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WATER QUALITY MONITORING OF THE CRANEY ISLAND DREDGE
MATERIAL DISPOSAL AREA, PORT OF HAMPTON ROADS,
VIRGINIA -- DECEMBER 1973 TO FEBRUARY 1975

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and

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Technical Report

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INTRODUCTION

Estuaries are regions of the marine environment which receive the greatest impact of man's activities, one of which is pipeline dredging. This form of channel and harbor maintenance is one of the most common practices along the southeastern Atlantic coastline. Earlier studies by Windom (1972) suggested that dredging of unpolluted sediments led to little changes in water quality. However, further investigations (Windom 1974) of confined and unconfined disposal areas indicated that water quality changes during dredging cannot be predicted from bulk analyses of the sediments. This has been further substantiated by Lee and Plumb (1974), as well as that immediate release of ammonia in confined areas, which might be toxic to the microphytic community, could lead to growth of unfavorable species which would be discharged from the diked area. It was also suggested that there might be a relationship between water quality and retention time within a spoil area, yet there was no clear indication that the characteristic of the effluent from a diked area would be improved by increasing the residence period of the dredged material within the confined zone.

Since coastal environments are of prime concern for marine fish production and serve both as the breeding and nursery grounds for many species of fish and as the home habitat for economically valuable invertebrates, a long-term effort to study the effluent from a large confined disposal area was considered important. In this initial attempt to understand the effects of dredge disposal and fill operations, a study was designed to monitor and evaluate the quality of water and suspended material leaving the Craney Island Disposal area located in the estuarine waters of Hampton Roads Harbor, near Norfolk, Virginia. This diked disposal site, which is operated and maintained by the Norfolk District of the U. S. Army Corps of Engineers, encloses approximately 2500 acres (ca. 10.3 km²) and receives about four million cubic yards annually.

Description of the Hampton Roads Harbor

The harbor of Hampton Roads, Virginia, is the largest estuarine section of the James River before it enters the lower Chesapeake Bay (Figure 1) and Atlantic Ocean at latitude 37°N longitude 76°W. The importance of the James

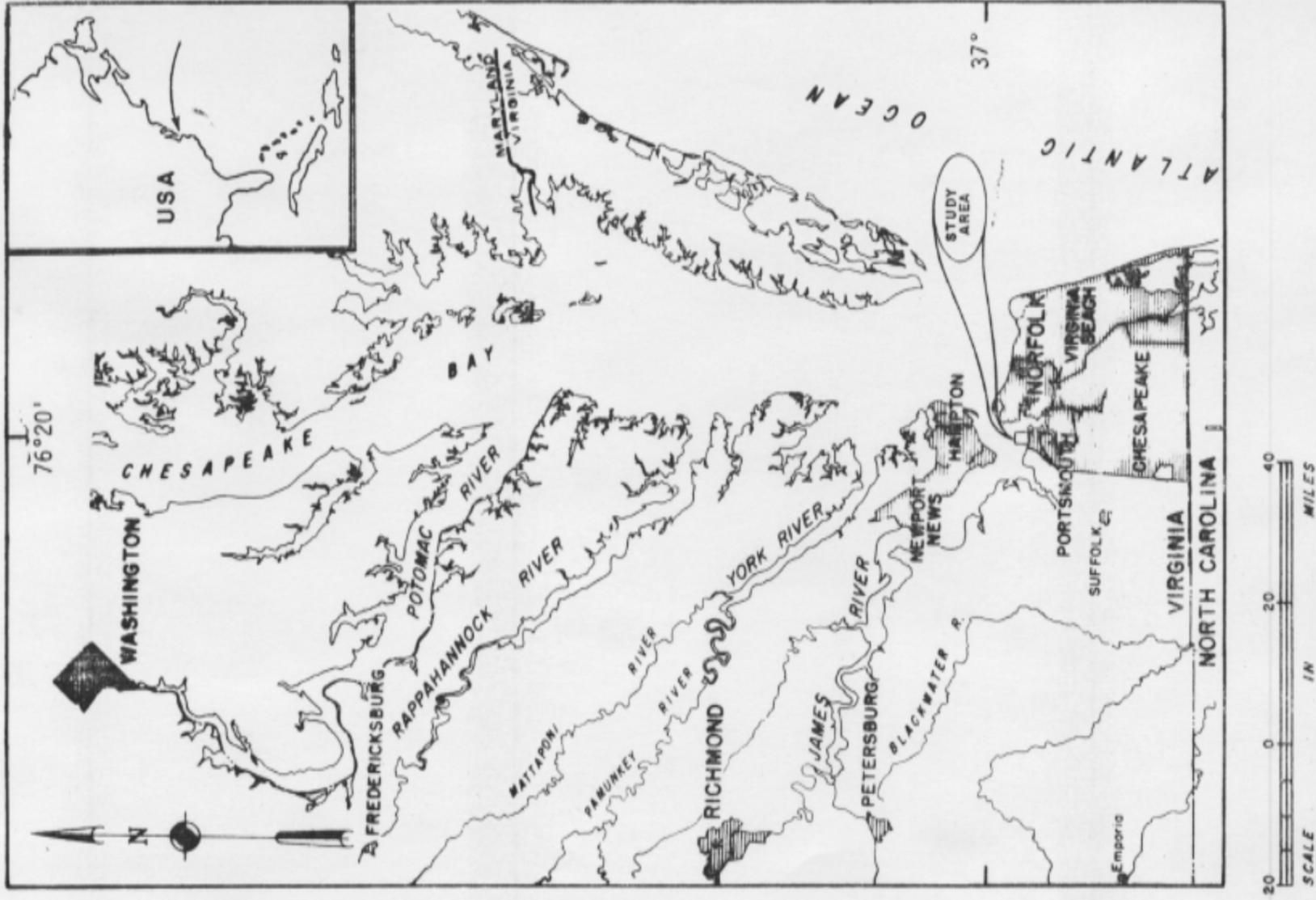


Figure 1. Location of the Corps of Engineers Craney Island Disposal Area, Port of Hampton Roads, Virginia, near the mouth of the James River. See Figure 2 for a detailed view of the study area.

River and the harbor of Hampton Roads to the economic and social well-being of the surrounding communities of Norfolk, Portsmouth, Chesapeake, Virginia Beach, Suffolk, Hampton, and Newport News has been documented by Pleasants (1973). Other important statistics concerning population and projected growth for the Hampton Roads area, notable land-use features, oil spills, small boat usage, closures of shellfish grounds, point discharges, estimated waste loadings from non-point sources, economic activity, and water utilization have been compiled by the Hampton Roads Water Quality Agency¹ (1974-1975). Included in the HRWQA report to the U. S. Environmental Protection Agency was an evaluation and documentation of water quality information for the James River Basin and other local bodies of water. Some further investigations of sediment and water quality in the study area have been conducted by Adams (1973-1975), Adams (1974), Adams et al. (1974, 1975a), Beauchamp (1974), Brehmer (1972), Guide and Villa (1972), Norfolk District Corps of Engineers (1974), Pheiffer et al. (1972), and the Virginia Institute of Marine Sciences (1971, 1972), while circulation and modeling studies were reported by Kuo et al. (1974), Fang et al. (1973), and the Virginia Institute of Marine Sciences (1973).

The normal tidal period at Hampton Roads is 12.42 hrs, with a rise duration of 6.10 hrs and a fall duration of 6.32 hrs (Cronin 1971). A physical description of the area from a transect connecting Fort Wool with Old Point Comfort (see Figure 2) at the eastern extremity of Hampton Roads and extending ten miles upstream on the James River (to a transect approximately two miles below the James River Bridge, which is used for U. S. Highways 12 and 258) is provided in Table 1. If the surface areas of the Elizabeth (transect of the hypothetical mouth is drawn from Sewells Point southwest to land), Hampton, and Lafayette Rivers and Willoughby Bay are excluded from the 0-5 mile portion of Hampton Roads and the Nansemond River from the 5-10 mile portion (see Table 1), then the Craney Island Disposal area would occupy approximately 7.6 percent of the mean low water surface area of the Hampton Roads Harbor.

The Norfolk area has an average frost-free growing season of 239 days and an annual mean rainfall of 45.2 inches (1934-1973). The average temperature for 1973 ranged from 39.7°F (4.3°C) in February to 78.5°F (20.3°C) in August, while the average wind velocity was 10.8 mph out of the west. Local climatological data are reported for the Norfolk Regional Airport at latitude 36°54'N longitude 76°12'W.

¹ Present address: HRWQA, Suite 51, Pembroke Three Building, Virginia Beach, VA.

Table 1. Tidal, areal, and volumetric statistics for the Hampton Roads Harbor. Mile "0" is the transect between Fort Wool and Old Point Comfort, while mile "10" is ten miles upstream on the James River (approximately two miles below the James River bridge). The Elizabeth River mouth is taken as a transect between Sewells Point southwest to land at Craney Island. Other rivers and Bay are treated with transects taken directly across their mouths. Units are in meters with exception of nautical miles (1853.25 meters). (Taken from Cronin 1971).

Location	Mean low water surface area ³ 10 ⁶ M ²	Mean low water volume ⁴ 10 ⁶ M ³	Intertidal volume ⁴ 10 ⁶ M ³	Mean high water volume ⁴ 10 ⁶ M ³	Tidal range M	Average depth M
James River (0-5) ¹	111.43	536.5	85.79	622.31	0.75	5.1 - 7.3
James River (5-10) ²	108.25	350.56	91.53	442.09	0.79	3.1 - 4.7
Elizabeth River	45.57	167.40	36.30	203.70		3.67
Lafayette River	6.31	8.81	4.97	13.78		1.40
Hampton River	1.21	1.77	0.90	2.67		1.46
Willoughby Bay	5.07	12.19	3.70	15.89		2.40
Nansemond River	24.92	58.12	25.89	84.01		2.33

¹ The 0 - 5 nautical mile statistics include the Elizabeth, Lafayette, and Hampton Rivers, and Willoughby Bay.

² The 5 - 10 nautical mile statistics include the Nansemond River.

³ Surface area of Craney Island disposal area included in calculations.

⁴ Volume of water within Craney Island disposal area not included in calculations.

Description of the Craney Island Disposal Area

The Craney Island Disposal area was established in 1957 to receive dredged materials from maintenance and deepening of shipping channels in the Hampton Roads Harbor and contiguous areas (Elizabeth River, James River, etc.). After upgrading of the dikes and filling, followed by compaction of the underlying substrate, the approximate capacity of the site has been estimated at 125 million cubic yards. At the present annual fill rate of about four million cubic yards, the disposal area (with levees to project elevation of 17 feet above mean sea level) could be utilized until 1979. As a result of the Craney Island replacement study (Norfolk District, USACE 1974) conducted by the Norfolk District of the Corps of Engineers, the District Engineer has recommended that the elevation and capacity of the disposal area be increased by gradually raising its levees from 17 to 29 feet above mean sea level. The useful life of the disposal area would then be extended to about 1989. The levee to 29 feet above msl would be located, for stability, approximately 1000 feet inland from the outer edge of the existing levee. The disposal area (ca. 10.3 km²) is located in the southeastern portion of Hampton Roads Harbor at the entrance to the Elizabeth River (Figure 2). It is a trapezoidal-shaped structure with each of the three levees extending approximately two miles in length.

An ecological study of Craney Island was conducted during the period from November 1972 to November 1973 (Marshall 1974), at which time the populations of birds, small mammals, vascular plants, aquatic and terrestrial insects, and plankton were examined. During this period, a seasonal water quality monitoring program was conducted at a location approximately one nautical mile west of the middle spillway. Tidal studies for each of the four seasons were also conducted at this location, and five sediment cores were processed for various chemical parameters.

A preliminary report (Adams, Aitkenhead, and Crouse 1975) at the Craney Island Disposal area for the period December 1973 to June 1974 has been submitted. The additional sampling period from August 1974 to February 1975 is included and evaluated in this technical report, along with the previous data. Briefly, water samples were collected for the analysis of dissolved and particulate species at the No. 1, middle (No. 2), and No. 3 spillways, which empty into the waters of Hampton Roads at the western side of the disposal area,

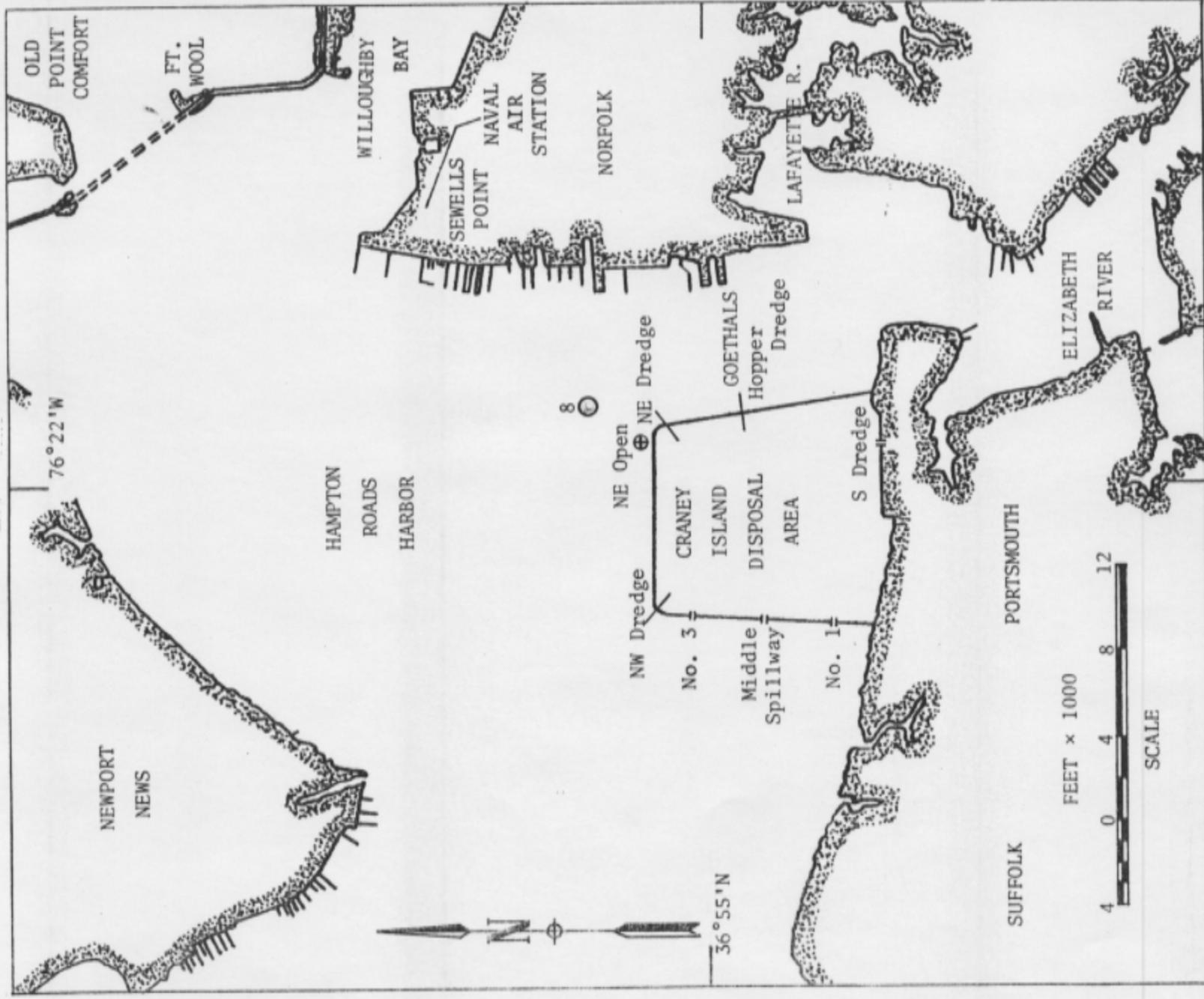


Figure 2. Approximate locations of the sampling sites at the U. S. Army Corps of Engineers' Craney Island Disposal area, Port of Hampton Roads, Virginia. No. 1, middle, and No. 3 are spillways, while NE Open is located on the open water side of the levee. The other positions designate dredge discharge locations. Station 8 represents a location of monthly collection by the Institute of Oceanography, ODU, for the Hampton Roads Sanitation District Commission during the period from January 1974 until April 1975.

and at the northeast corner of Crane Island on the open water side of the levee (considered as background). In addition, dredge pipes were sampled at 15 different times during the first nine months of the program, comprising 32 discrete samples. This should provide information concerning the quality of the sediments and water entering the disposal area. The following parameters were measured: temperature, salinity, pH, dissolved oxygen (and calculations of oxygen saturation), dissolved inorganic orthophosphate, nitrate, nitrite, ammonia, total phosphorus, fecal coliform, and total suspended solids. Samples for dissolved and particulate cadmium, mercury, and zinc were also collected and analyzed. In the latter portion of the program, total Kjeldahl nitrogen measurements were also conducted on samples collected from the spillway and background waters.

