

The Applicability of Single Species Bioassay for Estimating the Effects of a Refinery Effluent on an Estuarine Environment

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THE APPLICABILITY OF SINGLE SPECIES
BIOASSAY FOR ESTIMATING THE EFFECTS OF
A REFINERY EFFLUENT ON AN
ESTUARINE ENVIRONMENT

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ABSTRACT

The ability of single-species aquatic toxicity bioassays to predict the impacts of industrial effluents in receiving water ecosystems was evaluated. A refinery discharging into an estuary was chosen for the assessment. Effluent plume dispersion characteristics, analytical chemistry data, acute and chronic bioassay results, and biological ecosystem analyses were correlated to evaluate whether the bioassay results accurately reflected receiving water ecosystem impact findings. Bioassays indicated no toxic effects of the effluent (at concentrations of waste effluent occurring in the ecosystem), and no ecosystem impacts were discerned. In this limited sense, therefore, ecosystem condition was reflected by toxicity data.

The raw study data contained within the Appendix of this report related to Physical Characterization (Appendix A), Chemical Characterization (Appendix B), Field Biology Studies (Appendix C), and Bioassay (Appendix D) are available for consultation and review in the American Petroleum Institute library, 1220 L Street NW, Washington, D.C. 20005.

KEY WORDS

Bioassay
Effluent Bioassay
Virginia
Chesapeake Bay
Mysidopsis bahia

Single-Species Bioassay
Industrial Bioassay
NPDES--Refinery Effluents
York River
Refinery Effluents

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EXECUTIVE SUMMARY

The objective of this study was to evaluate the ability of single-species aquatic toxicity bioassays conducted on industrial effluents to predict the impacts of the effluents in receiving water ecosystems. This study was initiated in response to EPA protocols recommended for NPDES permits and by concern that draft EPA biomonitoring policy was placing excessive reliance on the information obtainable by such bioassays. This case study was conducted at the Standard Oil Company of Indiana (Amoco) refinery in Yorktown, Virginia, which discharges its process effluents and noncontact cooling waters into the York River estuary. The studies were conducted throughout 1982 and 1983.

The study had four major tasks: (1) characterization of the effluent discharge plume's dispersion behavior; (2) chemical characterization of the effluents, receiving waters, and York River sediments; (3) laboratory toxicity bioassays on the effluents; and (4) evaluation of ecosystem impacts as indicated by benthos and fouling plate studies. The results of these four study components were evaluated to determine whether the bioassay data accurately predicted ecosystem impact findings.

Plume characterization studies indicated that the receiving water body and its transport of the waste plume are exceedingly complex. In the refinery vicinity, the York estuary is stratified for most of the year. This stratification causes the summer chronic dissolved oxygen (DO) depletion in the deeper water. This study also showed that the DO can change on a bi-weekly basis when the spring tides are of sufficient magnitude and the freshwater flows are sufficiently reduced to allow vertical mixing, thus replenishing bottom DO. This biweekly cycle does not always occur, but during the summer low-DO period it can occur regularly.

The biweekly tidal cycle also affects the physical character of the refinery effluent plume within the York River. Regardless of whether

the plume is headed inland during the flood tide, headed seaward during the ebb, or spreading during the slack water period, its vertical distribution is controlled by the spring and neap tides. During a spring tide, vertical mixing results in up to 0.02 percent of the refinery process water reaching the bottom even in deeper areas. During the stratified neap tide conditions, the plume does not reach the bottom at the deeper stations. Because the stratified conditions occur approximately 75 percent of the time, this means that, at a minimum, 75 percent of the time the refinery plume is caught above the pycnocline and therefore has little or no quantifiable effect on water deeper than about 10 meters.

The plume studies also showed that the process water concentration in the York River estuary did not exceed 0.35 percent at any time during the survey and that, typically, the value was nearer 0.02 percent within the study area.

The chemistry studies found constituents to be typical for a refinery discharge.

Toxicity bioassays indicated demonstrable toxicity of the process effluent in acute (96-hour and shorter) tests and sublethal effects during a chronic (26-day) test. However, no effects occurred at test concentrations corresponding to effluent concentrations occurring in the York River.

Benthos stations were selected on the basis of metal and hydrocarbon contents of the sediments. This allowed comparisons of stations with high versus low concentrations of these parameters. Three replicates of samples collected twice at 30 stations were thoroughly analyzed to determine benthic community characteristics. No impacts attributable to the discharge of refinery effluents were discerned within the benthos study area.

Similarly, fouling organism communities collected on artificial fouling plate arrays distributed in the area of effluent discharge were extensively examined. Again, no impacts from the refinery effluent were evident.

The bioassays did accurately reflect the finding of "no impact" on the ecosystem based on environmental exposures resulting from effluent dilution. Nevertheless, this refinery would have failed bioassay-related regulatory criteria used in some states, based on the least favorable acute bioassay of the several tests conducted during this study.

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1.0 INTRODUCTION

This study was funded by the American Petroleum Institute (API) and was conducted by Environmental Science and Engineering, Inc. (ESE) during 1982 and 1983. It was initiated because of questions arising from draft regulations and policy discussions promulgated by the U.S. Environmental Protection Agency (EPA). The subject of the study and the approaches taken to attempt clarification of the issues are discussed below. Study results and conclusions are presented in subsequent chapters.

1.1 THE ISSUES

Federal and state agencies interact for the protection of water quality by controlling the discharge of toxic substances in toxic amounts as mandated in the Clean Water Act. Sections 308 and 402 of the Clean Water Act authorize EPA and the states to require National Pollutant Discharge Elimination System (NPDES) permit applicants to provide chemical and biological data necessary to assure compliance with water quality standards.

In January 1981, EPA issued a draft document (EPA, 1981) proposing the use of effluent toxicity testing as a criterion for Second Round NPDES Permit application evaluation. In this draft document, EPA stated:

"Toxicity may be used to identify dischargers with significantly toxic discharges, determine receiving water impacts, and establish permit limits..." (page 8)

Although EPA subsequently discussed the types of additional data required to evaluate receiving water impacts, this document nevertheless initiated API concerns that EPA was becoming oriented toward a great reliance on effluent toxicity data for making such evaluations. API concerns were specifically raised by the statement in the draft EPA document that:

"Water-quality-based limits are designed to prevent chronically toxic conditions from occurring in the receiving water. The

impact of a discharge is a function of the toxicity of the effluent and the dilution capacity of the receiving water at low flow."

(page 29)

API was concerned that this and similar statements indicated a de-emphasis of the myriad of additional factors affecting ecosystem impacts, such as receiving water quality, sediment types in the receiving water body, biotic communities present, population dynamics of the specific ecosystem, and similar ecosystem characteristics.

A further point of concern was initiated by the draft statement that:

"EPA has developed a standard testing procedure to screen wastewater discharges for acute toxicity. This procedure is detailed in 'Effluent Toxicity Screening Test Using Daphnia and Mysid Shrimp.'" (page 20)

This implied that EPA was inclined toward using single-species bioassays to extrapolate to the impacts of effluents on receiving water ecosystems. API questioned whether a sufficient scientific understanding of ecosystem dynamics exists to realistically permit such a simplistic approach.

This concern was subsequently emphasized by a previous draft of the present EPA Statement of Policy entitled "Policy for Development of Water Quality-Based Permit Limitations for Toxic Pollutants" (EPA, 1984). This policy states:

"There is now a general consensus that an evaluation of effluent toxicity, when adequately related to instream conditions, can provide a valid indication of receiving system impacts."

That such a consensus exists within the scientific community is questionable; there is considerable doubt that enough is known to "adequately" relate instream conditions to single-species bioassays in order to predict effluent impacts on complex ecosystem dynamics, except in

extreme circumstances (i.e., conditions of extreme, catastrophic toxicity).

API's concern was echoed by the Environmental Effects, Transport and Fate Committee of EPA's Science Advisory Board (EPA Board, 1983a), which concluded:

"...laboratory toxicity tests fail to account for interactions between species, ecosystem level effects, interactions with other chemicals, and modifications by local water quality characteristics. In addition, the non-specific stresses in a laboratory setting...are assumed to be equivalent to the non-specific stresses encountered in the environment. The species tested in the laboratory are assumed to reflect significant or important species in the environment."

"The Committee concluded that the sum of such assumptions made it essentially impossible to discern a logical framework which would guarantee achieving the protection of the environmental integrity of aquatic systems."

To address these issues, API sponsored this research project to attempt determination of whether information derived from single-species toxicity testing can be correlated with ecosystem data collected in the field. API is concerned that the ability of laboratory tests to predict potential ecosystem impacts has not been adequately verified by field studies. This project is one of many such studies that must be conducted to properly evaluate these issues.

