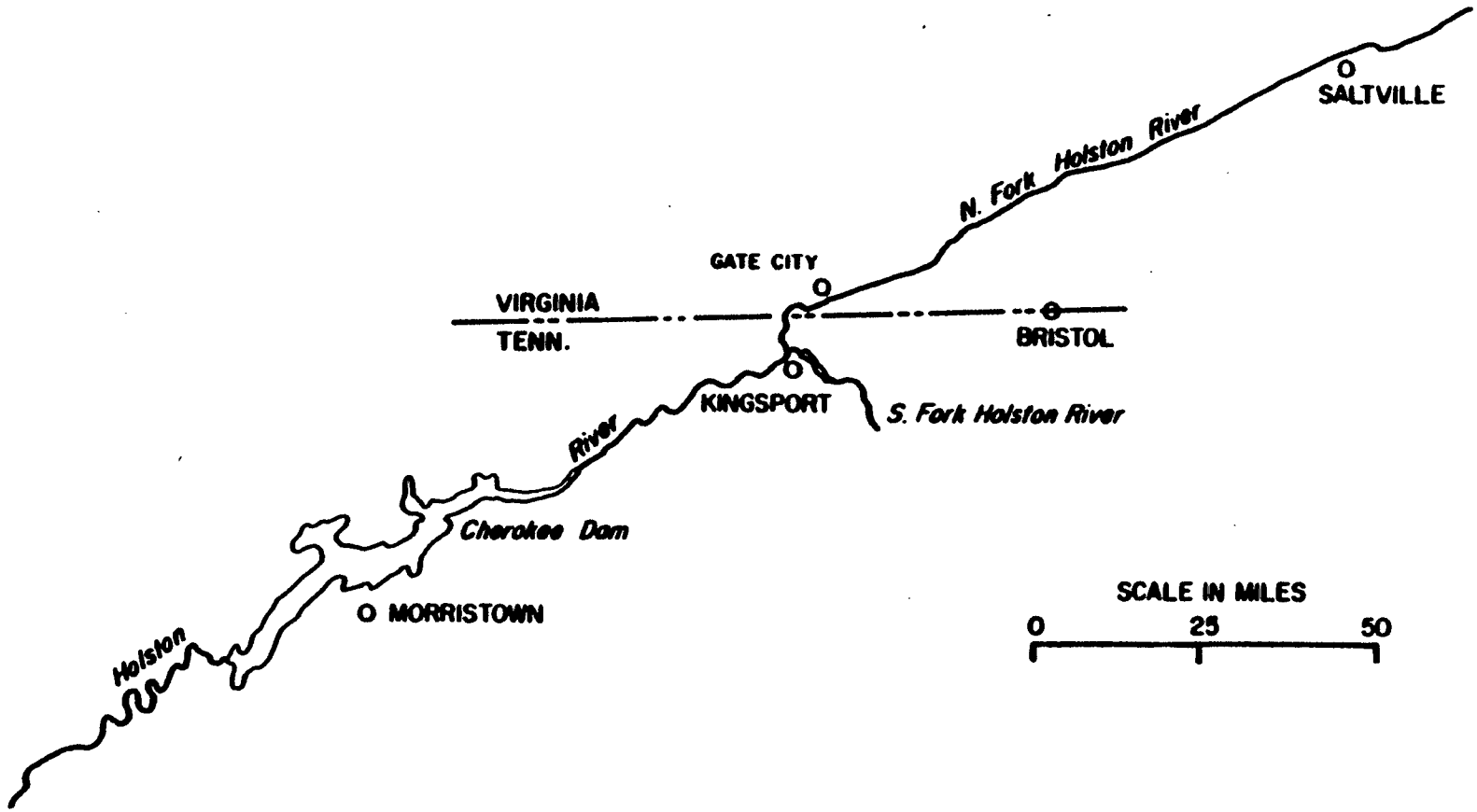


FIGURE 2. Holston River-Cherokee Reservoir System

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## 1.3 Contaminant Sources

The contaminant of concern is mercury (ROD, 1987). Mercury was used in chlor-alkali plant operations (1951 to 1972) and entered the environment via process wastewater streams. Mercury contaminated wastewater initially discharged directly to the NFHR and later to Pond 5.

## 1.4 Transport Pathways

The former chlorine plant site has been remediated with a clay cap. The Pond 5 outfall presently discharges to the NFHR. This discharge can contain up to 120 ppb mercury. The Pond 6 outfall also discharges to the NFHR. The discharge from Pond 6 contains insignificant quantities of mercury (i.e. <0.0002 mg/l). The sediments of the NFHR contain 3 to 9 ppm mercury near the site. Mercury concentrations in the sediments decrease downstream to less than 0.5 ppm at NFHRM 8.

Aquatic life in the NFHR is exposed to mercury through several pathways: the water column below Pond 5 outfall, suspended sediment and food sources contain mercury. These are generally the pathways available for uptake. This is not intended to be an in-depth discussion of the mechanism of uptake.

## 1.5 Data Gaps

The proposed ambient water toxicity studies will address the present data gaps and characterize the potential toxicity of discharges from Pond 5 and Pond 6 to NFHR aquatic life. Ambient water toxicity tests will be conducted using standard laboratory test organisms (i.e. daphnids, fathead minnows, juvenile mussels and algae). These studies will be conducted with ambient waters taken under two NFHR flow conditions, i.e. average and low flow. The highest ratios of outfall flows to river flows occur during average river flows. During storm events river flows respond much slower to rainfall. Flows generally peak several days after a rain event when the river has returned to normal. Thus the highest ratios of outfall effluent to river flow are found during normal river flows.

# 2.0 SAMPLING OBJECTIVES

## 2.1 Specific Objectives and Data Uses

A comprehensive bioassessment program for measuring mercury impact on NFHR aquatic communities involves the integrated use of both biological (i.e., benthic and fish surveys) and physio-chemical (i.e., sediment modelling) methods. The NFHR bioassessment program consists of five major tasks which evaluate the effects of present and past mercury discharge from the Site on the biotic integrity of stream communities of NFHR. The five tasks include (I) fish studies, (II) benthic studies, (III) mussel studies, (IV) ambient toxicity studies and (V) mercury fate and transport studies.

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The ambient water toxicity studies consist of two related studies, a mixing zone study and an ambient water toxicity study First, a mixing zone study of the Pond 5 outfall and Pond 6 outfall will be conducted. The objective of this study is to estimate the size of the mixing zone in the NFHR for each outfall. This will be accomplished using continuous dye injection into the outfall coupled with fluorometer measurements of river water. Data from the mixing zone study will be used to determine sample points for the ambient water toxicity studies. The objective of the ambient water toxicity study is to determine the toxicity of the Site effluent at various dilutions on standard aquatic test organisms.

## 3.0 SAMPLE LOCATION AND FREQUENCY

### 3.1 Field Test Sites

Mixing zone studies will be conducted at Pond 5 outfall located at NFHRM 81.72 and Pond 6 outfall located at NFHRM 81.55. Rhodamine dye will be continuously injected into the outfall effluent directly behind the outfall weir. After dye concentrations in the mixing zone reaches steady-state, water samples will be collected from six transects downstream of the outfall. Transects will be located 0, 60, 156, 310, 556 and 950 feet downstream. Seven locations spaced across each transect will be sampled. Transects and sample points are shown in Figure 3.

The mixing zone study will be used to identify the river locations of five logarithmic dilutions of Pond 5 effluent. Water samples for the toxicity tests will be collected from these locations. Control water for the ambient toxicity tests will be collected from the North Fork Holston River upstream of the Saltville Site at Mile 82.8.

### 3.2 Sample Collection

#### 3.2.1. Mixing Zone Study

Mixing zone water samples will be collected in glass bottles (~16 oz) from a minimum of six transects comprised of seven sampling locations within each transect. Samples will be placed on ice and returned to the laboratory. The rhodamine dye concentration in each sample will be measured using a fluorometer, following manufacturer's specifications.

These studies will be conducted with ambient waters taken under two NFHR flow conditions, i.e., average (4-15 cms) and low (<4 cms) flow. These flow conditions are appropriate because the highest ratios of effluent flow to river flow, i.e., worst case conditions, occur at these conditions. Another consideration in high flow sampling is safety. Past field work indicates a river flow rate of 17 cms (600 cfs) in the maximum condition under which sampling and field studies can safety be conducted. High flows can be evaluated properly on paper using data from two flow conditions.

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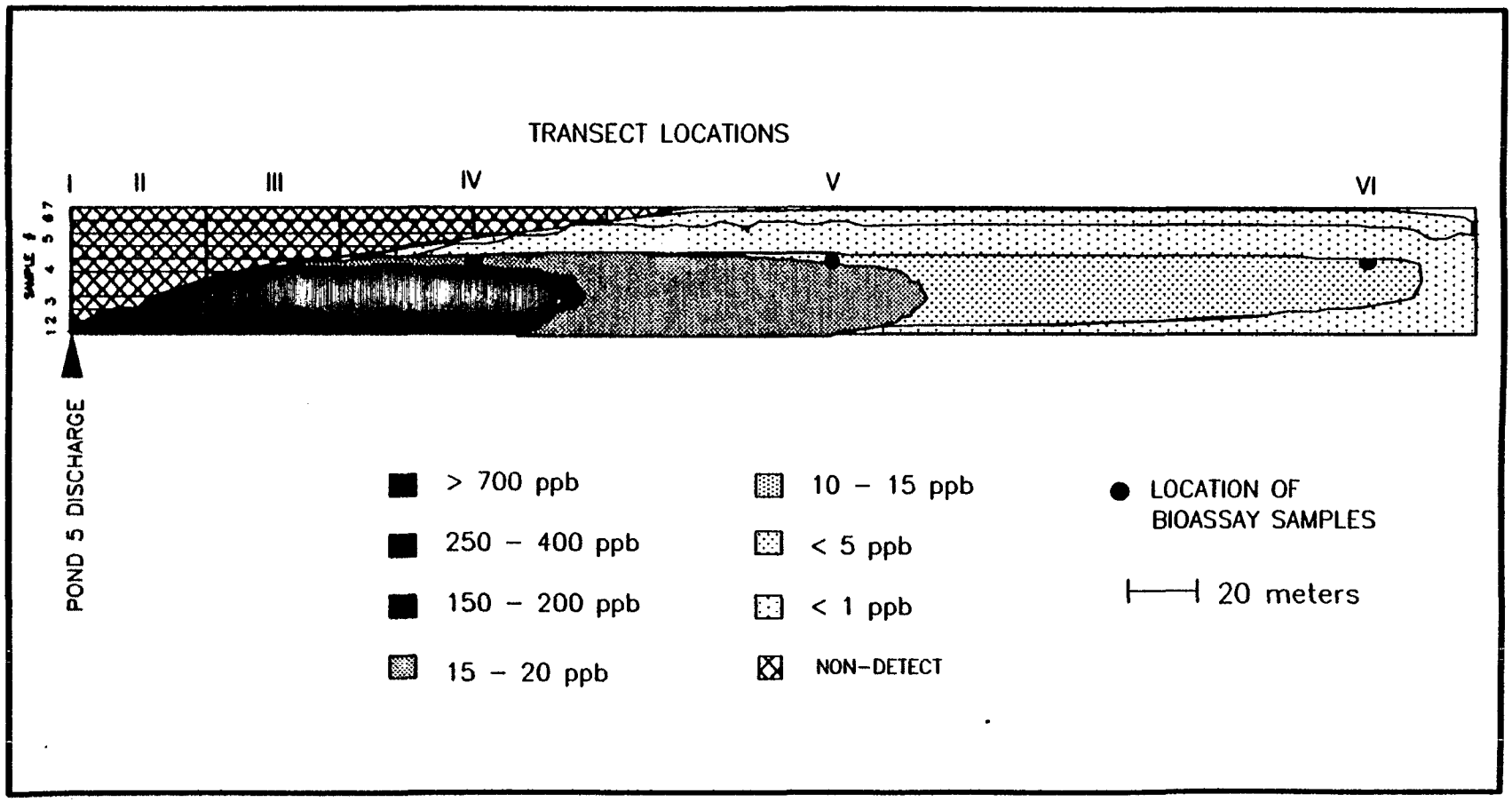


**FIGURE 3. Mixing Zone Study Sample Points**

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### 3.2.2. Ambient Water Toxicity

Ambient water samples will be collected from the river at five locations within the mixing zone of Pond 5's outfall effluent (representing five logarithmic dilutions of the discharge) as defined by continuous dye injection techniques. This technique was selected rather than laboratory dilutions because collecting water from designated points within the mixing zone is more representative of the concentrations of effluent than diluting an outfall sample in the laboratory.

