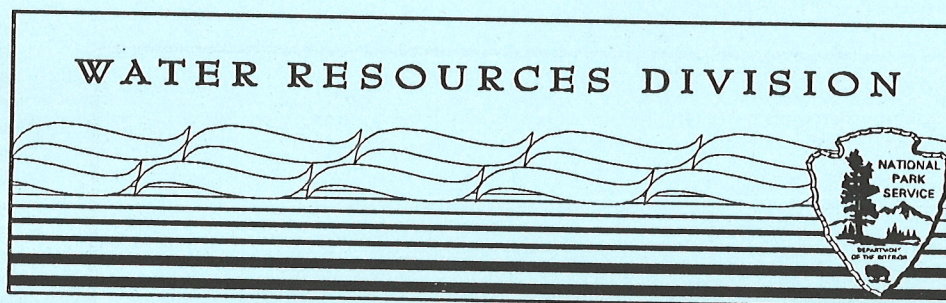


ASSESSMENT OF AN URBAN LANDFILL ON  
TRIBUTARY WATER QUALITY:  
FORT DARLING UNIT OF THE  
RICHMOND NATIONAL BATTLEFIELD PARK,  
VIRGINIA

Del Wayne R. Nimmo, Mary J. Willox, John F. Karish,  
John D. Tessari, Terri L. Craig, Ervin G. Gasser,  
and James R. Self

Technical Report NPS/NRWRD/NRTR-94/35



National Park Service - Department of the Interior  
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ASSESSMENT OF AN URBAN LANDFILL ON TRIBUTARY  
WATER QUALITY: FORT DARLING UNIT OF THE  
RICHMOND NATIONAL BATTLEFIELD PARK, VIRGINIA

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## SUMMARY

A toxicological assessment of a landfill, located in the Fort Darling Unit of Richmond National Battlefield Park (RICH), Virginia, was conducted from 1989-1992. After using acute and chronic toxicity tests, and priority pollutant analysis on water and sediments collected from a small unnamed tributary to the James River, and water collected from four monitoring wells constructed into the landfill, it was concluded that toxic conditions to aquatic life did not exist. For acute tests conducted on tributary water and sediments, three species of traditionally used aquatic organisms (*Ceriodaphnia dubia*, *Pimphales promelas*, *Hyaella azteca*) and one plant species (*Latuca sativa*) were used. For chronic tests conducted on tributary water, *Ceriodaphnia dubia* was used. Priority pollutant analyses of tributary water and sediments and water from the monitoring wells in the landfill also did not reveal organic or inorganic chemicals at hazardous levels. An analysis of metals in both tributary water and sediments suggest that metals entering the tributary through the landfill's leachates precipitate out of the water and armor the substrate preventing the establishment of permanent aquatic life.





## INTRODUCTION

Fort Darling, a unit of RICH, is commonly referred to as Drewry's Bluff. This Confederate stronghold successfully guarded the James River during several battles fought in Richmond during the Civil War. One important battle was fought on May 15, 1862 when four federal gunboats, including the famous Monitor, attacked the fort. Fortunately for the Confederates, the attacking boats were driven off. Fort Darling also served as the Confederate Naval Academy and Marine Corps Camp of Instruction during the war.

Between 1963 and 1972, a landfill adjacent to Fort Darling was operated by Chesterfield County, Virginia for disposal of residential and industrial waste. Shortly after the landfill was closed in 1972, Chesterfield County and the National Park Service (NPS) covered the landfill with topsoil then contoured and revegetated it. In 1975, 25 acres containing the landfill and additional acreage around the perimeter of the fill was donated to the NPS.