1.2 STUDY RATIONALE

ESE conducted a series of studies to attempt determination of relationships between single-species bioassay data and measurable effects of a petroleum refinery effluent on an estuarine environment. The studies were conducted at the Standard Oil Company of Indiana (Amoco) Yorktown

Refinery, Yorktown, Virginia. This site was selected by API as representative of the very complex estuarine conditions existing at many coastal refineries. In API's view, studies conducted at less complex sites are occasionally dismissed as simplistic; this potential fate was avoided by selection of the Yorktown site.

Through a framework of onsite bioassays, biological field studies (benthic and fouling communities), plume studies, extensive chemical characterization (effluent, receiving water, and sediments), and background information review, a comprehensive data base was assembled. From this information, correlations between laboratory predictions and ecosystem impacts were evaluated.

To achieve the study objectives, a phased approach was followed. This report presents and discusses the results obtained from all laboratory and field studies. Task efforts included: (1) physical characterization of the discharge plume; (2) acute and chronic bioassays using several laboratory-reared and indigenous species; (3) chemical characterization of effluents, ambient river water, and river sediment samples; (4) sediment particle size distribution; and (5) benthic and fouling community studies.

The following sections discuss the study site, the materials and methods of each task, and the task-specific results and discussion. The final section of the report integrates all the phases of this study, presents correlations between laboratory and field studies, and relates these findings to the proposed EPA (1983b) guidelines.

2.0 SITE DESCRIPTION

2.1 ENVIRONMENTAL SETTING--THE YORK RIVER BASIN

The purpose of the following discussion of historical data is to describe the York River and the factors that affect the physical nature of the river and to gain an understanding of how these factors might affect the physical character of the effluent plume issuing from the Amoco refinery.

The York River basin (Figure 2-1) is located in Virginia and has an area of 6,790 square kilometers (km²), comprised predominantly of forests, farmland, and marshland. Only 2 percent of the area is classified as urban (Weston, 1976). The major industries are lumbering, pulp and paper, petroleum refining, fabricated metals, textiles, fishing, and shellfishing. Figure 2-1 and Table 2-1 present the major point source industrial and municipal discharges for the York River basin.

Characteristically, the area has hot summers [July mean daily maximum air temperature of 31 degrees Celsius (°C)], relatively dry autumns, and mild wet winters (January mean daily minimum air temperature of -1°C). Precipitation, which annually averages 114 centimeters (cm), is generally lowest from September to January and highest in July and August, due to thunderstorms. An example of extreme precipitation was tropical storm Agnes which dropped 71 cm within 2 days in 1972. The prevailing winds are from the south to southwest at 4.5 meters per second (m/s) [10 miles per hour (mph)].

The York River proper begins approximately 50 kilometers (km) up-estuary of its mouth at the confluence of the Pamunkey and Mattaponi Rivers, and actually occupies only a small portion of the total York River basin. Typically, the York River is straight, wide [approximately 3,200 meters (m)], and deep (in excess of 7.5 m) throughout its length except for the area of Gloucester Point, where the river bends and its width is reduced to 780 m.

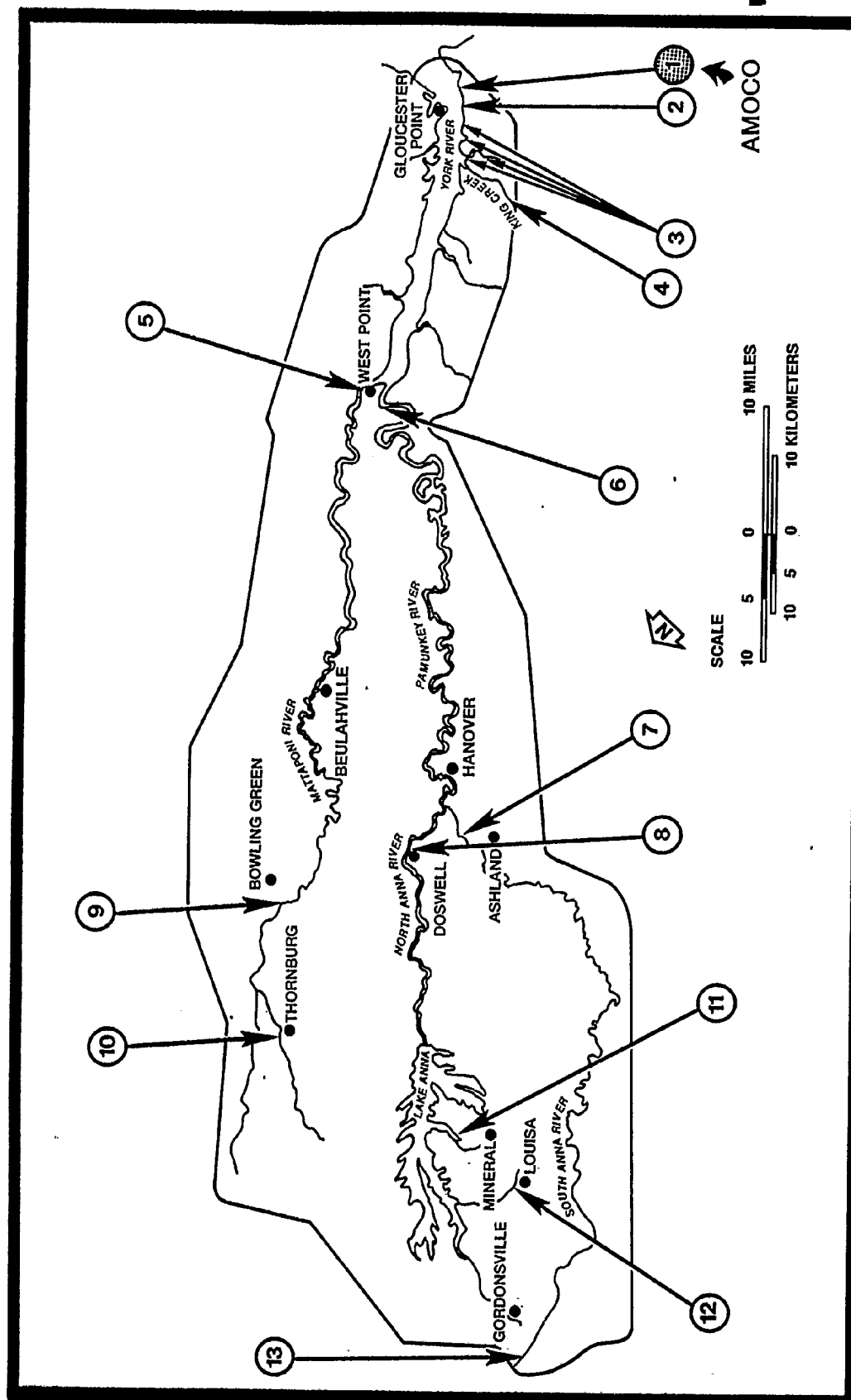


Figure 2-1
YORK RIVER BASIN AND MAJOR POINT DISCHARGES

SOURCE : WESTON, 1976.

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Table 2-1. Major Point Sources in the York River Basin (Measured Discharge Levels, Except Where Indicated Otherwise)

Major Point Sources	Map Reference Number*	Flow† (m ³ /day)	BOD ₅ ** (kg/day)	Oil and Grease (kg/day)
Amoco (Petroleum Refinery)	1	4,958††	322	283
VEPCO (Power Plant)	2	3,595,372	***	90
Combined Navy Weapons (Sewerage)	3	1,893†††	1,841†††	***
York and James City Co. Sewer District No. 1	4	1,211	14	***
West Point POTW****	5	1,476	50	***
Chesapeake Corporation (Pulp and Paper)	6	47,691	10,699	***
Ashland POTW	7	2,385	76	***
Doswell POTW	8	4,966	134	***
Bowling Green POTW	9	125	4	***
Thornburg POTW	10	95	3	***
Mineral POTW	11	76	2	***
Louisa POTW	12	106	4	***
Gordonsville POTW	13	1,351	58	***

*Refer to Figure 2-1.

†Annual average daily flow for 1981.

**Annual average daily BOD₅ load for 1981.

††Process water only.

***Not measured.

†††Based on projection by Weston, Inc. (1976) for 1977.

****Public Owned Treatment Work.

Source: Woodsin, Personal Communication, Virginia State Water Control Board, 1982.

The freshwater flow in the York River is generally greater from January through April, and less in July through September. Hyer et al. (1975) reported that the summer thunderstorms and associated precipitation have less effect on the river flow than do the spring rains. The York River is tidally influenced throughout its entire length and, therefore, does not have a flow gaging station. Flows cited for the York River are calculated from the sum of the flows of the Pamunkey and Mattaponi Rivers and multiplied by the drainage area ratio of 1.54 (Haas, 1977). Table 2-2 presents summary flow data. With an average flow of only 70 cubic meters per second (m^3/s), the York River contributes only about 3.2 percent of the total fresh water to the Chesapeake Bay drainage basin. In fact, Hyer et al. (1975) states that the salinity at the mouth of the York River is controlled more by freshwater flow from the other major rivers in Chesapeake Bay than by freshwater flow from the York River.