Water samples will be collected during average and low flow conditions and transferred under chain of custody to the laboratory for use in conventional toxicity tests. Samples will be collected in pre-cleaned amber glass bottles (~2 liter volume), placed on ice in insulated coolers, sealed and delivered to the laboratory. Toxicity tests will be initiated within 48 hours of sample collection. The specified protocol for cleaning glassware is provided in Section 6.2 of this document.

These studies will be conducted with ambient waters taken under two NFHR flow conditions, i.e., average (4-15 cms) and low (<4 cms) flow. Toxicity studies with all four organisms will be conducted under average flow conditions. During average flow, the ratio of pond effluent to river flow is higher than during low flow. Toxicity tests under low flow conditions will be conducted with fathead minnows and daphnids. If these toxicity studies indicate mixing zone toxicity, then the studies will be repeated with river samples collected downstream of the mixing zone. More frequent studies are unnecessary because sampling at average and low flow conditions accurately characterizes the potential toxicity of discharges from the Saltville Site. During most months, outfall and river flow conditions fall within these two flow conditions. High flows can be evaluated properly on paper and possibly in the laboratory.

## 3.3 Quality Assurance

The Quality Assurance Project Plan for the Saltville Waste Disposal Site Remedial Investigation and Feasibility Study, Saltville, Virginia will be in effect for this project. The goals of the QA program are to insure to the maximum extent possible that sample results are precise, accurate, representative, comparable, and complete.

Field quality assurance is the responsibility of the Field Sampling Coordinator. Frequent checks will be made to insure that all sampling procedures are followed. Random audits of field procedures will be conducted by the QA Officer to insure that specified protocols are being followed. The analytical quality assurance is described in detail in the Quality Assurance Project Plan (QAPjP).

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The calibration procedures specified by the analytical methods and instrument manuals will be followed. Frequency of calibration specified by the analytical methods or instrument manuals will be considered to be the minimum frequency. More frequent calibration may be required under severe

field conditions (e.g., rain, freezing temperatures). Calibration requirements of the method references will be met. All calibration checks must be documented in log books. At a minimum the following information must be recorded:

- Date of calibration
- Identification of standards used
- Instrument model and serial number
- Personnel performing calibration
- Results of calibration (including raw data and summary statistics
- Corrective action taken

Field instruments such as pH meters and conductivity meters will be calibrated daily (at a minimum) according to procedures specified by the Field Analytical Procedures and documented in field log books. Calibration must be performed with commercially-prepared, certified standards if available, e.g., pH buffers, conductivity standards, etc. Sources of all material used for calibration or for preparing calibration standards will be documented.

## 4.0 SAMPLE DESIGNATION

All water samples collected from the NFHR for the mixing zone studies and the toxicity tests will be assigned a unique sample identification number. The sample numbering system will be:

Txx - yyyyyD-zzz or Txx-yyyyyT-zzz

where:

Txx is the transect number
yyyyy is a five digit number (starting with 00001 with the first water sample collected and assigned sequentially)
D is the designation for mixing zone water samples
T is the designation for ambient water toxicity samples
zzz is the month/year collected (589 for May 1989)

## 5.0 SAMPLING PROCEDURES AND EQUIPMENT

### 5.1 Pre-Sampling Activities

Sampling and analytical personnel will be properly trained and experienced in the collection and analysis of aquatic toxicity data. Personnel employed in field sampling will be familiar with all equipment required to conduct toxicity studies. A minimum of two years of technical training or field experience in environmental toxicology or other similar discipline emphasizing proper scientific methods is required.

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Preparation for the sampling event can be divided into three primary areas:

1. Logistics of the event, including site access
2. Equipment preparation
3. Coordination with the analytical laboratory

The sampling coordinating team is responsible for all three areas. Olin will obtain site access for sampling points not on Olin property.

### 5.1.1 Logistics

The sampling team will insure that samples can be collected from all sampling points before an event is scheduled. At a minimum the team will contact the Olin Project Manager before mobilizing. Olin will arrange for all contacts with property owners for permission to enter their property where necessary to collect samples. The sampling team should check with property owners of any fenced or posted property.

### 5.1.2 Equipment Preparation and Calibration

All equipment to be used in the sampling effort will be checked for service before mobilizing. Any instruments used in water quality monitoring will be calibrated per manufacturers specifications prior to field measurements. Backup meters will also be taken into the field. Any maintenance or cleaning will be completed prior to moving into the field for sampling.

### 5.1.3 Coordination with Laboratory

The Field Sampling Coordinators will insure that the laboratory is prepared to receive any samples on the required schedule before collecting any samples. The laboratory will be notified of each sample shipment so that samples can be expeditiously unpacked, inspected, and entered into the analytical flow at the laboratory.

## 5.2 Field Procedures

It is the responsibility of Field Sampling Coordinator to insure that field activities and observations are documented. A field log book will be maintained to record the following information:

- General work description
- Samples collected and their identification number
- Date, time of sampling, weather conditions
- Sample location
- Field measurements and observations

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- Field sampling personnel
- SOPs employed
- Written discussion of any deviations from SOPs
- Chain-of-custody references for each sample

5.2.1. Mixing Zone Study

Mixing zones of Pond 5, Pond 6 and other influxes will be defined using continuous dye injection techniques as specified by Wilson (1986). A fluorescent molecule has the ability to absorb light at one wavelength and almost instantly emit light at a new and longer wavelength. The intensity of the emitted light is proportional to the intensity of the exiting light and the concentration of the fluorescent material present. By monitoring the intensity of the exiting light and the intensity of the emitted light, the concentration of fluorescent material can be determined. A known concentration of rhodamine dye will be directly injected into the point source effluent continuously for 2 to 3 hours. After the dye concentration in the mixing zone reaches steady-state, water samples will be collected from six transects downstream of the effluent source. Transects will be located 0, 60, 156, 310, 556 and 950 feet downstream of the source. Water samples will be collected in glass bottles (~16 oz) from seven sampling locations spaced across each transect as previously presented in Figure 11 of the "Work Plan Remedial Investigation and Feasibility Study, Operable Unit 3, Saltville Waste Disposal Site" (June 1989). Samples will be placed on ice and returned to the laboratory. The rhodamine dye concentration in each sample will be measured using a fluorometer, following manufacturer's specifications. Through this technique, the mixing zone will be defined for Pond 5, Pond 6, and any other influxes identified.

The changes in dye concentration will be used to define 5 points within the mixing zone that represent logarithmic dilutions of the effluent. These 5 points will be sampled for toxicity testing as defined in 5.2.2 below.

Samples for total mercury will be collected from each sample location. Samples will be preserved with acid to a pH less than 2 with nitric acid and transported to the laboratory for analysis. Alkalinity, hardness, temperature, conductivity, pH and dissolved oxygen will be field measured at each sample location within the mixing zone and at control water sampling points. Analytical procedures for alkalinity, hardness and dissolved oxygen are given in the QAPjP. Temperature, pH and conductivity will be measured electrometrically. Instruments will be calibrated daily following manufacturers specifications for each instrument.

5.2.2. Ambient Water Toxicity

The locations of five logarithmic dilutions determined during the mixing zone study will be identified. Ambient water samples for toxicity tests will be taken at these locations. Control water for ambient toxicity tests will be collected from an upstream control site located at NFHRM 82.8. Ambient water samples and control water samples will be collected in clean glass

sampling containers, labeled according to field log and chain-of-custody procedures, placed on wet ice, and returned to the laboratory for testing. The tests will be initiated within forty-eight hours of collection.

Toxicity test methods and procedures will be followed in compliance with EPA/600/4-85/013, "Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms" (Peltier 1985). Toxicity test methods and procedures for *Selenastrum* will follow EPA/600/4-89/001 "Short Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms" (Horning, 1989). These references summarize protocols for laboratory safety, quality assurance, facilities and equipment, effluent sampling and holding times, test species handling, data interpretation and utilization, report preparation, test organism culturing, equipment check lists and computer programs for calculating the LC50 and confidence intervals. Stock cultures of *Ceriodaphnia dubia, Pimephales promelas, Anodonta imbecillis* and *Selenastrum capricornutum* will be utilized as test organisms. Test conditions for static, non-renewal tests for each organisms are provided in Table 1-4, respectively.

Test concentrations will consist of whole ambient water samples collected within the mixing zone of the influxes. Replicate treatments will be conducted for each concentration containing 10 individuals per replicates. During each test, the organism in question will be placed in the containers specified in Tables 1-4, and maintained under the conditions specified in Tables 1-4. Visual observation of mortality will be made at the intervals specified for each test type in the EPA protocol (Peltier 1985 or Horning 1989). Copies of all chain-of-custody records, calibration records and lab sheets will be included with the final ambient water toxicity report. All reporting methods follow EPA guidelines (Peltier 1985 or Horning 1989).

Total mercury, alkalinity and hardness will be measured initially and at the end of each test. Analytical procedures for total mercury, alkalinity and hardness are given in the QAPjP. Temperature, conductivity, dissolved oxygen and pH will be electrometrically measured daily for each treatment. Instruments will be calibrated daily following manufacturers' specifications for each instrument.

If other areas of significant influx are identified during the RI, field conductivity (see QAPjP for procedure) measurements will be used to estimate flow and dilution. The measuring design would consist of transects established approximately perpendicular to the river's edge at intervals based on the extent of the influx, i.e., larger seepage zones would entail larger intervals. An appropriate number of sample points across the transect will be established based on a preliminary screening of the area influenced by the seepage.

## 5.3 Equipment Required

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The following equipment may be required for the ambient water toxicity studies:

TABLE 1

TEST CONDITIONS FOR *Ceriodaphnia dubia* STATIC ACUTE TOXICITY TESTS (WATER FLEA)

| | | |
|---|---|---|
| 1. | Temperature (°C) | 25 +/- 1°C |
| 2. | Light quality | Fluorescent/natural |
| 3. | Light intensity | Fluorescent/natural |
| 4. | Photoperiod | 14 hrs light/ 24 hr |
| 5. | Size of test vessels | 100 ml plastic |
| 6. | Volume of test solution | 50 ml |
| 7. | Age of organisms | Neonates, < 24 hour |
| 8. | No. of test organisms/rep | 10 |
| 9. | No. of reps/concentration | 2 |
| 10. | Total no. of organisms per concentrations | 20 |
| 11. | Feeding regime | None |
| 12. | Aeration | None |
| 13. | Dilution water | North Fork Holston River Water |
| 14. | Test duration | 48 hour static |
| 15. | Effect measured | Mortality |

Reference: Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms. 1985. EPA/600/4-85/013.

