Appendix S10
(Final Product)

FINAL REPORT

Risk Assessment and Evaluation of Selected Virginia Sites within the Coastal Zone
(SE-VDWM-4482-90)

CENTER FOR RISK MANAGEMENT OF ENGINEERING SYSTEMS

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FINAL REPORT

Risk Assessment and Evaluation of Selected Virginia Sites within the Coastal Zone

(SE-VDWM-4482-90)

Submitted to
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Department of Waste Management
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by

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Risk Assessment and Evaluation of Selected Virginia Sites within the Coastal Zone

FINAL REPORT

I. SUMMARY OF PROJECT GOALS

Specific goals for this project were outlined in the second quarter report dated April 6, 1990. The final agreed upon goals are as follows;

Evaluation of three potentially problematic sites. Site 1- Cheatham Annex in Williamsburg, VA., 2- L-Wood Wood Preservers in Kent, Va., and 3- Republic Creosoting.

Site 1 Cheatham Annex

1- Assess the hydrologic input and output of Hipps Pond.

2- Sample and analyze the pond sediments and water from varying depths for PAH's and the EP toxic metals.

3- Install nested pizometers to evaluate gradients around the pond.

4- Remeasure targeted analysis in both existing GW monitoring wells and in the several streams on the site.

5- Install seepage meters along the stream in the north ravine to investigate groundwater and surface water migration or contamination. Inject a sodium bromide tracer into the head of the stream to make dilution measurements.

Site 2 L-Wood Wood Preservers

1- Establish current levels of chromium, copper, and arsenic (CCA) concentrations in the ground water.

2- Evaluate surface water runoff for CCA.

3- Evaluate soils for CCA.

4- Perform a bench study of the leaching potential of treated lumber and soils from the site.

5- Model groundwater flow in an effort to evaluate back pumping existing ground water contamination into the on-site recycling system.

Site 3 Republic Creosoting

1- Assess published data on the following topics;

PAHs in sediments
Other Elizabeth River PAH problems
Tidal effect
Human and aquatic toxicity of PAHs

2- If possible pursue a PAH leaching study, varying physical conditions that may exist on the site.

A summary of a "Framework" for storing, compiling, comparing, and evaluating data has been developed. This framework could assist the staff of the Department of Waste Management in organizing information, making decisions, and planning strategies in dealing with complex non-NPL sites.

II. Evaluation of the Cheatham Annex Site

See separate report.

III. Evaluation of L-Wood Site

A. Summary of problem

L-Wood wood preservers is an approximately 16 acre site located in Kent, Virginia. Recent evaluations of the ground water at this site showed elevated levels of chromium in one well.

The primary source of contamination was the front of the pressure chamber where the treatment process takes place. The owners have installed a drip pad and more recently an awning for the pad. Secondary contamination may be taking place from the stored materials on the site. Treated lumber is stored on the site.

There is a question as to whether or not already contaminated ground water could be back-pumped and used to wash down the drip pad. The water would then go through the on-site treatment process.

A prominent mechanism for chemical movement is by mass transport through porous soil media. Contaminants distributed in the soil can move with water and potentially could contribute to surface and ground water contamination problems. Understanding how these compounds move is of prime importance in determining whether or not a source is contributing to contamination of water systems.

There are many factors in evaluating migration. Several are;

1) Solubility of the contaminants in water (under different conditions)

2) Partition Coefficient (Octanol Water)

3) pK (the behavior of weak acids and bases on the extent to which they exist as neutral or charged species)

4) Adsorption of contaminants onto solid phase materials

5) Water flow conditions, etc.

The L-Wood site has several specific problems. Copper, Chromium, and Arsenic (CCA) treated lumber is allowed to dry on the drip pad for 24 hours prior to storage on the main lot. There the surface has potential for direct contact. What is the level (potential) that CCA will leach from the dried treated lumber? What is the level (potential) that CCA will leach from the surface soils? How does this affect surface water and groundwater contamination?

The specific goals of the In Lab Leaching Evaluation is to determine how easily CCA can be released from their bound medium (sediment and mulch) into water, under varying conditions (salinity and pH). This will give us insight into the potential for these sources to contribute to Copper, Chromium, and Arsenic contamination of the wetland area behind Kent Wood.

B. Field survey and sampling

The field work focused around several goals;

1) Establish current levels of copper, chromium and arsenic (CCA) in the three existing wells.
2) Evaluate surface water run-off for CCA.
3) Evaluate soils for CCA.
4) Collect materials to perform in-lab leaching study of treated lumber and contaminated soils.

We did not sample the wells at the site nor were we able (financially) to install new wells to evaluate. Only one of the existing wells was in operable condition. The other two, one was broken off and the other was buried. This site has a history of voluntary compliance and support for both the Department of Waste Management and the Water Pollution Control Board. The water quality has been evaluated several times in the last ten years.

There was no surface water on the site available to sample on either of our two trips to the site.

The sampling site trip was conducted under the supervision of Mr. Glenn Metzler of the Department of Waste Management on June 26, 1990. Samples were collected to perform the leaching and soil studies.

1. Samples for the leaching study.

Ten samples of wood and soil from the site were collected. The samples collected for analysis are as follows;

sample #	type sample	description

#1	Treated wood	(wet)
#2	Treated wood	(wet)
#3	Untreated wood	
#4	Untreated wood	
#5	Contaminated soil	
#6	Contaminated soil	
#7	Uncontaminated soil	
#8	Uncontaminated soil	
#9	Treated wood	(dry)
#10	Treated wood	(dry)

2. Samples for the soil study

The same samples collected for the leaching study were used in the total metals evaluation. Samples of the wood were also analyzed. Both contaminated and uncontaminated samples were analyzed.

Notes: wet wood samples for both studies were removed from the pressure chamber just prior to leaving the site. Samples began the lab leaching study within 96 hours. The dry sample was a piece of lumber that had been out of the chamber for greater than one week (according to site supervisor). There were four contaminated soil samples collected, the first sample was used for the leaching experiment. The contaminated soil samples were taken where the ground had a greenish color. The samples were surface soils less than 2 inches deep.

Analytical Results

1. Leaching study

Samples of each sample type (250g) were placed in 3 liters of distilled water. Acetic acid was used to adjust half of the samples to ph 2. The samples were continuously shaken during the entire experiment. 100 ml aliquots were withdrawn at 24 hours, 48 hours, and 96 hours. The extracted alequots were subsequently analyzed by Atomic Absorbtion Spectroscopy for Copper, Chronium, and Arsenic concentrations. (EPA methods 7210, 7190, and 7061 respectively). The EPA's EPTox procedure is similar with the following basic differences;

1- 100 grams of sample is placed in 2 liters of water
2- the ph is adjusted to <ph5 (not to ph2) with acetic acid.
3- only one sample is evaluated (at 24 hrs.).

(Ref. "Chemical Concepts in Pollutant Behavior," I. Tinsely, Wiley-Interscience, 1988)

The data collected represents a relative concentration of the contaminants. Samples were analyzed between July 26 and July 30, 1990.

The results for these analyses are as follows (mg/L);

		Cu	Cr	As
1	24	<1	3.6	<1
	48	<1	3.6	1.4
	96	1.2	3.6	2.2
2	24	23.2	10.1	8.3
	48	37.5	16.1	14.4
	96	55.8	26.8	20
3	24	<1	<1	<1
	48	<1	<1	<1
	96	<1	<1	<1
4	24	1	<1	<1
	48	1.1	<1	<1
	96	1.3	<1	<1
5	24	<1	<1	<1
	48	<1	<1	<1
	96	<1	<1	<1
6	24	4.8	<1	<1
	48	5.0	2.4	1.1
	96	5.3	3.0	1.9
7	24	<1	<1	<1
	48	<1	<1	<1
	96	<1	<1	<1
8	24	<1	<1	<1
	48	<1	<1	<1
	96	<1	<1	<1
9	24	8.8	4.1	2.3
	48	21.4	8.8	3.9
	96	33.1	14.2	5.2
10	24	<1	<1	<1
	48	<1	<1	<1
	96	1.7	<1	<1

2. Soil analysis

Samples of each material (to include the wood samples) were analyzed for total metal (Cu, Cr, As). Samples of each type (1 gram) were digested in first Aqua-Regia and then Sulfuric acid. Samples were filtered and than analyzed by Atomic Absorbtion Spectroscopy for copper, chronium, and arsenic (EPA methods 7210, 7190, and 7061 respectively). Samples were analyzed between July 26 and July 30, 1990.

The results of these analyses are as follows;

	Total metals (µg/g) Cu	Cr	As
cont wd #1	1211.6	3917.5	556
cont wd #2	552.5	3892.5	496
dry cont wd	1120	5125	322
dry uncont wd	200	51	<25
cont soil #1	104	381	41.1
cont soil #2	96	565	64
cont soil #3	48	332.5	36
cont soil #4	45	295	32
uncont soil	<25	<25	<25

3. Data validation

Data validation of the analytical results was performed for the wood and soil samples analyzed. All samples were analyzed three times and the mean of the runs was the reported value. The data validation process involved an examination of instrument calibration procedures, instrument tuning, sample holding times, blanks, duplicates, interferences, and data assessment. Rejection of outlier values was determined using EPA's Fitness test.

Note: Blank samples were analyzed, their value was used to establish the baseline.