The surface salinity at the mouth of the York River generally ranges from 15 to 24 parts per thousand (ppt). Hyer et al. (1975) reported that salinity at the source of the York River (West Point) can reach as high as 17.2 ppt in the late fall, but decreases to less than 1 ppt in the spring.

Salinity, more than temperature, is responsible for density gradients that lead to stratification in the York estuary. According to Hyer et al. (1975), vertical salinity differences between top and bottom can vary from <1 to 8 ppt. These density gradients determine the depth and strength of the pycnocline (the region in the water column where density changes sharply with depth) which generally forms a distinction, or even a virtual barrier, between two distinct water masses. The pycnocline generally occurs between 4.5 and 12 m.

In addition to salinity, the depth and strength of the pycnocline are affected by several other factors, including bottom depth, river flow, wind-induced mixing, and tides. Hydroscience, Inc. (1975) reported that during the summer, at shallow sites (depth <9 m), the density gradient

Table 2-2. Summary Flow Data for the York River and its Tributaries

River	Maximum (m ³ /s)	Mean (m ³ /s)	Minimum (m ³ /s)
Pamunkey River at Hanover	1140	28.52	0.34
Mattaponi River at Beulahville	479	16.99	0.17
York River	--	70.09*	4.25†

*Calculated using drainage area ratio of 1.54.

†Calculated 7-day, 10-year low flow from Hydrosience, Inc. (1975).

Source: ESE [from U.S. Geological Survey (USGS), 1979].

was 0.056 ϵ units per meter (units/m), whereas the deep site gradient was 0.144 ϵ units/m.

According to both Hydrosience, Inc. (1975) and Haas (1977), freshwater flow in the York River affects the density gradient and, therefore, the degree of stratification. They agree that the higher freshwater flows in winter produce the greatest density gradients and, therefore, the greatest degree of stratification. Their findings are to be expected when one considers the dynamic classification of estuaries as defined by Pritchard (1967). The three major categories, in order of increasing tidal dominance over river flow, are: (1) highly stratified or salt-wedge estuary, (2) moderately stratified or partially mixed, and (3) vertically homogeneous or completely mixed. During the winter when freshwater flows are greater, the York estuary is similar to the highly stratified estuary where river flow is dominant over tidal action. As the river flow decreases, the York River more closely resembles a moderately stratified estuary.

In addition, Hydrosience, Inc. (1975) and Haas (1977) reported that winds affect the degree of stratification to a lesser extent. Haas (1977), however, reported that one of the dominant factors also affecting stratification in the York estuary is the tides. The semi-diurnal tides of the York estuary have a rather small range of 0.7 m and usually generate tidal currents on the flood and ebb tides of approximately 30 centimeters per second (cm/s). It is not, however, the daily fluctuation of the tides that affects the stratification in the York estuary. Rather, it is the biweekly cycle of lunar spring and neap tides, their associated currents, and time differences between tidal stages within the Chesapeake Bay in the vicinity of the York River that affect stratification.

Webb and D'Elia (1980) and Hayward et al. (1982) also reported that there was a strong positive correlation between destratification (and, therefore, complete vertical mixing) and spring tides. Destratification

was usually most intense approximately 4 days after the spring tide. Following destratification, the estuary once again began to stratify and became most stable during the neap tides. Not all spring tides produced vertical homogeneity. The spring high tide height had to be of sufficient magnitude (0.8 m, according to Hayward et al., 1982) to induce destratification. The periods of homogeneity were more numerous and intense in summer because of the annual cycle in magnitude of high tides. Also, because of decreased freshwater flow in the summer, destratification was more likely.

However, all authors (Hydroscience, 1975; Haas, 1977; Webb and D'Elia, 1980; and Hayward et al., 1982) maintain that variations in river flow and meteorological conditions are of secondary importance. For instance, during the increased flows associated with the tropical storm Agnes in 1972, the cycles of stratification and mixing proceeded according to the tides and were not measurably affected by increased flows.

To reiterate, the primary regulating factor for the York estuary's stratification-destratification cycle is the biweekly variation in tidal currents rather than the annual variation in river flows. This cycle is of particular importance when examining water quality parameters. This section of the report will only briefly discuss water quality as it will be examined in more detail in other sections of the report.

Perhaps the water quality parameter of most interest, both biologically and physically, is dissolved oxygen (DO). DO in the lower York River frequently drops below the Virginia State water quality standard of 4.0 milligrams per liter (mg/L), particularly during the summer and at depths greater than 12 m. Webb and D'Elia (1980) stated that:

"...the spring tidal destratification phenomenon has substantial effects on the distribution of oxygen and nutrients in the lower York River. Vertical mixing accompanying destratification replenishes oxygen in deep water, allowing aerobic processes to proceed again until oxygen is depleted. This mixing will also accelerate the input of benthic regenerated nutrients into the

euphotic zone. This pulsing of nutrients into the euphotic zone may support phytoplankton growth during stable conditions of the stratified period immediately after the destratification event."

It is emphasized that such DO "violations" in the lower York River are the result of natural rather than man-made phenomena.

To understand the dynamic physical structure of the York River, 14 data sets spanning 2 years (Appendix, Table A-1) provided by the Hampton Road Sanitation District (HRSD, 1982) were examined. These data were used because HRSD has done extensive and frequent sampling in the study area adjacent to the refinery.

Table 2-3 presents summary data for five of the HRSD stations for all 14 dates. The five stations examined by ESE are shown in Figure 2-2.

Historical data from two particular days were examined in greater detail. The first day, July 13, 1981, occurred during a neap tide; the second day, August 24, 1981, was during a spring tide. Selected parameters for three stations on both days were plotted versus depth (Figures 2-3 and 2-4). Figure 2-3 shows temperature, salinity, and density (as σ_t) versus depth; Figure 2-4 shows DO and DO as percent of saturation versus depth.

These two figures demonstrate several features of the York estuary discussed previously. The most obvious feature is the stratification that existed on July 13 during neap tide, where the lunar first quarter occurred on July 8 and the full moon occurred on July 16. On August 24 (2 days after a full moon, i.e., spring tide), the estuary was virtually homogeneous. The DO depletion, particularly in the deep water as presented in Figure 2-4, was very pronounced on July 13 (neap tide), whereas on August 24 there was only a slight decrease in DO with depth.

A final feature revealed in these figures is the tendency toward greater stratification in the deeper water. The density gradient between 6 and

Table 2-3. Summary HRSD Water Quality Data for the York River from October 1979 through September 1981

	YA-2			YA-1			YB-1			YO-4			YU		
	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min
Temperature (°C)	28.67 12 Aug 80†	17.14	4.34 19 Feb 81†	28.74 13 Jul 81	19.85	3.04 19 Feb 81	28.90 13 Jul 81	19.48	2.56 19 Feb 81	29.32 13 Jul 81	19.92	2.86 19 Feb 81	29.68 04 Aug 81	19.52	2.76 19 Feb 81
Salinity (ppt)	24.42 19 Feb 81	19.90	14.97 22 May 80	24.22 19 Feb 81	20.86	15.34 31 Oct 79	25.50 22 Jul 80	21.28	15.70 22 May 80	23.73 19 Feb 81	20.78	15.74 22 May 80	25.85 10 Sep 81	21.22	14.28 22 May 80
t _g †	14.11 24 Aug 81	6.86	-0.22 07 Apr 81	1.18 13 Jul 81	0.41	-0.08 04 Aug 81	5.72 22 Jul 80	1.65	-0.19 24 Aug 81	1.62 22 Jul 80	0.65	0.09 18 Jun 80	5.23 22 Jul 80	1.74	-0.05 24 Aug 81
Dissolved Oxygen (mg/L)	11.7 19 Feb 81	8.4	5.5 12 Aug 80	11.9 19 Feb 81	7.1	2.6 22 Jul 80	12.25 19 Feb 81	6.9	1.4 13 Jul 81	12.4 19 Feb 81	7.5	1.4 13 Jul 81	13.7 04 Aug 81	7.1	1.3 13 Jul 81
Oxygen Saturation (%)	109.6 24 Aug 81	94.6	66.4 22 May 80	116.2 13 Jul 81	85.3	48.5 10 Sep 81	136.2 13 Jul 81	82.9	18.8 13 Jul 81	131.5 13 Jul 81	88.7	49.2 13 Jul 81	203.0 04 Aug 81	85.1	17.5 13 Jul 81
Total Kjeldahl Nitrogen (mg/L)	0.88 22 Jul 80	0.46	0.06 19 Feb 81	1.95 22 May 80	0.47	0.05 05 Nov 80	0.99 20 Mar 80	0.47††	0.15 10 Sep 81	1.03 18 Jun 80	0.48††	0.07 19 Feb 81	1.64 18 Jun 80	0.53††	0.01 19 Feb 81
Nitrate-Nitrite (mg/L)	4.21 10 Sep 81	0.52	0.02 18 Jun 80	4.40 10 Sep 81	0.64	0.01 18 Jun 80	4.21 10 Sep 81	0.66††	0.02 20 Mar 80	3.68 10 Sep 81	0.30	0.01 18 Jun 80	4.26 10 Sep 81	0.56	0.02 22 Jul 80
Ammonia (mg/L)	0.72 20 Mar 80	0.23	0.00 19 Feb 81	0.84 22 May 80	0.17††	<0.001 18 Jun 80	0.48 20 Mar 80	0.19††	<0.001 18 Jun 80	0.96 20 Mar 80	0.21††	0.00 19 Feb 81	0.08 20 Mar 80	0.18††	0.00 19 Feb 81
Orthophosphate (mg/L)	0.15 13 Jul 81	0.06	<0.001 22 May 80	0.39 24 Aug 81	0.09	0.01 18 Jun 80	0.22 13 Jul 81	0.08	0.02 18 Jun 80	1.16 24 Aug 81	0.13	0.02 22 May 80	2.34 24 Aug 81	0.17††	<0.001 22 May 80
BOB (mg/L)	3.3 19 Feb 81 07 Apr 81	1.4	0.5 20 Mar 80	3.2 13 Jul 81	1.2††	0.3 18 Jun 80	5.6 13 Jul 81	1.3	0.3 12 Aug 80	5.3 13 Jul 81	1.6††	0.2 18 Jun 80	4.4 20 Mar 80	1.3	0.1 12 Aug 80
Total Suspended Solids (mg/L)	29 22 Jul 80	16	1 19 Feb 81	110 20 Mar 80	21	1 19 Feb 81	59 20 Mar 80	19	0 19 Feb 81	42 24 Aug 81	18	5 12 Aug 80	254 20 Mar 80	40	5 31 Oct 79