TABLE 2

TEST CONDITIONS FOR *Pimephales promelas* STATIC ACUTE TOXICITY TEST (FATHEAD MINNOW)

| | | |
|---|---|---|
| 1. | Temperature (°C) | 20.0 +/- 1.0°C |
| 2. | Light quality | Fluorescent/natural |
| 3. | Light intensity | Fluorescent/natural |
| 4. | Photoperiod | 14 hrs light/ 24 hr |
| 5. | Size of test vessels | 1000 ml glass |
| 6. | Volume of test solution | 750 ml |
| 7. | Age of organisms | 1-90 days |
| 8. | No. of test organisms/rep | 10 |
| 9. | No. of reps/concentration | 2 |
| 10. | Total no. of organisms per concentrations | 20 |
| 11. | Feeding regime | None |
| 12. | Aeration | None |
| 13. | Dilution water | North Fork Holston River water |
| 14. | Test duration | Fish: 96 hrs static |
| 15. | Effect measured | Mortality |

Reference: Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms. 1985. EPA/600/4-85/013.

TABLE 3

TEST CONDITIONS FOR *Anadonta imbecillis* STATIC ACUTE TOXICITY TEST (MUSSEL)

| | | |
|---|---|---|
| 1. | Temperature (°C) | 20.0 +/- 1.0°C |
| 2. | Light quality | Fluorescent/natural |
| 3. | Light intensity | Fluorescent/natural |
| 4. | Photoperiod | 14 hrs light/ 24 hr |
| 5. | Size of test vessels | 100 ml plastic |
| 6. | Volume of test solution | 50 ml |
| 7. | Age of organisms | Mussels: less than 30 days |
| 8. | No. of test organisms/rep | 10 |
| 9. | No. of reps/concentration | 2 |
| 10. | Total no. of organisms per concentrations | 20 |
| 11. | Feeding regime | None |
| 12. | Aeration | None |
| 13. | Dilution water | North Fork Holston River water |
| 14. | Test duration | 48 hrs static |
| 15. | Effect measured | Mortality |

Reference: Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms. 1985. EPA/600/4-85/013.

TABLE 4

TEST CONDITIONS FOR *Selenastrum capricornutum* STATIC CHRONIC TOXICITY TEST (ALGAE)

| | | |
|---|---|---|
| 1. | Temperature (°C) | 25.0 +/- 1.0°C |
| 2. | Light quality | Fluorescent/natural |
| 3. | Light intensity | Fluorescent/natural |
| 4. | Photoperiod | Continuous |
| 5. | Size of test vessels | 125 ml or 250 ml glass |
| 6. | Volume of test solution | 50 or 100 ml |
| 7. | Age of culture | 4 to 7 days |
| 8. | Initial cell density | 10,000 cells/ml |
| 9. | No. of reps/concentration | 3 |
| 10. | Shaking rate | Twice daily by hand |
| 11. | Dilution water | North Fork Holston River water |
| 12. | Test duration | 96 hrs static |
| 13. | Effect measured | Cell density |

Reference: Methods for Measuring the Acute Toxicity of Effluents to Freshwater and Marine Organisms. 1985. EPA/600/4-85/013.

5.3.1. Mixing Zone Study

- camera with film
- boat with motor and appropriate safety equipment
- gloves
- waterproof labels
- sample containers (plastic/glass)
- chain of custody forms
- coolers
- sample seals
- permanent markers
- utility box
- first aid kit
- flash lights/dive lights
- site map
- field log book
- Masterflex pump
- Tygon tubing
- Fluorometer (Turner Model No. 10)
- pH, Conductivity Meters and calibration supplies
- burets, beakers, flasks and reagents for alkalinity, dissolved oxygen and hardness as listed in the QAPjP

5.3.2. Ambient Water Toxicity Tests

- camera with film
- boat with motor and appropriate safety equipment
- gloves
- waterproof labels
- sample containers (plastic/glass)
- chain of custody forms
- coolers
- sample seals
- permanent markers
- utility box
- first aid kit
- flash lights/dive lights
- site map
- field log book
- aquaria
- stock cultures of test organisms
- dilution water
- thermometers

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- pipettes
- pH, D.O., Conductivity Meters and calibration supplies
- burets, beakers, flasks and reagents for alkalinity and hardness as listed in the QAPjP

## 6.0 SAMPLE HANDLING AND ANALYSIS

### 6.1 Sample Preparation

Water samples for the toxicity study will be placed on ice and will remain under custody until delivery to the laboratory.

### 6.2 Equipment Cleanup

All sample bottles and preparation equipment which contacts the test organisms or water samples will be thoroughly cleaned. This includes scales, calipers, processing pans, etc. The cleaning procedure is as follows:

1) Wash with tap water and laboratory detergent using a brush if necessary to remove particulate matter and surface films.

2) Rinse thoroughly with tap water.

3) Rinse with nitric acid solution.

4) Rinse three times with tap water and allow to air dry as long as possible.

### 6.3 Shipping Requirements

Samples will be shipped on ice to the laboratory in insulated coolers. Arrangements will be made to insure that the samples arrive at the laboratory in an expeditious manner to prevent violation of holding time requirements for toxicity tests.

### 6.4 Chain-of-Custody Record

Once a sample is collected, custody must be maintained. A sample is under custody if:

It is in the sampler's possession.

It is in the sampler's view, after being in the sampler's possession.

It is in the sampler's possession and then is placed in a secure area.

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It is in a designated secure area.

Chain-of-custody forms will be prepared for the sample prior to transporting samples from field sites. Each sample will be listed on the form. A chain-of-custody form is shown in Figure 4.

The following sample custody procedures will be utilized:

1) Each sample collected for the project will be entered on the chain-of-custody record. Field personnel will retain a copy of the chain-of-custody record.

2) The original chain-of-custody record plus one copy will accompany the sample containers during transport to document controlled custody.

3) If custody is relinquished through a common parcel carrier for delivery to the laboratory, the following protocol will be followed:

   - The method of sample shipment will be noted in the comment section on the chain-of-custody form.

   - The original chain-of-custody record plus one copy will be placed inside the shipping package.

   - The shipping package will then be sealed with a custody seal. The seal will be placed on the package in such a manner that the package cannot be opened without breaking the seal. The seal will serve to document that the samples remained unaltered during shipment through the common parcel carrier.

4) If the sample is shipped by air freight or express shipment, the air bill will become part of the chain-of-custody procedures.

5) The laboratory will assume custody of the samples upon receipt. A designated Sample Custodian will be charged with sample care and receipt and verification of custody seal condition. These observations will be noted by the Sample Custodian on the chain-of-custody form upon receipt. All sample damage and abnormalities will be noted on the forms. The Sample Custodian will sign the chain-of-custody form, retain the copy for the Laboratory's record, and forward the original to the Field Project Officer.

6) Sample preparation and analysis custody will be tracked by laboratory work sheets.

7) The laboratory will retain custody of the samples in a secure area until such time as the samples are ordered destroyed.

AR300114

# FIGURE 4

## OLIN CORPORATION

### CHAIN OF CUSTODY RECORD

| PROJ. NO. | PROJECT NAME |
|---|---|
| SAMPLERS: *(Signature)* | |

ANALYSES REQUIRED

Instructions: List samples individually. Write time in military time. Record sample type as water, soil, etc. and as grab or composite. Record special handling instructions or precautions in remarks section. Record method of shipment in comments section.

| Station or Sample No. | Date | Time | Sample Type | Number Of Containers | | | | | | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
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|---|---|---|---|---|---|
| Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* | Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* |
| Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* | Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* |
| Relinquished by: *(Signature)* | Date/Time | Received for Laboratory by: *(Signature)* | Date/Time | Comments | |

DISTRIBUTION: Original and Pink copies accompany sample shipment to laboratory. Pink copy retained by laboratory. Yellow copy retained by samplers.

8) A copy of the chain-of-custody record will be retained.

9) If samples are transferred to another laboratory, either as a whole or as a split sample, a new chain-of-custody form will be initiated.

## 6.5 Holding Times

Ambient toxicity tests must begin within 48 hours of sample collection. Water quality analysis will be conducted within the holding times specified in Table 4 of the QAPjP.

## 6.6 Record Keeping

All records will be maintained in bound books. A master log will be established which will contain the appropriate identity and traceability of each sample. The same code number will be used from sample acquisition through final data tabulation. Detailed notebooks will be maintained by laboratory personnel for samples, instruments and calibration standards.

# 7.0 REFERENCES


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AR300117

# FIELD SAMPLING PLAN FOR MERCURY FATE AND TRANSPORT STUDIES FOR THE SALTVILLE WASTE DISPOSAL SITE REMEDIAL INVESTIGATION AND FEASIBILITY STUDY SALTVILLE, VIRGINIA

OCTOBER 26, 1989

AR300118

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## 1.0 SITE BACKGROUND

### 1.1 Introduction

This Field Sampling Plan for Mercury Fate and Transport Studies (FSP-F/T) has been prepared for the Remedial Investigation/Feasibility Study (RI/FS) for the Saltville Waste Disposal Site, Saltville, Virginia. This document describes in detail the sampling and data gathering methods which will be used to achieve the data quality objectives needed to support decisions regarding remedial response activities. The FSP-F/T was prepared in accordance with the Interim Final EPA document "Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA" (OSWER Directive 9355.3-01), dated October 1988; EPA document "A Compendium of Superfund Field Operations Methods" (OSWER Directive 9355.0-14), dated December 1987; and EPA document "Data Quality Objectives for Remedial Response Activities-Development Process" (OSWER Directive 9355.0-7B), dated March 1987.

### 1.2 Site Description

The Saltville Waste Disposal Site is located along the North Fork of the Holston River (NFHR), between the town of Saltville and the community of Allison Gap in western Smyth County, Virginia, extending partly into Washington County, Virginia (see Figure 1). The NFHR lies adjacent to the southern border of the Site at North Fork Holston River Mile (NFHRM) 80.8 - 82.4 and flows southwest. The Saltville Waste Disposal Site includes the former chlorine plant site (FCPS), waste disposal Pond 5 and waste disposal Pond 6. Pond 5 discharges water into the NFHR at Mile 81.7. Pond 6 discharges water into the NFHR at Mile 81.5. Additional description of the Site is given in Section 2.0 of the RI/FS Work Plan.

The NFHR is a fast flowing mountain stream which originates approximately 48 miles above the former plant site. The stream flows southwest through a rural landscape to the confluence with the South Fork Holston River in Tennessee to form the Holston River. The Holston River flows in Cherokee Reservoir in Tennessee. Figure 2 is a schematic of the Holston-Cherokee system.

Upper watershed areas are primarily hardwood forest on steep slopes while the lower portion is less mountainous and is bordered by pasture and farmland. Land-use is dominated by agriculture, and little heavy industry is present within the watershed except that located in Saltville, Virginia.

The NFHR is characterized over most of its length by a coarse, rocky substrate with extensive riffle and pool areas. Daily discharge at NFHR Mile 85 ranges from 23 cfs at low flow (7Q10) to 16,500 cfs at peak storm discharges (USGS data). Over the course of the study area (NFHRM 85 to NFHRM 59), the river varies in width between 100 and 300 feet. Water depths at normal flow vary between a few inches in the riffle areas to 10 feet in the deeper pools.