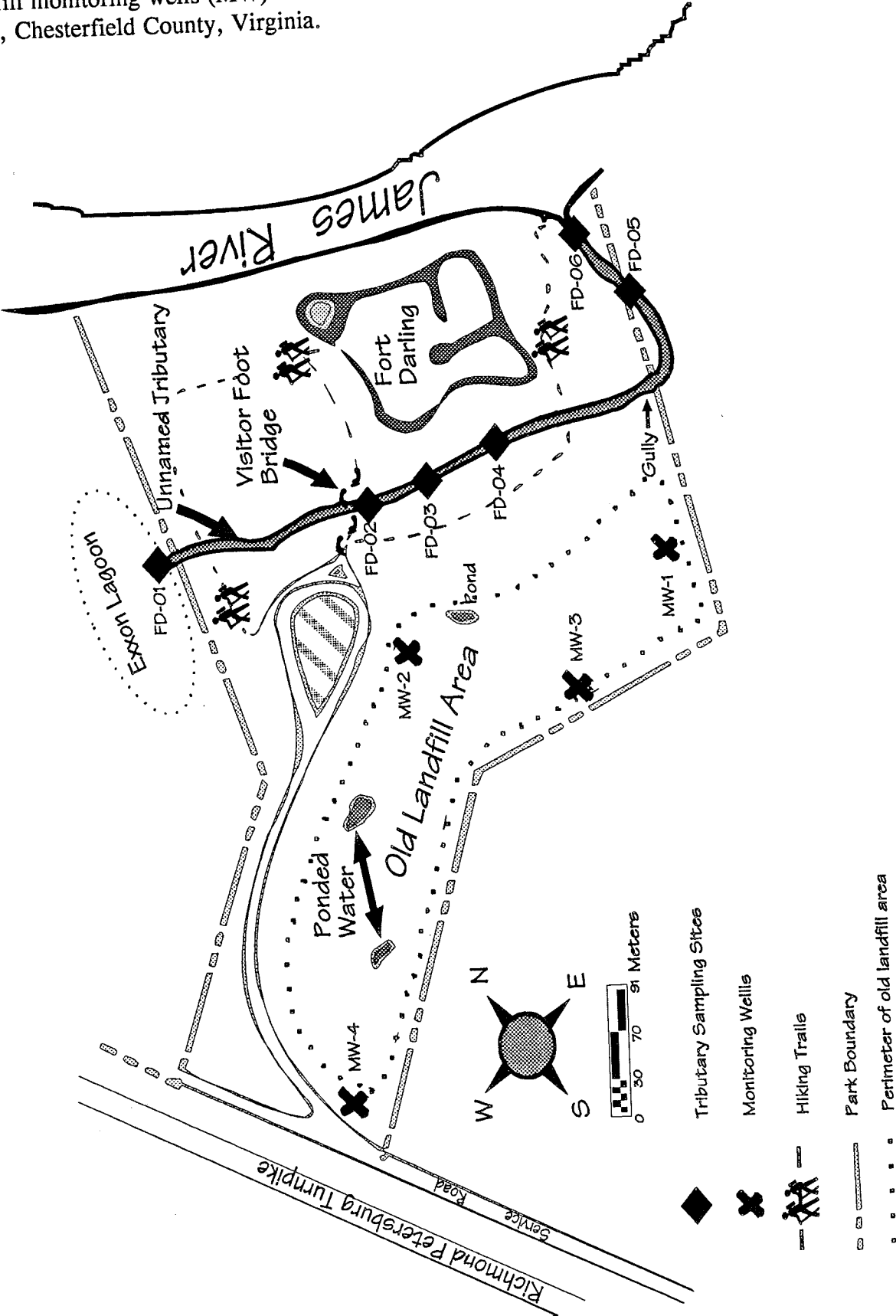
However, because the landfill was not monitored during its operation, the possibility of it containing hazardous wastes could not be discounted. Especially noticeable to park officials and the visiting public were orange-reddish leachates staining the banks, water, and substrates in a small unnamed tributary to the James River that encircles the bluff and earthen fortifications within the park unit (Figure 1). Additionally, due to subsidence at several locations on the landfill's earthen cap, water from precipitation continuously pools in the depressions and percolates through the cap. These pools are believed to add to the volume of leachates entering the tributary. An earlier site inspection report on the landfill's leachates further suggested that toxicants could be affecting the tributary's aquatic life (NUS Corporation 1985). Toxicants mentioned in the report were several polynuclear aromatic hydrocarbons (PAHs), iron, small quantities of cyanide, and traces of chlorinated benzenes, ethanes, and ethenes identified in tributary water and sediment samples. Concentrations of iron upstream from the landfill exceeded acceptable levels for protection of aquatic life. Furthermore, investigators who contributed to the report failed to find any aquatic life in the tributary which suggested that the leachates were toxic to aquatic life.

Because of these concerns, the objectives of this study were to:

- 1) analyze the impact of the leachates on the tributary's water for potential toxicity to aquatic life, and
- 2) assess the landfill's possible environmental risks to park resources.

To aid in the understanding of this report, the discussion centers as much as possible, on water and sediments in the tributary. During an initial reconnaissance, it was determined that it would not be possible to obtain representative water or sediment samples which would be affected by only an individual leachate site. Because the number of sites where leachates entered the tributary were so numerous and widely distributed, any sample would be influenced by more than one leachate site. In this report, the term "leachate site" refers to a specific location where it can be seen that a leachate is entering the tributary. This can be

**Figure 1.** Locations of six sampling stations (FD) in the unnamed tributary and of the four landfill monitoring wells (MW) within Fort Darling Unit of Richmond National Battlefield Park, Chesterfield County, Virginia.



identified by a prominent staining of the tributary substrate. Therefore, the study plan was modified to obtain samples of water and sediment from points in the stream equidistant above and below the most prominent stained areas of the tributary. All samples were taken in the channel midstream.

## METHODS

Six sampling stations, used for the duration of studies along the tributary, are diagrammed in Figure 1. The unnamed tributary, referred to in this report, is a small perennial stream usually with permanent water immediately after station FD-02. During the studies, natural water and leachate increased the volume in the tributary until its confluence with the James River. Station FD-01 is located at the point where water is released from the Exxon lagoon located on the other side of the security fence on the western boundary of the park unit. To our knowledge, there is no permanent flow at the FD-01 station. FD-01 was sampled only once which coincided with the reconnaissance for obtaining the initial samples. Station FD-02 was located immediately below the visitor foot bridge and above the initial signs of staining, or approximately 151 meters from the western park boundary; station FD-03 was located immediately below the initial leachate, or 70 meters below the visitor foot bridge; station FD-04 was located immediately below the greatest volume of leachate, or 121 meters below the foot bridge; station FD-05 was located below a gully confluence which contained flowing water only during wet conditions, or approximately 70 meters above the confluence with the James River; and station FD-06 was located immediately before the tributary's confluence with the James River. Four groundwater monitoring wells and two piezometers were installed in the landfill between October 24 and November 12, 1989. The location of the landfill's monitoring wells, constructed by Chesterfield County, are shown in Figure 1. The sequence of visits, tests, and dates of sampling at the Fort Darling Unit is listed in Table 1.

The landfill assessment work plan, although not identical, was modeled after a study published by Athey, et al. (1989). Standard U.S. Environmental Protection Agency (EPA) methods were used for sampling, preserving, and holding the tributary water and sediment samples collected from the unnamed tributary and monitoring wells constructed in the landfill (U.S. EPA 1983, Greene et al. 1989). Samples for acute tests with animals and plants were preserved by maintaining them on wet ice while collecting and transporting them to the laboratory. In the laboratory, samples were maintained at 4°C until they were tested or analyzed. Acute testing using daphnids (*Ceriodaphnia dubia*), amphipods (*Hyalella azteca*), fathead minnows (*Pimephales promelas*), and seed germination of lettuce (*Lactuca sativa*) also followed standard EPA methods (Weber et al. 1989, Greene et al. 1989). The tributary water was tested with daphnids and fathead minnows, and the sediment elutriates were tested with amphipods and lettuce; both water and sediment were collected from the identified sampling stations (Figure 1). To prepare elutriates, sediment samples were mixed with reconstituted (Recon) water as described by EPA (Peltier and Weber 1985). The hardness of the Recon water was 75 mg/L as CaCO<sub>3</sub> (similar to the hardness of station FD-04 which was 72 mg/L as



CaCO<sub>3</sub>). Four liters of water per one kilogram of sediment were first shaken for 48 hours, centrifuged for 30 minutes at 4000 rpm, and then tested.