METHODS AND MATERIALS

Sampling

Samples were collected with a polyethylene bucket (Cole-Parmer, Chicago, IL) from actively discharging dredge pipes, the No. 1, middle (No. 2), and No. 3 spillways, and the background waters adjacent to the northeast levee (see Figure 2). Water temperature was recorded immediately at the site. Dissolved oxygen was measured at the site with a polarographic probe from December 1973 to August 1974, while during the period from September 1974 to February 1975, 300-ml BOD bottles were filled and preserved in the field for laboratory titrations. Aliquots for nutrients, trace metals, pH, and suspended solids were taken from the bucket and stored in acid-washed polyethylene bottles after rinsing twice with the sample. Salinity samples were collected in citrate bottles. Samples for fecal coliform measurements were stored in plastic containers. Control measurements indicated no contamination for the fecal coliform measurement. The bottles were iced in a cooler for transport to the laboratory, where dissolved species were separated from particulate materials by filtering through either 0.45 μ Type AA Millipore (Millipore Corp., Bedford, MA), 0.45 μ Metrical GA-6 (Gelman Instr., Ann Arbor, MI), or 0.4 μ Nucleopore Type N040 (Nucleopore Corp., Pleasanton, CA) filters. The choice of filter was dictated by the specific analytical technique. Water samples for nutrient analyses, with the exception of dissolved ammonia which was analyzed within six hrs, were placed in acid-rinsed polyethylene bottles and frozen. Aliquots for dissolved trace metals were acidified to pH 1 with reagent grade or specially-prepared¹ conc HCl and stored in acid-rinsed polyethylene bottles. After filtration, filter pads which were used for the measurement of particulate trace metals were stored in plastic vials and frozen.

Locations

Specific locations of the sampling sites are provided in Figure 2, while times of collection are listed in Tables A1 and A2 in the Appendix. Data not reported for a specific discharge on any given collection day indicates a period

¹ Baker reagent grade conc HCl was purified with a sub-boiling Teflon still using the method outlined by Mattison (1972).

of inoperation or complete termination of dredge pumping at that site. In the case of spillways, samples were only collected under significant flow conditions. Sampling changed from the middle to No. 1 spillway in September 1974 because of curtailment of the former site as a discharge area.

Temperature

At each station, temperature was measured with a high precision bucket thermometer (Kahl Scientific Instr. Corp., El Cajon, CA) which has a stated accuracy of $\pm 0.02^{\circ}\text{C}$.

Salinity

Salinity samples were usually collected in 400-ml citrate bottles, which were fitted with porcelain caps and rubber washers to avoid evaporation. These were returned to the Institute of Oceanography where salinities were determined with a Hytech model 6620 (Bissett-Berman Co., San Diego, CA) salinometer. These bottles were usually opened and used for pH measurements, but this process was only momentary so that evaporation would be negligible. The salinometer was standardized with standard sea water, which was periodically calibrated with Copenhagen sea water (I.A.P.S.O. Standard Sea-Water Service, Charlottenlund, Denmark). Accuracy of this instrument is $\pm 0.003^{\circ}/\text{oo}$, as provided in the instruction manual. Starting in November 1974, salinities were calculated from usual conductivity measurements, however drift and temperature corrections were not considered (accuracy $\pm 0.01^{\circ}/\text{oo}$).

pH

During the first nine months of the program, pH was measured with a Corning research model 12 pH meter (Corning Scientific Instr., Medfield, MA) after water samples were returned to the laboratory. Beginning in September 1974, a Weston and Stack model 650 Multianalyzer (Rexnord Instr. Products, Malvern, PA) with an LN model 117342 combination electrode (Leeds and Northrup Co., North Wales, PA) was used for pH measurements in the laboratory. Each instrument was standardized and calibrated with pH 7 and pH 10 buffers before each set of water samples was measured. Analyses were conducted within three hours of collection; therefore, under these conditions the accuracy would be approximately ± 0.1 units.

Dissolved Oxygen

During the first nine months of the program (December 1973 to August 1974), an oxygen meter model 51A (Yellow Springs Instr. Co., Yellow Springs, OH) was used for the determination of dissolved oxygen in the field. This instrument was periodically checked with standard Winkler titrations (Strickland and Parsons 1972). Accuracy is approximately ± 0.2 mg/liter when calibrated at $\pm 5^{\circ}\text{C}$ of the water sample temperature. Starting in September 1974, oxygen samples were collected in 300-ml BOD bottles and preserved with manganous sulfate and alkaline potassium iodide (Strickland and Parsons op. cit.) at the site. Acidification and titration were also conducted as outlined in Strickland and Parsons (op. cit.). The stated precision at the 11.2 mg/liter level of dissolved oxygen is approximately ± 0.03 mg/liter about the mean of duplicate determinations (Strickland and Parsons op. cit.); however, this is the highest precision (at the 95 percent confidence level) for laboratory work under ideal conditions. Because of varying field conditions and changes during transportation, the uncertainty range would be appreciably greater (ca. ± 0.1 mg/liter).

Fecal Coliform Bacteria

The membrane filter technique, as outlined in Standard Methods for the Examination of Water and Wastewater (Taras et al. 1971), was used for the measurements of fecal coliform (*Escherichia coli*). During the first portion of the program (December 1973 to August 1974), water samples were analyzed by processing only one ml of water sample for incubation and counting. This could be the reason for the relatively low counts; therefore, starting in September 1974 fecal coliform measurements were improved by processing larger volumes (10 - 100 ml) through the filter pads before incubation in a Millipore constant temperature waterbath incubator (Millipore Corp., Bedford, MA; Cat. No. XX6300300) held at $44.5 \pm 0.2^{\circ}\text{C}$ for 24 hrs.

Total Phosphorus and Dissolved Orthophosphate-Phosphorus

Dissolved inorganic orthophosphate was determined by the single solution (Murphy and Riley 1962) ascorbic acid method as outlined in Strickland and Parsons (1972), where the absorption of the phosphomolybdic acid complex was measured at 885 nm on a Bausch and Lomb Spectronic 20 spectrophotometer (Bausch and Lomb Corp., Rochester, NY). In the latter part of the program, a Beckman

model DU (Beckman Instr., South Pasadena, CA) spectrophotometer fitted with a Gilford model 222 attachment (Gilford Instr., Oberlin, OH) was used for more precise measurements. Total phosphorus was determined on an unfiltered water sample by the persulphate digestion - autoclave method described in Standard Methods (Taras et al. 1971). Duplicate measurements were taken, whenever possible, and final values are reported as the average concentration. The stated precision at the 0.093 mg/liter level of orthophosphate is approximately ± 0.001 mg/liter about the mean of duplicate determinations (Strickland and Parsons 1972). This is expressed for the 95 percent confidence level.

Dissolved Inorganic Nitrate and Nitrite

During the first seven months of the program, December 1973 to June 1974, dissolved inorganic nitrate was determined by the cadmium-copper column reduction procedure (Morris and Riley 1973), as modified by Grasshoff (1964) and Wood et al. (1967). During the same period, dissolved nitrite was measured according to a procedure from Shinn (1941), as applied to sea water by Bendschneider and Robinson (1952). The procedural techniques are provided in Strickland and Parsons (op. cit.), where the stated precision at the 0.280 mg/liter level of nitrate is approximately ± 0.005 mg/liter about the mean of duplicate determinations (95 percent level of confidence). This procedure is based upon the assumption that the reduction efficiency of the cadmium-copper column is kept at a constant value (approximately 95 percent). The stated precision (Strickland and Parsons op. cit.) at the 0.014 mg/liter level of nitrite is approximately ± 0.003 mg/liter (at the 95 percent level of confidence) about the mean of duplicate measurements. Reported values are the average of duplicate determinations, where the absorbance was measured at 543 nm with a Bausch and Lomb Spectronic 20 spectrophotometer. Beginning in August 1974, dissolved inorganic nitrate and nitrite were measured with a modified Technicon I system (Technicon Corp., Tarrytown, NY) developed in the laboratories at the Institute of Oceanography from a variety of established methods. Originally, the Technicon Industrial method (No. 158-71W, December 1972) manifold with a granular copper-cadmium column was employed to detect dissolved nitrate plus nitrite. The granular copper-cadmium column was replaced with a 2-meter length (1-mm dia.) of copper-coated cadmium wire fitted inside a similar length of 1.3-mm i.d. Teflon tubing, as described by Stainton (1974) for

lake waters. The column provided a 95-105 percent reduction of nitrate to nitrite, and it was effective over the 0.005 to 1.000 mg/liter range. The automated method for dissolved inorganic nitrite was adapted from the Technicon Industrial method (No. 161-71W, January 1975) manifold, which was similar to the diazotization method outlined in Standard Methods (Taras et al. op. cit.). The stated coefficients of variation are ± 0.0004 at the 0.035 mg/liter level for nitrates and ± 0.0002 at the 0.014 mg/liter level for nitrites.

Dissolved Ammonia Nitrogen and Total Kjeldahl Nitrogen

Dissolved ammonia was determined on unfiltered water samples to prevent loss of ammonia as a gas. Inorganic ammonia, as dissolved and weakly absorbed species on particulate material (released to solution upon acidification with 0.01 N H_2SO_4), was measured using a modification of the phenol-hypochlorite method (Solórzano 1969) described in Strickland and Parsons (op. cit.). Absorbance was measured at 640 nm on a Bausch and Lomb Spectronic 20 spectrophotometer, and values represent an average of duplicate determinations. The stated precision at the 0.042 mg/liter level of ammonia is approximately ± 0.001 mg/liter about the mean of duplicate measurements (Strickland and Parsons op. cit.). This is expressed for the 95 percent confidence limit.

For determinations of total Kjeldahl nitrogen, unfiltered water samples were frozen upon return to the laboratory. The sample was heated to boiling in the presence of sulfuric acid, potassium sulfate, and mercuric sulfate catalyst. By this method, the amino nitrogen of most organic materials would be converted to ammonium bisulfate (total Kjeldahl nitrogen includes inorganic ammonia and organic nitrogen, but does not include nitrate and nitrite). The mercury ammonium complex is then decomposed by sodium thiosulfate, and the ammonia is distilled from the alkaline medium and absorbed in boric acid. The ammonia was determined by titration with 0.020 N H_2SO_4 . At the 1.5 mg/liter level of nitrogen, the precision is 54.7 percent and the accuracy is estimated at four percent, as listed in Standard Methods (Taras et al. 1971). Starting in January 1975, TKN was measured by digesting water samples in 30 ml micro-Kjeldahl flasks (Arthur H. Thomas Co., Philadelphia, PA) in a LabConCo fume hood. The sample was heated with a sulfuric acid and potassium sulfate-mercuric sulfate solution by refluxing to a clear or pale-yellow color (30 to 60 min). It was then cooled, diluted to slightly less than 50 ml with

deionized water, and neutralized with ammonia-free sodium hydroxide. With the further addition of deionized water, exactly 50.0 ml was analyzed colorimetrically by the method of Solórzano (1969) for dissolved ammonia. Concentrations were determined with a linear least squares calibration plot of analytical standards, prepared from ammonium chloride, which were identically processed by the method described above.

Dissolved Cadmium, Mercury, and Zinc

During the first seven months of the program (December 1973 to June 1974), the reactive concentrations of dissolved cadmium and zinc were measured on a 10 ml aliquot, with the procedure outlined by Princeton Applied Research, Princeton, NJ for the PAR model 174 Polarographic Analyzer. This is an anodic stripping voltammetric (ASV) method, with peak heights recorded on an Omnigraphic model 2000 X-Y Recorder (Bausch and Lomb, Rochester, NY) and compared to standards by the addition of known concentrations of each metal to the same solution matrix. The accuracy for these two metals by anodic stripping voltammetry was approximately ± 10 percent of the reported concentration. Dissolved mercury was determined by means of an acid digestion-permanganate oxidation, followed by chloride reduction and volatilization (Hatch and Ott 1968), as modified by the Perkin-Elmer Corporation (Perkin-Elmer Corp., Norwalk, CT) for use with their Coleman model MAS-50 flameless atomic absorption mercury analyzer. A linear least squares calibration plot was obtained using analytical standards, and sample concentrations were determined from the slope equations. The accuracy for dissolved mercury is estimated at approximately ± 10 percent of the reported concentration.

Starting in August 1974, dissolved cadmium and zinc were determined by a different method. Sample collection was similar as previously described. After return to the laboratory, 300-400 ml of sample were filtered and treated with conc HCl to a final concentration of 1-2 percent. Total dissolved metal concentrations were determined with a Perkin-Elmer model 303 atomic absorption spectrophotometer, equipped with a (flameless) graphite furnace accessory, Perkin Elmer model HGA-2100. A deuterium arc background corrector was used to correct for broad band absorbances,¹ and a Perkin-Elmer recorder readout accessory was combined with a Beckman 10-inch strip chart recorder for measuring the signal. Due to instrumental malfunctions and optical modifications associated with installation of the graphite furnace, analyses were not begun until December 1974.