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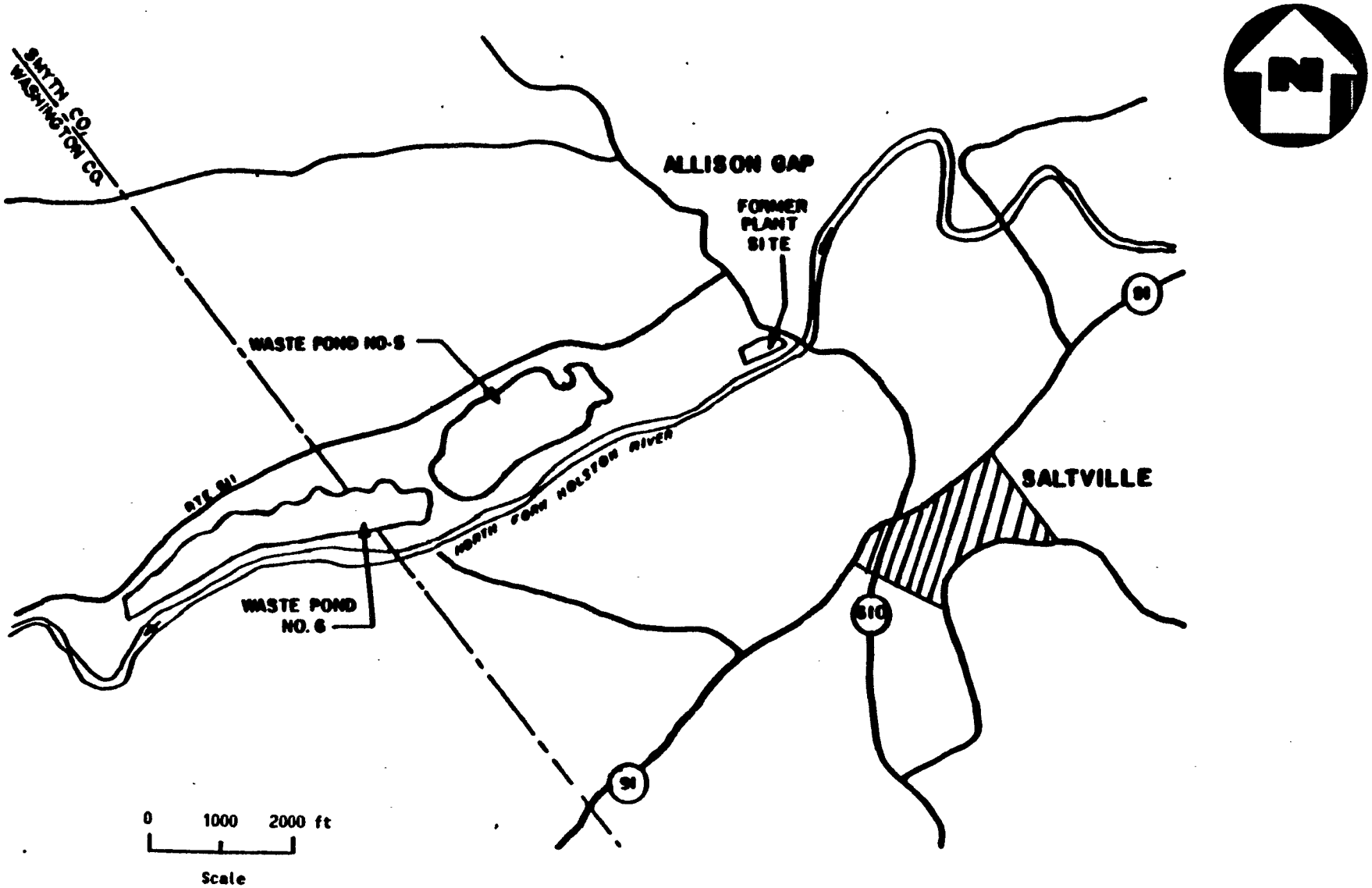


FIGURE 1. Saltville Waste Disposal Site-Area Map

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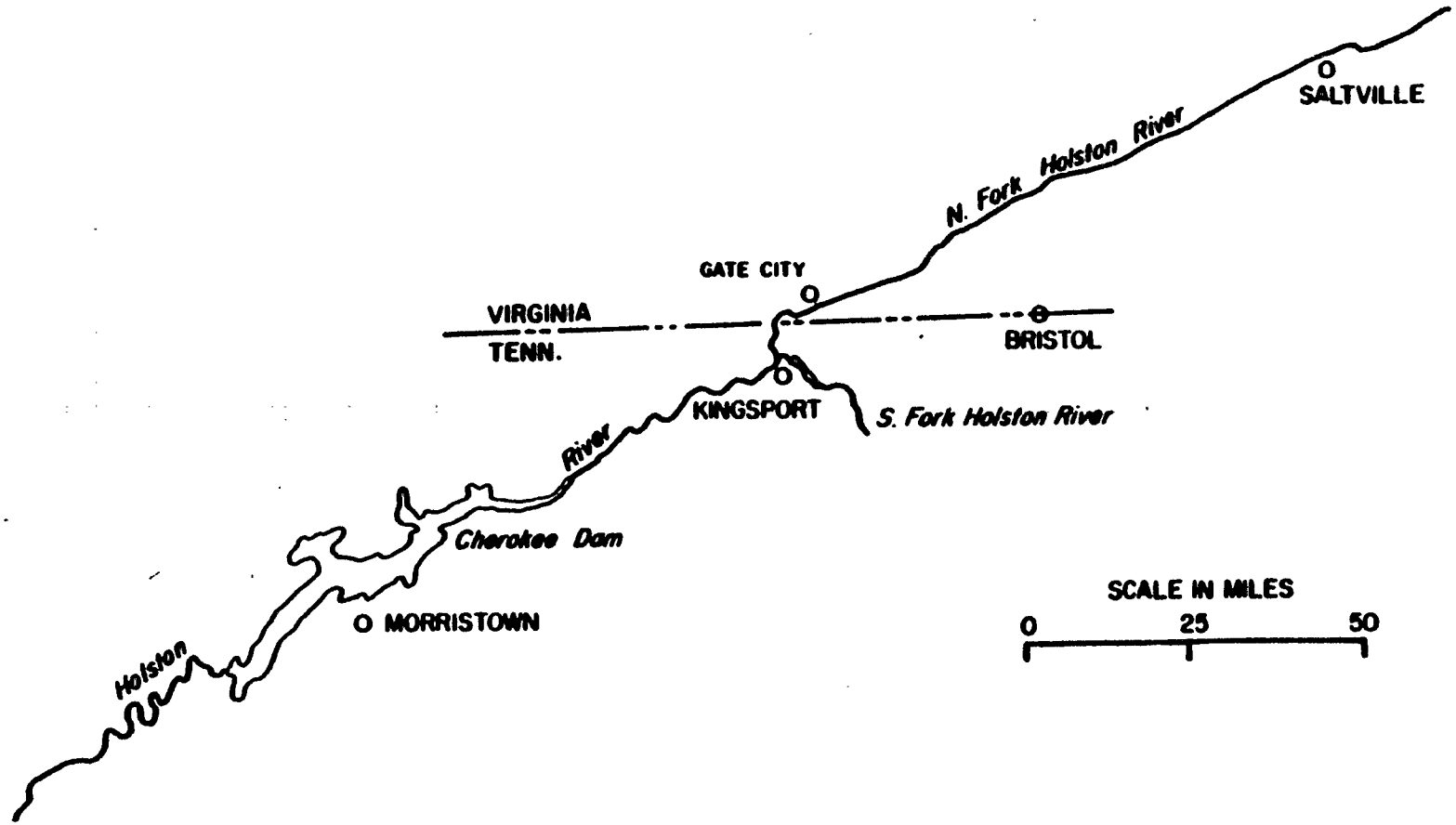


FIGURE 2. Holston River-Cherokee Reservoir System

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## 1.3 Contaminant Sources

The contaminant of concern is mercury (ROD, 1987). Mercury was used in chlor-alkali plant operations (1951 to 1972) and entered the environment via process wastewater streams. Mercury contaminated wastewater initially discharged directly to the NFHR and later to Pond 5.

## 1.4 Transport Pathways

One source of dissolved mercury to the NFHR appears to be the Pond 5 outfall. This discharge can contain up to 120 ppb mercury. Sediments of the NFHR near the site contain 3 to 9 ppm mercury. These may also contribute mercury to the water column.

The following points summarize the major processes controlling mercury transport and fate in the NFHR below Saltville: 1) dissolved-mercury adsorbs onto suspended sediments near Pond 5, 2) suspended sediment-mercury settles to the river sediments, 3) sediment bacteria begin to methylate mercury and benthic macroinvertebrates bioaccumulate mercury, 4) fish are exposed to dissolved-mercury, suspended sediment-mercury and benthic mercury (bioaccumulate through food and bioconcentrate from water). During high river flows: 5) river sediment-mercury is re-suspended as suspended sediment-mercury, 6) suspended sediment-mercury is diluted by suspended sediments entering NFHR from other tributaries in the watershed, and 7) suspended sediment-mercury is transported downstream through the NFHR system. It is possible that suspended sediment-mercury is not as dominant as assumed and that organic particulates such as algae and detritus adsorb a significant fraction of the mercury. This organic-mercury will exhibit little settling and will be transported downstream during low flows as well as during major storm events.

## 1.5 Data Gaps

EPA's 1986 Risk Assessment consultant, GCA, conducted fate and transport modelling utilizing selected data sets from previous studies (ORNL, 1980, Milligan et al, 1978). GCA selected EPA's Chemical Transport and Fate Model TOXIWASP (Ambrose 1983) to conduct their risk assessment. TOXIWASP is a time-variable compartment model for simulating the transport and transformation of chemicals (primarily organic chemicals) in the water column and the sediment of stratified lakes and reservoirs, large rivers and estuaries.

Model input requirements are extensive and include exchange coefficients between compartments (i.e., dispersion between segments, water column and sediment, sediment and water in bed material); segment volumes and flows; boundary conditions; and numerous environmental and pollutant characteristics and rate constants. The PC version of TOXIWASP is limited to 80 segments total: 40 water segments and 40 sediment segments. TOXIWASP limitations include: 1) requirements for extensive input not routinely available and 2) substantial manpower requirements (about two man-months) to have an operational model to the point of providing a rough understanding of its overall behavior/performance.

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GCA chose to model a 20 mile stretch of the NFHR extending downstream from the chlor-alkali plant. The NFHR was divided into four segments, each 5.7 miles long. Initial model conditions for the mercury concentrations in the sediment of the four segments were 6.8 ppm, 3.4 ppm, 2.1 ppm and 1.9 ppm, respectively, going downstream. Sediment scour rates and settling rates were taken from TVA studies (Milligan, 1979) which applied regression analysis to historical data for the Saltville and Gate City monitoring stations. The model was run under four flow conditions i.e., 42, 97, 327 and 1100 cfs (5-, 30-, 70-, 95- percentiles), and three mercury discharge concentrations from Pond 5 (i.e., 0 g/day, 10 g/day, 27 g/day).

The modelling report concluded that, at present conditions, mercury concentrations in the sediments below Pond 5 will remain above 0.5 ppm for more than 10 years for the entire 20 mile stretch modeled. GCA assumed that sediment concentrations above 0.5 ppm would result in fish tissue concentrations exceeding the FDA limit of 1.0 ppm methylmercury.

The GCA modelling efforts and previous models by Oak Ridge National Laboratory (Dilution Modelling) and the Tennessee Valley Authority (TVA) (Sediment Transport Modelling) identify the important processes affecting mercury fate and transport in the NFHR system. These processes include daily mercury loading (Pond 5 and other sources); daily water balance; daily suspended solids and sediment transport (re-suspension/deposition). Unfortunately, data characterizing these processes do not exist. Our approach therefore, is to sample the parameters which control these processes and to use simple algebraic algorithms to correlate them on a daily basis (Brown et al., 1988).