Conclusions

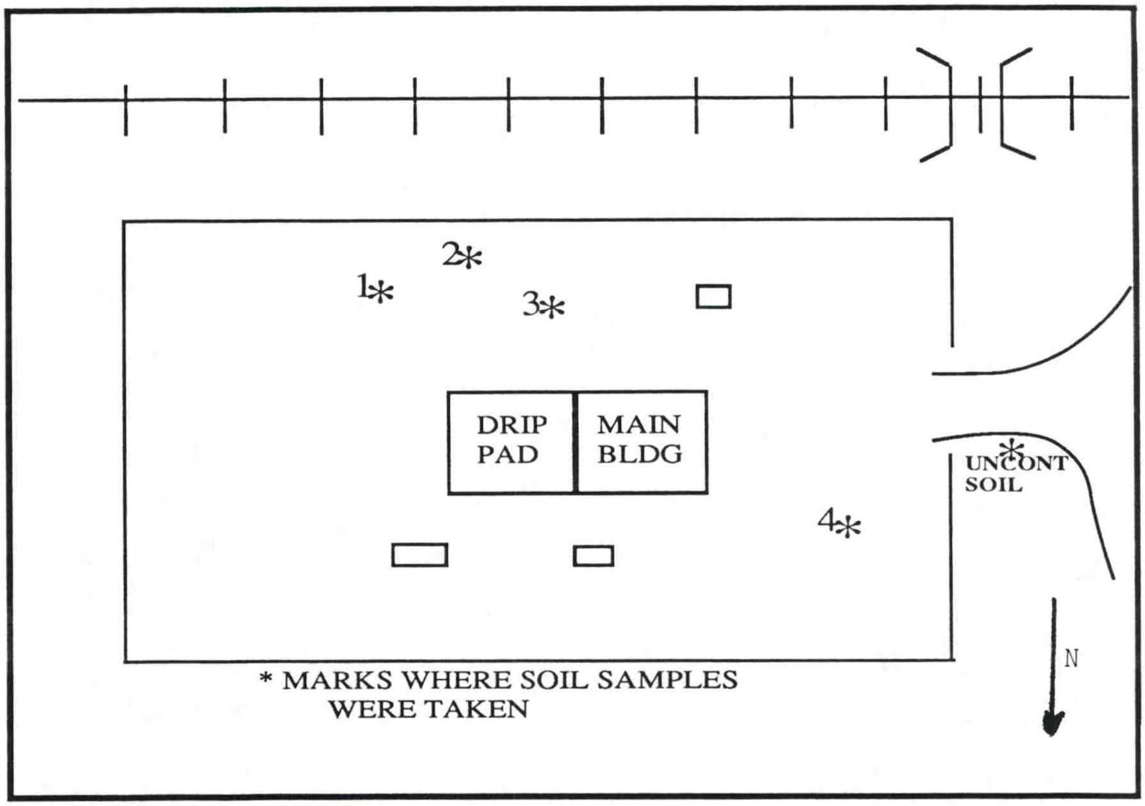
Both the treated wood and contaminated soil can leach. There are several factors which affect the amount of leaching. Time out of the treatment chamber and acidity conditions are the major factors identified. There is a significant increase in the leaching under acidic conditions (both in soil and wood). The "wet" wood, wood collected right out of the pressure chamber showed a four fold increase in leaching.

The results do indicate leaching potential out in the storage yard. The wood can leach to the ground which is evident from the results but also visually evident at the site where there are patches of green dirt under where treated wood is stored. Once in the ground CCA can leach to ground/surface waters.

Recommendations

These results suggest that allowing the wood to dry longer on the drip pad or washing the wood on the drip pad could significantly lower its ability to contribute as a source of contamination.

Another leaching study evaluating length of stay on the drip pad and/or washing conditions may help evaluate alternatives.



MAP #1

C. Groundwater Flow Investigation

The task is to analyze, using existing data, groundwater flow at the L-wood site, and to determine the likelihood that pumping from monitoring well M-1 will reverse the gradient in the water table over a substantial portion of the site.

Approach

The site is approximately 775' by 480', bounded on the south by a C & O rail line, and on the east by woods bordering a pond and a swampy area (Figure 1). A brief description of observations obtained upon a visit to the site included in Appendix 1. In this study, the portion of the groundwater of concern is contained in unconsolidated river terrace deposits extending the surface to approximately 4 meters in depth. This water-table aquifer is bounded below by the Calvert formation which acts as a confining bed.

A simple, steady-state groundwater model of the site was prepared. The finite-difference equations were written for a rectangular area that extended approximately 500 meters to the west of the site, and approximately 40 meters to the south and east of the site. Boundary conditions were fixed at these exterior boundaries to ensure that they would not unduly influence the analysis of the perturbation created by pumping from well M-1. A grid spacing of 7.6 meters was used.

Water level data in four monitoring wells (M-1 through M-4) and in four piezometers (P-1 through P-4) were recorded by Emergency Special Services (ESS) in May 1986 (Figure 1; Sullivan and Kohler, 1989). These data indicate that the shallow groundwater in the river terrace deposits underlying the site drains to the southeast, toward the Chickahominy River.

A plane was fit to the water-table elevation data. This was taken to represent the slope of the water table in the region. The data were extrapolated to the boundaries of the finite-difference grid. The heads at the boundaries were fixed at these values for all simulations.

The finite-difference model for a typical grid point (i,j) is

$$h_{i+1,j} + h_{i,j+1} - 4h_{i,j} + h_{i-1,j} + h_{i,j-1} = Q_{i,j} / T \qquad (1)$$

where T is the transmissivity of the aquifer and $Q_{i,j}$ is the pumping rate at the (i,j) node. To simulate conditions at the L-wood site therefore requires estimates of the pumping rate, Q, and the aquifer transmissivity, T.

The transmissivity is the product of the hydraulic conductivity, K, and aquifer thickness, b. Aquifer thickness at the site is approximately two meters (Sullivan and Kohler, 1989). Measurements of the hydraulic conductivity are not available. Based on the boring logs (the aquifer material is described as a coarse sand), a probable K value would be expected to within the range of 10-4 to 10-2 ms^{-1}.

Wells developed in the shallow aquifer of the Coastal Plain can be expected to yield on the order of 6 x 10-4 m^3s^{-1} (about 10 gpm). An upper limit of about 6 x 10^{-3} m^3s^{-1} might be expected.

A "likely" value of Q/T for the L-wood site is 0.5 m ($T = 2 \times 10^{-3}$ m^2s^{-1}; $Q = 10^{-3}$ m^3s^{-1}). We also considered a Q/T of one order-of-magnitude higher in our analyses.

Results

To answer the question about possible groundwater flow reversals near monitoring well M-1 as a result of pumping from that well, several simulations were performed. The model was run for Q/T = 1m, 0.25m, 0.5m, and 5m. All pumping was assumed to occur at M-1.

With Q/T = 0, the result is a uniform flow to the southeast (Fig. 2a; Fig. 3a). Successively increasing Q/T at well M-1 causes larger areas in the vicinity of the well for which any contaminant plume would be "pulled back" by pumps (Figs. 2b, c, d; Figs. 3b, d). For the "likely" value of Q/T (0.5m), only a relatively small area in the vicinity of the pumping well is strongly affected (Fig. 2c; Fig. 3c). For a Q/T value a factor of ten greater, there is a strong reversal of ground-water glow in the southeast corner of the site.

Conclusion

The reversal of groundwater flow near a pumping well on the L-wood site will be significant only if: 1) the transmissivity of the shallow aquifer is on the order of $2x10^{-4}$ m^2s^{-1} (K of approximately 9.1 m d^{-1} rather 91 m d^{-1}); or 2) pumping could be maintained at 10-2 m^3s^{-1} (about 200 gpm rather than 20 gpm). Additional field study would be required to answer this question definitively.

Appendix 1

On 18 October 1990, Rob Hoelscher and Charlie Hall of the Department of Environmental Sciences, University of Virginia, visited the L-Wood site for a brief assessment of the hydrological factors at the site and to assess what hydrological measurements might be necessary to determine off-site groundwater seepage rates. Generally, the site has very low relief with a low surface gradient oriented towards the lake/swamp area on the eastern boundary. If the attitude of the water table is related to topography, the presence of conspicuous surface drainage features suggests that subsurface gradients should also be aligned towards the east/southeast.

We examined the western margin of the swampy area at the intersection with the site. A fairly well defined escarpment (1m high) is aligned along the margin of the swamp. It is probable that groundwater inflow to the swamp occurs under hydrostatic conditions. That is, the relatively flat groundwater table would supply water to the pond by horizontal seepage. The most effective method of measuring fluxes across the site boundary/swamp margin would be to install several transects of piezometers leading away from the swamp. Tracer tests and/or slug tests could provide further information about the hydraulic nature of the aquifer in the area.

List of Figures

Figure 1. Schematic plan view of the L-Wood site. (from Sullivan and Kohler, 1989)

Figure 2. Contour map of the water table from output or the mathematical model. The arrows indicate the direction of the groundwater flow. The edges of the graphs are the approximate boundaries of the L-Wood site. Labels on the axes are grid point numbers. (20 grid spaces on the y axis, for example, represent a distance of 152.4m or 800 ft.)

Figure 3. Perspective representation of the water table over the L-Wood site. In a), the water table slope from the northwestern corner of the site to the southeastern corner. In b),c), and d) the progressive lowering of the cone of depression as Q/T is increased is shown.

FIGURE 1.