Differences between the measurements of dissolved cadmium and zinc by these two methods (ASV versus graphite furnace atomic absorption) will be evaluated in the discussion section of this report.

In order to bring water samples to the appropriate concentration ranges and to minimize both matrix effects and sodium chloride absorption in the graphite furnace, samples were diluted with Super-Q (Millipore Corp., Bedford, MA) deionized water. Inspection of the recorder trace during atomization showed multiple or consecutive peaks. It is possible that these were due to different species of the metal in the natural water sample. Addition of two percent perchloric acid (double-vacuum distilled from Vycor) gave a single peak during atomization, indicating complete oxidation of any organically-associated metal. This phenomenon was observed for both cadmium and zinc, and distilled water blanks showed that the intensified peak height was not due to contamination. Peak heights were read off the recorder chart paper and converted from percent absorption to absorbance. The method of standard additions was used to account for matrix effects, which are extremely significant in a method as sensitive as the graphite furnace. Sample peak heights were converted to concentration by using a linear least squares program, which consisted of the calculation of slope from the absorbance of the sample plus two standards and a blank. Each determination (blank, sample, sample plus the first standard addition, and sample plus the second standard addition) was conducted until the relative standard deviation of the peak measurement was better than eight percent (duplicate or triplicate measurements). Average error for the standards as calculated from slope equations was less than ten percent, and generally three to five percent. Accuracy and precision is conservatively estimated at ± 10 percent for cadmium and zinc measurements during the second portion of the monitoring program.

Total Suspended Solids

Total suspended solids were measured according to the method outlined in Strickland and Parsons (op. cit.) for the determination of microscopic materials in sea water. Filters were dried to constant weight by heating at 130°C. Accuracy of replicate measurements was estimated at ± 0.5 mg/liter using a Mettler H10T analytical balance (Mettler Instr. Corp., Princeton, NJ).

Particulate Cadmium, Mercury, and Zinc

During the initial period of the program (December 1973 to June 1974), particulate cadmium and zinc were determined by filtering the samples through 1-3 Gelman or Nucleopore filters. The concentration of particulate suspended material would usually dictate the number of filter pads necessary for metal analysis. The suspended material and filter(s) were digested in nitric acid (Anderson 1974), an average filter weight was subtracted for computing the concentration of particulates on the filter pad (rather than taring each filter separately), and the diluted nitric acid was aspirated into a single-slot burner of a Perkin-Elmer model 503 atomic absorption spectrophotometer. Sample concentrations were determined from slope equations using analytical standards for each metal. Particulate mercury was determined by the Hatch and Ott (1968) method using similar filtering, standardization, and digestion techniques as described above. When large concentrations of suspended materials were present, the accuracy of the particulate metal measurements is estimated at approximately ± 10 percent of the reported concentration. However, when there was negligible particulate material on the filter pads, and thus a weak signal was measured for the respective metal, the accuracy is probably significantly poorer (at least 25 percent; however, this has not been determined).

Starting in August 1974, particulate cadmium, mercury, and zinc were determined by similar analytical techniques with the exception that filtering of the water sample was handled differently. In order that maximum accuracy would be obtained, each filter was weighed prior to filtration, then dried at 60°C for 48 hrs to constant weight. Several filters were collected for each sample, and the weight of suspended solids determined to better than ± 0.5 mg. The filters and solids were digested with 1:1 HCl - HNO_3 for 3-5 hrs at $95 \pm 5^{\circ}\text{C}$ (Anderson 1974). The mixture was diluted to 100.0 ml with Super-Q deionized water. Concentrations were determined by flame aspiration into a Perkin-Elmer model 503 atomic absorption spectrophotometer, and these were compared with standards made up in a similar acid matrix and analyzed under identical conditions. Sample concentrations were derived from linear least squares calibration equations of the standards, after correcting for blanks using filters digested with the same amount of acid. Values are provided as micrograms of the metal to gm dry weight of suspended solids.

RESULTS

Untreated data for the monitoring program at the Craney Island Disposal area are located in the Appendix. Tables A1 and A2 provide collection times and the key to sample numbers (which appear in later figures depicting the variations of each parameter) for the period 28 December 1973 to 20 February 1975. Tables A3 and A4 list the parameters at the spillways and northeast open background sampling site for the period 28 December 1973 to 28 June 1974. Tables A5 to A8 provide similar information for the time period from 6 August 1974 until 20 February 1975. During the time period from December 1973 until February 1975, a total number of 60 discrete samples were collected from three spillways, and 50 discrete samples from the northeast open water site. Effluent data from sampling four dredge pipes at 15 different times (32 discrete samples) are provided in Tables A9 and A10.

The results section will be divided into the dredge pipe effluent data entering the Craney Island Disposal area; then each parameter will be reported for the spillways (effluent leaving the disposal area) and these will be related to the northeast open water site. Statistical treatment of the data will be reported at the 95 percent level of confidence (or approximately two sigma).

Dredge Pipe Effluent Sampling

Dredge pipes were sampled only during the first portion of the monitoring program (December 1973 to August 1974). Water temperature at the dredge pipes indicated a normal seasonal range from a low of 7.05°C during the winter to 25.25°C in the early summer. Salinity ranged from 10.850 to 25.484 ‰. pH ranged from 7.38 to 8.54 with a mean of 7.91 ± 0.68 (n = 31). Dissolved oxygen was zero at one time (other values on the same day were as high as 9.6 mg/liter) and as high as 10.9 mg/liter (105 percent saturation) in March 1974. The arithmetic mean was 4.45 ± 6.34 mg/liter (n = 31). The statistics for the dredge pipe effluent data are provided in Table 2.

Measurements for the various nutrients provided a range for dissolved inorganic orthophosphate of 0.000 to 1.091 mg/liter (mean of 0.264 ± 0.640 mg/liter; n = 31), while total phosphorus was 0.043 to 4.133 mg/liter (mean of 0.893 ± 1.974 mg/liter; n = 31). For the dissolved inorganic nitrogen compounds, the concentration of ammonia, as expected, exceeded the

Table 2. Statistics for the dredge pipe effluent material (both dissolved and particulate) entering the Crane Island Disposal area, Port of Hampton Roads, Virginia during the period from 28 December 1973 until 28 June 1974 (when appropriate, data for 6 August 1974 are included).

	Units	Range	Mean	Std. Dev. (± 2 sigma)	n
Salinity	‰	10.850 - 25.484	--	--	--
Temperature	°C	7.05 - 25.23	--	--	--
pH		7.38 - 8.54	7.91	0.68	31
Fecal coliform	colonies per 100 ml	0 - 250	79	164	31
Dissolved oxygen	mg/l	0.00 - 10.90	4.45	6.34	31
Oxygen saturation	%	0 - 105	50	62	31
PO ₄ - P	mg/l	0.000 - 1.091	0.264	0.64	31
Total phosphorus	mg/l	0.043 - 4.133	0.893	1.974	31
NO ₃ - N	mg/l	0.003 - 0.869	0.152	0.362	31
NO ₂ - N	mg/l	0.002 - 0.213	0.022	0.076	31
NH ₄ - N	mg/l	0.060 - 59.94	5.780	22.12	31
Diss. cadmium ¹	mg/l	0.000 - 0.009	0.004	0.006	31
Diss. mercury	mg/l	0.000 - 0.027	0.005	0.014	31
Diss. zinc ¹	mg/l	0.007 - 0.214	0.053	0.096	30
Part. cadmium	µg/g	0.40 - 426	47.3	166	31
Part. mercury	µg/g	0.03 - 4.18	0.70	1.71	25
Part. zinc	µg/g	22.3 - 745	111	289	31

¹ Measured as reactive concentration by anodic stripping voltammetry (ASV).

others with a range of 0.060 to 59.94 mg/liter (mean of 5.780 ± 22.12 mg/liter; $n = 31$). Nitrates ranged from 0.003 to 0.869 mg/liter (mean of 0.152 ± 0.362 mg/liter; $n = 31$), while nitrites were 0.002 to 0.213 mg/liter (mean of 0.022 ± 0.076 mg/liter; $n = 31$).

Dissolved cadmium and zinc, which were both measured by anodic stripping voltammetry (ASV), ranged from 0.000 to 0.009 mg/liter and 0.007 to 0.214 mg/liter, respectively. The mean for dissolved cadmium was 0.004 ± 0.006 mg/liter ($n = 31$), while more than one third (12) of the dredge pipe effluent samples were 0.001 mg/liter or less. Only one dredge effluent sample (6 August 1974) was determined, in triplicate, by the graphite furnace technique for total dissolved cadmium, and this measurement (0.263 mg/liter) was almost 30 times greater than the largest concentration by ASV. Dissolved zinc had a mean concentration of 0.053 ± 0.096 mg/liter ($n = 30$). Again, one dredge effluent sample, collected on 6 August 1974, was measured by graphite furnace. This value (0.399 mg/liter) was only double the highest dissolved zinc measurement by ASV. Dissolved mercury ranged from 0.000 to 0.027 mg/liter, with a mean of 0.005 ± 0.014 mg/liter ($n = 31$).

Measurements of the particulate metals resulted in the following statistics; cadmium was 0.40 to 426 $\mu\text{g/g}$ (mean of 47.3 ± 166 $\mu\text{g/g}$, $n = 31$), mercury was 0.03 to 4.18 $\mu\text{g/g}$ (mean of 0.70 ± 1.71 $\mu\text{g/g}$, $n = 25$), and zinc was 22.3 to 745 $\mu\text{g/g}$ (mean of 111 ± 289 $\mu\text{g/g}$, $n = 31$).

Several factors are important in determining sedimentary parameters (dredge data) such as trace metal and nutrient composition. First, the source should be considered, i.e., if there are sufficient concentrations of unstable dissolved species, dredged sediments should reflect this input as adsorbed or rapidly released species (due to dredging agitation and disturbance). Organic versus inorganic components are likewise determinants of composition, especially for nitrogen and phosphorus, but also in the case of many trace metals. Sediment texture is important in the evaluation of various particulate components. This pertains primarily to inorganic particles, such as fine sand. Because of the greater surface to weight ratio of fine particles, trace metals and other charged species would be in greater concentration on the smaller size fraction, and conversely, coarse-grained particulates would be expected to have less of these species. Lastly, there is the dredging operation and the sampling of the effluent to consider. It is common practice for operators to raise the dredge head off the sediment to allow overlying water to clear the dredging

apparatus and discharge pipes. Therefore, a sample of the pipe effluent might be more representative of the overlying waters than of the sediment itself. This would hold true primarily for dissolved rather than particulate species. Dredge parameters, then, can be expected to exhibit a broad range of values, and averages should be viewed with caution as being representative of average input qualities.

Spillways and NE Open Background Sampling

During the first portion (December 1973 to August 1974) of the monitoring program, the middle spillway ($n = 19$) was sampled exclusively. Starting in September 1974 and continuing until February 1975, the No. 1 spillway ($n = 31$) was sampled exclusively until 31 January 1975, when dredging resumed and the increased volume activated the middle ($n = 5$) and No. 3 ($n = 5$) spillways. As described in the previous section, dredge pipe effluent samples were not collected during the second portion of the program. Statistics for the two portions of the monitoring program are provided in Tables 3 and 4.

Physical parameters. Due to the smaller volume of water within the Craney Island Disposal area as opposed to that of Hampton Roads Harbor, water temperatures within Craney Island tended to be more sensitive to atmospheric thermal fluctuations than the NE Open water. This was most evident when abrupt temperature changes occurred, for example, on a relatively warm (for the season) day, such as 16 October 1974, the No. 1 spillway was 23.77°C and the NE Open water measured 20.75°C . On the coldest day in November (Nov. 27, 1974; ranged from -1.7° to 8.3°C at the Norfolk Airport), the No. 1 spillway was 3.86°C , while the NE Open water was 9.17°C . Overall, the temperatures were similar during periods when small diurnal temperature ranges were predominant. Temperature data are presented in Figure 3. Salinity at the Northeast Open water site ranged from 9.408 ‰ to 21.939 ‰.

Dissolved oxygen, pH, and bacteria. From December 1973 to August 1974, dissolved oxygen (Figure 4) ranged from 5.4 to 11.5 mg/liter (mean of 8.71 ± 2.70 mg/liter) at the middle spillway, while the NE Open was 6.20 to 11.80 mg/liter (mean of 9.20 ± 3.10 mg/liter). There was also very little difference in the dissolved oxygen data between the first and second portions of the program. The mean for the entire sample period at the spillways was 9.18 ± 2.68 mg/liter, while the NE Open was 8.90 ± 2.97 mg/liter. Dissolved oxygen was usually greater than 100 percent of the saturation value (on 16 occasions it was greater than 110 percent, as compared to 10 times at the NE Open site) during plankton bloom conditions, as evident by a green coloration of the spillway waters. Dissolved oxygen at the spillways was always above 6 mg/liter with the exception of one time (6 August 1974) when it was 5.4 mg/liter.

Table 3. Statistics for particulate and dissolved materials at the middle spillway and the NE Open background sampling site during the monitoring program at the Craney Island Disposal area, Port of Hampton Roads, Virginia, from 28 December 1973 until 28 June 1974 (when appropriate, data for 6 August 1974 are included).

	Units		Range		Mean	Std. Dev.	
						(± 2 sigma)	n
Salinity	‰						
	M Spill ¹		10.076	20.174	--	--	--
NE Open ¹		9.408	21.939	--	--	--	--
Temperature	°C						
	M Spill		5.50	26.40	--	--	--
NE Open		6.70	23.83	--	--	--	--
pH							
	M Spill		7.82	9.24	8.52	0.72	19
NE Open		7.71	8.73	8.12	0.46	20	
Fecal coliforma	Colonies per 100 ml						
	M Spill		0	200	18	98	20
NE Open		0	1	0	0	21	
Dissolved oxygen	mg/l						
	M Spill		5.4	11.5	8.7	2.7	20
NE Open		6.2	11.8	9.2	3.1	21	
Oxygen saturation	%						
	M Spill		64	124	100	32	20
NE Open		69	125	100	30	21	
PO ₄ - P	mg/l						
	M Spill		0.000	0.264	0.065	0.134	20
NE Open		0.000	0.090	0.032	0.048	21	
Total phosphorus	mg/l						
	M Spill		0.058	1.369	0.287	0.558	20
NE Open		0.014	0.169	0.094	0.070	21	
NO ₃ - N	mg/l						
	M Spill		0.018	0.465	0.130	0.234	20
NE Open		0.004	0.263	0.101	0.144	21	
NO ₂ - N	mg/l						
	M Spill		0.001	0.280	0.049	0.164	20
NE Open		0.001	0.063	0.013	0.029	21	
NH ₄ - N	mg/l						
	M Spill		0.011	13.76	2.208	7.109	20
NE Open		0.011	4.532	0.488	1.938	21	
Diss. cadmium ²	mg/l						
	M Spill		0.000	0.019	0.005	0.010	19
NE Open		0.001	0.056	0.010	0.026	20	
Diss. mercury	mg/l						
	M Spill		0.000	0.021	0.006	0.016	19
NE Open		0.000	0.023	0.006	0.014	20	
Diss. zinc ²	mg/l						
	M Spill		0.010	0.149	0.054	0.072	19
NE Open		0.012	0.116 ³	0.047	0.059	19	
Suspended solids	mg/l						
	M Spill		49	3430	461	1728	20
NE Open		4	92	32	48	21	
Part. cadmium	µg/g						
	M Spill		0.75	133	21.5	68.8	20
NE Open		0.47	103	13.2	50.1	21	
Part. mercury	µg/g						
	M Spill		0.115	1.160	0.345	0.597	16
NE Open		0.045	1.150	0.261	0.543	15	
Part. zinc	µg/g						
	M Spill		12.3	667	87.3	289	20
NE Open		12.9	374	57.2	163	21	

¹ M Spill is middle spillway, NE Open is northeast open water sample (see Figure 2 for station locations).