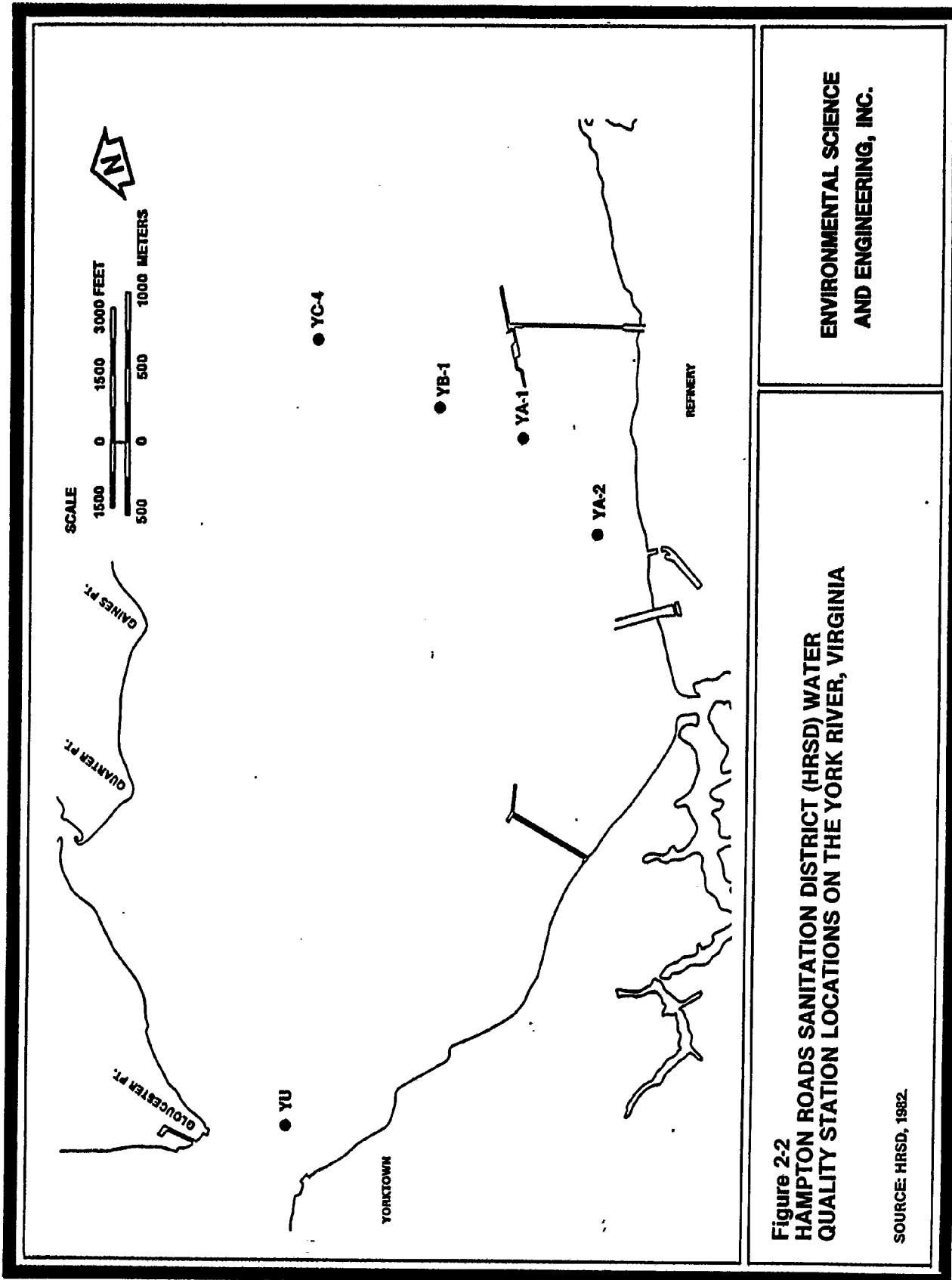
*Mean calculated from surface and bottom values for all dates.

†Date of occurrence of maximum and minimum values.

**Bottom t, minus surface t.

††Values below detection limit present in data set.

Source: ESE (from Hampton Roads Sanitation District, 1982).



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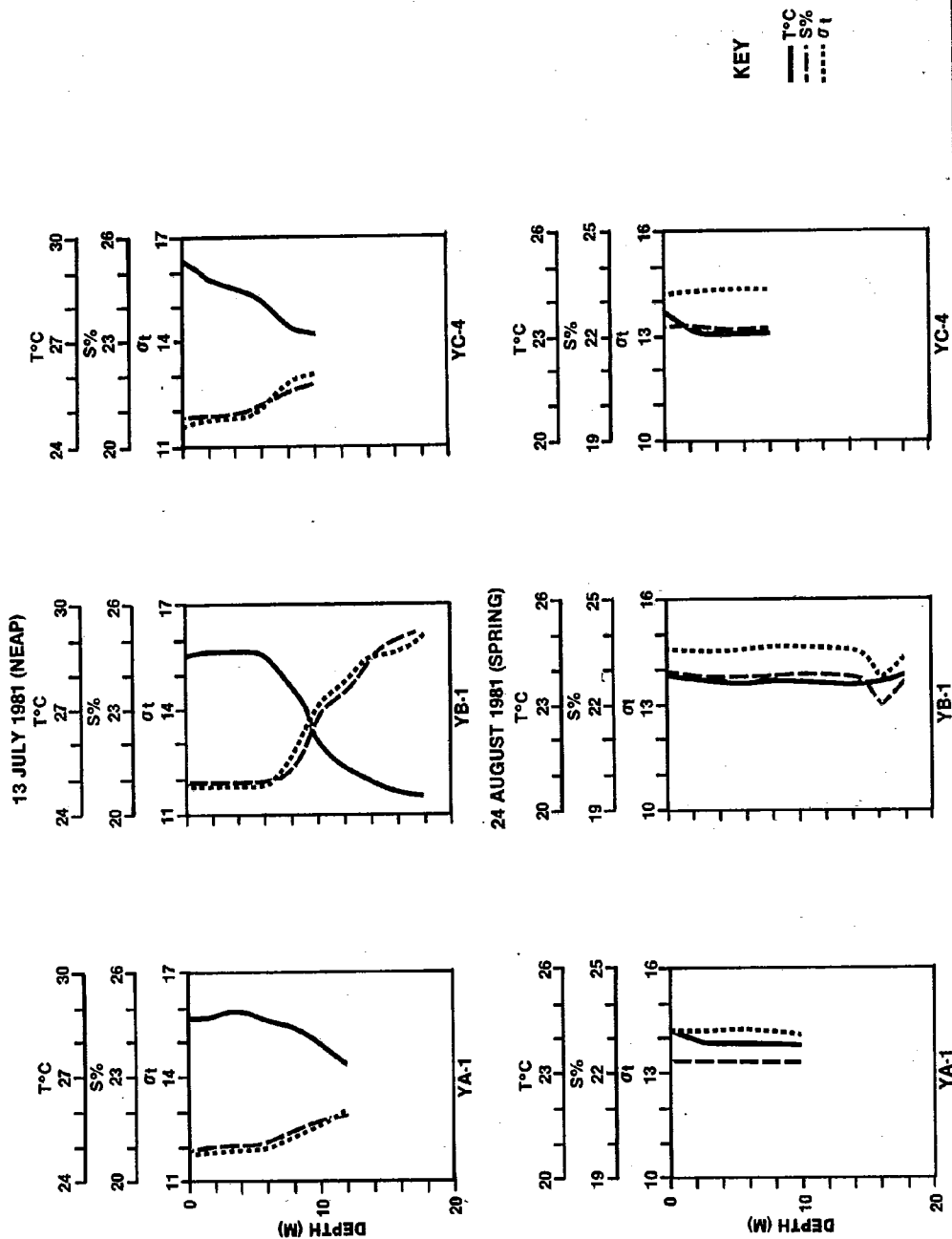