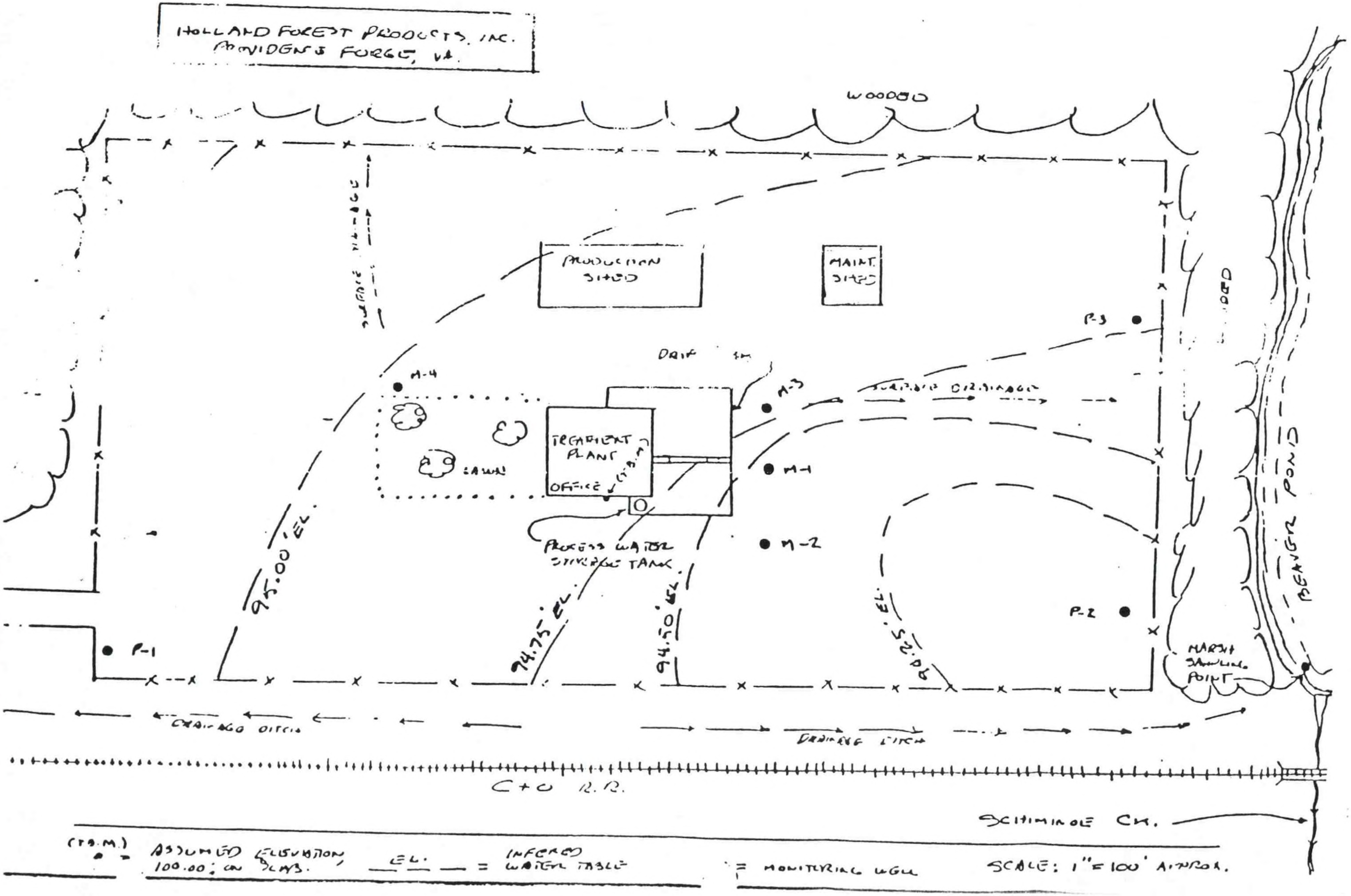
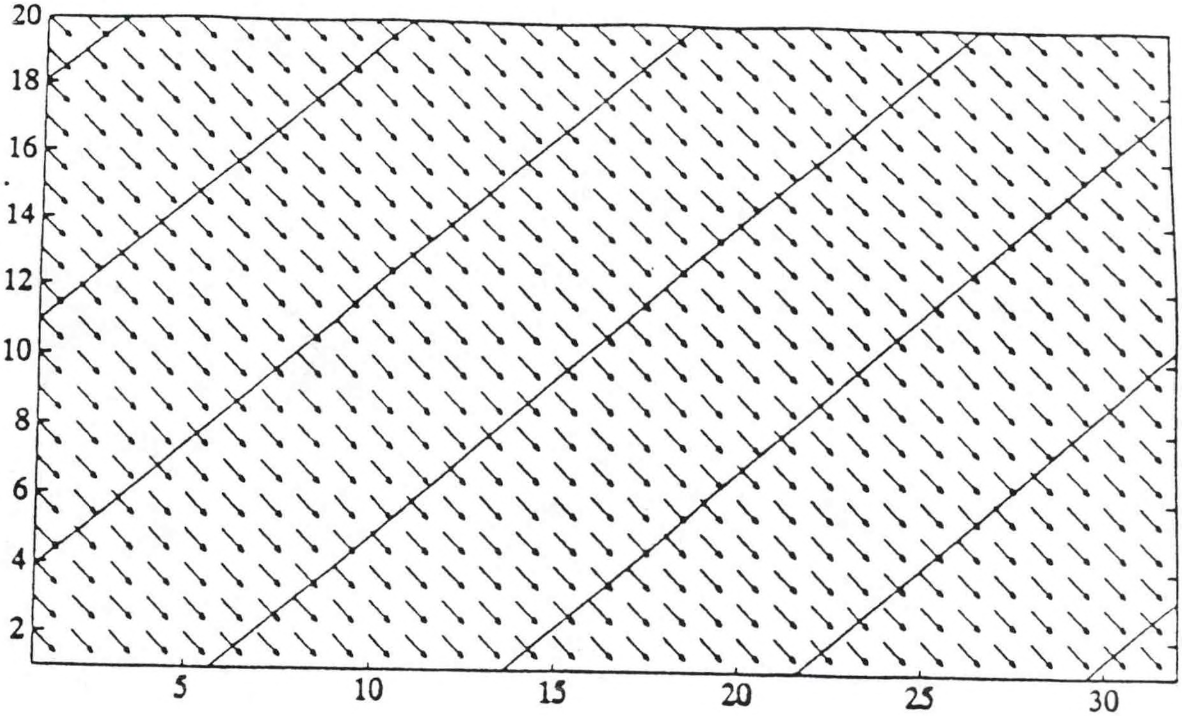
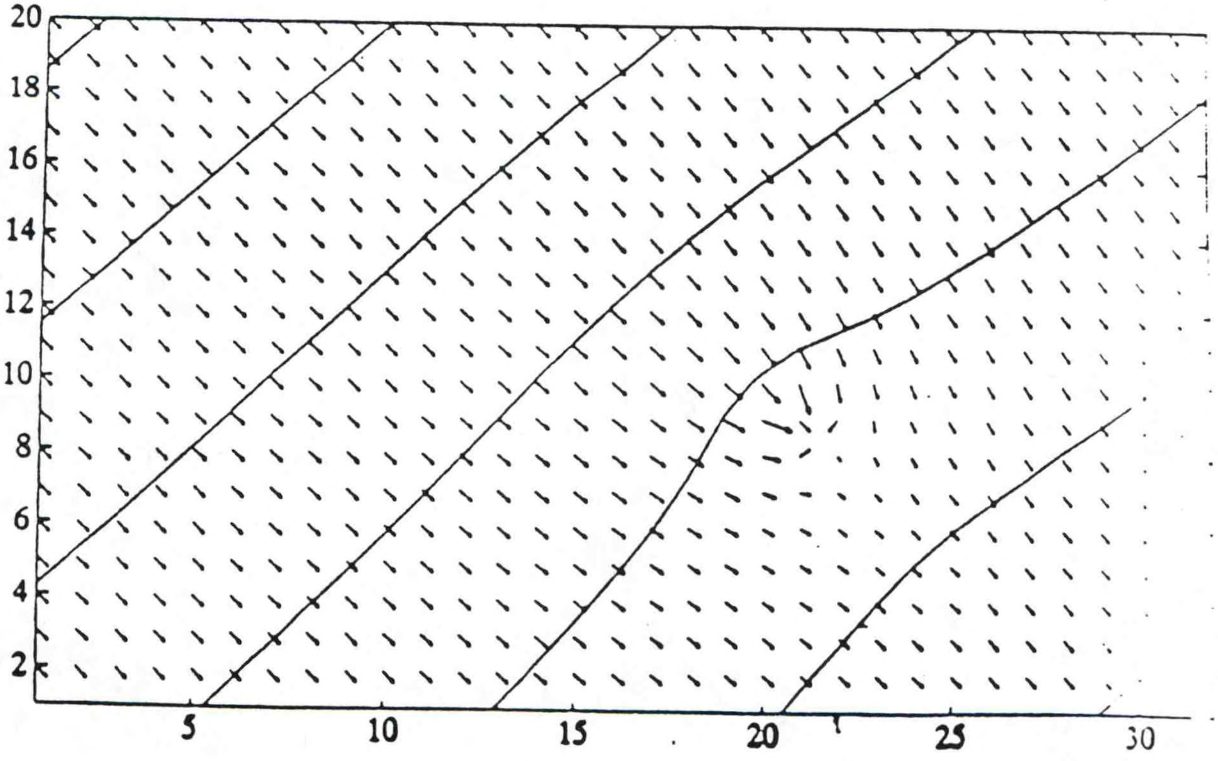

HOLLAND FOREST PRODUCTS, INC.
PROVIDENCE FORGE, VA.
WOODED
WOODED
BEAVER POND
PRODUCTION SHED
MAINT. SHED
SURFACE DRAINAGE
SURFACE DRAINAGE
DRIP SH
TREATMENT PLANT
OFFICE
(T.B.M.)
LAWN
PROCESS WATER STORAGE TANK
M-1
M-2
M-3
M-4
P-1
P-2
P-3
95.00' EL.
94.75' EL.
94.50' EL.
94.25' EL.
MARSH SAMPLING POINT
DRAINAGE DITCH
DRAINAGE DITCH
C+O R.R.
SCHIMINOE CK.
(T.B.M.) ● = ASSUMED ELEVATION 100.00; ON SLAB.
— EL. — = INFERRED WATER TABLE
● = MONITORING WELL
SCALE: 1" = 100' APPROX.