² Measured as reactive concentration by anodic stripping voltammetry (ASV).

³ One value (0.424 mg/l) rejected due to possible contamination.

Table 4. Statistics for particulate and dissolved materials at the No. 1 spillway and the NE Open background sampling site during the monitoring program at the Craney Island Disposal area, Port of Hampton Roads, Virginia, from 18 September 1974 until 20 February 1975.

	Units	Range	Mean	Std. Dev. (± 2 sigma)	n
Salinity	#1 Spill ¹	10.24 - 17.894	---	---	---
	NE Open ¹	13.63 - 21.939	---	---	---
Temperature	#1 Spill	3.20 - 24.12	---	---	---
	NE Open	4.18 - 24.80	---	---	---
pH	#1 Spill	8.28 - 9.08	8.62	0.49	30
	NE Open	6.78 - 8.19	7.83	0.64	29
Fecal coliforms per 100 ml	#1 Spill	0 - 217	64	118	30
	NE Open	0 - 20	3	8	29
Dissolved oxygen mg/l	#1 Spill	6.14 - 12.18	9.49	2.46	30
	NE Open	6.95 - 12.08	8.14	4.74	29
Oxygen saturation %	#1 Spill	71 - 145	99	42	30
	NE Open	66 - 149	94	48	29
PO ₄ - P mg/l	#1 Spill	0.013 - 0.340	0.085	0.130	30
	NE Open	0.023 - 0.262	0.064	0.110	29
Total phosphorus mg/l	#1 Spill	0.095 - 0.445	0.235	0.190	24
	NE Open	0.049 - 0.243	0.103	0.100	23
NO ₃ - N mg/l	#1 Spill	0.007 - 2.832	0.440	1.620	28
	NE Open	0.073 - 3.801	0.567	1.564	28
NO ₂ - N mg/l	#1 Spill	<0.006 - 0.089	0.028	0.050	30
	NE Open	<0.006 - 0.141	0.027	0.068	29
NH ₄ - N mg/l	#1 Spill	0.007 - 2.679	0.419	1.242	30
	NE Open	0.019 - 0.214	0.108	0.088	29
Total Kjeldahl N mg/l	#1 Spill	2.15 - 9.92	4.95	3.68	22
	NE Open	0.17 - 2.43	1.42	1.46	21
Diss. cadmium ² mg/l	#1 Spill	0.005 - 0.254	0.051	0.096	30
	NE Open	0.013 - 0.076	0.036	0.028	29
Diss. mercury mg/l	#1 Spill	0.001 - 0.014	0.005	0.007	30
	NE Open	0.001 - 0.005	0.003	0.003	29
Diss. zinc ² mg/l	#1 Spill	0.035 - 0.586	0.175	0.256	30
	NE Open	0.028 - 0.282	0.109	0.116	29
Suspended solids mg/l	#1 Spill	54 - 660	254	354	30
	NE Open	14 - 345	96	202	29
Part. cadmium ug/g	#1 Spill	6.82 - 237	107	263	30
	NE Open	<0.5 - 90.3	17.2	40.3	29
Part. mercury ug/g	#1 Spill	0.082 - 1.50	0.650	0.689	30
	NE Open	0.008 - 0.908	0.429	0.539	29
Part. zinc ug/g	#1 Spill	35.8 - 664	239	347	30
	NE Open	8.62 - 462	87.8	213	29

¹ #1 Spill is no. 1 spillway, NE Open is northeast open water sample (see Figure 2 for station locations).

² Measured as total dissolved metal by graphite furnace atomic absorption.

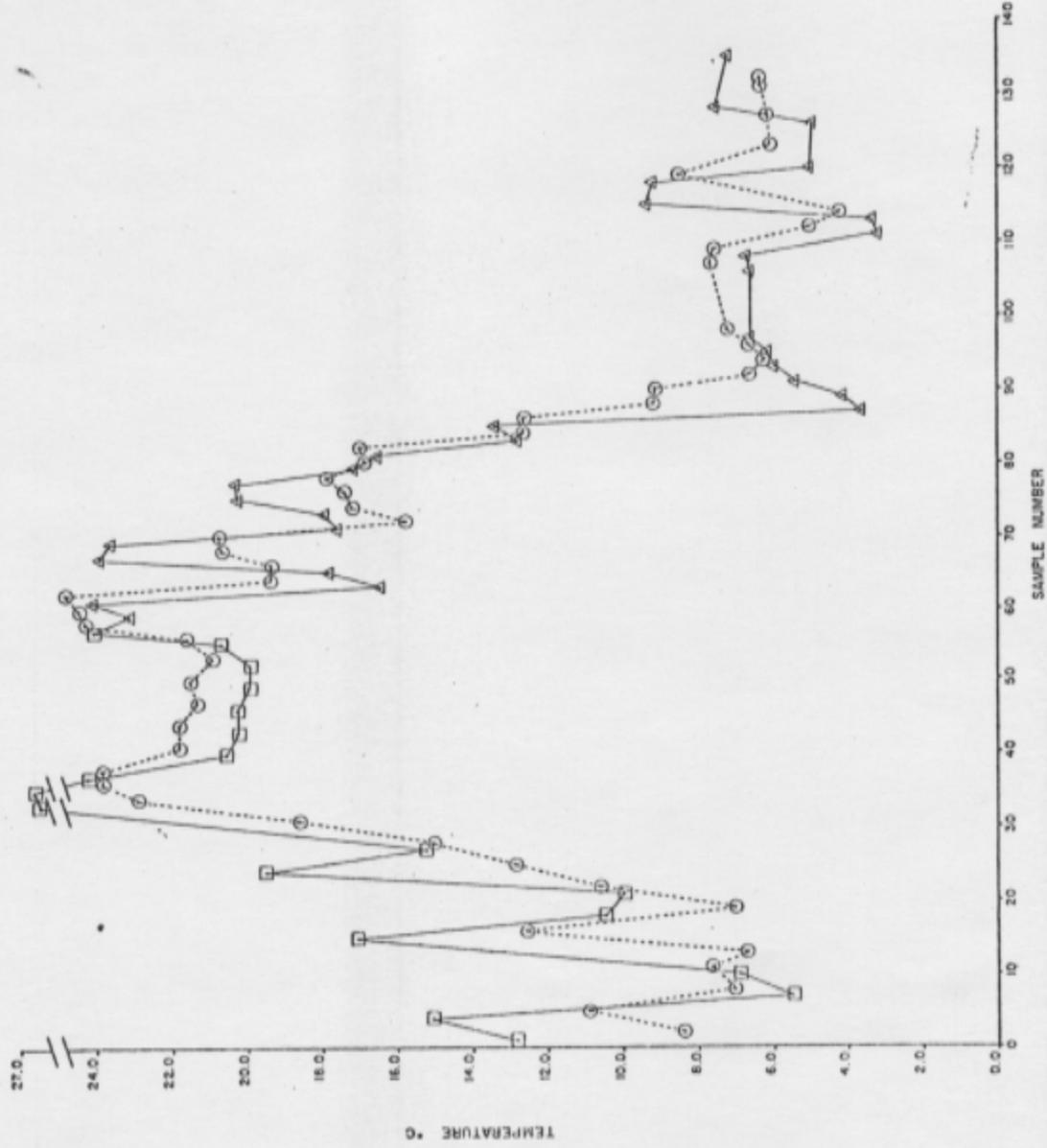


Figure 3. Temperature ($^{\circ}\text{C}$) at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from December 1973 to February 1975; \square = middle spillway, Δ = No. 1 spillway, \odot = northeast open water. Note the scale break above 24°C .

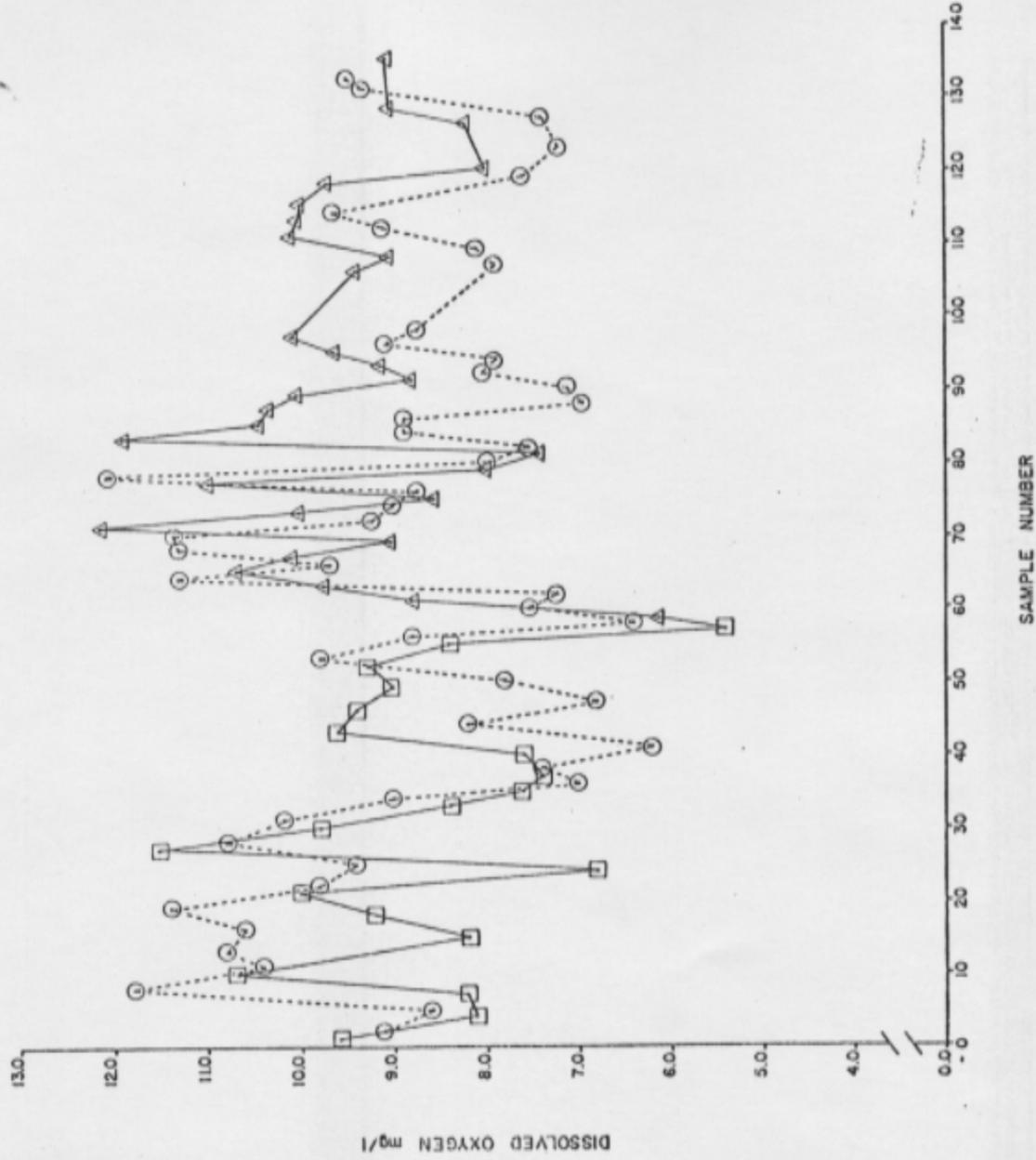


Figure 4. Dissolved oxygen (mg/l) at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from December 1973 to February 1975; \square = middle spillway, Δ = No. 1 spillway, \odot = northeast open water. Note the scale break between 0 and 4 mg/liter.

The values for pH at the spillways were higher (averaged 0.4 to 0.9 units greater) than at the NE Open water site, with the exception of two occasions (Figure 5). During the first portion of the program, pH ranged from 7.82 to 9.24 (mean of 8.52 ± 0.72) at the middle spillway, while the NE Open site was 7.71 to 8.73 (mean of 8.12 ± 0.46). In the second portion of the program, the No. 1 spillway ranged from 8.28 to 9.08 (mean of 8.62 ± 0.49), while the NE Open was 6.78 to 8.19 (mean of 7.83 ± 0.64). The mean for the total sampling period at the spillways was 8.57 ± 0.60 , while the NE Open was 7.95 ± 0.63 pH units.

As seen in Figure 6, fecal coliform bacteria (*Escherichia coli*) counts at the spillways exceeded 100 colonies per 100 ml on eight occasions only. During the second portion of the program (when more accurate results were obtained because of improved techniques), the NE Open water site was usually below ten colonies, while the No. 1 spillway ranged between zero and 217 colonies (mean of 64 ± 118).

Nutrients, total phosphorus, and total Kjeldahl nitrogen. During the first portion of the program, dissolved inorganic orthophosphate (Figure 7) ranged from less than detection (<0.001 mg/liter) to 0.264 mg/liter (mean of 0.065 ± 0.134 mg/liter) at the middle spillway, while the NE Open water site was <0.001 to 0.090 mg/liter (mean of 0.032 ± 0.048 mg/liter). During the second portion of the program, the range at the No. 1 spillway was 0.013 to 0.340 mg/liter (mean of 0.085 ± 0.130 mg/liter), while the NE Open was 0.023 to 0.262 mg/liter (mean of 0.064 ± 0.110 mg/liter). The mean for the entire sample program was 0.076 ± 0.133 mg/liter at the spillway, while the NE Open was 0.050 ± 0.095 mg/liter. A large increase in dissolved orthophosphate was evident in April and again in September 1974 (also present at the NE Open water site during September), which probably stimulated plankton growth. In both months, phosphate values dropped rapidly to background levels (ca. 0.06 mg/liter) within one month, indicating biological utilization. Total phosphorus (Figure 8) ranged from 0.058 to 1.369 mg/liter (mean of 0.287 ± 0.558 mg/liter) at the middle spillway during the first portion of the program, while the NE Open site was 0.014 to 0.169 mg/liter (mean of 0.094 ± 0.070 mg/liter). If the one high value (1.369 mg/liter¹ on 18 January 1974) at the middle spillway was

1 Both the presence of an active dredge effluent at the NW corner of Craney Island and the high suspended solids at the middle spillway suggest that this datum point cannot be discarded as analytical error.