Figure 2-3
VERTICAL PROFILES OF TEMPERATURE, SALINITY AND SIGMA-T
FOR THREE STATIONS ACROSS THE YORK RIVER DURING NEAP AND
SPRING TIDES (FROM HAMPTON ROADS SANITATION DISTRICT)

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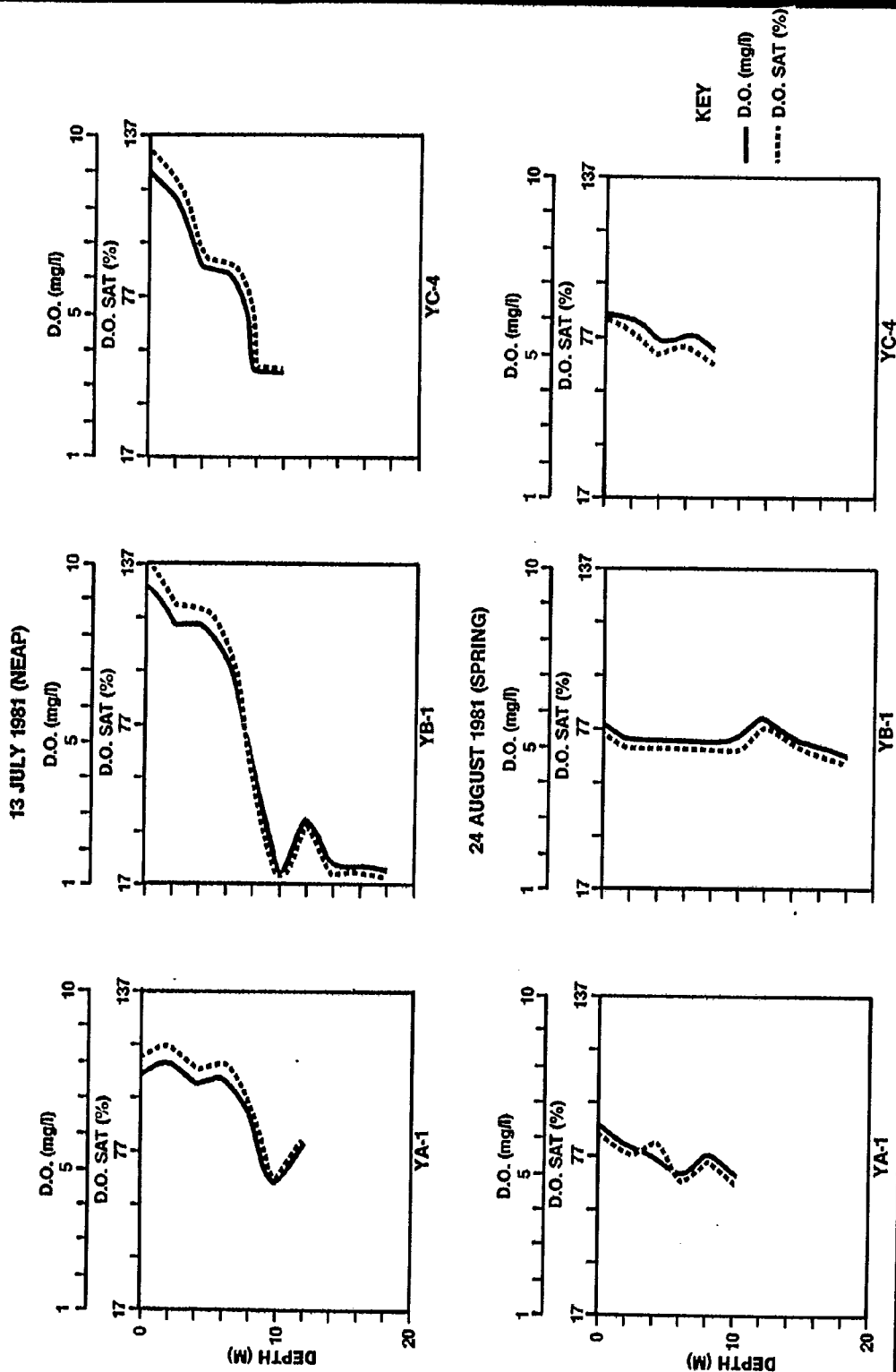


Figure 2-4
VERTICAL PROFILES OF DISSOLVED OXYGEN CONCENTRATION AND SATURATION FOR THREE STATIONS ACROSS THE YORK RIVER DURING NEAP AND SPRING TIDES (FROM HAMPTON ROADS SANITATION DISTRICT)

ENVIRONMENTAL SCIENCE
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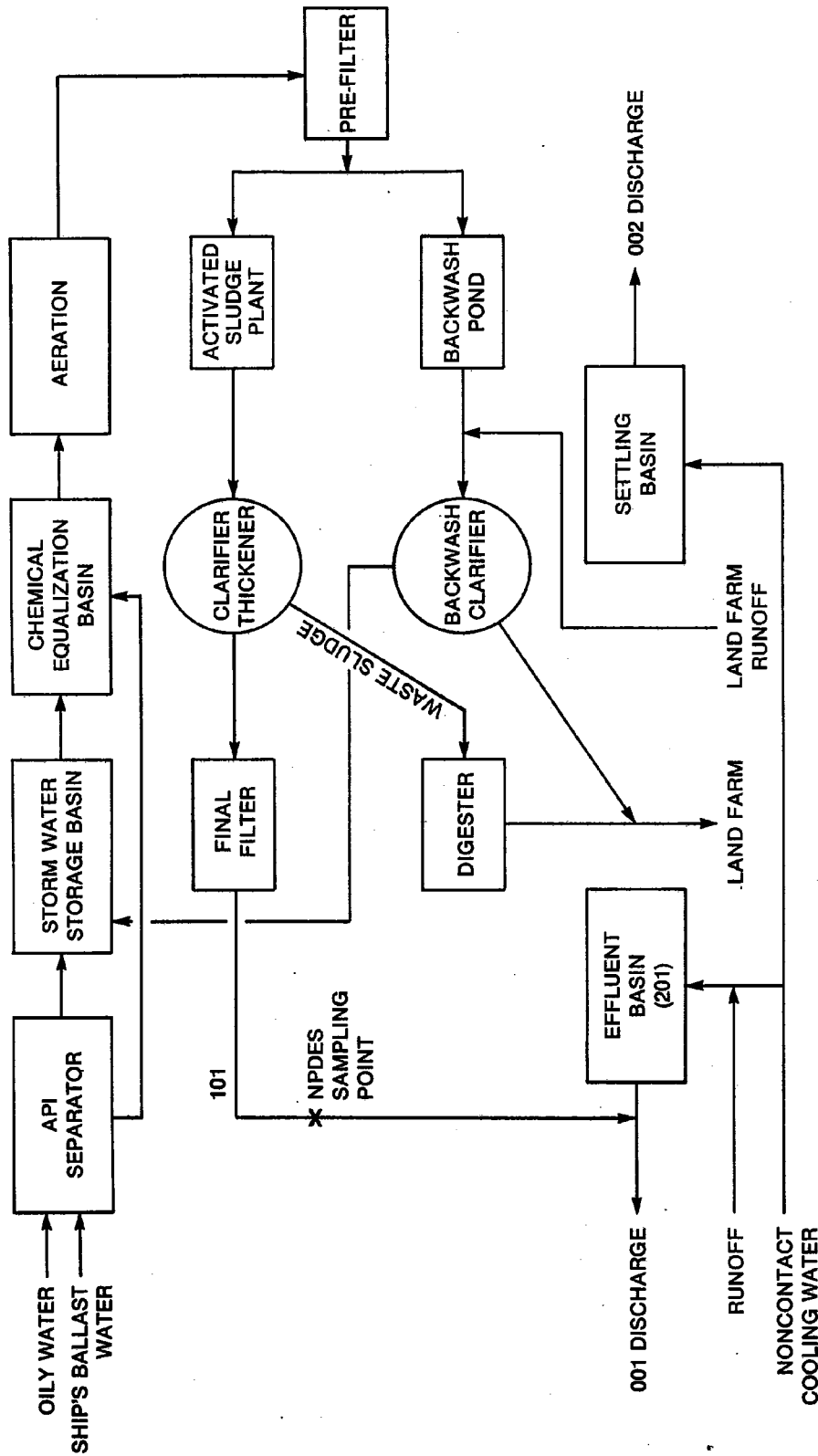
10 m is 0.5 μ units/m at Station YB-1 (depth = 18 m) and approximately 0.2 μ units/m at Stations YA-1 and YC-4 (depth $\leq$ 12 m).