Model development is a stepwise process. First the important parameters must be identified and secondly the precision which the parameters can be sampled and analyzed must be determined. For complex systems this becomes an iterative process. A basic model with parameters that can be sampled and measured with some degree of confidence is of greater use than a complex model with parameters which cannot be verified.

## 2.0 SAMPLING OBJECTIVES

### 2.1 Specific Objectives

A comprehensive bioassessment program for measuring mercury impact on NFHR aquatic communities involves the integrated use of both biological (i.e., benthic and fish surveys) and physio-chemical (i.e., sediment modelling) methods. The NFHR bioassessment program consists of five major tasks which evaluate the effects of present and past mercury discharge from the Site on the biotic integrity of stream communities of NFHR. The five tasks include (I) fish studies, (II) benthic studies, (III) mussel studies, (IV) ambient toxicity studies and (V) mercury fate and transport studies.

AR300126

The objective of the mercury fate and transport studies is to develop a computer model which simulates the movement of water, sediment and mercury in the NFHR. The model will be used in the risk assessment and the analysis of alternatives in the feasibility study. An assessment of the fate and

transport of mercury in the NFHR will provide a tool to aid in understanding any long-term effects of mercury on the aquatic communities of the stream and to assess effects of potential remedial actions for OU-2 and OU-3 on the NFHR.

One area of interest in the NFHR is on fish bioaccumulation of mercury (Hg) and potential risks to human health from consuming mercury contaminated fish. Yet the mechanisms operating in the river ecosystem that lead to mercury uptake remain incompletely described and quantified. This task will contribute to the understanding of mercury source, transport and fate in the NFHR by providing 1) time-varying watershed model of river flow, suspended sediment (SS) dynamics, mercury transport, 2) daily flow-weighted measurements of suspended sediments and mercury upstream of Pond 5 (NFHR Mile 82.5), 3) daily suspended sediments and mercury concentrations downstream of Pond 6 (NFHR Mile 80.8) and at the Holston streamflow gage (NFHR Mile 59.3) and 4) weekly suspended sediments-mercury measurements from riverine settling trays placed at 6 locations within the study reaches. These data will document the patterns of flow, suspended sediments, and mercury transport from the NFHR under a variety of seasonal and hydrologic conditions. These data will enable more accurate estimates of mercury transport and fate in the NFHR, and will be used to calibrate the transport model. The calibrated model can then be tested against future data to verify the model and thereafter used with confidence to simulate future mercury conditions following alternative treatment or control measures at the Saltville Site.

## 2.2 Uses of Data

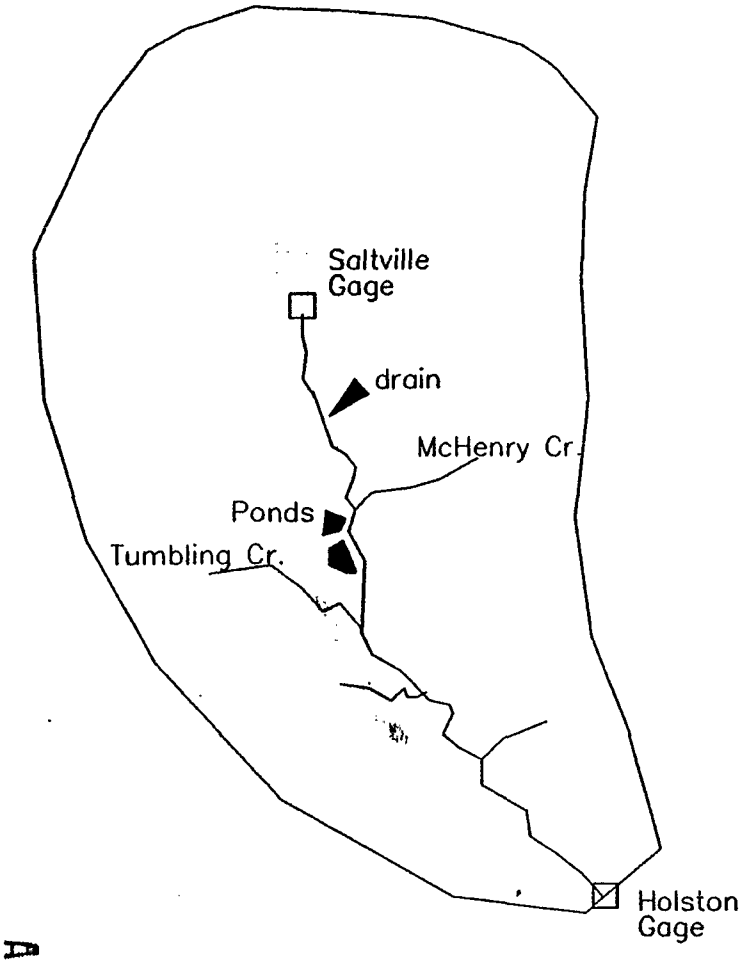
The model will be developed specifically for the Saltville-NFHR situation in a modular manner that will allow future data and conceptual improvements to be incrementally added to the model description. The model will include the Saltville mercury source within the context of the entire NFHR watershed above Holston. The model will operate on a PC-AT using FORTRAN and include eight major elements:

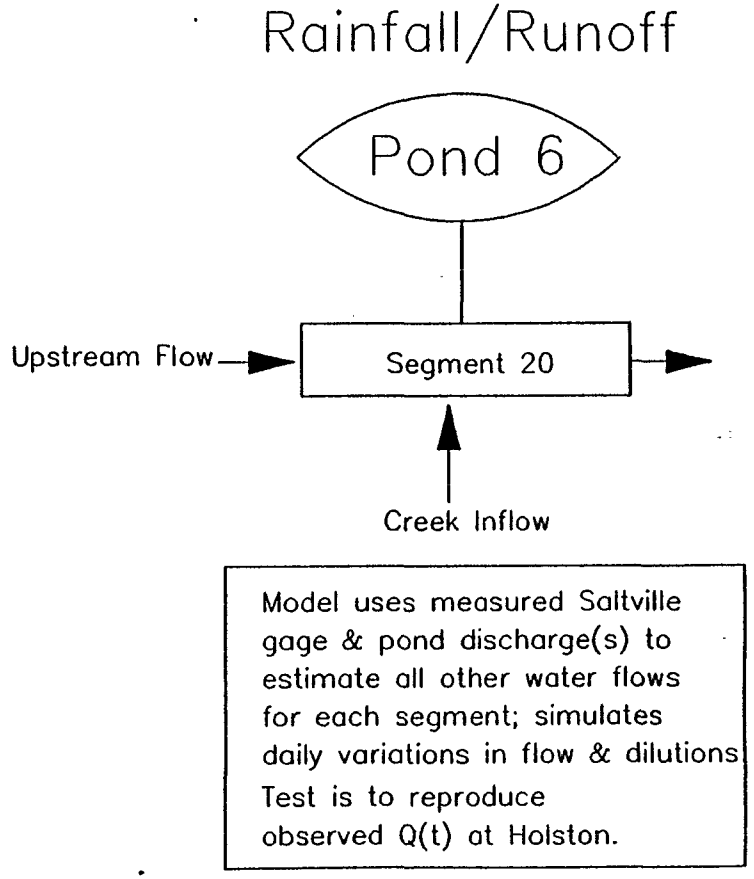
1) A daily water budget will provide the information required to run the hydrologic module of the model and allow prediction of river flows. The timing and size of precipitation events, estimation of evapotransporation and calculation of daily soil moisture budgets are the primary components of the hydrologic module. The baseflow and surface runoff components of flow will be distinguished by soil moisture/flow timing relationships calculated from the available historical database (i.e., if soils are saturated, flow occurs primarily as surface runoff; if soils are dry, rainfall infiltrates the soil and reaches the river primarily as baseflow). A similar water budget of Ponds 5 and 6 will allow the outfall flow to be divided into surface runoff and percolation flow components. Figure 3 shows an example of water balance for a selected segment.

AR300427

2) The channel hydraulics will be simulated by dividing the river into 1-mile segments and using algebraic relationships for depth, width, convergence area, velocity, and volume as a function of river flow. These relationships follow power equations of the form :

Figure 3. Water Budget Module.

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$$H = 0.25\ Q^{0.4}$$
$$W = 50\ Q^{0.2}$$
$$V = 0.08\ Q^{0.4}$$

where:

H = channel depth
W = channel width
Q = flow
V = velocity

Figure 4 shows an example of the channel hydraulics module. These simple equations will adequately describe the changes in segment hydraulic properties with streamflow and allow dynamic evaluation of time variation of flows and sediment. The upstream inflow will be measured at the Saltville USGS gage (NFHRM 85.0). The downstream segment flow will be incremented by the local drainage area, which increases by approximately 75% (3% per mile) between the Saltville gage and the former Holston USGS gage, which will be the downstream end of the model. This calculation will account for dilution of salt and mercury concentrations caused by inflow from tributaries to the system.

3) A daily suspended sediments (SS) module will simulate the runoff source for suspended sediments, and estimate the transport of this suspended sediments material down the NFHR to Holston. Figure 5 describes the components of suspended sediments and bottom sediments portion of the model. Daily suspended sediments measurements made by TVA at the Gate City gage during the late 1930's and early 1960's will initially be used to develop and calibrate the suspended sediments transport module. Evaluation of this dataset will allow quantification of the relationship between flow and suspended sediments. This relationship will be determined by calculation of flow/SS regressions, modified by soil moisture conditions to account for seasonal variation. The proposed measurements of suspended sediments will be used to validate the suspended sediments transport formulation.

4) The bottom sediment component will simulate the deposition, re-suspension, and downstream movement of the fine sediment material that coats the cobble substrate of the NFHR (See Figure 5.). Because of the dynamic settling and re-suspension terms, the depth of this material changes with river flow and suspended sediments conditions, and may exhibit downstream patterns. Measurements of the net downstream movement of this bottom sediment material will be obtained with multiple sediment traps placed across several transects, both upstream and downstream the Saltville site. These data will allow the modeled patterns of re-suspension and net downstream movement of the bottom material to be calibrated.