Figure 5. pH at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from December 1973 to February 1975; \square = middle spillway, \triangle = No. 1 spillway, \odot = northeast open water.

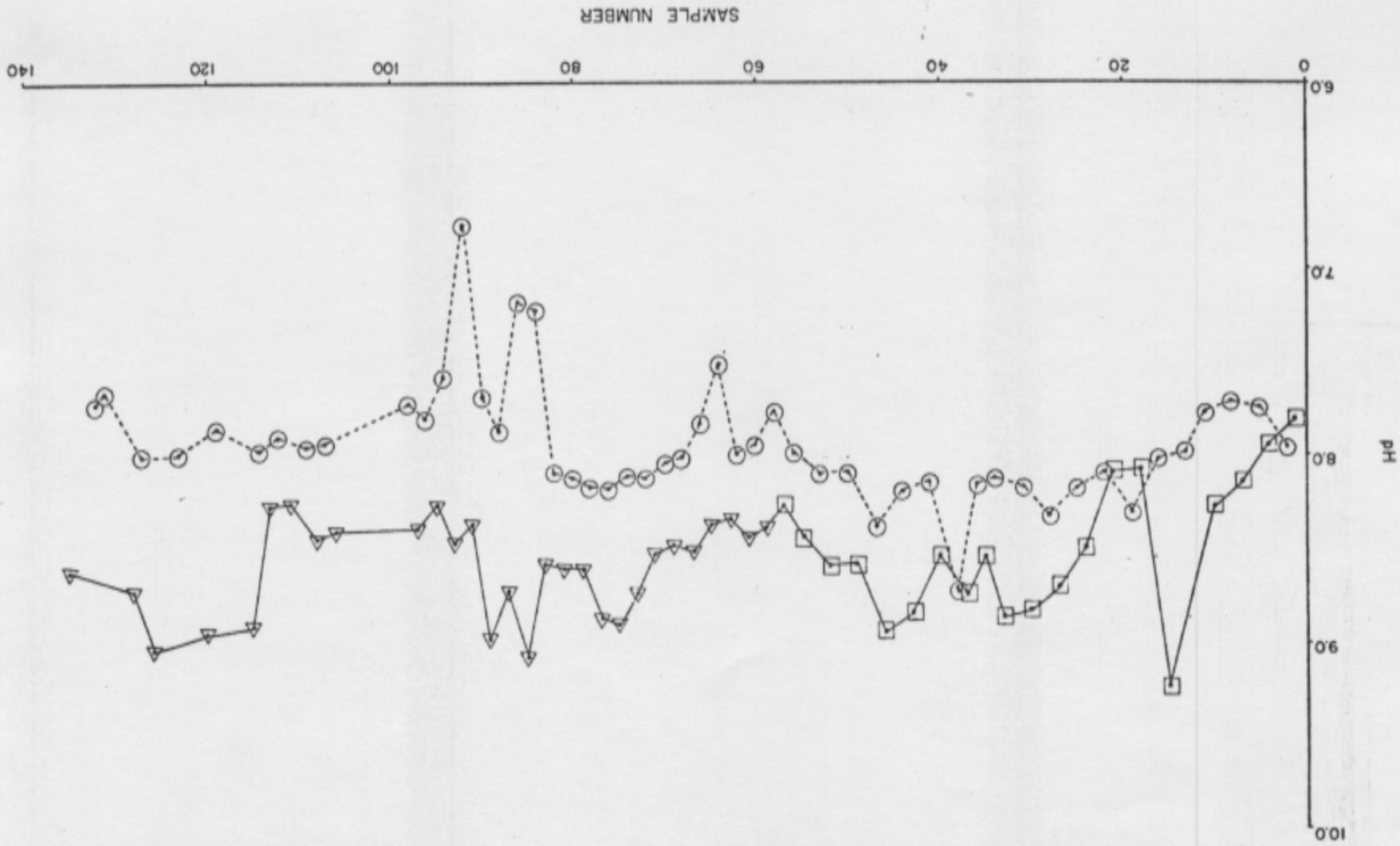
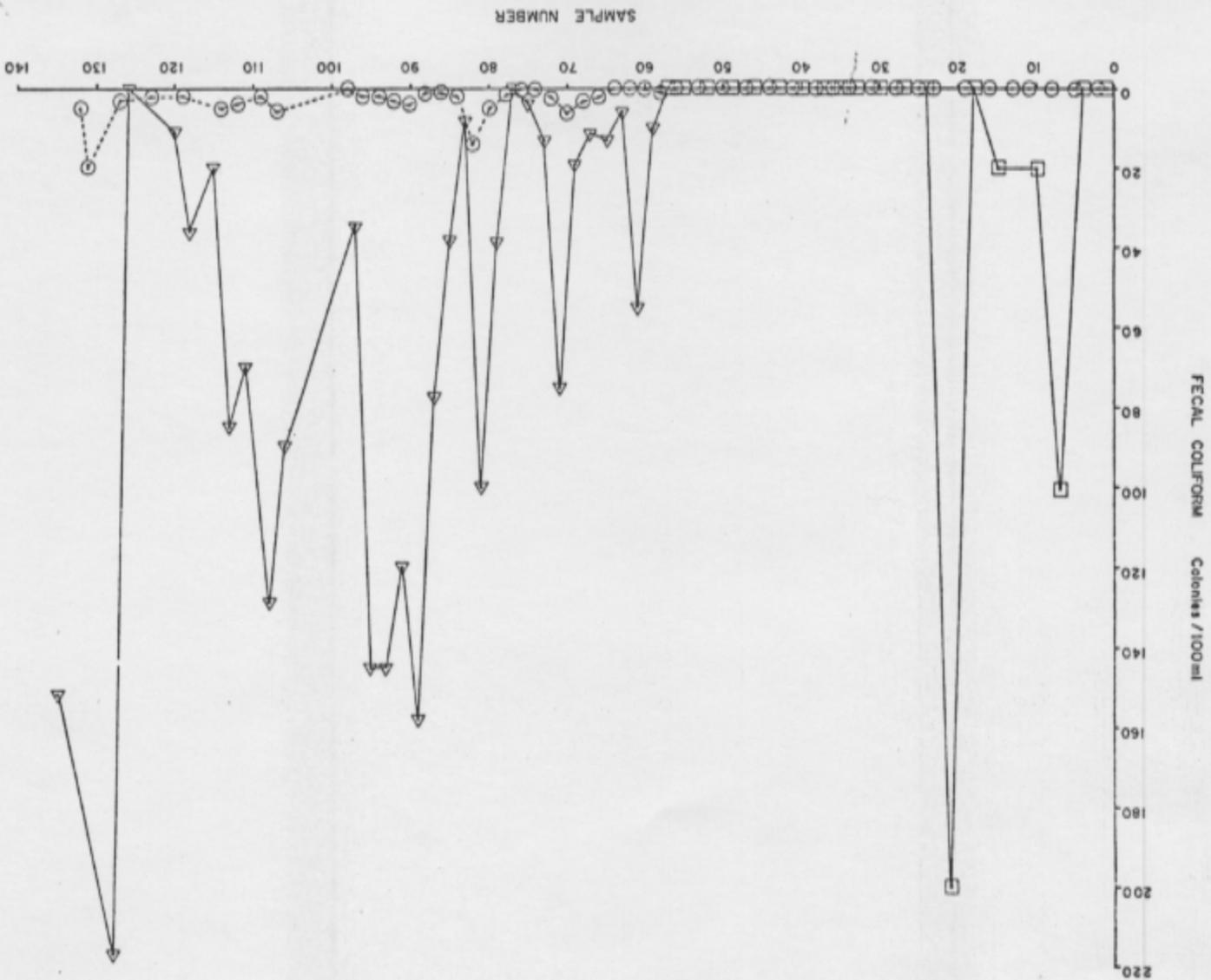


Figure 6. Fecal coliform (*Escherichia coli* - colonies/100 ml) at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from December 1973 to February 1975; \square = middle spillway, ∇ = No. 1 spillway; \odot = northeast open water. After sample number 58, there was a change in the processing technique.



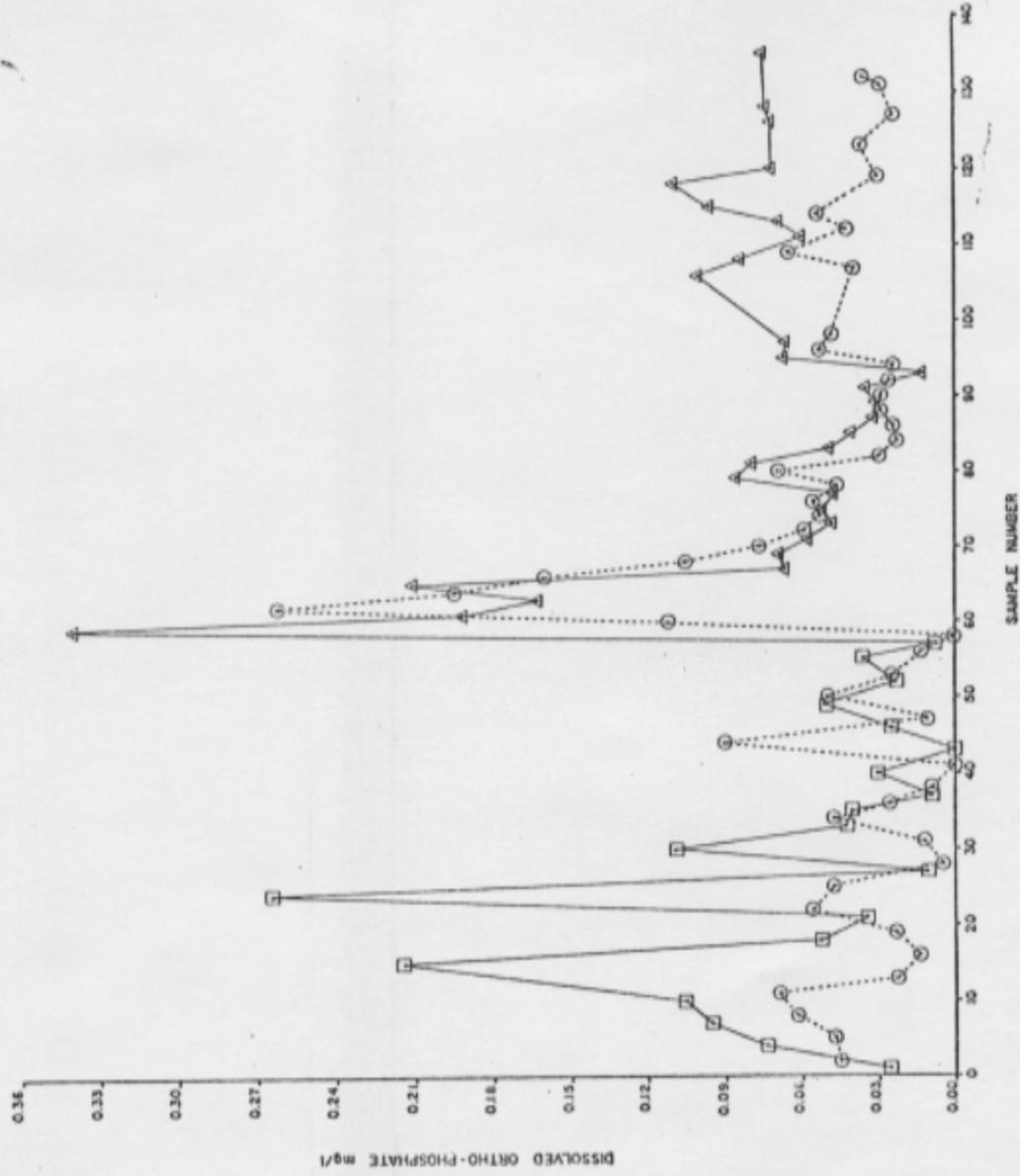


Figure 7. Dissolved ortho-phosphate (mg/l) at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from December 1973 to February 1975; \square = middle spillway, \triangle = No. 1 spillway, \odot = northeast open water.