2.2 STUDY SITE--THE AMOCO YORKTOWN REFINERY

The Amoco refinery was chosen by API for this research study. The refinery and waste treatment facility operate continuously. The major products of the refinery are gasoline, butane, heptane, LPG, coke, sulfur, and No. 2 fuel oil. The major raw material is crude oil. The Federal Standard Industrial Code (SIC) for Amoco is 2911.

Figure 2-5 is a wastewater treatment diagram for the refinery (Wilson et al., 1981). The process wastewater (Outfall 101) joins the non-contact cooling water (Outfall 201) to form the final effluent (Outfall 001), which is discharged into the York River through a 60-inch (in) line approximately 600-m offshore and at a depth of approximately 6 m. The only noticeable change in the physical appearance of the receiving water at the point of discharge was the appearance of air bubbles in the river water.

According to Wilson et al. (1981), water enters the refinery treatment plant from fresh water, salt water, storm runoff, and tanker (ship) ballasts. The fresh water is used in the crude oil refining process and in boiler steam generation. This water then goes through the oily water sewer to the API separator. Area runoff combines with the plant wastewater and the ship ballast water and are sent to the API separator for initial treatment. These wastewaters pass through a chemical equalization basin followed by an aeration basin. The effluent is pre-filtered and again aerated. Backwash from the prefilters is discharged to a backwash pond before entering a clarifier. Effluent from the second aeration tank is then discharged into the activated sludge plant and then into a clarifier to reduce settleable material before the final filters. Sludge from the clarifier goes to the digester and then to a land farm. The effluent produced after final filtration comprises Outfall 101, the NPDES sampling point for the refinery.



2-14

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Figure 2-5
AMOCO YORKTOWN REFINERY WASTEWATER TREATMENT
DIAGRAM

SOURCE: Wilson et al., 1981.

Salt water is used for area washdowns and non-contact cooling water. The non-contact cooling water (Outfall 201) is stored in the effluent holding basin prior to combining with final treated process water (Outfall 101) for discharge (Outfall 001). The process water [1.008 million gallons per day (MGD)] is diluted by the non-contact cooling water (56.067 MGD) prior to discharge (Outfall 001). Therefore, based on these projected average values (NPDES Permit Number VA0003018 for Amoco), the percent treated process water at time of discharge (Outfall 001) should average 1.8-percent process water.



3.0 MATERIALS AND METHODS

3.1 PHYSICAL CHARACTERIZATION

3.1.1 Objectives

The objective of this task was to describe the physical characteristics of the Amoco effluent plume discharged into the York River estuary. The effects of the environment on the physical behavior of the refinery plume and the plume effects on the environment were also investigated.

The results from this task aided in the determination of possible environmental impacts from the Amoco plume by defining the effluent concentration isopleths in the York estuary, thereby allowing a direct demonstration of the areas of anticipated possible acute and chronic impact, if any. In addition, the plume characterization physically portrayed the position of the effluent plume (and concentrations) under various environmental conditions so that not only the effluent concentrations were known, but the periods of exposure of the different communities could be estimated. The physical characterization study also defined the positions of the plume with respect to the benthic and water column communities; these results were used in the program design of the field biology sampling schemes.

ESE conducted a historical data survey and two field surveys to physically characterize the York River estuary and evaluate the dispersion of the refinery discharge plume. The historical data survey was conducted throughout the study period. The field surveys were conducted in March and June 1982 during spring and neap tides, respectively. Each field survey consisted of hydrographic and water quality sampling, and dye plume surveys. Techniques are described in the following sections.

3.1.2 Historical Data Survey

The first step in the historical data survey was to conduct a computer search of eight data bases using specific geographic and topical key words. This search yielded more than 100 citations. The most relevant

articles or their abstracts were obtained and examined in detail. The computer search also included an EPA STORET retrieval. This procedure retrieved existing water quality and discharge data for the general study area.

In addition to the computer searches, ESE conducted a search throughout the University of Florida and the Virginia Institute of Marine Sciences (VIMS) libraries.

In an effort to obtain unpublished data, several institutions and agencies were contacted or visited, including VIMS, the Virginia State Water Control Board, and HRSD. HRSD regularly conducts water quality sampling in the vicinity of the refinery and made its data readily available to ESE.

3.1.3 Hydrographic and Water Quality Survey

The hydrographic and water quality surveys consisted of in situ measurements of temperature, conductivity (and, hence, salinity), DO, pH, currents, and water quality sampling for laboratory analyses.

In situ physico-chemical measurements were made with a Model 4041 Hydrolab®. Current speed and direction were measured with an ENDECO® Model 110 deck readout current meter. All data were recorded on field data sheets.

Surface grab samples were taken for laboratory water quality analyses. The preservation and analytical techniques used are described in the chemical characterization sections of this report.

A physical and chemical reconnaissance survey of the York River in the vicinity of the Amoco Yorktown Refinery was conducted on March 9, 1982.

Representative ambient water was collected on March 5, 1982, to be used in fluorometer calibrations and pre-dye injection tests. These tests

included comparisons of ambient water and effluent water background fluorescence levels with distilled water, as well as recovery ratio tests.

The background tests were conducted to determine if any variability existed in background fluorescence or if the background fluorescence was unusually high. In either case, the amount of dye injected would be increased. The background level was determined by placing ambient water and effluent water in a cuvette and reading its fluorescence on a fluorometer. This reading was then compared to readings made with distilled water.

The recovery ratio tests involved adding a known amount of dye to ambient water or effluent discharge water, and distilled water. Fluorescence and temperature were then measured for each sample periodically throughout a 96-hour period. Any changes in the fluorescence of the discharge or ambient water versus the distilled water indicated that the dye was affected by constituents in the discharge or ambient water. If this had occurred, the amount of dye injected would have been increased to compensate for this effect.

The remainder of the ambient water was used to calibrate both the laboratory and survey fluorometers. In each case, the calibration involved the serial addition of a known amount of dye to the ambient water producing solutions of known concentrations. The fluorescence and temperature of each solution were then measured. Solution temperature is an important parameter as fluorescence of Rhodamine WT dye varies with temperature. The fluorescence was corrected to 25.0°C, and these values were plotted against dye concentrations to yield calibration curves. These curves were then used to convert fluorescence and temperature measurements made in the field to dye concentrations.

ESE used fluorescent Rhodamine WT dye continuously injected for a minimum of 2 days into the refinery effluent to tag the effluent plume.

The injection rate of the concentrated dye was 15 milliliters per minute (ml/min). The injection rate was checked several times per day to ensure constant dye delivery. Fluorescent dye was chosen for these studies because the dye could be tracked in the field, whereas chemical tracers existing in the discharge would be ambiguous and require chemical analysis. To define the dye plume, ESE used its automated high-speed data acquisition system (DAS). The DAS was controlled by an Esterline-Angus® Model PD 2064 Data Logger, which was interfaced with a thermistor (accurate to $\pm 0.1^{\circ}\text{C}$), a Turner Designs® Model 10 Fluorometer, and a DECCA® Model 202-MS20 Trisponder® Navigation System (DTNS). The DTNS is a short-range microwave navigation system which provides accurate triangulation position fixing based on the distances from two shore-based reference stations. This system is accurate to ± 1 m and has a range of up to 80 km. The fluorometer was calibrated before each study using known dye standards.

Each dye survey was conducted in two parts. The first part was a complete horizontal survey of the surface concentrations of dye. Surface water (approximately 0.5 m deep) was pumped continuously through a fluorometer located on the survey vessel. The fluorescence, water temperature, and position from the DECCA were automatically recorded by the data logger. The survey vessel, instrumented in this manner, traversed the plume along several transects with the data logger automatically recording fluorescence, temperature, sampling location, and time at approximately 15-second intervals. In this manner the distribution of surface dye concentration was mapped.

Immediately following the horizontal survey, a survey of the vertical distribution of dye and temperature was conducted. Dye, temperature, and position were sampled at several depths at each station using the same instrumentation. The sampling at depth was done by lowering the intake hose to the proper depth prior to activating the data logger.