The reference and culture water used to rear and acutely test the daphnids was well water collected from the Colorado Division of Wildlife's Research Well located in Fort Collins, Colorado. For the chronic (Weber et al. 1989) tests, the reference waters were EPA Recon water and a natural surface water from the Poudre River, located in Colorado. Standard EPA methods for sampling, transporting, and holding samples for analysis of metals and priority pollutants were used (U.S. EPA 1984a).

## RESULTS

The initial reconnaissance and sampling of tributary water and sediments were conducted on June 15 and 16, 1989. On the morning of June 15, water was unexpectedly released from the Exxon lagoon which provides the primary flow in the tributary above the leachates during wet conditions. At the time of release, the flow was estimated at approximately three cubic feet per second. Because the release lasted for two hours, it was sampled. After obtaining permission from the Exxon Superintendent, sediment from the Exxon lagoon outside park property was also sampled. Due to the release, however, sampling of tributary water and sediments downstream were postponed for 24 hours. Analysis of the physical parameters of tributary water, obtained during the reconnaissance, is presented in Table 2. Noted at stations FD-03 and FD-04 are instream concentrations of oxygen below 5.0 mg/L and, at all stations, pH values below 6.5, the EPA's dissolved oxygen and pH criteria for aquatic life (U.S. EPA 1986).

Data from the acute tests were not subjected to statistical analysis because of insufficient mortality of the test organism tested with the site water. Mortality of fathead minnows and daphnids at all sites was  $\leq 10$  percent, the majority of sites produced 0 percent mortality. Mortality of amphipods was  $\leq 20$  percent at any site. It was determined that the tests using the lettuce seeds for germination could not be analyzed for variance because the compartments in the test containers had physical connections, i.e., they were not divided into three physically-separate compartments. The lettuce germination tests had to be considered as duplicates.

Data from the chronic daphnid tests were subjected to statistical analysis using the procedures presented in U.S. EPA (1989). The response or endpoint used in the analysis was the number of young produced per living adult female at the end of the test. Survival of adult daphnids in all tests and at all sites exceeded 90 percent therefore, reproduction became the biological endpoint. The calculation of the average number of live young produced per adult female for each dilution provided a measure of the effect of the site water on the species. The procedures suggest that either an inhibition concentration (IC) estimate be calculated for the reproduction or hypothesis testing be used to obtain a no-observable effect concentration (NOEC), or, in the case of this study, a series of dilutions.

**Table 1.** Sequence of visits, tests, and dates of sampling in the Fort Darling Unit of Richmond National Battlefield Park, Virginia.

Sampling Dates	Station	Description	Types of Tests or Analyses
June 15, 1989	FD-01	Exxon lagoon	Initial reconnaissance and sampling for acute toxicity tests. Tributary water and sediments were tested using plants and animals.
June 16, 1989	FD-02	Below visitor foot bridge	
	FD-03	Below initial leachate	
	FD-04	Below greatest volume of leachate	
	FD-05	Below gully	
	FD-06	Immediately above confluence with James River	
December 6, 1989	FD-03	Below initial leachate	Priority pollutant analyses were conducted on tributary water and sediments collected below the landfill.
	FD-04	Below greatest volume of leachate	
October 11, 1990	FD-03	Below initial leachate	Chronic toxicity tests with <i>Ceriodaphnia dubia</i> and analyses of metals were conducted on tributary water and sediments collected below the landfill.
	FD-04	Below greatest volume of leachate	
July 24, 1991	FD-02	Below visitor foot bridge	Analyses of metals in water and sediments were conducted in the tributary basin above and below the landfill.
	FD-03	Below initial leachate	
	FD-04	Below greatest volume of leachate	
	FD-05	Below gully	
	FD-06	Immediately above confluence with James River	
	MW-1	Four monitoring wells constructed in the landfill	Priority pollutant analyses, conducted by the National Park Service, of water samples collected from monitoring wells constructed in the landfill.
	MW-2		
	MW-3		
	MW-4		
April 17, 1992	MW-1	Four monitoring wells constructed in the landfill	Priority pollutant analyses, conducted by Chesterfield County, of water samples collected from monitoring wells constructed in the landfill.
	MW-2		
	MW-3		
	MW-4		

We used the Shapiro-Wilkes's Test for normality and the Bartlett's Test for homogeneity of variance on both dilution series involving samples of water from FD-03 and FD-04. Both series were normally distributed and heterogenous for variance. Because of mortality in the FD-03 series of dilutions, and unequal replicates, we used the non-parametric Wilcoxon Rank Sum Test with the Bonferroni adjustment. For the FD-04 dilution series the replicates were equal, therefore, the Steel's Many-one Rank Test was used to determine the NOEC.

Acute (96-hour) toxicity tests of tributary water and sediment samples collected June 15 and 16, 1989, indicated no evidence of toxicity to fatheads and amphipods from either the tributary water or sediment elutriates (Tables 3 and 4). There was also no evidence of acute toxicity in 48-hour tests with daphnids (Table 5), and no observed effects on the germination of lettuce seeds exposed to elutriates for 120 hours (Table 6). Although the germination of lettuce seeds in elutriates from all tributary stations was less than that in reconstituted water, the results indicated that the two highest percentages of germination were directly below the initial leachate, FD-03, and where there was the greatest volume of leachate, FD-04 (Table 6).