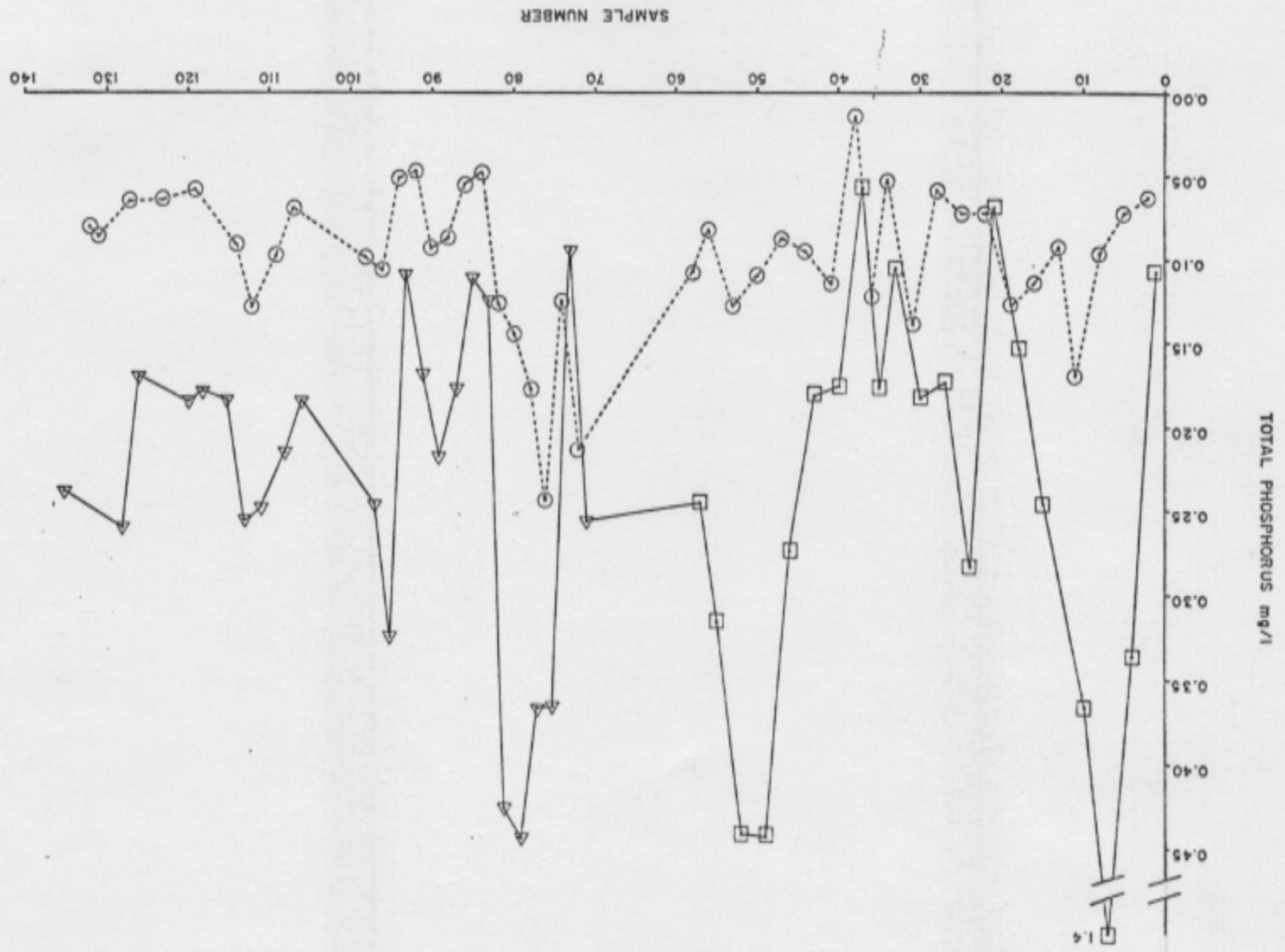
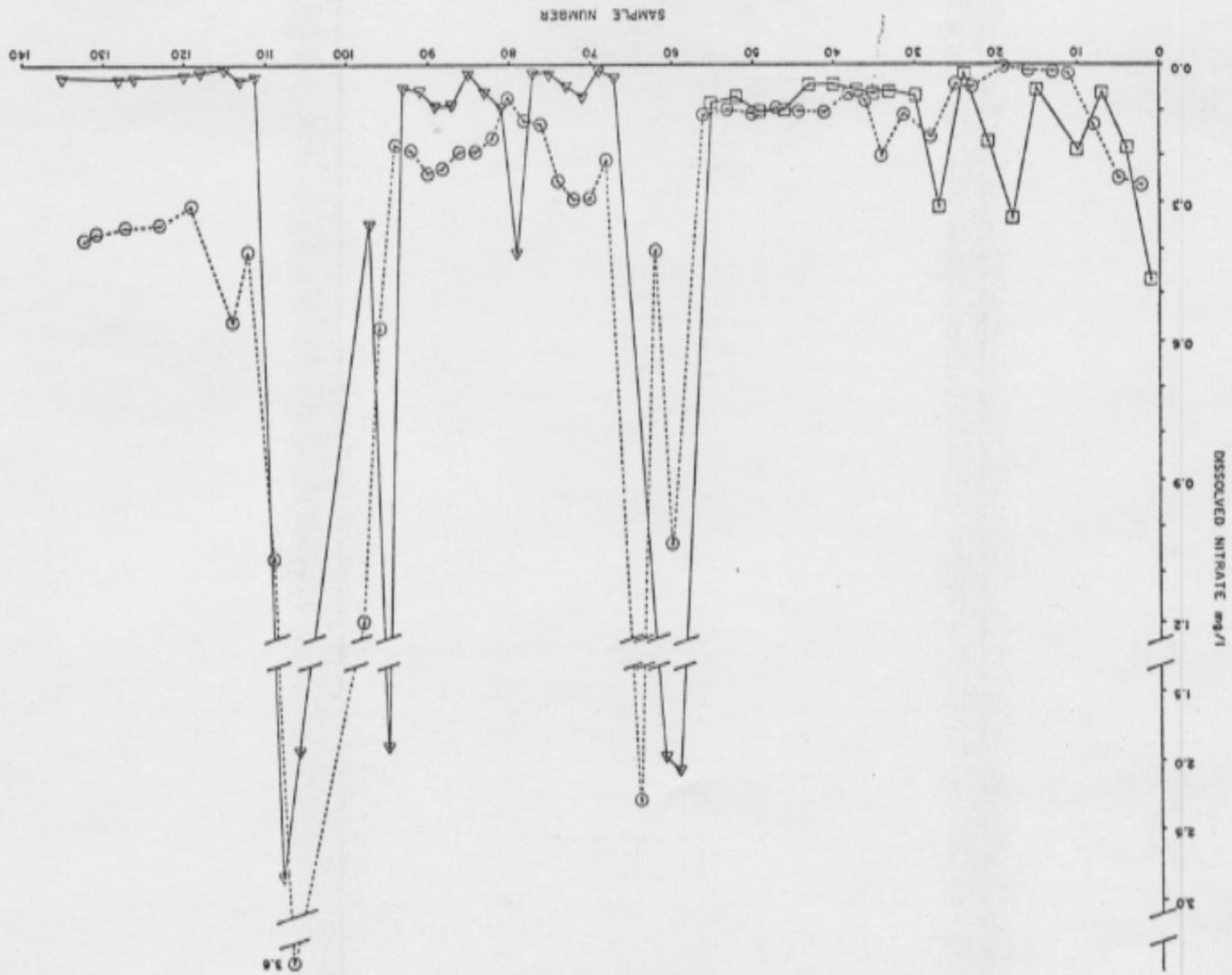


Figure 8. Total phosphorus (mg/l) at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from December 1973 to February 1975; \square = middle spillway, \triangle = No. 1 spillway, \odot = northeast open water. Note the scale break above 0.45 mg/liter.

removed from the data, the highest measurement was 0.444 mg/liter (mean of 0.227 ± 0.460 mg/liter), while values of total phosphorus at the NE Open water site closely resembled the previous seven months (range of 0.049 to 0.243 mg/liter; mean of 0.103 ± 0.100 mg/liter). The mean of the entire sampling program at the spillways was 0.256 ± 0.395 mg/liter, while the NE Open was 0.099 ± 0.087 mg/liter. The difference between total phosphorus and dissolved inorganic orthophosphate (middle spillway ranged from 0.02 to 1.27 mg/liter, No. 1 spillway was 0.047 to 0.359 mg/liter, while the NE Open water site was 0.005 to 0.177 mg/liter) indicated that suspended material in the spillways, primarily plankton, was at times laden with phosphorus. The concentration maximum in orthophosphate in September 1974 at the No. 1 spillway seemed to stimulate plankton growth, for a rapid increase in total phosphorus occurred shortly thereafter. This is a reasonable explanation; however it is purely speculative since indicators of plankton populations, such as chlorophyll measurements, were not obtained during the first year of this monitoring program.

In the case of the dissolved nitrogen compounds, inorganic nitrate (Figure 9) ranged from 0.018 to 0.465 mg/liter (mean of 0.150 ± 0.234 mg/liter) at the middle spillway during the first portion of the monitoring program, while values were lower (range of 0.004 to 0.263 mg/liter; mean 0.101 ± 0.144 mg/liter) at the NE Open water site. However, starting in September 1974, the measurements at the No. 1 spillway (range of 0.007 to 2.832 mg/liter; mean of 0.440 ± 1.624 mg/liter) included two periods of abnormally high levels of nitrate. This was also evident in the background waters (see Figure 9), where the range was 0.073 to 3.801 mg/liter (mean of 0.567 ± 1.564 mg/liter). The mean of the entire program at the spillways was 0.315 ± 1.298 mg/liter, while the NE Open site was 0.376 ± 1.252 mg/liter. Except for three occasions, dissolved nitrites (Figure 10) were less than 0.100 mg/liter at the spillways. This parameter ranged from 0.001 to 0.280 mg/liter (mean of 0.049 ± 0.164 mg/liter) at the middle spillway during the first portion of the program, while the NE Open site was 0.001 to 0.063 mg/liter (mean of 0.013 ± 0.029 mg/liter). Beginning in September 1974, the levels of nitrite were lower (sampling was done at the No. 1 spillway) with a range of <0.006 to 0.089 mg/liter (mean of 0.028 ± 0.050 mg/liter), while on two occasions in September concentrations exceeded 0.100 mg/liter (overall range was <0.006 to 0.141 mg/liter; mean of 0.027 ± 0.068 mg/liter) at the NE Open water site. The mean of the entire sample program at the spillways was

Figure 9. Dissolved nitrate (mg/l) at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from December 1973 to February 1975; \square = middle spillway, \triangle = No. 1 spillway, \odot = northeast open water. Note the scale breaks above 1.2 and 3.0 mg/liter, and the scale change above 1.2 mg/liter.



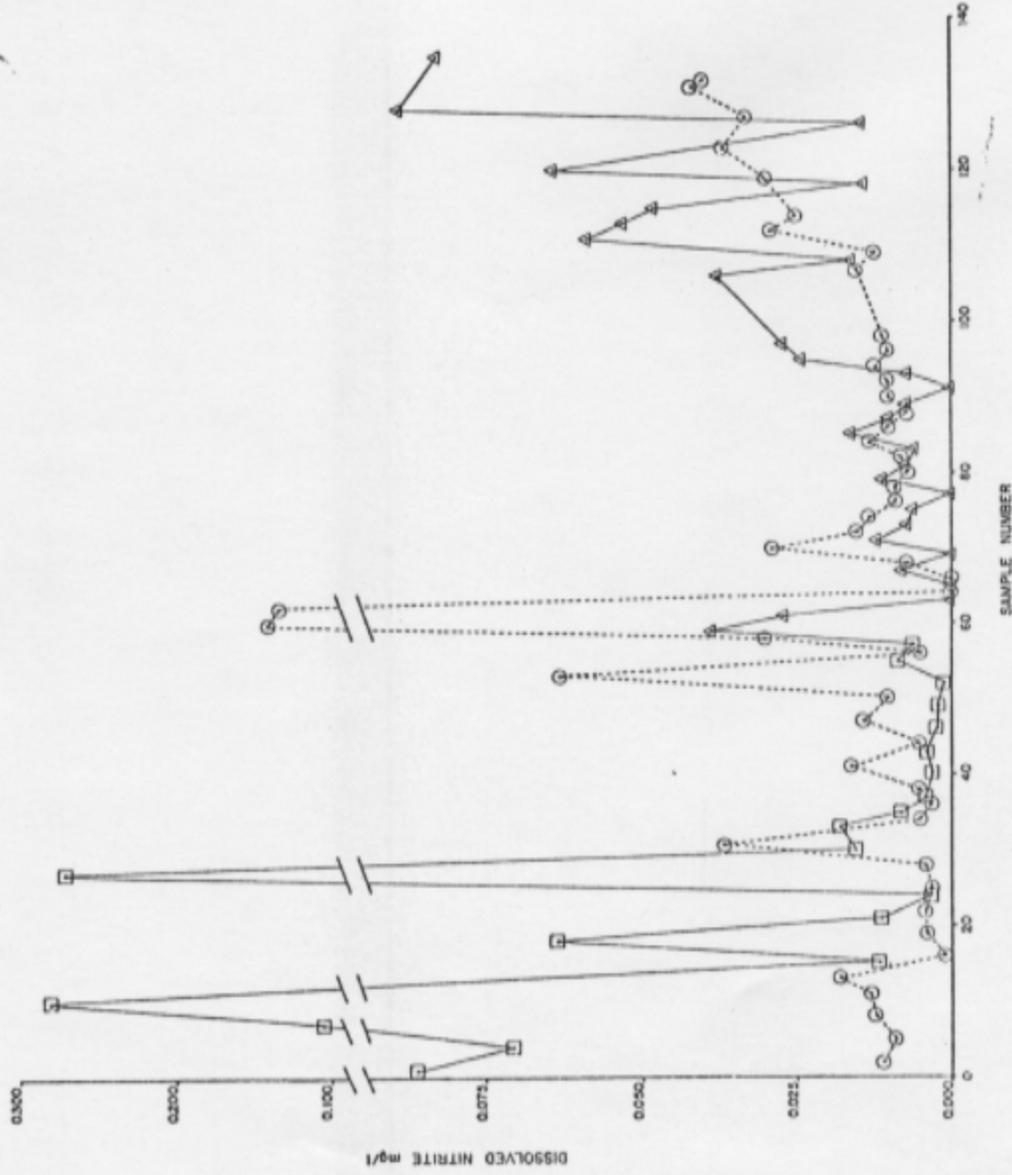


Figure 10. Dissolved nitrite (mg/l) at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from December 1973 to February 1975; \square = middle spillway, Δ = No. 1 spillway, \circ = northeast open water. Note the scale break below 0.1 mg/liter and the different scale above 0.100 mg/liter.

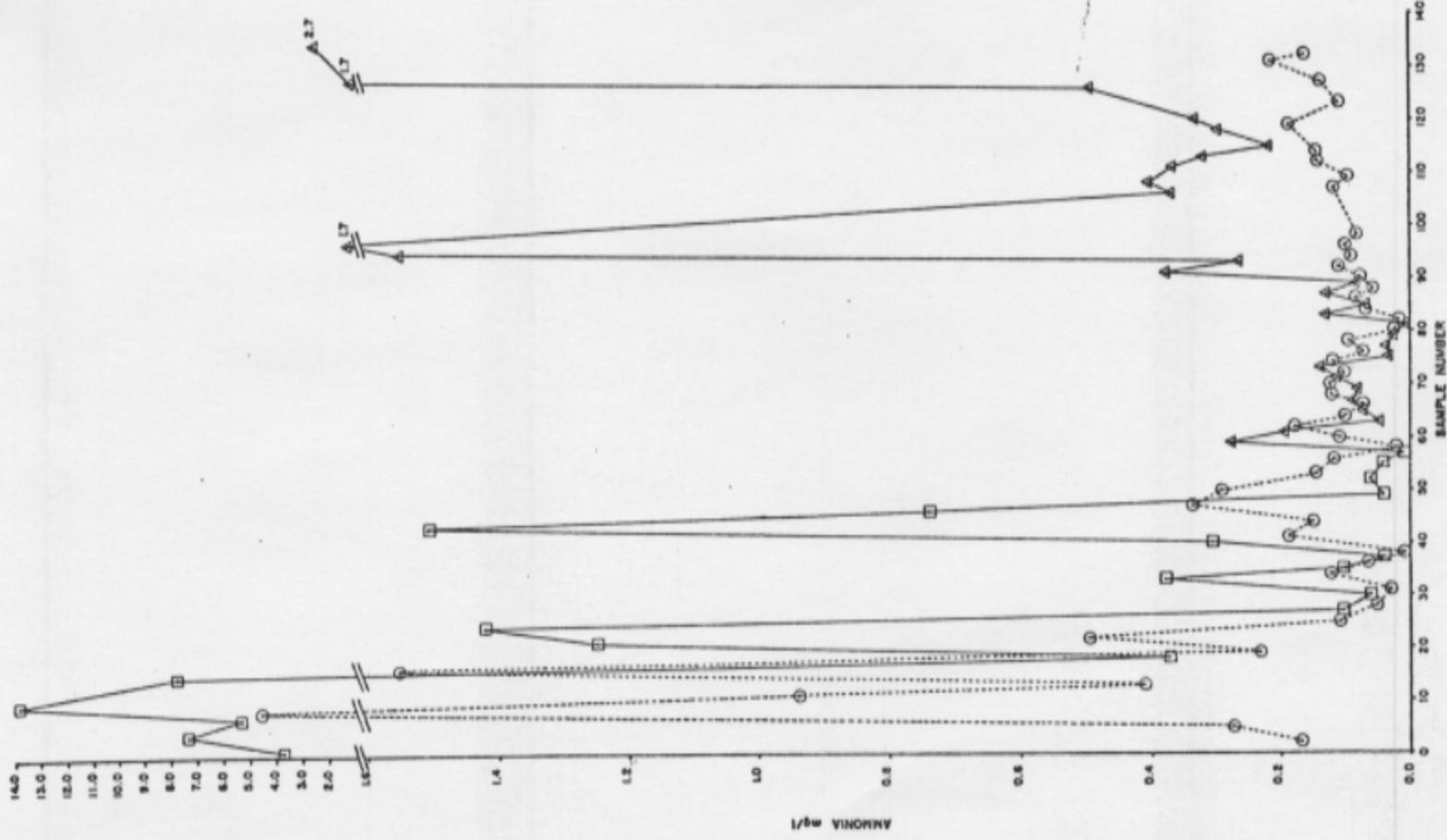


Figure 11. Ammonia (mg/l) at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from December 1973 to February 1975; \square = middle spillway, Δ = No. 1 spillway, \odot = northeast open water. Note the scale break and scale change above 1.6 mg/liter.