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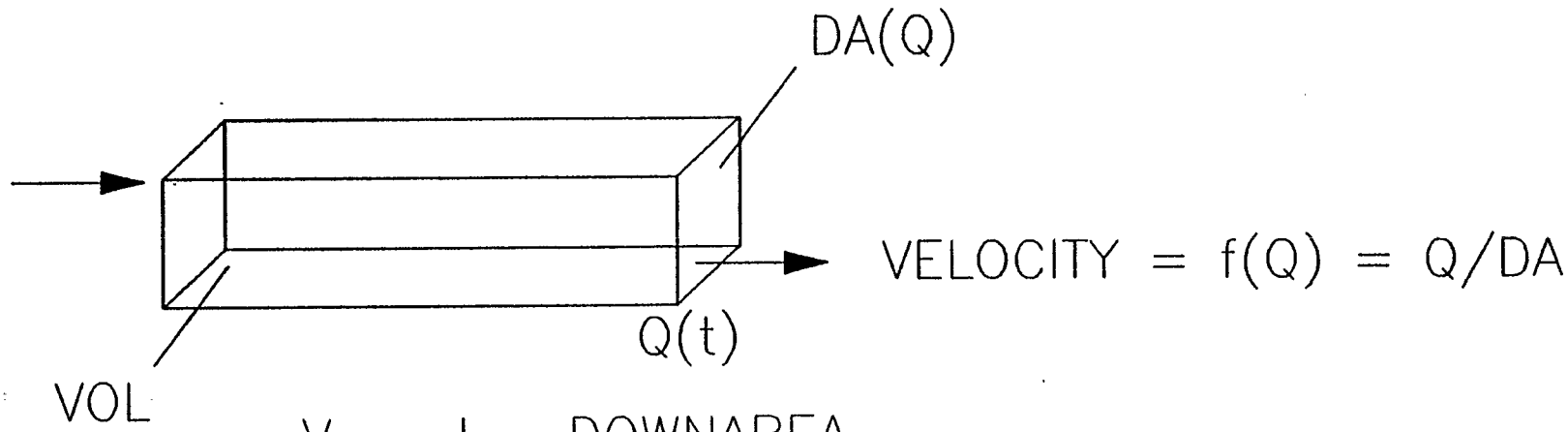
# FIGURE 4. CHANNEL HYDRAULICS MODULE.




$$V_L = L_o \quad \text{DOWNAREA}$$

$L_o$ = LENGTH

DOWNAREA = D(Q)*W(Q)
D = 0.25 $Q^{.4}$
W = 50 $Q^{.2}$
VELOCITY = 0.08 $Q^{.4}$

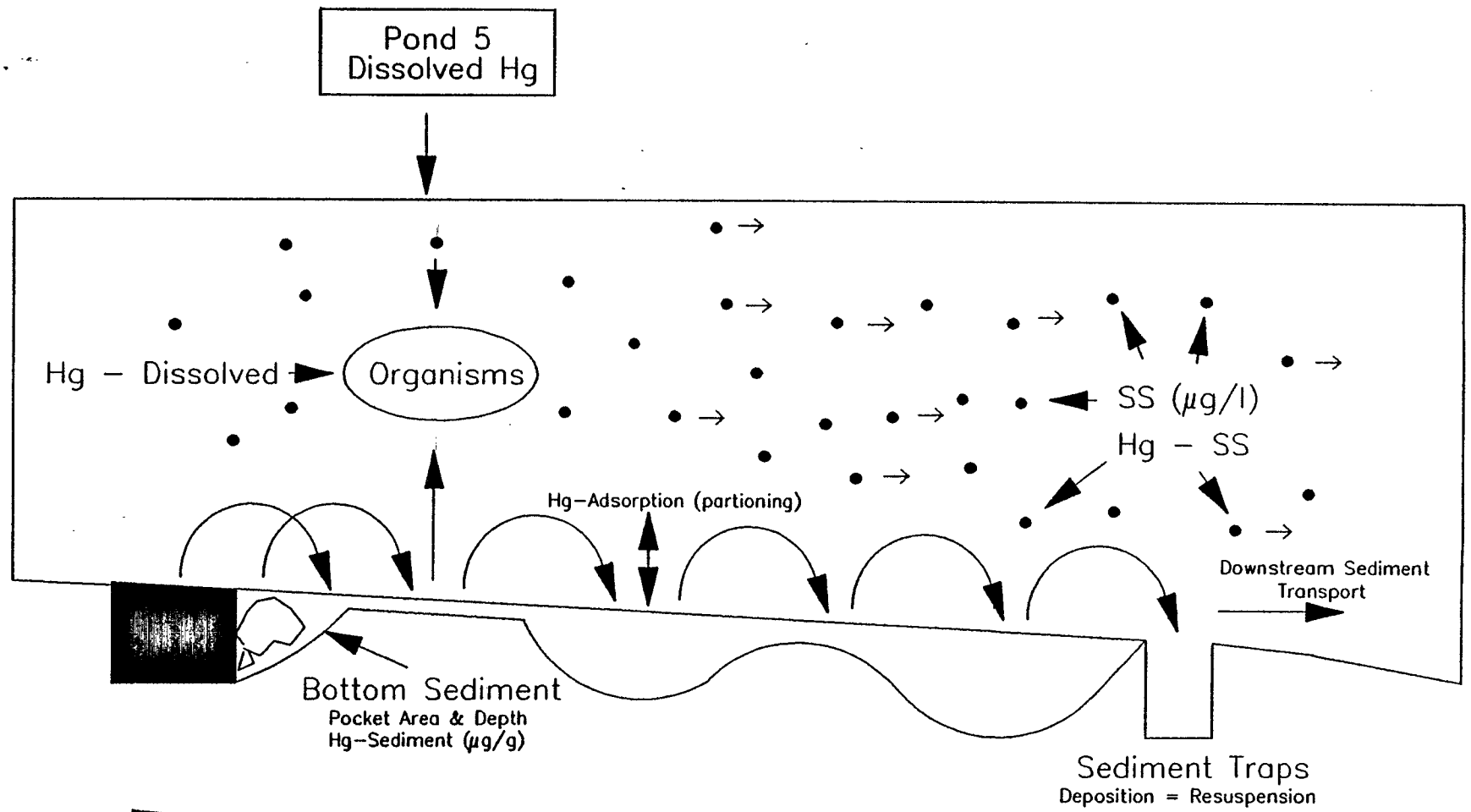
Coefficients derived from typical Appalachian streams.

This allows the daily changes in channel hydraulics to be incorporated. More accurate representation of water transport, settling depth, and shear velocity (bottom resuspension).

AR300130

# Figure 5. Daily Suspended Solids Transport Module

Daily SS Concentration * Daily Flow = Daily SS Transport




How much Hg precipitated?
Take samples of deposits in plume
Determine $Ca/SO_4/Mg/Hg$ Ratios (μg/g)

AR300131

5) The source term for mercury from Pond 5's outfall has been measured directly for several years. This daily data will be used to develop an accurate simulation of mercury runoff and leaching under existing conditions. This portion of the model will be extremely important since proposed treatment and control alternatives will be accurately considered in the model simulations. The suspended sediments-mercury concentrations depend on the source of mercury from the Saltville Site.

6) A total dissolved solids (TDS) mass balance will be modeled to allow the seepage source for TDS and mercury to be estimated. Data from the assessment of groundwater flow from Pond 5, Pond 6 and the FCPS can be incorporated in the future. Figure 6 shows the components used to develop the TDS mass balance estimates for the system. This will require measurements of TDS from the known point sources (Brine Field, Pond 5 outfall, and Pond 6 outfall) as well as river concentrations. Continuous measurements of conductivity will be made with periodic grab samples for TDS. The Pond 5 TDS measurements will be utilized to estimate the precipitation of salts onto the bottom sediments directly below the Pond 5 discharge using saturation chemistry relationships between pH and mineral precipitation reactions. These "theoretical" relationships will be validated by field verification of mixing zone water quality.

7) The adsorption of mercury onto suspended sediments and organic materials is an important mechanism that produces the observed partitioning of mercury between dissolved, suspended sediments, and organic substances in the NFHR. Precipitation of salts from the Pond 5 discharge may contribute to sediment adsorption of the dissolved mercury source by a process known as co-precipitation. The co-precipitation process will be evaluated through analysis of precipitate samples for mercury. The proposed data collection at downstream sites will provide information necessary to calibrate this portion of the model. Previous studies of mercury transport and fate (i.e., Poplar Creek at Oak Ridge) can be used to formulate this portion of the model, since the biochemical mechanisms operating in the NFHR are expected to be similar to those at other sites.

8) Finally, the model will include formulations linking the mercury concentrations in the dissolved, suspended sediments, organics, and river sediment fractions to those found in the benthos and fish species. Although these are the most crucial relationships, there is considerable uncertainty associated with these bioaccumulation mechanisms. However, the continuing measurements of bioaccumulated mercury concentrations outlined in other tasks will be more thoroughly integrated and interpreted using the proposed transport and fate modeling framework. Basically, the bioaccumulation module will follow the pharmacokinetic approach of Hartung (Young, 1988). The model uses a series of exponential equations to describe biological accumulation, storage and persistence of mercury in fish.

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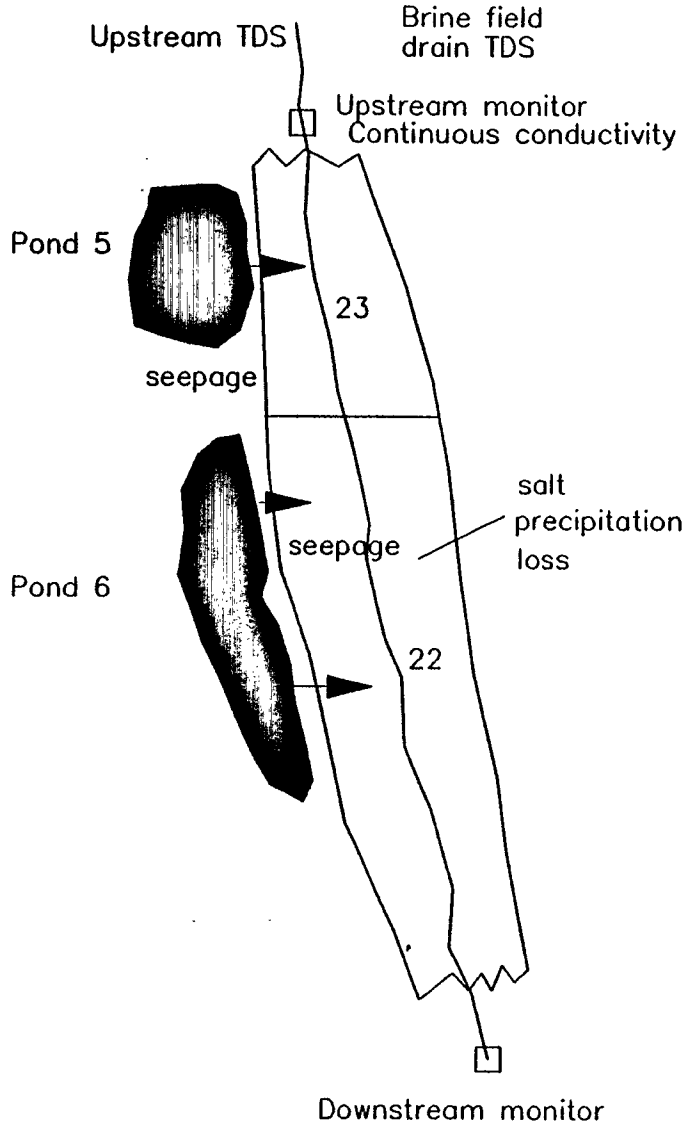
# Figure 6. TDS Mass Balance Estimation.




Demonstrate daily patterns of conservative TDS loads & concentrations above & below Saltville site.

Compare with measured Hg balance – to demonstrate loss of Hg onto bottom sediments.

Cl vs. TDS/conductivity shows magnitude of precipitation.

Difference between estimate of Downstream & Upstream Ponds = Seepage.

AR300133

## 3.0 SAMPLE LOCATION AND FREQUENCY

### 3.1 Collection Sites

The fate and transport studies will utilize three automated monitoring sites on the NFHR. The stations will be located at Mile 82.5, Mile 80.8, and Mile 59.3 (see Table 1 and Figure 7). The monitoring site at Mile 82.5 is located at the upstream end of Pond 5. The monitoring site is located approximately 2000 feet downstream of the Saltville POTW discharge and the brine field drain. This distance should provide adequate time for the inputs to the NFHR to become adequately mixed with the river water. The rocky river bed along this section shortens the mixing zone. The monitoring station at Mile 80.8 is located approximately 200 feet downstream of Pond 6. Pond 6 outfall is 0.9 miles upstream. The monitoring station at Mile 59.3 is located at the site of a former NFHR gaging station operated by USGS. Historical river data is available at this location.