FIGURE 2.

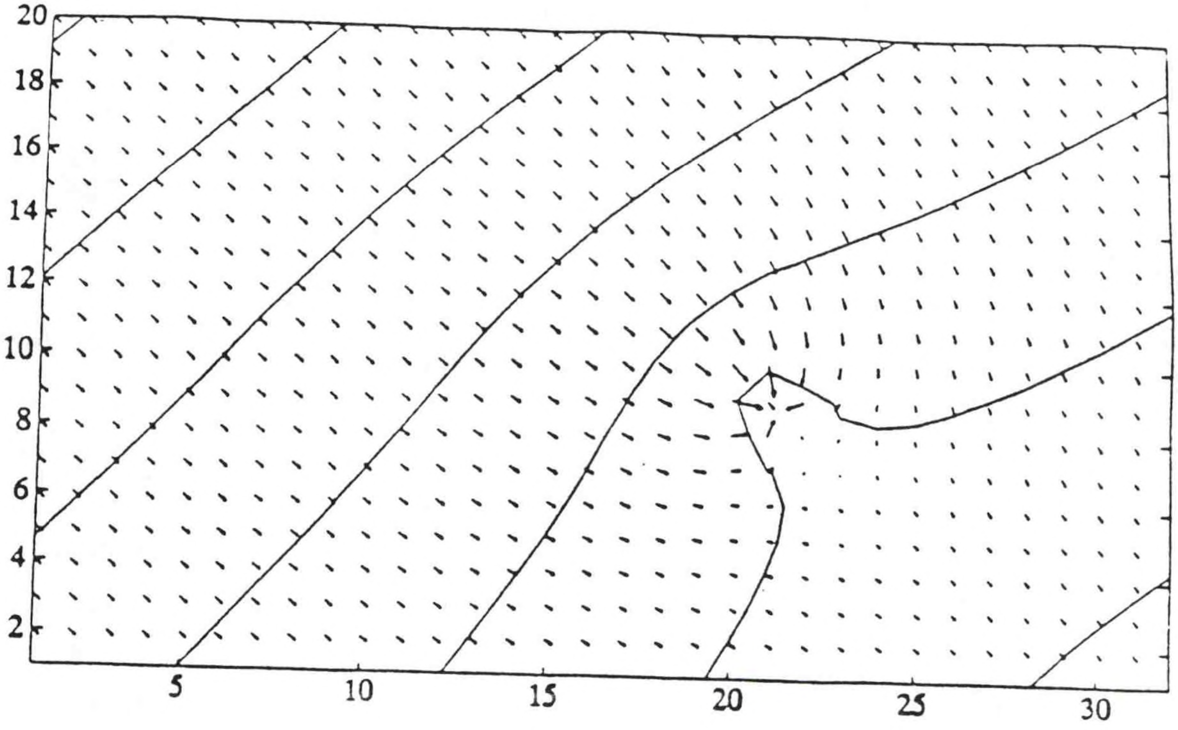


a) Q/T=0 m

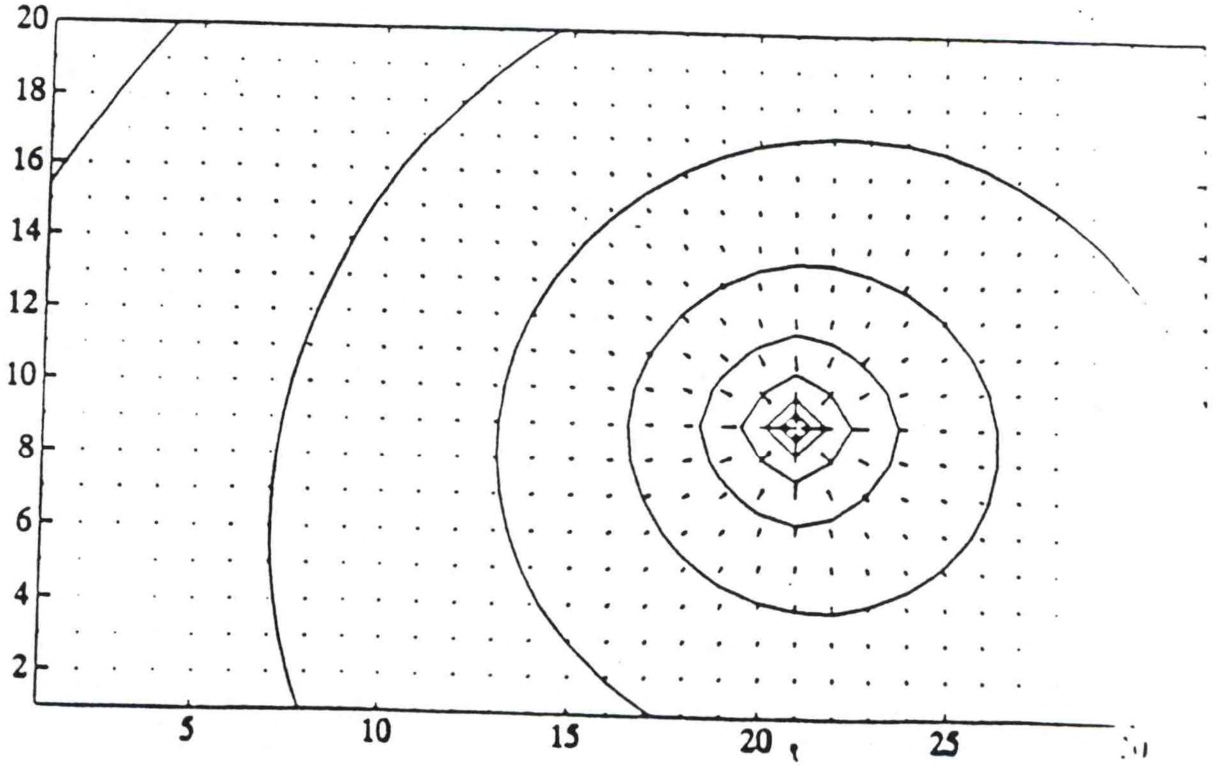


b) Q/T=0.25 m

FIGURE 2 (continued).

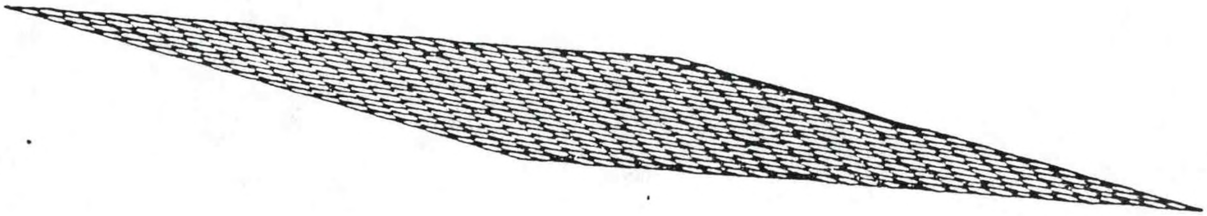


c) Q/T=0.50 m

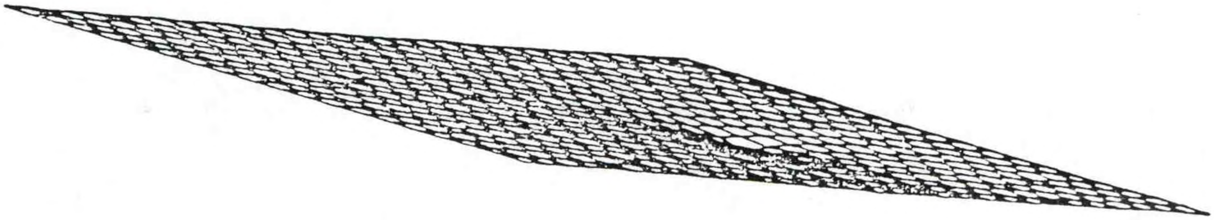


d) Q/T=5.0 m

FIGURE 3.



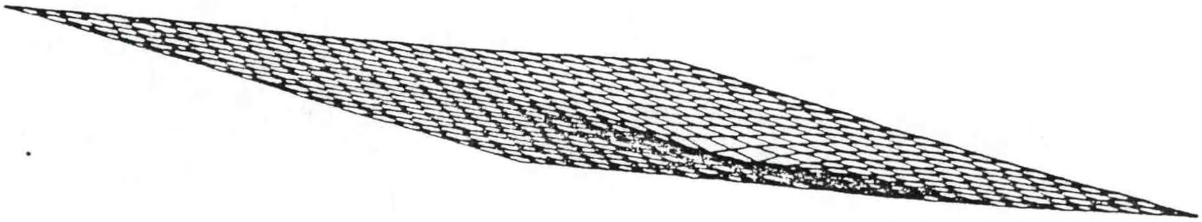
a) $Q/T=0$ m



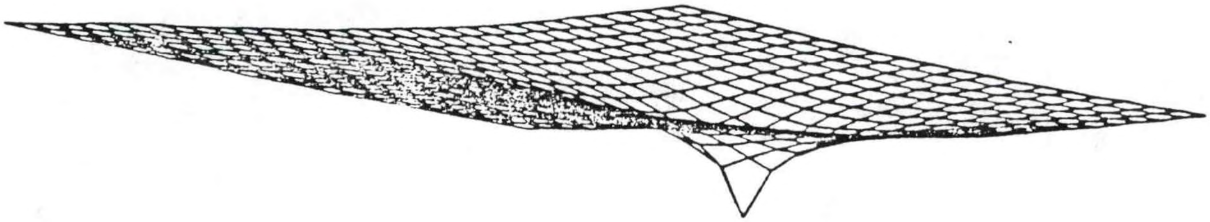
b) $Q/T=0.25$ m

L-Wood site
Department of Environmental Sciences
University of Virgina

FIGURE 3 (continued).



c) Q/T=0.5 m



d) Q/T=5.0 m

L-Wood site
Department of Environmental Sciences
University of Virgina

IV. Evaluation of the Republic Creosoting Site

A. INTRODUCTION

Republic Creosoting Company operated a coal tar and creosote refinery along the Southern Branch of the Elizabeth River in Chesapeake, Virginia, from 1917 to 1972. Specializing in preserving lumber with creosote and tar, this process generated two types of contaminants: pine bark shavings from the treated lumber that were distributed over approximately four acres of the northern portion of the site, and a tar waste that was stored in above ground tanks.