The magnetic data cassette from the data logger (and its backup paper tape) was returned to ESE for analysis. The data from the horizontal and vertical surveys were transferred to ESE's computer. The computer converted the two ranges for each station into X/Y coordinates and plotted these stations at a predetermined scale. The data were then tabulated and plotted for inclusion in this report.

3.2 CHEMICAL CHARACTERIZATION

3.2.1 Objective

Chemical data were gathered from the Amoco effluent, from the receiving and mixing waters, and from sediment samples taken from areas near the outfall. It was the objective of the chemical characterization studies to aid in the assessment of the wastewater toxicity and in defining the area of impact of the Amoco wastewater plume. Chemical characterization data of the effluent, the receiving water, and sediments were incorporated with the ecological data, to provide a more thorough evaluation of the wastewater's impact to the estuarine system. The chemical characterization data obtained from the sediment analyses were used extensively in the design of the benthic study.

The study objective was achieved through a phased approach. Phase I was a reconnaissance trip designed to develop a broad data base on the effluent. Phase II involved further characterization of the effluent concurrent with bioassay tests and also included the analysis of 60 sediment samples to define the area impacted by the plume, if any. The third phase of the study involved the analysis of effluent and 30 additional sediment samples to provide additional information on the zone of presumed impact.

3.2.2 Reconnaissance--Phase I

The reconnaissance trip had two major objectives. The first was to establish a broad chemical data base on the effluent and the receiving water with a special effort to characterize the unknown organic compounds by gas chromatography/mass spectrometry (GC/MS). Chemical characterizations of (1) the discharge plume under two sets of tidal conditions, (2) an ambient (dilution) water sample, and (3) a sediment sample collected near the outfall were conducted. The second objective of the reconnaissance trip was to attempt to limit the number of parameters necessary to characterize future samples with respect to their biological significance and potential toxicity.

Three types of samples were collected for chemical characterization during the reconnaissance trip: one wastewater effluent sample, three receiving water samples (one ambient and two plume samples), and one sediment sample.

The effluent composite sample (Outfall 101, process water) consisted of automatically composited subsamples and manual grab samples taken according to methods published in the Federal Register, Volume 45 (1980), Number 98 for NPDES outfall sampling. The effluent sample was collected over a 24-hour period. An ISCO automatic sampler set to sample 400 milliliters (ml) every 15 minutes was used to collect a 24-hour composite for all chemical fractions except cyanide, volatile organics, and hydrocarbons. These three fractions were manually collected composites (one-fourth of each sample was collected every 6 hours).

The receiving water samples (one ambient and two plume samples) were grab samples; the various fractions were preserved similarly to the effluent sample. The sediment sample was taken with a Ponar® grab, and the sample was iced for preservation.

The sampling locations were:

- Effluent: Sample taken from the NPDES sampling point (sump) for Outfall 101 (process water).
- Plume 1: Sample taken next to outfall, Station 1EBB of physical characterization study (Figure 3-1)
- Plume 2: Sample taken from Station 1FLOOD of the physical characterization study (Figure 3-1).
- Ambient: Sample taken from the York River, upstream and across the river from the Amoco refinery. The exact sampling point was below the Highway 17 bridge, at Gloucester Point. This was the dilution water source for bioassay.
- Sediment: Sample taken from near the outfall pipe (near plume 1 sample, Figure 3-1).

The analytical methods utilized in the analyses of the samples are listed in Tables 3-1 through 3-3. The methods used in the analyses of the water samples were EPA-approved methods, while the methods for the analyses of the sediment sample utilized modifications of the

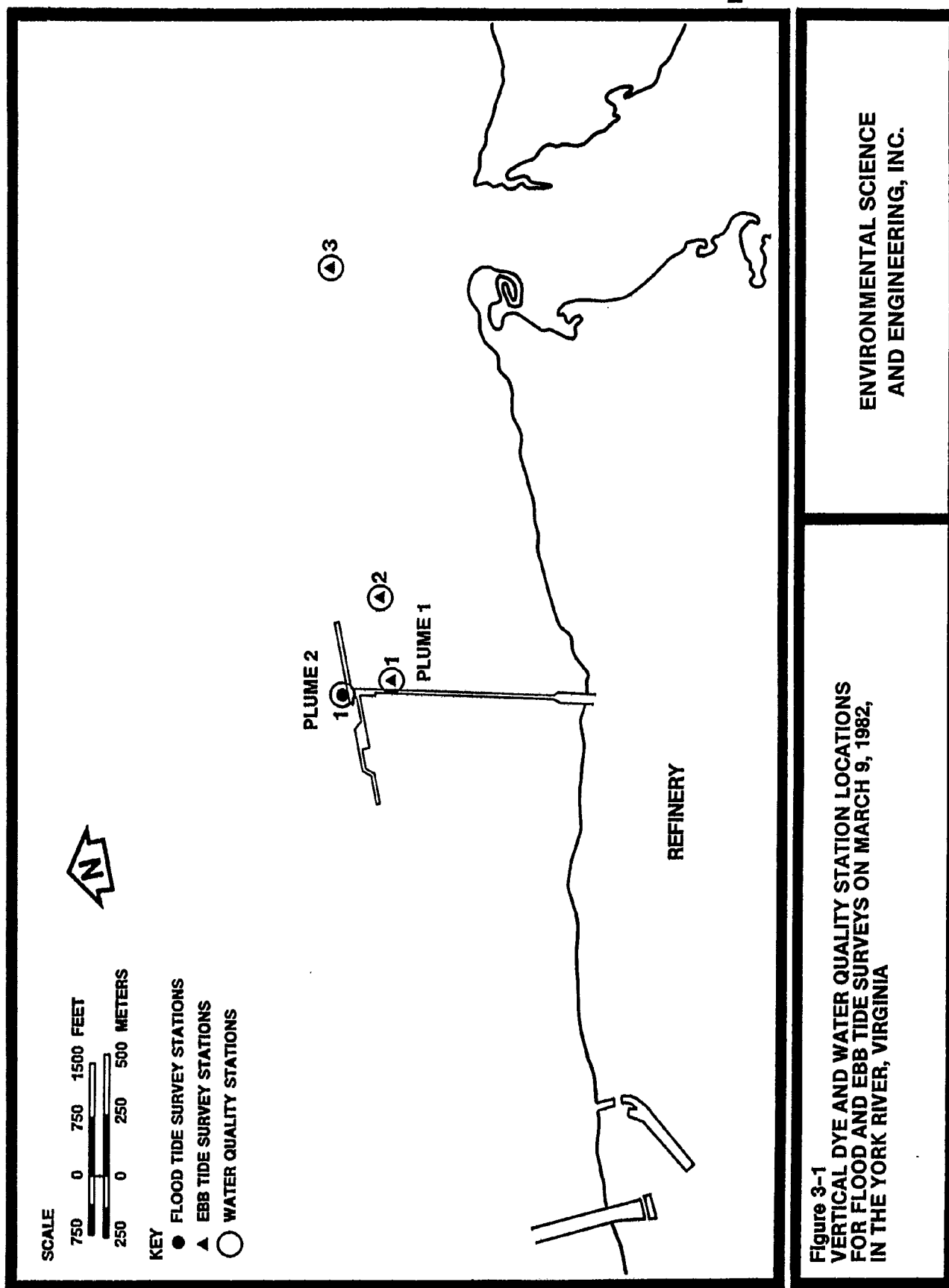


Table 3-1. Phase I Analytes and Methods for the Chemical Characterization of Wastewater

Analytes	Methods Utilized
A. Traditional Analyses	
Biochemical Oxygen Demand (BOD)	BOD Method* (No. 507)
Chemical Oxygen Demand (COD)	COD Method† (No. 410)
Total Organic Carbon (TOC)	TOC Method † (No. 415.1)
Total Suspended Solids (TSS)	TSS Method* (No. 209)
Ammonia	Ammonia Method* (No. 417)
Bromide	Bromide Method† (No. 320.1)
Sulfate	Sulfate Method† (No. 375.1)
Cyanides	Cyanide Method† (No. 335.3)
Temperature (Field)	Thermometric Method† (No. 170.1)
Dissolved Oxygen (Field)	Membrane Electrode Method† (No. 360.1)
pH (Field)	Electrometric Method† (No. 150.1)
B. Metals Analyses	
Aluminum	ICAP Method**
Barium	ICAP Method**
Boron	ICAP Method**
Cobalt	ICAP Method**
Magnesium	ICAP Method**
Manganese	ICAP Method**
Tin	ICAP Method**
Antimony	ICAP Method**
Chromium	ICAP Method**
Nickel	ICAP Method**
Thallium	ICAP Method**
C. Petroleum Hydrocarbon Analysis	
	Extraction and Capillary GC/MS
D. Volatile Compound Analyses	
Xylenes	EPA Method 624**
Benzene	EPA Method 624**
Toluene	EPA Method 624**
Ethyl Benzene	EPA Method 624**
Identify Other Major Unknown Peaks	Manual and Computerized Library Searches
E. Base/Neutral Compound Analyses	
Acenaphthene	EPA Method 625**
Acenaphthylene	EPA Method 625**
Anthracene	EPA Method 625**
Benzo(a)anthracene	EPA Method 625**