**Table 2.** Initial reconnaissance of water parameters of unnamed tributary in the Fort Darling Unit of Richmond National Battlefield Park, Virginia, on June 15-16, 1989.

Station	Description	Temperature °C	Conductivity μmhos/cm	Dissolved Oxygen mg/L.	pH	Approximate Flow (cubic feet per second)
FD-01 <sup>1</sup>	Exxon Lagoon	35	700	6.2	5.6	3.0
FD-02	Below visitor foot bridge	22	860	7.0	6.1	0.5
FD-03	Below initial leachate	20	4100	3.6	5.3	1.0
FD-04	Below greatest volume of leachate	20	4000	2.8	5.4	1.5
FD-05	Below gully	22	2000	7.6	5.4	2.0
FD-06	Immediately above confluence with James River	20	2200	7.0	5.6	3.0

<sup>1</sup>Station FD-01 is an intermittent discharge from the Exxon lagoon and on this occasion was sampled on June 15, 1989. All other samples were obtained on June 16, 1989.



**Table 3.** Results of acute<sup>1</sup> fathead minnow<sup>2</sup>, *Pimephales promelas*, toxicity tests conducted on tributary water in the Fort Darling Unit of Richmond National Battlefield Park, Virginia, June 15-16, 1989.

Station	Description	Mortality <sup>3</sup>	pH	Temp. °C	Dissolved Oxygen mg/L	Alkalinity CaCO <sub>3</sub>	Hardness CaCO <sub>3</sub>
FD-01	Exxon Lagoon	0%	6.5	22	6.4	<2	16
FD-02	Below visitor foot bridge	6%	6.8	22	6.0	14	20
FD-03	Below initial leachate	0%	7.6	22	6.6	60	42
FD-04	Below greatest volume of leachate	10% <sup>4</sup>	7.6	22	6.3	78	72
FD-05	Below gully	0%	7.3	22	6.3	40	52
FD-06	Immediately above confluence with James River	0%	7.3	22	6.6	32	40

<sup>1</sup>96-hour test. Test results are based on three replicates of five fish each.

<sup>2</sup>Six-day-old larval stage. Minnows were fed hatched brine shrimp, *Artemia*, throughout test.

<sup>3</sup>Percent mortality is based on an average of all three replicates.

<sup>4</sup>One replicate was accidentally destroyed during the tests.

**Table 4.** Results of acute<sup>1</sup> amphipod, *Hyalella azteca*, toxicity tests conducted on sediment elutriates collected from unnamed tributary in the Fort Darling Unit of Richmond National Battlefield Park, Virginia, June 15-16, 1989.

Station	Description	Mortality <sup>2</sup>	pH	Temperature °C	Dissolved Oxygen mg/L
FD-01	Exxon lagoon	0%	6.1	22	4.8 <sup>3</sup>
FD-02	Below visitor foot bridge	0%	6.3	22	6.3
FD-03	Below initial leachate	20%	6.8	22	6.4
FD-04	Below greatest volume of leachate	0%	6.8	22	6.5
FD-05	Below gully	10%	6.6	22	6.0
FD-06	Immediately above confluence with James River	0%	7.0	22	6.3

<sup>1</sup>96-hour test with elutriates (4 liters of EPA reconstituted water/1.0 kg of sediment). Test results are based on two replicates of ten animals each.

<sup>2</sup>Percent mortality is based on an average of both replicates.

<sup>3</sup>Although the recorded 4.8 mg/L dissolved oxygen is lower than the other samples, it did not violate EPA's methods requirement (Peltier and Weber, 1985) that dissolved oxygen, during testing, not fall below 3.5 mg/L.

**Table 5.** Results of acute<sup>1</sup> daphnid, *Ceriodaphnia dubia*, toxicity tests conducted on tributary water in the Fort Darling Unit of Richmond National Battlefield Park, Virginia, June 15-16, 1989. Temperature, dissolved oxygen, alkalinity, and hardness were recorded in the Fort Collins, Colorado, laboratory while preparing for testing.

Station	Description	Mortality <sup>2</sup>	pH	Temp. °C	Dissolved Oxygen mg/L.	Alkalinity CaCO <sub>3</sub>	Hardness CaCO <sub>3</sub>
FD-01	Exxon lagoon	5%	6.4	26	6.5	<2	16
FD-02	Below visitor foot bridge	10%	7.7	26	6.7	14	20
FD-03	Below initial leachate	0%	7.8	26	7.0	60	42
FD-04	Below greatest volume of leachate	0%	7.8	26	7.3	78	72
FD-05	Below gully	10%	6.6	26	7.3	40	52
FD-06	Immediately above confluence with James River	0%	7.0	26	6.6	32	40
DOW <sup>3</sup>	Well water	0%	7.7	26	6.7	280	320

<sup>1</sup>48-hour tests. Test results are based on two replicates of ten animals each.

<sup>2</sup>Percent mortality is based on an average of both replicates.

<sup>3</sup>Because the Colorado Division of Wildlife's research well water (located in Fort Collins, Colorado) was used as a culture water, it was used for this study as a reference water.



**Table 6.** Results of lettuce, *Lactuca sativa* L., germination tests conducted on sediment elutriates<sup>1</sup> collected from an unnamed tributary in the Fort Darling Unit of Richmond National Battlefield Park, Virginia, June 15-16, 1989.

Stations	Description	Percent Germination <sup>2</sup>
FD-01	Exxon lagoon	73
FD-02	Below visitor foot bridge	70
FD-03	Below initial leachate	93
FD-04	Below greatest volume of leachate	83
FD-05	Below gully	67
FD-06	Immediately above confluence with James River	80

<sup>1</sup>Seven mL of elutriate per petri dish; 48-hours of dark followed by 72-hours of light; temperature maintained at 26°C. Test results are based on three replicates of thirty seeds each.