Today, this site, hereafter referred to as Republic Creosote, is owned by McLean Construction Company, who uses the land as a supply yard for their marine construction operations. The two open tanks that were on the site have been removed. They contained roughly 2,000 gallons of dried sludge, highly concentrated with polynuclear aromatic hydrocarbons (PAHs). The four acres of contaminated mulch also contain percentage levels of PAHs. The concern is that PAHs are leaching and migrating into the groundwater and that they are being transported to the Elizabeth River, via surface runoff, thereby contributing significantly to the already high levels of PAHs in this river.

The above perceived problems were summarized by the Department of Waste Management:

> The site, operated by Republic Creosoting Company from 1917-1972, is located in Chesapeake, Virginia, on the south branch of the Elizabeth River. During that time the property was owned by Reilly Tar and Chemical Corp. It is presently owned by McLean Contracting Company which uses it as a supply yard for their marine construction operations. The main activity at the site by Republic was creosote and tar treatment of wood. This also involved refining coal, tar, and creosote. Two open deteriorating tanks, which contain a sludge of nearly 100% polynuclear aromatic hydrocarbons (PNAs), remain on site. There is also a four-acre area of mulch which came from treated lumber shavings. The soils of this area are contaminated with PNAs up to 34%. Aqueous samples from a drainage ditch running through the mulch area contained significant amounts of lead, cadmium, cyanide, and mercury. Lead was also found in high concentrations in the soil near one of the sludge tanks.
>
> The high levels of PNAs are a hazard if contacted. They are severe dermal irritants and can cause skin tumors. They are readily absorbed through the skin, where they exert toxic and/or carcinogenic effects. PNAs bind tightly to soil but they may be carried with it into the surrounding waters. In most organisms they are metabolized quickly, preventing bioaccumulation, but shellfish are an exception. Lead, cadmium, cyanide, and mercury are toxic to aquatic organisms at low concentrations. Samples were also taken from the drainage ditch, which empties into a marshy area adjacent to the Elizabeth River.

Background

POLYAROMATIC HYDROCARBONS (PAH)

Polycyclic aromatic hydrocarbons have a wide range of physical and chemical properties which determine their unique toxicities; several PAHs have been identified by the USEPA as priority pollutants. In August, 1989 Havens Laboratories, Inc. identified percentage levels of seven of these hazardous PAHs in the mulch samples, including acenaphthene, fluoranthene, naphthalene, pyrene, benzo (a) pyrene, chrysene, and anthracene. The physical/chemical properties, including solubilities, parition coefficients (octanol/water), absorption coefficients, as well as degradation and metabolic rates of these compounds, all contribute to the individual leaching and migration patterns of these chemicals in surface runoff and groundwater transport and eventually to the toxicity problems found in the river.

As is the case at Republic Creosote, PAHs are found as a major component of creosote. Creosote is a flammable, heavy, oily liquid. The PAHs themselves, are essentially odorless solids at room temperature, with low vapor pressures and high melting points. The vapors of the caustic creosote liquid can cause ulceration, gangrene, pigmentation, itching, burning, and vesiculation on the skin. Eye complications have been reported, as have cardiovascular collapse and death after ingestion of creosote. The EPA Carcinogen Assessment Group has listed creosote as a carcinogen. It is used as a disinfectant, waterproofing agent, and antiseptic. This coal tar is also used as a wood preservative, such as in treatment of telephone poles, docks and boat landings. Creosote is the distillate produce produced during high temperature carbonization of bituminous coal. In pure creosote, PAHs can comprise up to 90% of the total composition, with the other 10% being aliphatic hydrocarbons. Of the 90% the lower molecular weights PAHs, such as naphthalene, of three or fewer rings, are predominant, and at least 40% of the compounds are USEPA priority pollutants.

The environmental behavior of creosote depends on its chemical composition. In seawater, creosote separates into three fractions, a floating fraction, and sinking fraction, and a fraction that dissolves. This separation results from differences in solubility, molecular weight, and absorption affinity to sediment particles of the various hydrocarbons. The floating layer consists of a creosote mixture of low and high molecular weight PAHs absorbed on fine grain particles which remain suspended in the water, and therefore are easily transported. The sinking layer consists of PAHs probably attached to sediments too heavy to be carried along by the river current. The dissolved fraction is made up of the lowest molecular weight PAHs which are slightly soluble.

SITE

Republic Creosote covers 23 acres in the industrialized region of Chesapeake, Virginia along the Southern Branch of the Elizabeth River. (See site map in Figs. 1 and 2 by NUS Corp.) It lies on the eastern bank at 100 Republic Road. To the north, the site is bordered by Continental Oil Company, Norfolk and Portsmouth Belt Line Railroad to the east, and Lone Star Industries, were on the south central part of the site. Though the plant is no longer in operation, McLean Construction, the present owners, are utilizing original building foundations. Half the property was used in wood treatment processing. Bark shavings from the milling of lumber to be creosoted were disposed of, via land farming, on the northern section of the property. This contaminated mulch area covers about 4 acres, 2-4 feet thick, which as mentioned, McLean Construction now uses as a supply yard for their marine construction operations.

OWNERSHIP HISTORY

Originally, Reilly Tar and Chemical Corporation owned the land, and was operated by Republic Creosote from 1917 to 1972. Lone Star Industries then bought the land, renting it out to a junk dealer, but sold it to McLean Construction Company in 1976. McLean Construction is a dredging company which operates all along the river.

ENVIRONMENTAL SETTING

Water Supply: The public water supply comes from Norfolk Water Works, which does not utilize groundwater but relies on reservoirs. These reservoirs are Little Creek, Lakes Lawson, Smith, Whitehurst, and Wright, and are located approximately 8 miles northeast of the site. There are no private wells in use near Republic Creosote. (Norfolk Water Works.)

Surface Waters: Republic Creosote lies in an estuarine area, subject to tidal influences. The Southern Branch of the river flows north, into the Chesapeake Bay. According to the Virginia State Water Control Board, this river is used for recreational purposes, such as crabbing and fishing. (NUS 1984.) Workers at the site reported to us that the site floods 2 to 3 times each year.

Geology and Soil: Located within the Virginia Coastal Plain Province, the site sediment consists of marine deposits, underlain by nonmarine deposits. There exists unconsolidated sand, silt, clay, gravel, and shells. The permeability of these soils is reported as being moderately slow, ranging from 0.2 to 0.6 inches per hour.

Groundwaters: The water table ranges from the surface to a depth of one foot below the surface. There exist three acuifers, which are: The Water Table Aquifer, the upper Artesian Aquifer or Yorktown Aquifer, and the lower Artesian. Due to the location along the banks of the Elizabeth River, the groundwater tends to be salty. (NUS 1984.)

In 1984, NUS Corporation did a field study which found the mulch area heavily contaminated with PAHs. This was not surprising, as the mulch came from creosote treated wood chippings. From their sample data summary it was revealed that the only water sample which contained contaminant was located at the edge of the mulch fill area in the drainage ditch. Also, the mulch areas as not covered at this time, leaving the mulch exposed to surface water runoff. No testing to check for migration and soil leaching was done downstream of this area.

Havens Laboratories Inc. performed soil and surface water analyses in 1989. By this time, McLean Construction Corporation had covered the mulch fill area with 2-6 feet of dredging sediment (observed during site trips). Subsequent testing revealed PAHs in the sediment and mulch, with none in the water samples. There appeared to be Aquatic biota thriving around the site, in many of the surface water pools although no specific kiota evaluation was performed.

Total metals analysis and EPTOX metals analysis performed by Havens Laboratory shows little contamination for many samples (see Tables 1-2 for results of the metals determinations and Table 3 reports on the PAH analysis).

The fact that PAH contamination was only found in sediment and soil samples correlates with absorption characteristics of PAHs. As mentioned, PAHs have a strong affinity for organic compounds, making its attachment to the mulch strong. Also, the greater size of the mulch contributed to the PAH affinity here. If the PAHs were to migrate, they would then absorb onto the sediment. Solubility characteristics of PAHs also agree with sample findings. PAHs are virtually insoluble, and tend to settle out if stagnant.

B. Review of pertinent literature

The purpose of the literature review, was to assess to what extent, if at all, the PAHs can and are leaching and migrating from Republic Creosote into the Southern Branch of the Elizabeth River and how much this source is contributing to the overall pollution of the river. Clues to the answers can be found after thoroughly assessing the PAH contamination problem around the site, up and down the Southern Branch, and in the Chesapeake Bay area. These would include leaching and migration rates of PAHs, as well as absorption and partition coefficients specific to the types of particulates found at Republic Creosote.