0.033 ± 0.113 mg/liter, while the NE Open was 0.020 ± 0.054 mg/liter. Measurements of ammonia (Figure 11) at the middle spillway during the first portion of the program indicated high level transient spikes (values exceeded 1 mg/liter on eight occasions, while half of these were greater than 5 mg/liter) with a range of 0.011 to 13.76 mg/liter (mean of 2.208 ± 7.109 mg/liter). With the exception of two occasions, values were less than 1 mg/liter at the background NE Open water site during this same period (range of 0.011 to 4.532 mg/liter; mean of 0.488 ± 1.938 mg/liter). Starting in September 1974, ammonia concentrations at the No. 1 spillway were only greater than 1 mg/liter on four occasions (range was 0.007 to 2.679 mg/liter; mean of 0.419 ± 1.242 mg/liter). The NE Open water site was usually less than 0.2 mg/liter, with a range of 0.019 to 0.214 mg/liter (mean of 0.108 ± 0.088 mg/liter). The mean of the entire sample program at the spillways was 0.422 ± 1.177 mg/liter, while the NE Open site was 0.180 ± 0.494 mg/liter. In the latter part of the program (starting the end of October 1974), samples were collected for total Kjeldahl nitrogen (Figure 12) at the No. 1 spillway. Values of TKN at the No. 1 spillway ranged from 2.15 to 9.92 mg/liter (mean of 4.95 ± 3.68 mg/liter), while concentrations were always less at the NE Open water site (range was 0.17 to 2.43 mg/liter; mean of 1.42 ± 1.46 mg/liter).

Total suspended Solids, Dissolved and Particulate Metals. Cadmium, mercury, and zinc were measured in both the dissolved state (0.45 µ filtration) and as metals associated with the suspended particulates. During the first portion of the program (December 1973 to June 1974), dissolved cadmium and zinc were analyzed by anodic stripping voltammetry (ASV), which provides a measurement of the reactive ion concentration of these two metals. Dissolved mercury was measured by flameless atomic absorption spectrophotometry, which is thought to be a measurement of the total concentration of dissolved mercury, i.e., dissolved organically- and inorganically-complexed species as well as inorganic mercury. The range for dissolved cadmium (using ASV techniques) at the middle spillway (Figure 13) was <0.001 to 0.019 mg/liter (mean of 0.005 ± 0.010 mg/liter) while only on two occasions did the concentrations exceed 0.010 mg/liter (ca. 10 ppb). The range at the NE Open water site was greater (0.001 to 0.056 mg/liter; mean of 0.010 ± 0.026 mg/liter), while values exceeded 0.010 mg/liter on five occasions. Dissolved mercury (Figure 14) ranged from less than detection (<0.001 mg/liter) to 0.021 mg/liter (mean of 0.006 ± 0.016 mg/liter) at the middle spillway. Out of the 19 measurements, eight were below detection

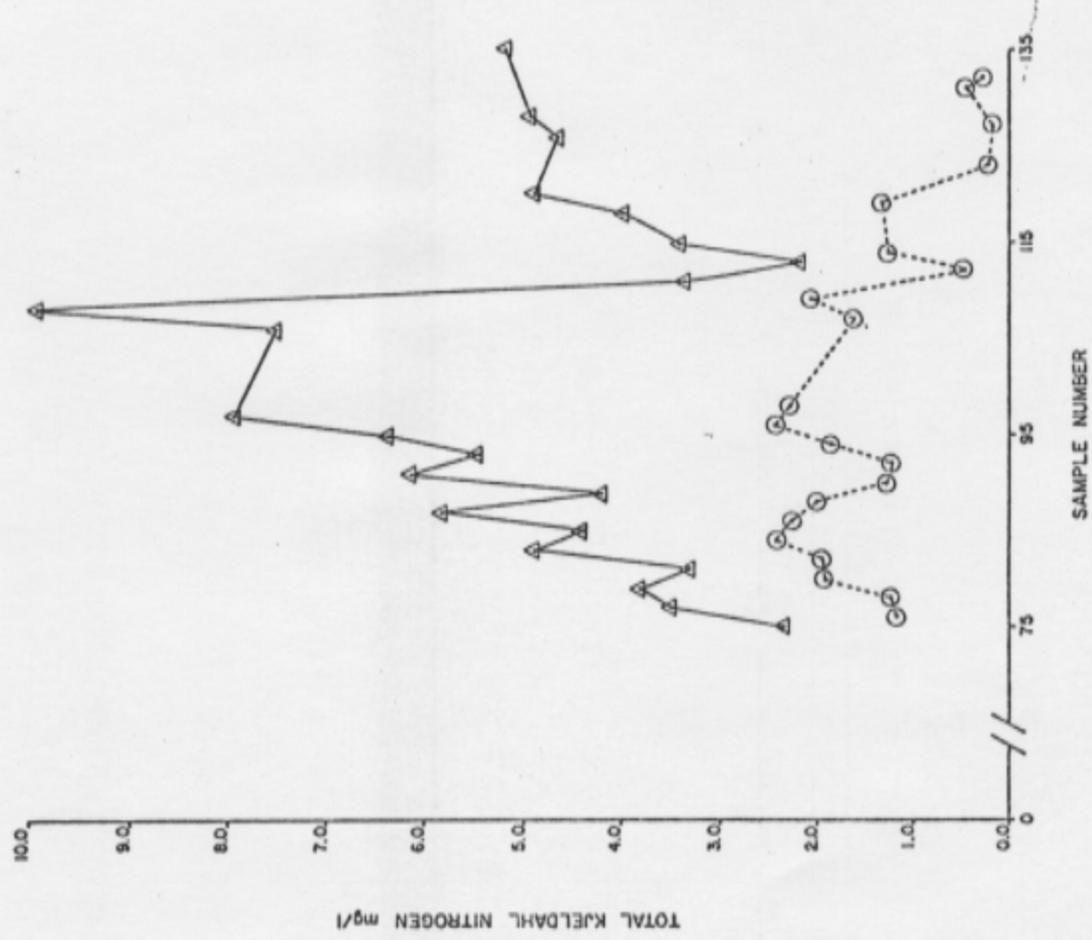


Figure 12. Total Kjeldahl nitrogen (mg/l) at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from October 1974 to February 1975; □ = middle spillway, Δ = No. 1 spillway, ○ = northeast open water. Samples were not collected before 30 October 1974 (sample number 75).

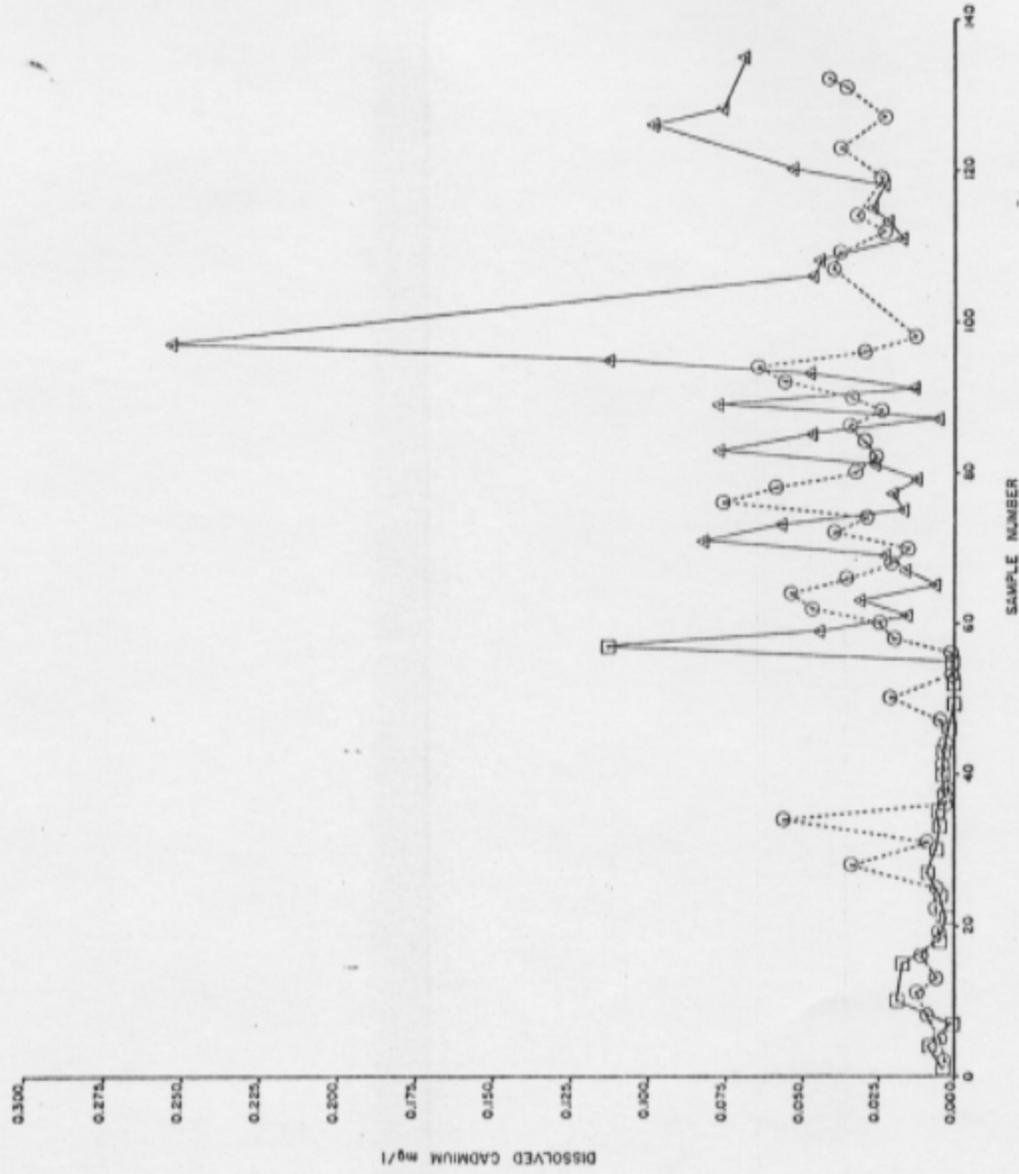


Figure 13. Dissolved cadmium (mg/l) at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from December 1973 to February 1975 (sample numbers 0-58 by ASV; sample numbers 59-135 by graphite furnace AA); \square = middle spillway, \triangle = No. 1 spillway, \odot = northeast open water.