<sup>2</sup>Germination in controls tested in EPA reconstituted water (hardness = 75 mg/L as CaCO<sub>3</sub>) was 97%.

Results of the priority pollutant analysis of tributary water and sediments, sampled on December 6, 1989, did not indicate elevated concentrations of organic pollutants, but did indicate the presence of high concentrations of metals in the sediments (Table 7). There were no elevated concentrations of metals in water samples collected from stations FD-03 or FD-04 except for concentrations of iron which averaged about 21 mg/L at station FD-03 and about 8 mg/L at station FD-04. Further, there were no significant differences in metals in the unfiltered samples when compared to filtered samples which indicated that the metals in the water at these two stations were in the soluble fraction. In contrast, sediments from the two stations indicated (1) the presence of metals in the mg/kg range concentrations and (2) that sediments sampled from station FD-03 had metal concentrations two to four times greater than sediments sampled from station FD-04 (Table 7) located further downstream.

Chronic daphnid tests on tributary water collected on October 11, 1990, below the initial leachate (station FD-03), and immediately below the greatest volume of leachate (station FD-04), did not reveal significant ( $p=0.05$ ) daphnid lethality or reduced reproduction at any dilution (Table 8). There were also no significant differences in toxicity between reference waters (EPA reconstituted and Poudre River, Colorado water) or upstream tributary water.

Finding substantial metal concentrations in sediments and elevated iron concentrations in water collected on December 6, 1989 but not finding toxicity to laboratory animals or plants

suggested that metals were not a toxic factor in the tributary. Further, there was no evidence of chronic toxicity to daphnids tested in tributary water sampled on October 11, 1990. However, the question of metals coming from sources other than the landfill prompted additional sampling of metals in the tributary basin. Results of water sampling on July 24, 1991, suggested that the primary sources of metals, such as aluminum and iron, were entering the tributary via the leachates at, and immediately below station FD-02, and increasing in concentration at station FD-03 (Table 9). Although discoloration was not observed when sampling at station FD-02, aluminum and iron were detected in the water, indicating that these metals may be naturally occurring in the basin soils. However, based on data at the downstream sites, more iron and aluminum, as well as additional metals, appear to enter the tributary via the leachates above stations FD-03, FD-04, and FD-05. Additional metals were detected at station FD-06.

Results of July 24, 1991, sediment sampling and analyses indicated the presence of substantial metal concentrations (Table 10). The highest concentration of aluminum was 36,700 mg/kg at station FD-03, the highest concentrations of copper, zinc, and lead were identified at station FD-04, and the highest concentrations of nickel, cadmium, and iron (51,600 mg/kg) were at station FD-05.

Independent priority pollutant analyses were conducted July 24, 1991, and April 17, 1992, on water samples collected from four monitoring wells (MW) constructed in the Chesterfield County Landfill (Figure 1). The NPS with a cooperative agreement with Colorado State University through a contract laboratory conducted the first analysis in 1991. The second analysis (1992) was conducted by Chesterfield County, Virginia, through a contract laboratory. Data from both analyses did not reveal high concentrations of inorganics or organics in any of the wells although the presence of organics indicated the possibility of industrial contamination. The NPS analysis identified 1,2-dichloroethene at 11.0  $\mu\text{g/L}$  and tetrachloroethene at 18  $\mu\text{g/L}$  in MW-3 and chloroform was measured at 68  $\mu\text{g/L}$  in MW-4. By comparison, the Chesterfield County analysis indicated that MW-3 contained chloromethane at a concentration of 7.0  $\mu\text{g/L}$ ; dichlorodifluoromethane at 11  $\mu\text{g/L}$ ; 1,2-dichloroethenes (total) at 21  $\mu\text{g/L}$ , and trichloroethene at 12  $\mu\text{g/L}$ . Monitoring well MW-3 was the only well that indicated a match of chemically-related organic compounds in both analyses. Because MW-3 and MW-4 are located at the south boundary of the landfill (Figure 1) and the ground water flows northeast to the James River, it is possible that MW-3 and MW-4 are influenced by organics originating outside park boundaries. Most important, though, was that in both analyses the metal concentrations were low, just above the instrument's limits of detection. It is important to note for purposes of discussion later, that the pH values of the ground water obtained from the monitoring wells were acidic. For example, on July 24, 1991, MW-1, MW-2, MW-3, and MW-4 had pH values of 6.3, 5.0, 5.6, and 3.8, respectively. On April 17, 1992, MW-1, MW-2, MW-3, and MW-4 had pH values of 5.6, 5.0, 5.5, and 4.7, respectively.

**Table 7.** Concentrations of elements identified in unfiltered and filtered<sup>1</sup> tributary water and sediment collected at sampling stations FD-03 and FD-04 on December 6, 1989 in the Fort Darling Unit of Richmond National Battlefield Park, Virginia.