1) PAHs in sediments

Suspended sediments and bottom sediments are the most important reservoir of the major creosote components in the Elizabeth River. This is due to high molecular weight PAHs remaining in solution due to their relative insolubility, especially in areas close to the source of contamination. This settling out has also been shown to occur downstream as well. PAHs have a strong affinity for particulate matter, and as a result, the contaminated fine particle sediments which are easily transported away from the source, distribute the PAHs over a wider area. Settled PAHs can also be resuspended as a result of weathering processes, currents and tides and drudging. The most important hydrographic phenomena involve the transportation of minute quantities of dissolved PAHs and particulate contaminants in surface water flows, scouring and subsequent transport of surficial sediments and sediment bedload transport. This is an important fact to consider in evaluating Republic Creosote, as the site is low-lying, and susceptible to groundwater and surface soil saturation and transportation from these processes. This high degree of water saturation, due to the site being low-lying, along with the physical laws which influence hydrologic flow (surface gradients, gravity, and diffusion), cause higher transportation rates of contaminants. Weathering and/or transport processes tend to result in PAH assemblages that are depleted in lower molecular weight PAHs relative to unaltered creosote. This is due to the aqueous solubilities and degradabilities of PAH, which tend to increase with decreasing molecular weight. One would expect that high molecular weight PAHs, being resistant to degradation and being insoluble, would be greater concentrations in areas affected by weathering processes than in close-to-source settlements. Gradients in environmental contaminants, such as PAHs, are generated by a complex system of interacting physical, chemical, geological and biological events. There are two major effects of the PAH distribution gradient resulting from sediment transport. The first effect is that mixing processes cause conservative and persistent pollutants, such as PAHs, to decrease in concentration as one move's further from the source. The second is that the processes of mixing, dilution and transport increase the geographic area within which aquatic organisms are exposed to the contaminants from a single source.

2) Other Elizabeth River PAH problems

There are other sources of PAHs. These are important to identify so that their contribution to the pollution of the Elizabeth River can be differentiated from Republic Creosote's. In addition to coal tar creosote from wood treatment plants, combustion of various organic matters, and crude petroleum product also are sources of PAHs. Petroleum contains 60% aliphatic hydrocarbons and 20-25% aromatic hydrocarbons. This is a considerable difference ratio critical in distinguishing between PAH sources. Indeed, Huggett et al. (1987) determined that PAH contamination of sediments in the industrialized Southern Branch of the Elizabeth River came from many sources, including creosote plants, petroleum tank farms and the presence of wet- and dry-docks.

Several studies examining the bioaccumulation and bioavailability of PAHs in clams, oysters, and worms have been performed. Bender et all. found residues in clams and oysters. Residue levels in these species: 1- reflected different sources for individual PAHs within the river systems; 2- revealed concentration gradients with distance. Bioaccumulation of unsubstituted PAHs in Baltic clams and clam worms in the Chesapeake Bay has also been documented. Huggett et al. (1984) documented bioavailability and bioaccumulation in transplanted oysters.

PAH residues were highest 19 km from the mouth, this is not the site of Republic Creosote. This area was the site of a major petroleum spill. Republic Creosote is approximately 2 km downstream from this major spill. Bieri et al. confirmed this PAH residue data, but also concluded that there was little doubt that other sources of contamination exist, although it is difficult to detect their presence with the high background near the site of the spills.

Other wood treating sites near Republic Creosoting handling creosote are, Atlantic Wood Industries (down stream), Eppinger and Russell, and Bernuth Lembcke (up stream). All of these sites have been or still are contributing to the PAH contamination of the Elizabeth River. As of January 11, 1990, creosote was still being used at two of these sites, Atlantic Wood Industries and Bernuth Lembcke. Between 1960-1963 a fire at Eppinger and Russell caused a release of pure creosote into the Elizabeth River at their site.

3) Tidal effects

The Republic Creosoting site is located in a tidal region of the southern fork of the Elizabeth River. Several times a year the northern half of the property has been known to flood. Even when the property does not flood ground water levels can approach the surface. These constantly shifting waters can support facilitated transport of PAHs using contaminated fine particulates. The transport can occur through either continuously direction changing ground water movement or by surface water runoff (either flooding or raining).

4) Human and aquatic toxicology

Toxicology is the study of the harmful interactions between chemical and biological systems. Assessing the toxicity of PAHs on surrounding biota at Republic Creosote is a measure of potential risk to the ecologic community in the Southern Branch of the Elizabeth

River. Risk is taken to mean the possibility of suffering harm from a hazard, which in this case is PAHs. The risk assessment, therefore, would be an analysis identifying a hazard (the substance causing harm), the event causing the harm (Republic Creosote's case this would be dredging and topographical distribution of PAH contaminated mulch), as well as an estimate of potential harm.

There are four parameters which need to be explored in order to assess the toxicity of PAHs in a biological system: absorption, distribution, metabolism, and excretion. In order to be exert toxicity, PAHs need to come in contact with a biological system, and in the case of Republic Creosote, this biological system is aquatic organisms. Rates and sites of absorption are factors influencing eventual toxicity in these organisms.

Distribution of PAHs to those tissues which may be the site of action is an important aspect of their toxicology. PAHs exhibit a significant degree of solubility in lipids which would lead one to expect that after initial absorption into the blood stream, PAHs would tend to accumulate in fatty tissues. Lorenz and Shear (1936), however, were able to detect PAH in tumors produced several months after a single subcutaneous injection into mice. This would indicate that PAHs are transformed into soluble metabolites and/or do not readily diffuse into tissues, thus suggesting that accumulation in the body is favorable over fatty tissues. Studies performed, however, have recorded detectable PAH levels in both organs and fatty tissues.

Excretion of toxic substances from a biological system is important, as the more time PAHs spend in a biological system, the greater the likelihood of toxicity to the organism. Metabolism and bodily distribution have the greatest effect in this area. The liver and kidneys are both involved in the two possible excretory routes. Although toxins may be metabolically altered within these two organs, toxic agents show selective distribution to and possibly concentration within the liver and kidney, so that the likelihood of toxic damage is increased here.

It is evident, that examining information on absorption, distribution, metabolism, and excretion, is essential in studying the bioaccumulation of PAHs in aquatic organisms. Toxicity data of PAHs along the Southern Branch of the Elizabeth River, however, is limited. Gathering sufficient material on the above four parameters in order to properly and justifiably estimate PAH risk could not be accomplished.

There is evidence that the bioavailability of PAHs along the Elizabeth River is causing abnormality, bioaccumulation, and fatality within several fish species. These species include winter flounder, summer flounder, hogchoker, toadfish, weakfish, and bluefish. The predominant disease is fin-rot. Laboratory studies indicate that this is due to exposure to contaminated sediments. In a 1984 analysis by Huggett et al., fish biomass studies along the Southern Branch revealed decreasing abnormalities and increased biomass with increasing distance from high PAH sediment areas. Low biomass and abundance of fish correlate with the region 19-21 km upstream from the river mouth where the highest contaminated sediments were found. Cataracts were also found in fish. There is a sharp increase in frequency of cataracts starting at 19 kilometers from the rivers mouth. Individual species have increased frequency with size. In a 1989 paper by Roberts et al., fish with lesions were also found approximately 19 km. away from the mouth of the river.

In other studies, the effects of PAH-contaminated sediments were tested, with the conclusion being that low molecular weight PAHs are more toxic than higher molecular weight compounds. This being due to the low molecular weight PAH's greater solubility, and subsequent greater bioavailability.

Degradation of PAHs is dependent on several factors, some of which can be related to the conditions found at Republic Creosote. Photolysis degrades high molecular weight PAHs faster than low molecular weight PAHs. The river water's turbidity, therefore, must be a consideration in this risk evaluation. If the river water is fast flowing, causing resuspension of contaminated particulate matter, a greater amount if PAHs will be subject to photolytic degradation. Metabolism of the compounds by marine organisms and biota would also have to be considered in assessing how much of the original source contaminant remains as a hazard on and around the site. Field and laboratory studies have shown that organisms throughout the phylogenetic scale can incorporate and metabolize PAHs. Information on metabolism is important in assessing the fate and effects of chemicals, especially since biotransformation may result in the production of more toxic or mutagenic products.

There is evidence supporting the idea that PAH metabolism is related to the carcinogenic activity of PAHs, although the mechanism of the carcinogenic activity is not yet clear. Understanding the metabolism of PAHs is necessary in order to assess potential risk to surrounding biota at Republic Creosote. The water-soluble diols formed from these hydrocarbons combine with tissue constituents in the cells to form a complex which is presumable the cause of the effects which carcinogens produce. The resulting change in electronic configuration is the probable explanation for the carcinogenic activity of PAHs. The altered configuration results in the PAH (or a metabolic derivative) binding to a nucleoprotein irreversibly. If the bond nucleoprotein happens to be a key enzyme in cellular function, its loss would result in metabolic changes, which may initiate the neoplastic process.

C. PAH leaching evaluation

We were unable to conduct a field effort to study the leaching potential of PAHs at Republic Creosoting. At best this study would have told us that PAHs could/would leach from the sediments and wood shavings at the site. Information concerning exposure or risk would have to be extrapolated at best. The literature study clearly showed that PAHs are leaching from the sediments and are causing adverse toxilogical effects to aquatic species.

Since it is clear that PAH contaminated anything is a potential hazard, evidence of contribution to the Elizabeth River problem is what is needed. In 1989 at Atlantic Wood Industries a river sediment survey was conducted. The survey took sediment samples up-river, down-river, and in front of Atlantic Wood Industries site (This site is less than 1 kilometer down river from the Republic Creosoting site). The samples up-river showed minimal concentrations of PAHs. There was a sharp increase in concentration at the AWI site with a gradual decreasing down-river (plum). The contamination did not extend across the channel in the center of the river. This is clear evidence to show that AWI has contaminated the river. This same type of evidence is needed at the Republic Creosoting site.