Table 3-1. Phase I Analytes and Methods for the Chemical Characterization of Wastewater (Continued, Page 2 of 2)

Analytes	Methods Utilized
Benzo(a)pyrene	EPA Method 625**
3,4-Benzo-fluoranthene	EPA Method 625**
Benzo(ghi)perylene	EPA Method 625**
Benzo(k)fluoranthene	EPA Method 625**
Bis(2-chloroethoxy)methane	EPA Method 625**
Chrysene	EPA Method 625**
Dibenzo(ah)anthracene	EPA Method 625**
Fluoranthene	EPA Method 625**
Fluorene	EPA Method 625**
Naphthalene	EPA Method 625**
Phenanthrene	EPA Method 625**
Pyrene	EPA Method 625**
Identify Other Major Unknown Peaks	Manual and Computerized Library Searches
F. Acidic Compound Analyses	
Cresols	EPA Method 625**
Identify Other Major Unknown Peaks	Manual and Computerized Library Searches

Sources: ESE.

*APHA et al., 1980.

†EPA, Environmental Monitoring and Support Laboratory, 1983b.

**EPA, 1979a.

Table 3-2. Phase I Analytes and Methods for the Chemical Characterization of Receiving Water Samples

Analytes	Methods Utilized
Level 1. Routine Field Parameters	
Temperature	Thermometric Method† (No. 170.1)
Dissolved Oxygen	Membrane Electrode Method† (No. 360.1)
pH	Electrometric Method† (No. 150.1)
Conductivity	Specific Conductance Method† (No. 120.1)
Level 2. Intensive Analysis	
<u>A. Traditional Analyses</u>	
BOD	BOD Method* (No. 507)
COD	COD Method† (No. 410)
TOC	TOC Method† (No. 415.1)
TSS	TSS Method* (No. 209)
Ammonia	Ammonia Method* (No. 417)
Bromide	Bromide Method† (No. 320.1)
Sulfate	Sulfate Method† (No. 375.1)
Cyanides	Cyanide Method† (No. 335.3)
<u>B. Metals Analyses</u>	
Aluminum	ICAP Method**
Barium	ICAP Method**
Boron	ICAP Method**
Cobalt	ICAP Method**
Magnesium	ICAP Method**
Manganese	ICAP Method**
Tin	ICAP Method**
Antimony	ICAP Method**
Chromium	ICAP Method**
Nickel	ICAP Method**
Thallium	ICAP Method**
<u>C. Petroleum Hydrocarbon Analysis</u>	Extraction and Capillary GC/MS
<u>D. Volatile Compound Analyses</u>	
Xylenes	EPA Method 624**
Benzene	EPA Method 624**
Toluene	EPA Method 624**
Ethyl Benzene	EPA Method 624**
Identify Other Major Unknown Peaks	Manual and Computerized Library Searches

Table 3-2. Phase I Analytes and Methods for the Chemical Characterization of Receiving Water Samples
(Continued, Page 2 of 2)

Analytes	Methods Utilized
E. Base/Neutral Compound Analyses	
Acenaphthene	EPA Method 625**
Acenaphthylene	EPA Method 625**
Anthracene	EPA Method 625**
Benzo(a)anthracene	EPA Method 625**
Benzo(a)pyrene	EPA Method 625**
3,4-Benzo-fluoranthene	EPA Method 625**
Benzo(ghi)perylene	EPA Method 625**
Benzo(k)fluoranthene	EPA Method 625**
Bis(2-chloroethoxy)methane	EPA Method 625**
Chrysene	EPA Method 625**
Dibenzo(ah)anthracene	EPA Method 625**
Fluoranthene	EPA Method 625**
Naphthalene	EPA Method 625**
Phenanthrene	EPA Method 625**
Pyrene	EPA Method 625**
Identify Other Major Unknown Peaks	Manual and Computerized Library Searches
F. Acidic Compound Analyses	
Cresols	EPA Method 625**
Identify Other Major Unknown Peaks	Manual and Computerized Library Searches

Sources: ESE.

*APHA et al., 1980.

†EPA, Environmental Monitoring and Support Laboratory, 1983b.

**EPA, 1979a.

Table 3-3. Phase I Analytes and Methods for the Chemical Characterization of a Sediment Sample Taken Near the End of Outfall 001 Pipe

Analytes	Methods Utilized
<u>Volatiles</u>	
Benzene	Modified EPA Method 624*
Xylenes (total)	Modified EPA Method 624*
Toluene	Modified EPA Method 624*
Ethylbenzene	Modified EPA Method 624*
<u>Extractables</u>	
Acenaphthene	Modified EPA Method 625*
Acenaphthylene	Modified EPA Method 625*
Anthracene	Modified EPA Method 625*
Benzo(A)anthracene	Modified EPA Method 625*
Benzo(A)pyrene	Modified EPA Method 625*
Benzo(B)fluoranthene	Modified EPA Method 625*
Benzo(K)fluoranthene	Modified EPA Method 625*
Benzo(g,h,i)perylene	Modified EPA Method 625*
Bis(2-chloroethoxy)methane	Modified EPA Method 625*
Chrysene	Modified EPA Method 625*
Dibenzo(a,h)anthracene	Modified EPA Method 625*
Fluoranthene	Modified EPA Method 625*
Fluorene	Modified EPA Method 625*
Naphthalene	Modified EPA Method 625*
Phenanthrene	Modified EPA Method 625*
Pyrene	Modified EPA Method 625*
Cresols (total)	Modified EPA Method 625*
<u>Metals</u>	
Antimony	ICAP Method*
Chromium	ICAP Method*
Thallium	ICAP Method*
Nickel	ICAP Method*
Aluminum	ICAP Method*
Barium	ICAP Method*
Boron	ICAP Method*
Cobalt	ICAP Method*
Magnesium	ICAP Method*
Manganese	ICAP Method*
Tin	ICAP Method*
<u>Traditionals</u>	
Oil and Grease	Method 739 Oil and Grease in Sediments
Moisture Content	EPA Method for Moisture Content**

Sources: ESE.

*EPA, 1979a.

†EPA, 1979b.

**EPA, 1969.

EPA-approved methods. These modifications involved changes in the sample workup. The volatiles were analyzed by taking an aliquot of the sediment and adding 5 ml of organic-free water in the purging chamber. The sample was then analyzed as described in EPA Method 624. The extractable fractions were prepared by taking an aliquot of the sediment, adding 100 ml of organic-free water, adjusting the pH to 12, and serially extracting three times utilizing methylene chloride and a Polytron Tissumizer®. This base/neutral fraction was then concentrated and analyzed according to EPA Method 625. Another 100 ml of organic free water was added to this same sediment aliquot, adjusted to pH 2, and serially extracted as described for the base/neutral fraction. This acid extract was then concentrated and analyzed according to EPA Method 625. The metals analysis utilized a nitric acid digestion of the sediment followed by analysis by ICAP. The oil and grease determination was by a freon Soxhlet extraction procedure followed by gravimetric measurement. The moisture content of the sediment was done by standard EPA methods utilizing a weight difference after drying the sample.

3.3.3 Phase II.

At the conclusion of the reconnaissance phase, the data were reviewed by ESE and API personnel. A list of parameters was developed to help define the area of impact of the plume. Based on the plume characterization results, a sampling grid was established and 60 sediment samples were taken (September 1983) to provide data from the anticipated zone of impact. The parameters selected included 7 metals, total organic extractables (TOE), and petroleum hydrocarbons. The specific parameters are listed in Table 3-4. Each of these parameters was selected on the basis of its occurrence in the reconnaissance survey sample and its presumed utility in helping to trace pollutant accumulation areas in sediments of the receiving water body. For example, manganese occurred at a much higher concentration in the reconnaissance survey effluent sample than in the ambient water sample. It was, therefore, analyzed in subsequent samples to attempt determination of its fate after discharge and its areas of accumulation, if they exist. Because the primary

Table 3-4. Analytes for the Chemical Characterization of the Sediment Samples Taken During Phase II of the Study

Analytes

Moisture Content

Total Extractable Organics

Total Petrogenic Hydrocarbons

Aliphatic Petrogenic Hydrocarbons

Aromatic Petrogenic Hydrocarbons

Unresolved Petrogenic Hydrocarbons

Total Petrogenic Hydrocarbons, Including Unresolved

Cadmium

Chromium

Lead

Manganese

Selenium

Vanadium

Zinc

Source: ESE.