Sample Sites →	FD-03 Below initial leachate			FD-04 Below greatest volume of leachate		
	Unfiltered Water (mg/L)	Filtered Water (mg/L)	Sediment (mg/kg)	Unfiltered Water (mg/L)	Filtered Water (mg/L)	Sediment (mg/kg)
Aluminum	<0.1	<0.1	13,700	<0.1	<0.1	7,300
Iron	21.4	21.6	17,600	8	8.39	1,610
Manganese	1.68	1.69	300	1.18	1.69	100
Titanium	0.02	0.01	800	0.02	0.01	600
Zinc	<0.01	<0.01	99	0.01	0.01	27
Nickel	<0.01	0.01	9.1	0.01	0.01	4.1
Barium	0.21	0.21	266	0.15	0.15	46
Vanadium	0.01	<0.01	170	0.01	<0.01	28
Arsenic	0.002	0.002	8.8	<0.001	0.001	7.7
Chromium	<0.01	<0.01	25	<0.01	<0.01	12
Strontium	0.11	0.12	23	0.09	0.09	6
Copper	<0.01	<0.01	16	<0.01	<0.01	5
Molybdenum	<0.01	<0.01	4.3	<0.01	<0.01	<1.0
Cadmium	<0.01	<0.01	1.2	<0.01	<0.01	<1.0
Lead	<0.05	<0.05	28	<0.05	<0.05	15
Selenium	<0.001	<0.001	1.2	<0.001	<0.001	0.7
Mercury	<0.001	<0.001	<0.05	<0.001	<0.001	<0.05
Silicon <sup>2</sup>	6.12	6.19	---	7.6	7.65	---
Boron <sup>2</sup>	0.54	0.54	---	0.28	0.29	---

<sup>1</sup>Water samples were filtered through a 0.45  $\mu$ m membrane. Elements that pass through the membrane are considered as the dissolved fraction (U.S. EPA 1984a).

<sup>2</sup>Silicon and boron were not reported in the sediment samples because they require special digestion methods prior to analysis by ICP.

**Table 8.** Results of seven-day chronic<sup>1</sup> daphnid (*Ceriodaphnia dubia*) tests conducted on tributary water collected from stations FD-03 and FD-04 on October 11, 1990, in the Fort Darling Unit of Richmond National Battlefield Park, Virginia.

Station FD-03		Dilutions <sup>2</sup>			
	100%	75%	56%	32%	10%
Percent survival	100	100	90	90	90
Reproduction, mean $\pm$ SD (# young/female)	27.1 $\pm$ 3.7	27.3 $\pm$ 4.2	26.3 $\pm$ 4.6	25.3 $\pm$ 4.7	26.6 $\pm$ 2.3
Hardness <sup>2</sup> (mg/L as CaCO <sub>3</sub> )	58	63	70	175	178
Alkalinity (mg/L as CaCO <sub>3</sub> )	55	42	55	49	58
pH	6.7	6.6	6.7	7.1	6.9
Station FD-04		Dilutions <sup>2</sup>			
	100%	75%	56%	32%	10%
Percent survival	100	100	100	100	100
Reproduction, mean $\pm$ SD (# young/female)	17.7 $\pm$ 3.5	23.6 $\pm$ 2.9	21.0 $\pm$ 2.3	30.1 $\pm$ 4.3	23.3 $\pm$ 2.2
Hardness <sup>3</sup> (mg/L as CaCO <sub>3</sub> )	68	70	51	82	148
Alkalinity (mg/L as CaCO <sub>3</sub> )	70	58	54	54	46
pH	6.9	7.3	6.7	7.3	6.6
Reference waters <sup>4</sup>	EPA reconstituted		Poudre River, Colorado		
Percent survival	100		100		
Reproduction, mean $\pm$ SD (# young/female)	27.6 $\pm$ 8.7		29.3 $\pm$ 7.3		
Hardness (mg/L as CaCO <sub>3</sub> )	75		52		
Alkalinity (mg/L as CaCO <sub>3</sub> )	46		62		
pH	7.5		7.2		

<sup>1</sup>Test results are based on replicates of ten animals each.

<sup>2</sup>EPA's reconstituted fresh water was used for dilution water because of the possibility of pollutants from sources upstream in the tributary.

<sup>3</sup>Greater dilution of site waters increased hardness. Total hardness is associated with the sum of calcium and magnesium. However, the polyvalent metals such as aluminum, iron, manganese, strontium and zinc, in high concentrations, are also involved in hardness and interfere with a true measure of hardness. Therefore, based on calculations of polyvalent metals in 100% FD-03 water, the true hardness should have been 119 mg/L as CaCO<sub>3</sub> (American Public Health Association 1975).

<sup>4</sup>Two reference waters were used as comparisons for this study: EPA reconstituted and Poudre River, Colorado water. The river water was used as a natural reference that closely resembled the pH, hardness, and alkalinity of the unnamed tributary.



## DISCUSSION AND CONCLUSIONS

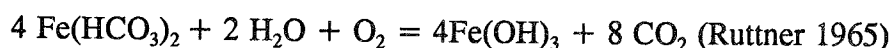
We are not able to address the direct biological limitations of dissolved oxygen and low pH measured during the initial reconnaissance (Table 2) because on-site seasonal or annual data are not available from this tributary.

Concentrations of dissolved oxygen were above 6.2 at all locations in the stream except for sites FD-03 (below initial leachate) and FD-04 (below greatest volume of leachate) which measured 3.6 and 2.8 mg/L, respectively. The low concentrations at these two sites probably reflect oxygen-demanding materials in the leachates that entered the stream. These could have been organic substances from the landfill, from upstream sources, or leachate metals that were being oxidized from either the landfill or from upstream sources. In addition, due to the extreme cut banks and heavy vegetation cover along the tributary, there was minimal opportunity for photosynthesis to appreciably increase the amount of oxygen in the water. However, during the acute and chronic tests in the laboratory, ranges of dissolved oxygen in the tributary water and sediment samples were compatible with the maintenance of test species under laboratory conditions (Tables 3-5). One possible reason for increases in dissolved oxygen in samples during the toxicity tests is that oxygen is introduced during disturbance of the sample while obtaining it. Also, the preparation of the sample for testing increases the dissolved oxygen concentration. Further, the tests are conducted in containers with a large ratio of surface area to volume that promotes the maximum exchange of gases during the tests. It is imperative during the tests to maintain oxygen concentrations at 60% saturation to avoid the confounding effects of low dissolved oxygen and toxicants that might be involved.