D. Conclusion

Data has been cited to illustrate that the Elizabeth River and Bay area have reached threatening levels. The fragile ecosystem of the Chesapeake is beginning to show signs of deterioration. Fin-rot, lesions, biaccumulation, and fataility frequencies in the aquatic biota are reported. PAHs, being the predominant organic pollutant of this area, have shown to be a significant cause for these anomalies. It has not been conclusively shown to date, that Republic Creosote is a source of PAH contamination. Testing has only confirmed the presence of PAHs in the mulch, as well as on the covering sediment. However, since this sediment is material McLean Construction dredged up from the Elizabeth River, it is impossible to know whether the sediment contamination came from the mulch (which would indicate some form of migration), or from the migration of sediments in the river itself. The mobility of the particulate matter would depend on the hydrogeologic conditions in this tidally influenced area. Since Republic Creosote is heavily affected by tidal processes, and also has a shallow water table, it would be difficult to assess the effects of the tides.

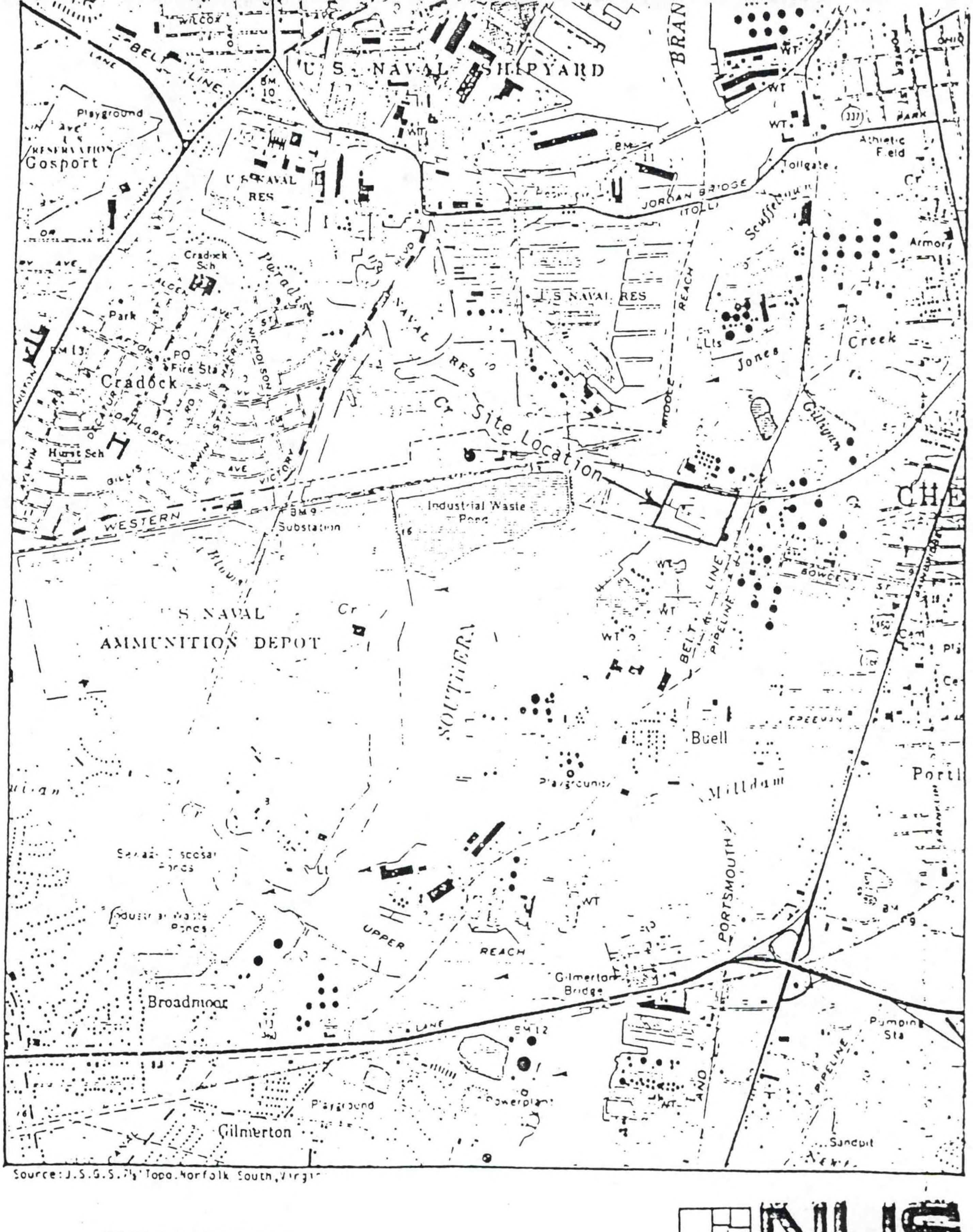
E. Recommendations

Performing extensive leaching studies of PAHs in the sediments and mulch at Republic Creosote might help in assessing the problem at this site. A better method with more conclusive results might be a similar study to that performed at Atlantic Wood Industries, a river sediment evaluation.

Remedial Actions could start with;

* Promoting photoxidation of contaminated sediments and mulches. This might decrease bioavailability of PAHs to aquatic organisms.

* Bioreclamation is another possibility in decreasing PAH concentrations on the Site.



Source: U.S.G.S. 7½' Topo. Norfolk South, Virginia

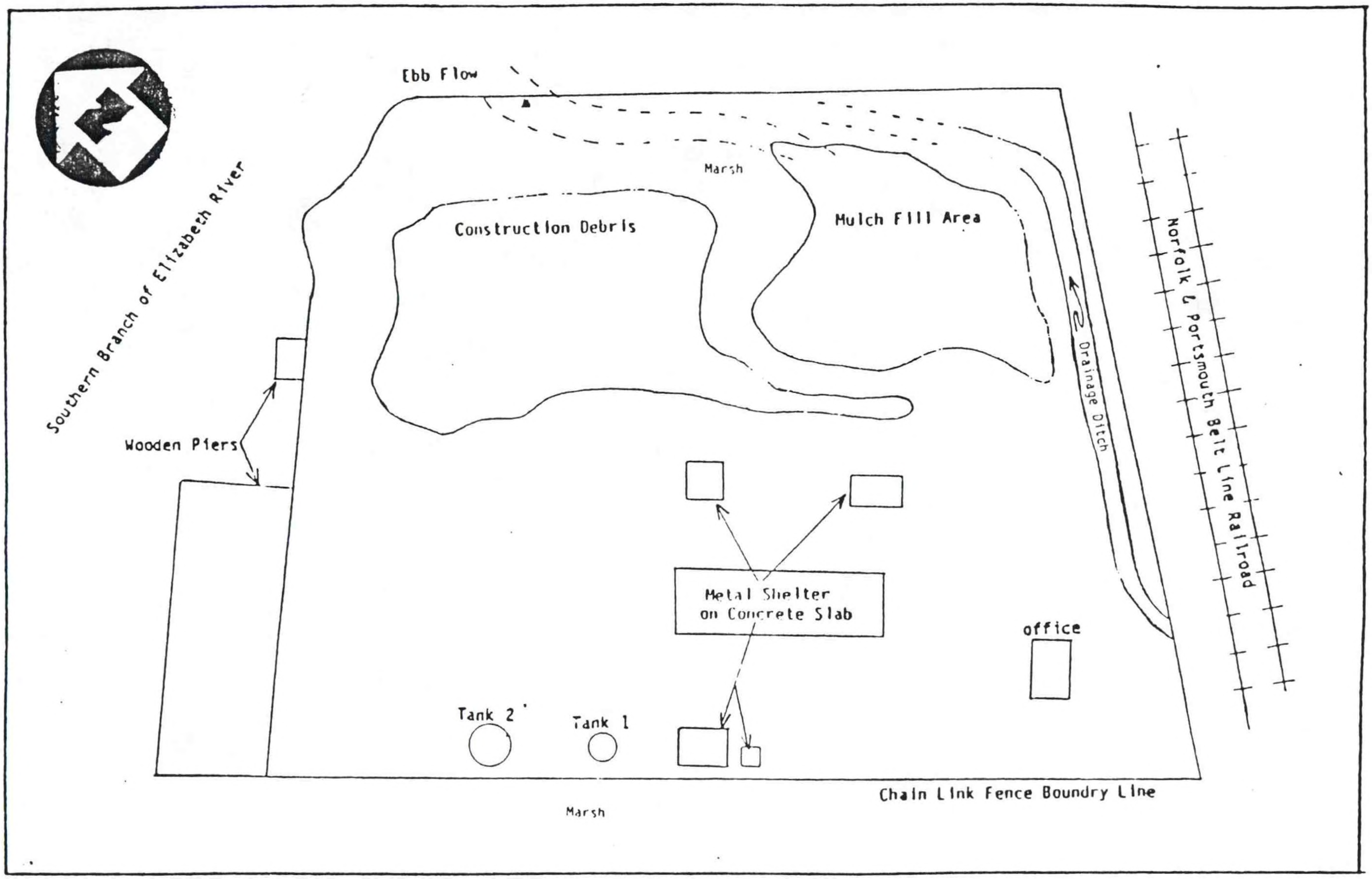
SITE LOCATION MAP

Republic Creosoting Co., Chesapeake, Virginia

Scale: 1:24,000

Figure 1

NUS CORPORATION
A Halliburton Company



SITE SKETCH

Republic Creosoting Co., Chesapeake, Virginia

NOT TO SCALE

NUS CORPORATION
A Halliburton Company

Figure 2

Table 1: Total Metal Analysis (Havens Laboratory, 8/11/89). Concentrations are in parts per million (mg/L). Locations of stations are shown in Figure 1.