Sediment traps will be employed at six sites to collect transported sediment. A conceptual design of the sediment traps is shown in Figure 8. Four sets of these traps will be installed at the six sites. The six sites are Mile 82.5, Mile 80.8, Mile 80.0, Mile 76.6, Mile 72.0, and Mile 61.0 (see Table 1). Site selection was based on the location of the automated monitoring sites, fish and benthos collection stations and river channel characteristics.

The USGS presently operates a gaging station at Mile 85.0. This will remain operational during the study and will provide data on river water elevations and flows.

### 3.2 Sample Collection

The proposed sampling design will provide data to accurately document the transport and fate of the mercury discharged from the Saltville Site. Table 1 summarizes the location and type of monitoring stations to be installed in the study area. The three automated monitoring sites are designed to interface each parameter to a "data logger" system. These systems contain non-volatile RAM (Random Access Memory) cartridges which are loaded to personal computer spreadsheet format. These systems will be serviced twice per week and the data packs replaced once per week. Table 2 shows the parameters to be monitored and the frequency of collection.

Several measurements are necessary to conduct the total dissolved solids (TDS) balance. Daily (5 days per week) flow and TDS measurements will be made at the brine field and Pond 6 discharge pipes. The daily (5 days per week) Pond 5 measurements (i.e., flow, TDS, total mercury) currently being conducted by Olin will continue during this study.

Daily flow-weighted river samples will be obtained and total volatile suspended sediments, turbidity, TOC, and mercury measurements will be made. Other adsorbed metals (Al, Fe, and Mn) will be measured along with mercury as a means of normalizing for clay content and because mercury tends to adsorb to these metals preferentially. Ten percent of the samples will be analyzed for the total mercury concentration, dissolved-mercury, suspended sediments-mercury, and organics-mercury

TABLE 1

LOCATION OF FIELD SAMPLE COLLECTIONS - FATE AND TRANSPORT STUDIES

| NFHRM | DESCRIPTION | FLOW (USGS) | AUTOMATED MONITORS* | SEDIMENT TRAPS |
|---|---|---|---|---|
| 85.0 | USGS Gaging Station | X | | |
| 82.5 | Upstream Point of Pond 5 | | X | X |
| 80.8 | Downstream Point of Pond 6 | | X | X |
| 80.0 | Historical Study Sites | | | X |
| 76.6 | Historical Study Sites | | | X |
| 72.0 | Historical Study Sites | | | X |
| 61.0 | Historical Study Sites | | | X |
| 59.3 | Former USGS Gaging Station | | X | |

* AUTOMATED MONITORS:

Turbidity, conductivity, temperature, pH, dissolved oxygen, water samples, flow.

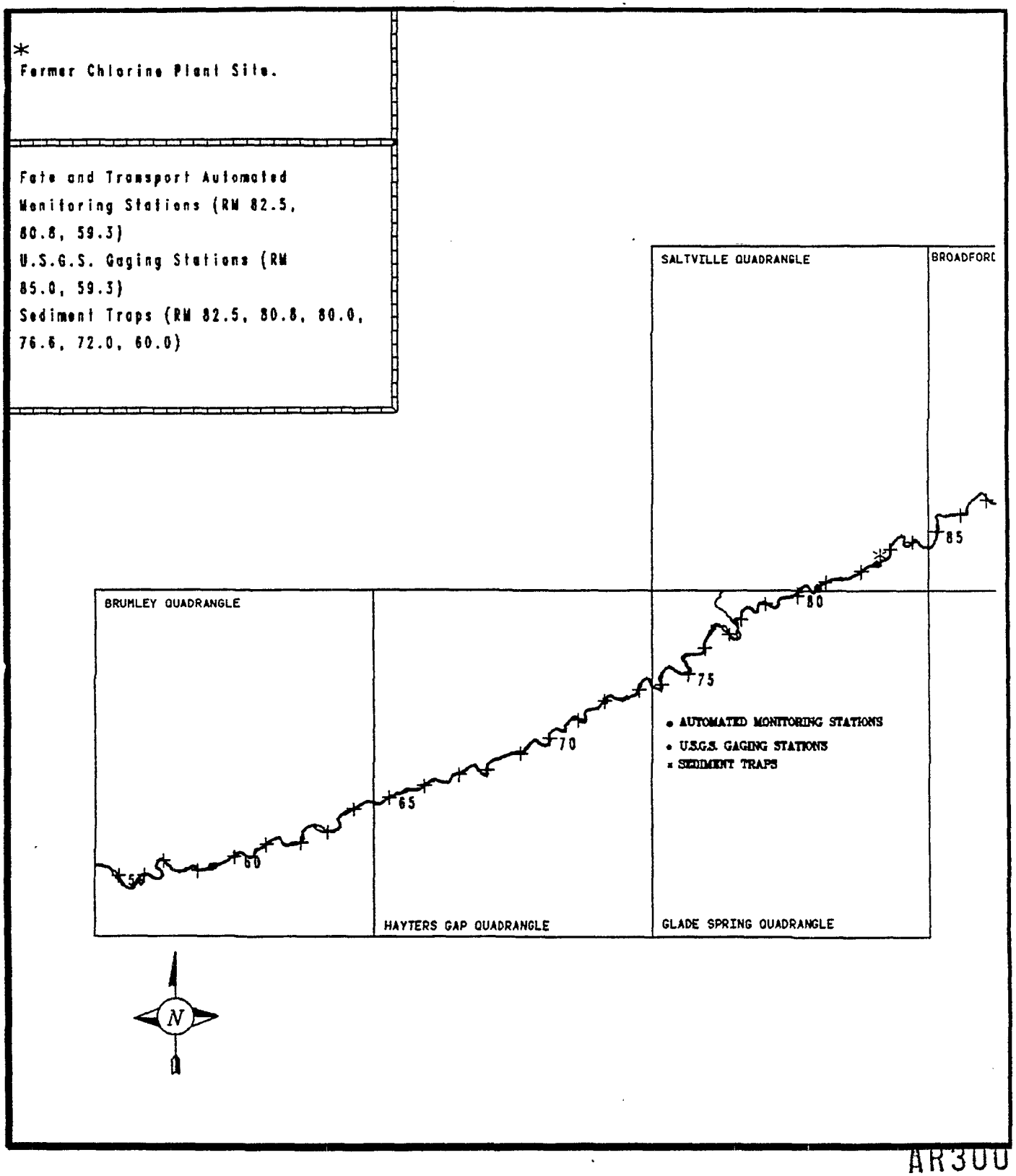



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**FIGURE 7. Mercury Fate and Transport Study Locations**

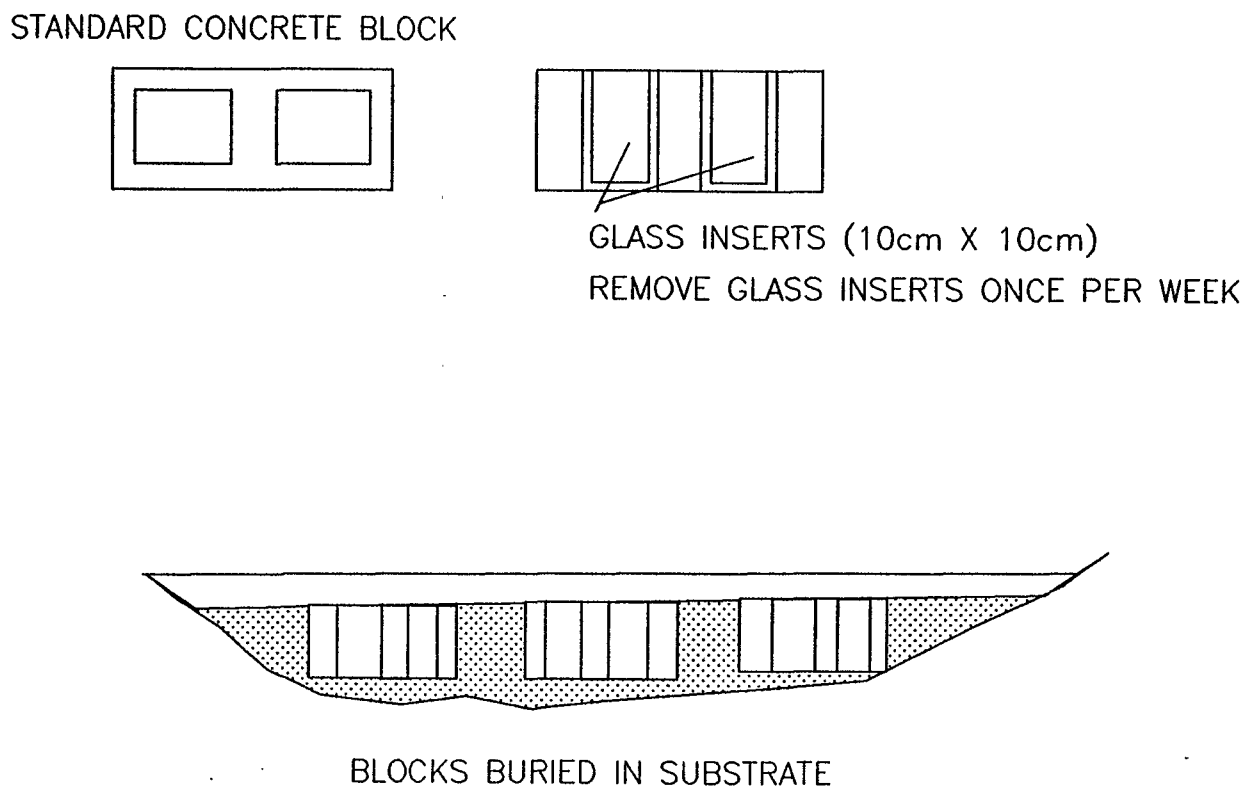


**FIGURE 8. Sediment Accumulation Trap**

TABLE 2

MONITORING PARAMETERS AND FREQUENCY

| Parameters | Automated Stations | Sediment Traps | Pond 5 Discharge | Pond 6 Discharge | Brine Field |
|---|---|---|---|---|---|
| Turbidity | C | | D | D | D |
| Conductivity | C | | | | |
| Temperature | C | | | | |
| Depth | C | | | | |
| pH | C | | D | D | D |
| Dissolved Oxygen | C | | | | |
| Water Samples | C(W)* | | | | |
| Total Dissolved Solids | W | | D | D | D |
| Suspended Solids | W | W | | | |
| Volatile Suspended Solids | W | W | | | |
| Total Organic Carbon | W | W | | | |
| Total Mercury | W | W | D | D | D |
| Iron, Aluminum, Manganese | W | W | | | |
| Chloride | W | W | D | D | D |
| Flow** | | | C | D | D |

* Water samples - 3 samples/day collected once/week; if no stormflow samples are composited; analyzed s during storm events.

** Flow measured daily by calculation and weekly by measurement.

C = continuous; W = weekly; D = daily (5 days per week)

fractions to allow the partitioning to be more accurately predicted in the transport and fate model. Gradient centrifuge techniques will be evaluated as method to separate the organic-bound mercury fraction from the mineral-sorbed mercury fraction.

Riverine sediment accumulation traps will be placed along the NFHR at six sites. These traps will be placed in the stream bed at four locations across the stream to trap transported sediments. The deposited materials will be collected weekly and analyzed for total and volatile sediment weight, particle size, TOC, and Hg, Al, Fe, and Mn content. The effects of low flow and storm events along the river will be identified from these weekly collections. Following major flushing events, the sediment-mercury concentrations are expected to be lower; following extended low flows these sediment-mercury concentrations are expected to build up. This combination of sampling activities is expected to be quite useful in model development and calibration.