The pH of samples collected on June 16 from the tributary ranged from 5.3 to 6.1 (Table 2). In order to obtain reference water in the vicinity of the landfill which was more neutral and relatively free from urban development, other streams were investigated as possible reference sources. On June 15, 1989, the pH of a small stream about 9.6 kilometers away from the site known as Licking Creek had a pH of 4.2, whereas the pH of a small stream flowing from Chickahominy Bluff, located about 12.8 kilometers from the landfill, had a pH of 5.9 and was also influenced by urban development. Because we could not find a suitable field reference site, it was decided to use a laboratory-derived water as the reference medium.

During the process of collecting, shipping, and testing water samples in the Fort Collins, Colorado laboratory, pH of the water samples increased. This increase in pH was possibly due to the alteration of sample characteristics during holding time. The pH in the laboratory ranged from 6.5 to 7.6 in the fathead minnow tests (Table 3) and 6.4 to 7.8 in the daphnid tests (Table 5). We instituted precautions against such changes by maintaining the sample at 4°C and initiating testing immediately upon receipt of the samples at the laboratory. One explanation for this change is due to a change in metals from the reduced to oxidized form. For example, if the iron within the sediment was in the form of ferrous bicarbonate,  $\text{Fe}(\text{HCO}_3)_2$ , and the sample was aerated, oxidation to insoluble ferric hydroxide could have

taken place according to the following formula:



With the precipitation of the ferric hydroxide and evolution of carbon dioxide, the pH would have shifted towards a more alkaline condition.

The results of acute toxicity tests and chemical analyses on water and sediments suggest that the threat of leachates from the landfill on the unnamed tributary's aquatic communities within the Fort Darling Unit of Richmond National Battlefield Park are minimal. No acute toxicological effects of tributary water were observed in the tests with the daphnids or larval fathead minnows. Elutriates from the sediments were tested for toxicity using amphipods and lettuce seeds germination. No acute toxicity to the amphipods was observed, and although diminished germination of the lettuce seeds was observed after exposure to the elutriates, the percentage of germination was greater in samples collected from stations below the prominent areas of leachates, FD-03 and FD-04, than either above or below these sites (Table 6).

Perhaps the most definitive test for determining toxicity was the chronic tests using the daphnids on water samples from stations FD-03 and FD-04 (Table 8) where there was no evidence of chronic toxicity. The importance of the daphnid test is that it encompasses about two and a half life cycles of the species where the endpoints involve survival and reproduction. Diminished survival and/or reproduction, if observed, are considered important. The first observation was that there was no dose-response relationship of survival or reproduction with percentage dilution of the site waters. Average survival of the daphnids in all dilutions was  $\geq 90\%$  and average reproduction in all waters equalled or exceeded 17.7 young per female. Although less reproduction was found in 100% site water from station FD-04, the variability in reproduction of each individual prevented the findings as significant.

Priority pollutant analyses did not reveal organic compounds in the tributary, but many metals were identified. Aluminum and iron in the sediment samples were measured in the thousands of parts-per-million concentrations (Tables 7 and 10). Zinc, nickel, arsenic, chromium, copper, cadmium, and lead were also detectable in sediments. However, relatively low metal concentrations were identified in the water samples (Tables 7 and 9). Iron identified in water collected from stations FD-03 and FD-04 ranged from 8 to 21.6 mg/L and manganese ranged from 1.18 to 1.69 mg/L (Table 7). In a later sampling of water, aluminum ranged from  $<0.1$  to 13.1 mg/L; iron ranged from  $<0.01$  to 8.48 mg/L; and manganese ranged from 0.04 to 2.71 mg/L (Table 9).

In general, concentrations of metals appear to increase in the water (Table 9) and sediments (Table 10) downstream from where the leachates confluence with the unnamed tributary. However, there were some exceptions. Aluminum, iron, manganese, copper, zinc, molybdenum, and cadmium were identified in water and sediment samples collected from site FD-02 which is believed to be upstream from the influence of the leachates (Tables 9 and 10).

Aluminum and iron were high in water and sediments at station FD-03 and in general, were attributable to the leachates. In sediments, manganese measured highest at station FD-03, copper, zinc, and chromium were highest at FD-04, and iron and nickel were highest at FD-05. Also, lead was two orders of magnitude higher at FD-04 than at upstream station FD-02. An interesting observation is that since metals were identified at upstream station FD-02. Are some metals entering the tributary from some other source/s upstream or are they naturally occurring in the soils? Perhaps this is an appropriate future study. Comparisons of metals in water collected at station FD-03 suggest additional monitoring may be necessary to determine their frequencies and sources. For instance, aluminum was  $< 0.1$  mg/L in tributary water obtained on December 6, 1989 (Table 7) whereas 13.1 mg/L of aluminum was measured in water obtained seven months later on July 24, 1991 (Table 9). This suggests that wide fluctuations in aluminum are occurring in the tributary.

Concentrations of aluminum, copper, and cadmium in water collected from the tributary were above the acute water criteria (established by the EPA based on a hardness relationship value of 50 mg/L). Acute criteria for metals are typically derived on the basis of a one-hour average concentration that is not to be exceeded more than once in three years on average. The protection provided by the acute value is mathematically-derived to provide protection against an acute concentration for 95% of the species in a national database. In water collected on July 24, 1991, from stations FD-02 and FD-03, aluminum concentrations were measured at 3.6 and 13.1 mg/L respectively—concentrations above the acute EPA criterion of 0.75 mg/L (U.S. EPA 1988).