Sample	Ag	As	Ba	Cd	Cr	Hg	Pb	Se
3115	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	<0.005	<0.001
3117	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	<0.005	<0.001
3119	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	<0.005	<0.001
3121	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	<0.005	<0.001
3123	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	<0.005	<0.001
3125	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	<0.005	<0.001
3127	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	<0.005	<0.001
3129	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	<0.005	<0.001
3131	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	<0.005	<0.001
3133	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	<0.005	<0.001
3135	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0170	0.010	<0.001
4135	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	0.010	<0.001
4143	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	0.008	<0.001
4150	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	<0.005	<0.001

Table 2: EP TOX Metals Analysis (Havins Laboratory, 8/11/89). Samples analyzed by EPA method 3010, EP Toxicity. Concentrations are in parts per million. Locations of stations are as shown in Figure 1.

Sample	Ag	As	Ba	Cd	Cr	Hg	Pb	Se
4131	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	0.032	<0.001
4133	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	<0.005	<0.001
4137	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	0.010	<0.001
4139	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	0.026	<0.001
4141	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	0.007	<0.001
4145	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	<0.005	<0.001
4147	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	0.016	<0.001
4149	<0.001	<0.001	<0.02	<0.001	<0.002	<0.0002	0.007	<0.001

Table 3: PAH Analytical Results (Havens Laboratory, 8/11/89).

RLI # (fld#)	Acenaphthene	Fluoranthene	Naphthalene	Pyrene	Benzo(a) Pyrene	Chrysene	Anthracene
74466 3116	-	-	-	-	-	-	-
74468 3118	-	-	-	-	-	-	-
74470 3120	-	-	-	-	-	-	-
74472 3122	-	-	-	-	-	-	-
74474 3124	-	-	-	-	-	-	-
74476 3126	-	-	-	-	-	-	-
74478 3128	-	-	-	-	-	-	-
74480 3130	-	-	-	-	-	-	-
74482 3132	-	-	-	-	-	-	-
74484 3134	-	-	-	-	-	-	-
74486 3136	-	-	-	-	-	-	-
74487-489 3137-39	-	-	-	-	-	-	-
74490 3140	-	-	-	-	-	-	-
74491 3141	-	-	-	-	-	-	-
74492 4130	-	-	-	-	-	-	600
74494 4132	9800	17500	500	11000	-	4200	160000
74496 4134	120	160	-	-	-	-	300
74498 4136	-	-	-	-	-	-	50
74500 4138	11200	32000	1200	16000	1500	4000	200500
74502 4140	7400	31000	-	15000	-	5800	185000
74504 4142	235	-	-	-	-	-	950
74506 4144	8900	25000	-	11000	-	-	110000
74508 4146	8700	10000	-	11000	-	-	95000
74510 4148	9600	10000	-	11000	-	-	85000

all results are in ppm
analysis by PID/GC

V. FRAMEWORK FOR STORING COMPILING, COMPARING, AND EVALUATING DATA SYSTEM

A framework was designed to assist the Department of Waste Management (DWM) in performing evaluations of sites suspected of potential risks. The framework is only a support mechanism for the decision making process. It will format data and provide simple or elaborate mechanisms of explosure evaluation, in an effort to allow the knowledgeable evaluator access to pertinent data (or to let him/her know that pertinent data is missing). This effort is not meant to replace CERCLA site evaluation protocols, but to support them.

A. Summary of Framework

Phase 1 (Supported by ERIES):

1. COMPILATION OF DATA - Data can be acquired in many forms and types, at different times and locations, and from many sources. Data collected under different conditions using different procedures must be compared. Subjective and objective information is available, which makes examining the data difficult at best. This first part of the framework is basically an interactive program designed to format the data in a simple, uniform manner so that it can be more easily examined. It also will assist in insuring that all the available data is collected by helping define the pertinent data needed. The format should allow clerical staff to enter data.

The data is compiled into two general groups: analytical data and site characteristics data. Either analytical data is target-selected or it can be collected generally, utilizing large unknown parameters. Site characterization data is necessary for exposure evaluation.

2. REVIEWING AND COMPARING DATA - This multicomponent section start by defining a specific format for looking at data. Quantitative data can be displayed as a two-dimensional plot of multi-dimensional data and viewed as follows, for example:

Qualitative data, both analytical and site-characteristic, will be in lists. At all times within this format, subjective statements in the quality of data can be entered. This can include the age, reliability of the data, etc., and should correspond to a 1-to-5 quality scale where 1 = good and 5 - bad. The review can be as simple as a list of compiled data (both analytical and characteristic) or comparisons of analytical data. Characteristic data is needed for modeling and exposure assessment. The ability to compare related data allows one to track trends.

3. USE OF THE INITIAL DECISION TOOLS TO EVALUATE EXPOSURE - This is broken down into two basic groups of procedures:

a) Best case/worst case analysis of contaminants at the sites. This is a powerful tool allowing one to predict the worst possible case and subsequently compare it to threshold values. In many cases the evaluation process may be terminated at this point, when the worst case does not exceed the minimum threshold. When minimal data has been collected and or when there are numerous gaps in characteristics data, creating larger uncertainties in the modeling and evaluation processes, exposure evaluation can still be estimated using this "Monte Carlo" analysis.

This analysis program begins by making an estimate of the variables and assuming either a uniform or log-normal distribution. By making numerous calculation runs, randomly choosing the distributed variables using the low parameters and then the high parameters, one can generate a worst case/best case probability plot of distribution versus concentration. Subsequent insertion of TLV information on top of this information allows one to judge the probability of whether the concentration has the potential to exceed the threshold values anywhere on the site.

b) Simplified models to assist in predicting movement and, eventually exposure. Simplified models do not require extensive site-characteristic data, which is often unavailable and always difficult to acquire. There are numerous models available. The data base support system program will have three specific simplified models built in to evaluate specific problems.

- Surface water models to evaluate both running and standing water bodies.
- A groundwater model to evaluate point source contamination (2-dimensional).
- A point source surface contaminants model to show effects on undefined aquifer systems (3-dimensional).

Phase 2:

4. COMPLEX MODELING - The goals are to ensure the effective use of models for appropriate problems. It is necessary to define all quantitative inputs required by the program and to define the variability in default values and ranges as a function of output. Most complex models require a great deal of effort to run, so it is absolutely imperative that any changes in defaults or even in input variables fall within acceptable limits. Where these limits are and what they mean is critical to the effective use of models.

5. ESTIMATING EXPOSURE - This utilizes EPA procedural manuals as a guideline.

6. ESTIMATING RISK - This is aimed at estimating risk as it directly relates to human health and subsequently to the environment.

7. EVALUATING CONSEQUENCES AND RESPONSES - Once an evaluation has been performed and immediate risk has been estimated, it would be very beneficial at this point to be able to answer the questions, "What about the risk if we don't do anything?" or "What about the risk if we perform a particular remedial action or procedure?" These kinds of questions can be addressed in several different procedures. For example, at the Monte Carlo and simple model level, new concentration levels at source, etc., can be estimated and plugged into the programs, thus modeling the conditions under question.

B. Environmental Risk Information and Evaluation System (ERIES)

COMPUTER ASSISTED DECISION SUPPORT SYSTEM

ERIES is a phase I (edition 1.0) program designed to provide maximum utility in support of the first half of the "Framework." ERIES is a knowledge based (KB) system. It can rearrange multiple sets of data and compile them into readily evaluatable formats of information. The comparison mode allows the user to look at trends, determine localization, and track concentrations with respect to both location and time.

ERIES is a menu driven, user friendly KB decision support system. A brief description of the program follows:

a. Title and Abstracts

These pages allow an evaluator the ability to screen sites. You can menu-select a site (by title or number) and then examine the following basic information.

Title Page - basic information about the site: name, address, contacts, etc.

Sources Page - an interactive listing of sources of information used to develop the KB and those which are available.

Abstract - brief description of problem and notes on any litigation or pending regulatory action.

b. Knowledge Base Data Entry

This section is where entry of analytical and site characteristic data are made.

Analytical and Characteristic Data - includes five menu options:

1. Source surface data base
2. Surface water data base
3. Unsaturated zone data base
4. Groundwater data base
5. Analytical Reference data base

Source Surface Data Base

- How many sources have been identified?
- Source #1?
- Status of source? stopped, still contaminating?
- Analytes and data

Surface Water Data Base
- How many?
- Surface water #1?

- Is it flowing or standing water?
- Characteristics: width, depth, velocity, volume, temperature, rain fall (amount/period)?

Unsaturated Zone Data Base

- How thick?
- Percolation?
- Transmissivity?
- Compaction?
- Soil types?
- Analytes and data

(NOTE: The unsaturated zone knowledge base is not completed at this time.)

Groundwater Data Base

- Aquifer information
    - name?
    - depth?
    - hydraulic conductivity?
    - pumping rate?
    - direction of flow?
    - flow rate?
- Monitoring information
    - how many monitoring wells?
    - monitoring well #1
        - how deep?
        - internal diameter of casing?
        - casing type?
        - water depth?
        - analytes and data

Analysis Reference Interacting Data Base

- Location of sample? (keyed to map of site area)
- Data and time of sampling?
- Analytes, group, and/or targeted compounds? In the form (chemical, <TLV>, <results>, <method>).

(NOTE: < > is data supplied by the operator.)

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