### 3.3 Quality Assurance

The Quality Assurance Project Plan for the Saltville Waste Disposal Site Remedial Investigation and Feasibility Study, Saltville, Virginia will be in effect for this project. The goals of the QA program are to insure to the maximum extent possible that sample results are precise, accurate, representative, comparable, and complete.

Field quality assurance is the responsibility of the Field Sampling Coordinator. Frequent checks will be made to insure that all sampling procedures are followed. Random audits of field procedures will be conducted by the QA Officer to insure that specified protocols are being followed. The analytical quality assurance is described in detail in the Quality Assurance Project Plan (QAPjP).

The calibration procedures specified by the analytical methods and instrument manuals will be followed. Frequency of calibration specified by the analytical methods or instrument manuals will be considered to be the minimum frequency. More frequent calibration may be required under severe field conditions (e.g. rain, freezing temperatures). Calibration requirements of the method references will be met. All calibration checks must be documented in log books. At a minimum the following information must be recorded:

- Date of calibration
- Identification of standards used
- Instrument model and serial number
- Personnel performing calibration
- Results of calibration (including raw data and summary statistics)
- Corrective action taken

The effectiveness of this procedure is directly dependent upon the amount of mercury present in the sediment sample. The detection limit of analytical technique for mercury will determine the utility of this method. Methods for distinguishing organic mercury from inorganic mercury will also be

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evaluated. Specifically the procedure developed by the National Research Council of Canada (Schintu 1989). Once established, the above method will be added to the QAPjP.

Automated field instruments such as pH meters and conductivity meters will be calibrated twice per week (at a minimum) according to procedures specified by the Field Analytical Procedures and documented in field log books. Calibration must be performed with commercially prepared, certified standards if available, e.g., pH buffers, conductivity standards, etc. Sources of all material used for calibration or for preparing calibration standards will be documented.

## 4.0 SAMPLE DESIGNATION

Each sample collected will be assigned a unique sample identification number. The sample numbering system will be:

Sxx - yyyyyW-zzz or Sxx - yyyyyS-zzz

where

Sxx is the site number
yyyyy is a five digit number (starting with 00001 with the first sample collected and assigned sequentially.
W is for water samples
S is for sediment samples
zzz is the month/year collected (589 for May 1989)

Each sample will be labeled including:

- Sample number
- Date
- Time
- Sample location
- Sampler name
- Project name
- Analysis required
- Preservative added

## 5.0 SAMPLING PROCEDURES AND EQUIPMENT

### 5.1 Pre-Sampling Activities

Preparation for the sampling event can be divided into three primary areas:

1) Logistics of the event, including site access

2) Equipment preparation
3) Coordination with the analytical laboratory

The sampling coordinating team is responsible for all three areas. Olin will obtain site access for sampling points not on Olin property.

5.1.1 Logistics

The sampling team will insure that samples can be collected from all sampling points before an event is scheduled. At a minimum the team will contact the Olin Project Manager before mobilizing. Olin will arrange for all contacts with property owners for permission to enter their property where necessary to collect samples. The sampling team should check with property owners of any fenced or posted property.

5.1.2 Equipment Preparation and Calibration

All equipment to be used in the sampling effort will be checked for service before mobilizing. Any instruments used in water quality monitoring will be calibrated per manufacturers specifications prior to field measurements. Water quality monitors utilized for continuous field measurements will be checked and calibrated twice per week. Any maintenance or cleaning will be completed during these checks.

5.1.3 Coordination with Laboratory

The Field Sampling Coordinators will insure that the laboratory is prepared to receive any samples on the required schedule. The laboratory will be notified of each sample shipment so that samples can be expeditiously unpacked, inspected, and entered into the analytical flow at the laboratory.

## 5.2 Field Procedures

The three automated monitoring sites located at Mile 82.5, Mile 80.8 and Mile 59.3 will be equipped with monitors which will continuously measure water turbidity, conductivity, temperature, depth, pH and dissolved oxygen. Electronic data loggers will be used to record the data. Continuous measurements will be made and stored in non-volatile random access memory within the data logging unit. The memory recording cartridges will be exchanged weekly. The data logger and measurement equipment will be inspected at least twice a week for re-calibration and operation verification.

All equipment will be housed in a small concrete block or metal building at each site. A pump will transfer a continuous slipstream of river water from the hydraulic center of the channel to the monitoring equipment and then back to the river. This will permit all equipment and probes to be housed in the building for protection from vandalism.

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Continuous water samplers will be utilized at the three automated stations to collect daily flow-weighted water samples during normal flow. It is anticipated that three 8-hour composite samples will be collected each day. Water samples will be analyzed individually during storm events and composited by day during normal flow. These samples will be analyzed for the constituents listed in Table 2.

Velocity-discharge measurements will be made once per week. This data will be used to prepare stage-discharge graphs for each monitoring site.

Sediment traps will be placed at four locations across the stream at six transect sites. Each trap will contain two glass containers where the sediment accumulates. The containers will be removed weekly and replaced with clean containers. More frequent collection may occur during a series of storm events. The sediment at each transect will be composited and analyzed for the constituents listed in Table 2.

USGS will continue to operate the gaging station at NFHR Mile 85.0. Stage elevation is recorded every 30 minutes.

Pond 5 outfall, Pond 6 outfall and the Brine Field drain will be sampled daily (5 days per week) for the parameters listed in Table 2. Weirs will be installed on Pond 6 outfall and the Brine Field drain. Pond 5 has a weir. The flow from the Brine Field and Pond 6 will be measured manually when sampled.

It is the responsibility of Field Sampling Coordinator to insure that field activities and observations are documented. A field log book will be maintained to record the following information:

- General description of the work
- Samples collected and their identification number
- Date, time of sampling, weather conditions
- Sample location
- Field measurements and observations
- Field sampling personnel
- SOPs employed
- Written discussion of any deviations from SOPs
- Chain-of-custody references for each sample

## 5.3 Equipment Required

Three monitoring stations on the NFHR will be constructed. Each station will consist of a small building (concrete block or metal) which will house the monitoring equipment. Water will be pumped from the river to the building and back to the river on a continuous basis. This slipstream will be monitored continuously for pH, conductivity, temperature, dissolved oxygen and turbidity. This slipstream will be sampled periodically for wet analysis. A pressure transducer will be installed in the river to monitor water depth. Equipment for each monitoring station will include:

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- Continuous monitoring and sensors for pH, conductivity, temperature, turbidity, dissolved oxygen and water depth.

- Data logger system with RAM cartridges to record data from the continuous monitors

- Calibration solutions, standards and equipment as recommended by manufacturers of the equipment.

- Sequential water samplers capable of collecting 24 individual samples

- Sample bottles (minimum of 3 sets for each sampler)

The other equipment required for fate and transport studies include:

- sediment collection trays (24 trays)
- water velocity meter with measuring rod
- 200-foot tape measure
- waterproof labels
- chain-of-custody forms
- coolers
- ice (wet or Blue™)
- sample seals
- permanent markers
- utility box
- first aid kit
- flash lights/dive lights
- site map
- field log book
- tap water
- alconox™
- nitric acid solution (5%)
- deionized water

## 6.0 SAMPLE HANDLING AND ANALYSIS

### 6.1 Sample Preparation

Water and sediment samples collected will remain under custody until delivery to the laboratory. Copies of the chain-of-custody forms will be included in the final report. Sediment samples will be homogenized by the procedure in Appendix B of the QAPjP.

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## 6.2 Equipment Cleanup

All sampling equipment and bottles which contact the samples will be thoroughly cleaned. This includes bottles, pumps, tubing, processing pans, etc. The cleaning procedure is as follows:

1) Wash with tap water and laboratory detergent using a brush if necessary to remove particulate matter and surface films.

2) Rinse thoroughly with tap water.

3) Rinse with 5% nitric acid solution

4) Rinse three times with tap water and allow to air dry as long as possible.

## 6.3 Shipping Requirements

Water samples will be shipped on ice to the laboratory in insulated coolers. Sediment samples may be packed with ice at the option of the sampler. Water and sediment samples will be shipped in separate coolers. Arrangements will be made to insure that the samples arrive at the laboratory in an expeditious manner.

## 6.4 Chain-of-Custody Record

Once a sample is collected, custody must be maintained. A sample is under custody if:

- It is in the sampler's possession.
- It is in the sampler's view, after being in the sampler's possession.
- It is in the sampler's possession and then is placed in a secure area.
- It is in a designated secure area.

Chain-of-custody forms will be prepared for the sample prior to transporting samples from field sites. Each sample will be listed on the form. A chain-of-custody form is shown in Figure 9.

The following sample custody procedures will be utilized:

1) Each sample collected for the project will be entered on the chain-of-custody record. Field personnel will retain a copy of the chain-of-custody record.

2) The original chain-of-custody record plus one copy will accompany the sample containers during transport to document controlled custody.

3) If custody is relinquished through a common parcel carrier for delivery to the laboratory, the following protocol will be followed:

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# FIGURE 9.

## OLIN CORPORATION

### CHAIN OF CUSTODY RECORD

| PROJ. NO. | PROJECT NAME |
|---|---|
| SAMPLERS: *(Signature)* | |

ANALYSES REQUIRED

Instructions: List samples individually. Write time in military time. Record sample type as water, soil, etc. and as grab or composite. Record special handling instructions or precautions in remarks section. Record method of shipment in comments section.

| Station or Sample No. | Date | Time | Sample Type | Number Of Containers | | | | | | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
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|---|---|---|---|---|---|
| Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* | Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* |
| Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* | Relinquished by: *(Signature)* | Date/Time | Received by: *(Signature)* |
| Relinquished by: *(Signature)* | Date/Time | Received for Laboratory by: *(Signature)* | Date/Time | Comments | |

DISTRIBUTION: Original and Pink copies accompany sample shipment to laboratory. Pink copy retained by laboratory. Yellow copy retained by samplers.

- The method of sample shipment will be noted in the comment section on the chain-of-custody form.

- The original chain-of-custody record plus one copy will be placed inside the shipping package.

- The shipping package will then be sealed with a custody seal. The seal will be placed on the package in such a manner that the package cannot be opened without breaking the seal. The seal will serve to document that the samples remained unaltered during shipment through the common parcel carrier.

4) If the sample is shipped by air freight or express shipment, the air bill will become part of the chain-of-custody procedures.

5) The laboratory will assume custody of the samples upon receipt. A designated Sample Custodian will be charged with sample care and receipt and verification of custody seal condition. These observations will be noted by the Sample Custodian on the chain-of-custody form upon receipt. All sample damage and abnormalities will be noted on the forms. The Sample Custodian will sign the chain-of-custody form, retain the copy for the Laboratory's record, and forward the original to the Field Project Officer.

6) Sample preparation and analysis custody will be tracked by laboratory work sheets.

7) The laboratory will retain custody of the samples in a secure area until such time as the samples are ordered destroyed.

8) A copy of the chain-of-custody record will be retained.

9) If samples are transferred to another laboratory, either as a whole or as a split sample, a new chain-of-custody form will be initiated.

### 6.5 Holding Times

Samples collected for mercury analyses will be analyzed within 28 days as specified in Table 4 of the QAPjP. Aqueous samples for total mercury will be acidified with nitric acid to a pH less than 2.0 as a preservative. Water samples for dissolved mercury will be filtered and then acidified. All samples will be collected in glass containers. Holding times for water samples for other analysis will follow those holding times listed on Table 4 of the QAPjP.

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## 6.6 Record Keeping

All records will be maintained in bound books. A master log will be established which will contain the appropriate identity and traceability of each sample. The same code number will be used from sample acquisition through final data tabulation. Detailed notebooks will be maintained by laboratory personnel for samples, instruments and calibration standards.

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