Copper and cadmium concentrations, identified in samples collected from station FD-02 on July 24, 1991, were also greater than EPA's chronic criterion of 0.009 mg/L for copper (U.S. EPA 1984b) and 0.0018 mg/L for cadmium (U.S. EPA 1984c). Generally, a chronic metal criterion is typically derived to provide species protection based on a value not to exceed a four-day average metal concentration more than once in three years on average. The derivation of a chronic criterion is based on the ratio of acute and chronic values from life-cycle tests. Although some of the acute and chronic criteria were exceeded in the tests for metals, the chemical form of the metal, i.e., whether it is dissolved, ionized, or bound to complex inorganic or organic materials, determines its availability and hence, its toxicity to test species (Nelson et al. 1986).

The absence of a permanent aquatic community may be due to physical factors in the basin. The first may be a lack of permanent substrates in the tributary which is needed for the colonization of primary producers (plants) and consumers (macroinvertebrates). The only "permanent" substrates are the red-orange oxides which form precipitates that armor the tributary. Another physical factor is the periodic release of water from the Exxon lagoon at the tributary's headwaters which flushes out the basin periodically, i.e., including the unconsolidated leachates.

**Table 9.** Metal concentrations (mg/L) identified in tributary water collected on July 24, 1991, in the Fort Darling Unit of Richmond National Battlefield Park, Virginia.

Sampling Sites →  Metals ↓	FD-02 Below visitor foot bridge	FD-03 Below initial leachate	FD-04 Below greatest volume of leachate	FD-05 Below gully	FD-06 (A) <sup>1</sup> Immediately above confluence with James River	FD-06 (B) <sup>1</sup> Immediately above confluence with James River
Aluminum	3.6	13.1	<0.1	<0.1	<0.1	<0.1
Iron	2.53	8.48	0.13	<0.01	<0.01	0.26
Manganese	0.12	0.04	1.25	2.71	0.98	0.85
Copper	0.09	<0.01	<0.01	<0.01	<0.01	<0.01
Zinc	0.03	0.01	<0.01	<0.01	<0.01	<0.01
Nickel	<0.01	<0.01	<0.01	0.01	0.01	<0.01
Molybdenum	0.06	<0.01	<0.01	0.02	0.02	0.02
Cadmium	0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Lead	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Mercury	<0.001	0.003	0.003	0.004	0.003	0.002
Chromium	<0.01	<0.01	<0.01	<0.0	<0.01	<0.01
Barium	0.02	0.06	0.02	0.03	0.03	0.03

<sup>1</sup>Replicate samples collected from the same sampling station were analyzed to determine the inherent variation.

**Table 10.** Metal concentrations (mg/kg) identified in sediment samples collected on July 24, 1991, in the Fort Darling Unit of the Richmond National Battlefield Park, Virginia.

Sampling Sites → Metals ↓	FD-02 Below visitor foot bridge	FD-03 Below initial leachate	FD-04 Below greatest volume of leachate	FD-05 Below gully	FD-06 (A) <sup>1</sup> Immediately above confluence with James River	FD-06 (B) <sup>1</sup> Immediately above confluence with James River
Aluminum	27,600	36,700	21,700	28,400	7,340	7,630
Iron	9,650	26,800	23,500	51,600	26,800	11,800
Manganese	190	330	180	120	130	200
Copper	6	10	12	10	6	6
Zinc	42	28	63	42	28	21
Nickel	6	7	10	12	4	4
Molybdenum	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cadmium	0.3	1.1	1.3	2.7	1.5	0.6
Lead	<0.1	3	93	17	16	6
Mercury	<0.05	<0.05	<0.05	0.09	<0.05	<0.05
Chromium	3.2	1.2	10.7	10.6	9	4.1
Barium	50	108	113	132	46	60

<sup>1</sup>Replicate samples, collected from the same sampling station, were analyzed to determine the inherent variation.

Fort Darling and the landfill rest on unconsolidated valley-fill alluvium of the James River valley. Local geologic formations contain an iron-rich mineral, glauconite  $[K_{1.5}(Fe,Mg,Al)_{4-6}(Si,Al)_8O_{20}(OH)_4]$ , from which the alluvium may be derived. A high iron content was verified in a petrographic study of core samples taken from the landfill cover and tributary banks. In addition, soluble iron of 30 mg/L was measured in water sampled from MW-3 by Chesterfield County on November 26 and 27, 1990 (Central Virginia Laboratories & Consultants 1990). As water moves through the landfill under acidic pH conditions of 4.7 to 5.6, iron is probably mobilized in the reduced state as  $Fe_2+$ . Although it was not possible to verify, iron could continue to be in the  $Fe_2+$  reduced state in the cavity of the landfill. After surfacing as leachate and entering the tributary, the iron is oxidizing and precipitating from the water in a colloidal or amorphous state, "scavenging" or taking the other minerals out of solution. Other

research suggests that the hydrous oxides of manganese and iron furnish the principal control on the sedimentation of cobalt, nickel, copper, and zinc in soils and freshwater sediments (Jenne 1968). Although metals in the tributary water were measurable and sediment metals were identified in the high parts-per-million, the absolute concentrations of metals are not reliable predictors of toxicity. As was noted by Chapman and McCrady (1977) in their work with copper toxicity, it is not the concentration of—but the form of the metal that determines its availability and toxicity to organisms.

It is highly probable that the toxicity tests, conducted on shipped samples from Fort Darling, could have provided different results if "fresh" samples had been tested the day of collection. Unfortunately, this was not possible. In studies conducted elsewhere (Nimmo et al. 1990), investigators identified toxicity in samples obtained from three mining sites when tested the same day. In a related study in which the metal manganese was present at high concentrations from a tailings drain, toxicity to daphnids and fathead minnows was not identified when the sample was held at 4° C for only 24 hours, but was identified when tested the same day it was collected. When collected, the sample with manganese appeared clear but within an hour, an observed reddish precipitate had begun to form and deposit on the bottom of the sample container. Future toxicological analyses of the water and sediments in the basin should include the testing of "fresh" samples instead of shipped samples.

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