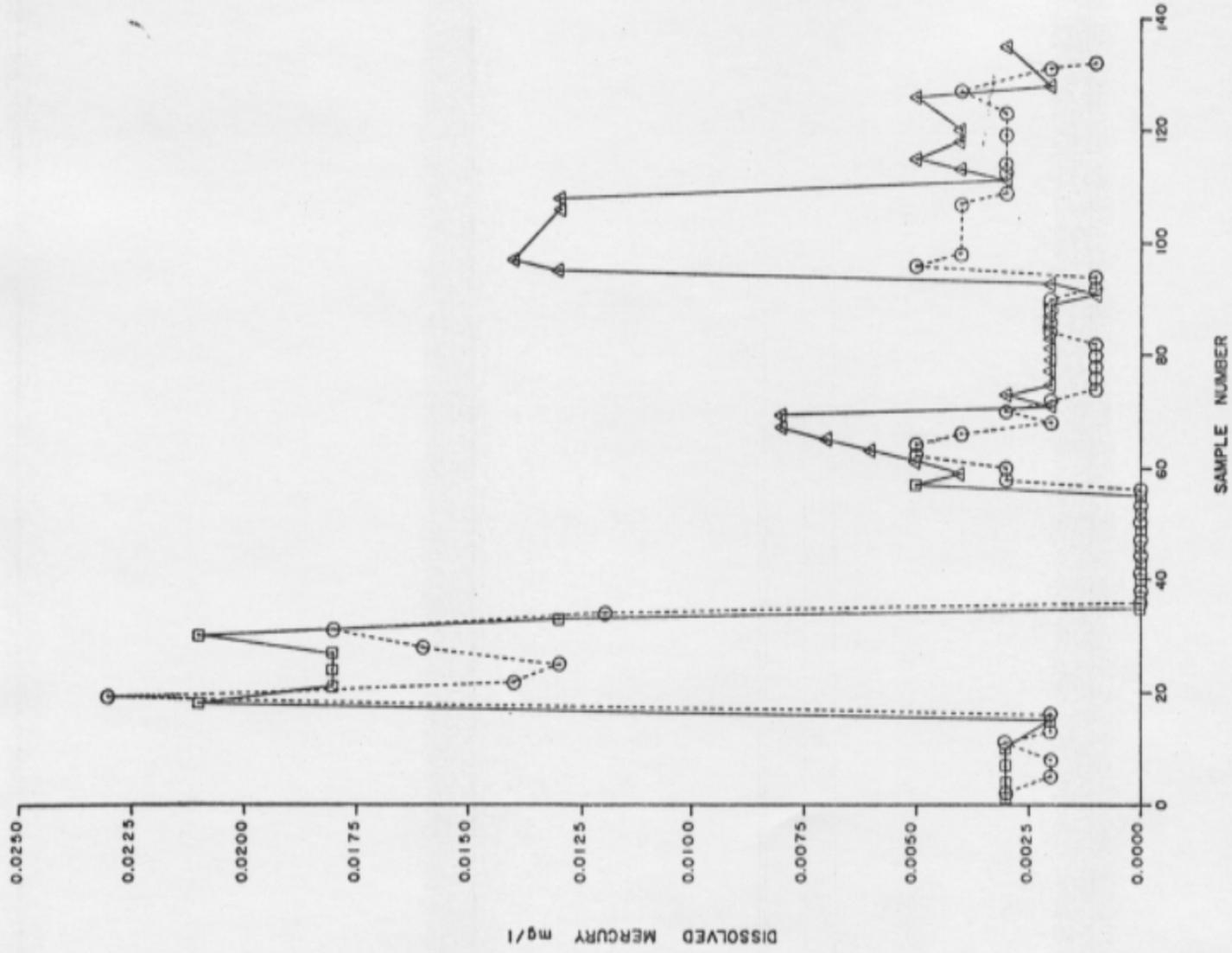
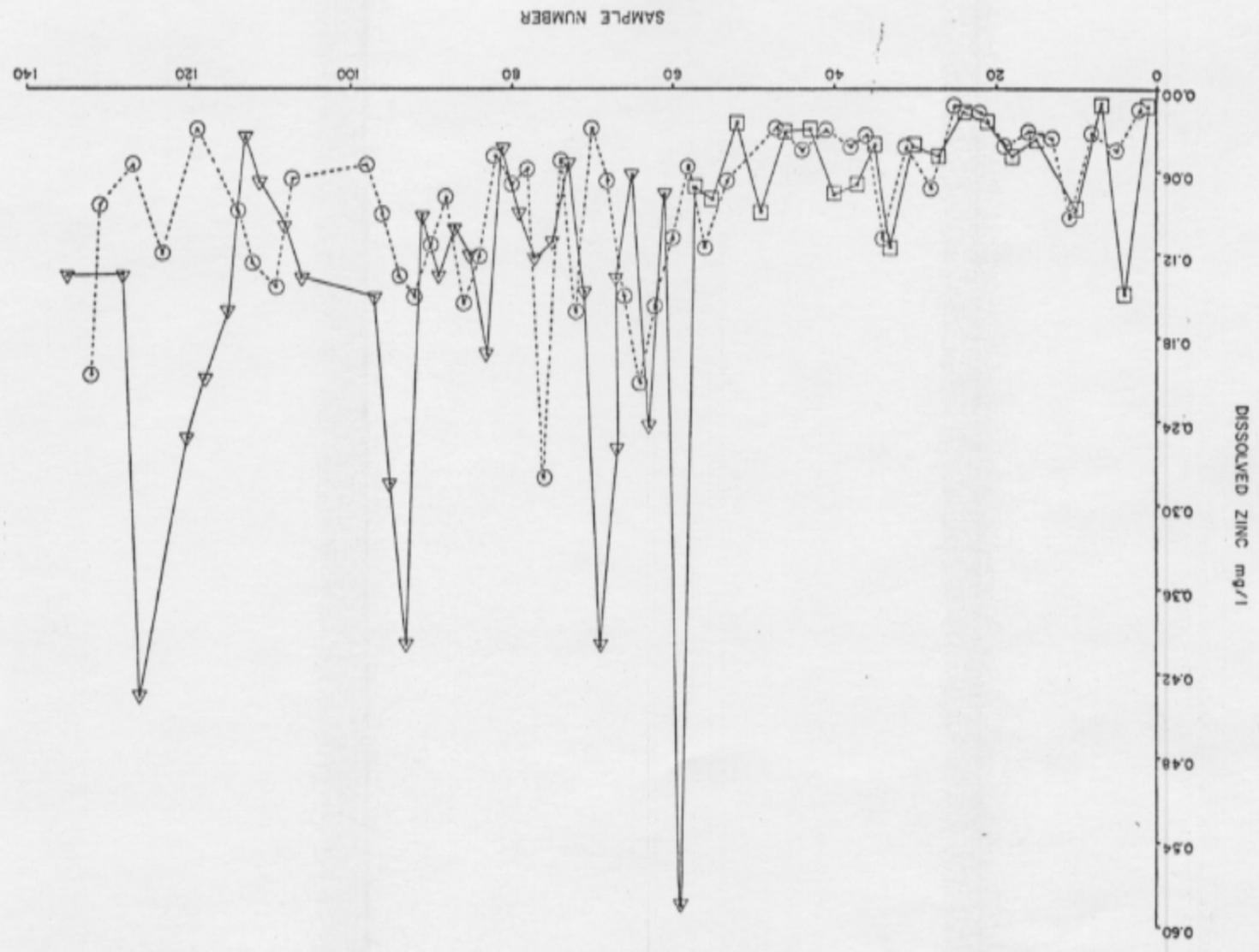


Figure 14. Dissolved mercury (mg/l) at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from December 1973 to February 1975; \square = middle spillway, Δ = No. 1 spillway, \odot = northeast open water.

Figure 15. Dissolved zinc (mg/l) at the middle and No. 1 spillway and northeast open water. (see Figure 2 for locations) from December 1973 to February 1975 (sample numbers 0-58 by ASV; sample numbers 59-135 by graphite furnace (AV); \square = middle spillway, ∇ = No. 1 spillway, \odot = northeast open water).



limits. At the NE Open water site, dissolved mercury concentrations were similar (range from <0.001 to 0.023 mg/liter; mean of 0.006 ± 0.014 mg/liter). Dissolved zinc (Figure 15) ranged from 0.010 to 0.149 mg/liter (mean of 0.054 ± 0.072 mg/liter, all by ASV techniques) during the same time period at the middle spillway, while this was 0.012 to 0.116 mg/liter (mean of 0.047 ± 0.059 mg/liter) at the NE Open water site.

Starting in August 1974, dissolved cadmium and zinc were analyzed by a different method (graphite furnace atomic absorption), which would provide an indication of the total dissolved species of metal present. Dissolved cadmium ranged from 0.005 to 0.254 mg/liter (mean of 0.051 ± 0.096 mg/liter) at the No. 1 spillway, while 40 percent of the measurements exceeded 0.050 mg/liter. Only nine values (30 percent) were less than the maximum concentration reported for the middle spillway by ASV technique. The range at the NE Open site was 0.013 to 0.076 mg/liter (mean of 0.036 ± 0.028 mg/liter), while very few measurements (five, or 17 percent of the data) were above 0.050 mg/liter. Dissolved mercury ranged from 0.001 to 0.014 mg/liter (mean of 0.005 ± 0.007 mg/liter) at the No. 1 spillway, while at the NE Open site values indicated a similar trend (range from 0.001 to 0.005 mg/liter; mean of 0.003 ± 0.003 mg/liter) except that none of the data were above 0.005 mg/liter. In the case of the spillways, ten samples (32 percent) were greater than 0.005 mg/liter during the same time interval. Dissolved zinc ranged from 0.035 to 0.586 mg/liter (mean of 0.175 ± 0.256 mg/liter) at the No. 1 spillway, while the NE Open site was 0.028 ± 0.282 mg/liter (mean of 0.109 ± 0.116 mg/liter). Thirteen values (43 percent) of the measurements in the second portion of the program (by graphite furnace atomic absorption) were greater than the largest value (0.116 mg/liter) by the ASV method.¹ In the case of the No. 1 spillway, 39 percent (12 discrete data points) were greater in concentration than the maximum value (0.149 mg/liter) at the middle spillway, while 13 percent (4 measurements) were more than double the maximum concentration found by the ASV method.

Suspended matter at the spillways and NE Open water site (Figure 16) was collected on 0.45 micron filters. During the first portion of the program (December 1973 to June 1974), values ranged from 49 to 3430 mg/liter (mean of 461 ± 1728 mg/liter) at the middle spillway, while the NE Open was 4 to 92 mg/liter (mean of 32 ± 48 mg/liter). A similar trend was observed at the NE Open site during the

¹ Because GFAA provides a measurement of the total concentration of a specific metal in solution, it is expected to be greater than data obtained by ASV.

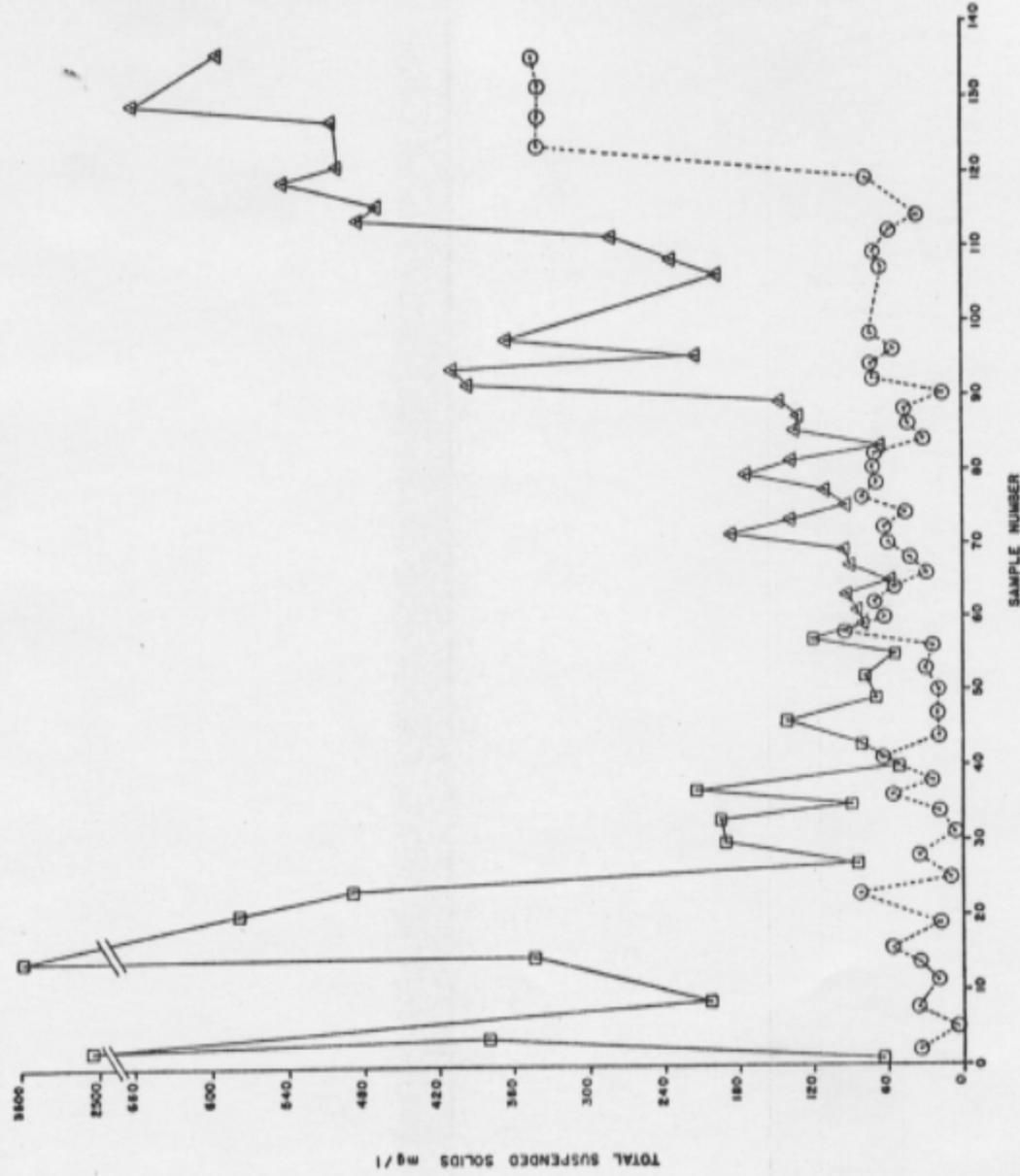


Figure 16. Total suspended solids (mg/l) at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from December 1973 to February 1975; ◻ = middle spillway, Δ = No. 1 spillway, ⊙ = northeast open water. Note the scale break and the different scales above 660 mg/l.

second portion of the monitoring program (range was 14 to 345 mg/liter; mean of 96 ± 202 mg/liter) with exception of the last month when concentrations increased to 340 mg/liter. Suspended solids ranged from 54 to 660 mg/liter (mean of 254 ± 354 mg/liter) at the No. 1 spillway during the second portion of the program. The yearly mean of both spillways was 237 ± 356 mg/liter and 67 ± 169 mg/liter at the NE Open water site. The concentration of suspended solids at the spillways reflected the levels of nutrients at the sampling site. For example, during the period from late March until mid May 1974 particulates ranged from 189 to 578 mg/liter (with the exception of one measurement of 83 mg/liter) while dissolved orthophosphate (see Figure 7) and ammonia (see Figure 11) were at higher levels. Again in early December 1974 and continuing through the latter part of February 1975 (when seasonal temperatures were lowest; see Figure 3), the increase in suspended solids indicated a corresponding higher level of ammonia and nitrates (see Figure 9), while the concentration of orthophosphate was above 0.06 mg/liter.

The particulate metals were measured by atomic absorption spectrophotometry after the suspended materials on filter pads were released to solution by acid digestion. During the first portion of the program, particulate cadmium (Figure 17) ranged from 0.75 to 133 $\mu\text{g/g}$ dry weight at the middle spillway, while the arithmetic mean was 21.5 ± 68.8 $\mu\text{g/g}$. Concentrations at the NE Open water site during the same period of time ranged from 0.47 to 103 $\mu\text{g/g}$ (mean of 13.2 ± 50.1 $\mu\text{g/g}$). During the second portion of the monitoring program particulate cadmium ranged from 6.82 to 237 $\mu\text{g/g}$ (mean of 107 ± 263 $\mu\text{g/g}$) at the No. 1 spillway, while the NE Open water site was <0.5 to 90.3 $\mu\text{g/g}$ (mean of 17.2 ± 40.3 $\mu\text{g/g}$). The relative standard deviation for the spillway measurements [$(2S/\bar{X}) \times 100\%$] improved from 321 to 246 percent, while observations from the NE Open water site changed from 379 to 235 percent. The same analytical problems were evident with the particulate mercury data (Figure 18); however, fluctuations were not as great as with the cadmium and zinc measurements. Concentrations of particulate mercury from December 1973 to June 1974 ranged from 0.115 to 1.160 $\mu\text{g/g}$ (mean of 0.345 ± 0.597 $\mu\text{g/g}$) at the middle spillway, while the NE Open water site was 0.045 to 1.150 $\mu\text{g/g}$ (mean of 0.261 ± 0.543 $\mu\text{g/g}$). During the second portion of the program, these values also were higher (ranged from 0.082 to 1.500 $\mu\text{g/g}$ at the No. 1 spillway, while the NE Open water site was 0.008 to 0.908 $\mu\text{g/g}$), and there was less fluctuation in the data (mean of 0.650 ± 0.689 $\mu\text{g/g}$ for the No. 1 spillway,

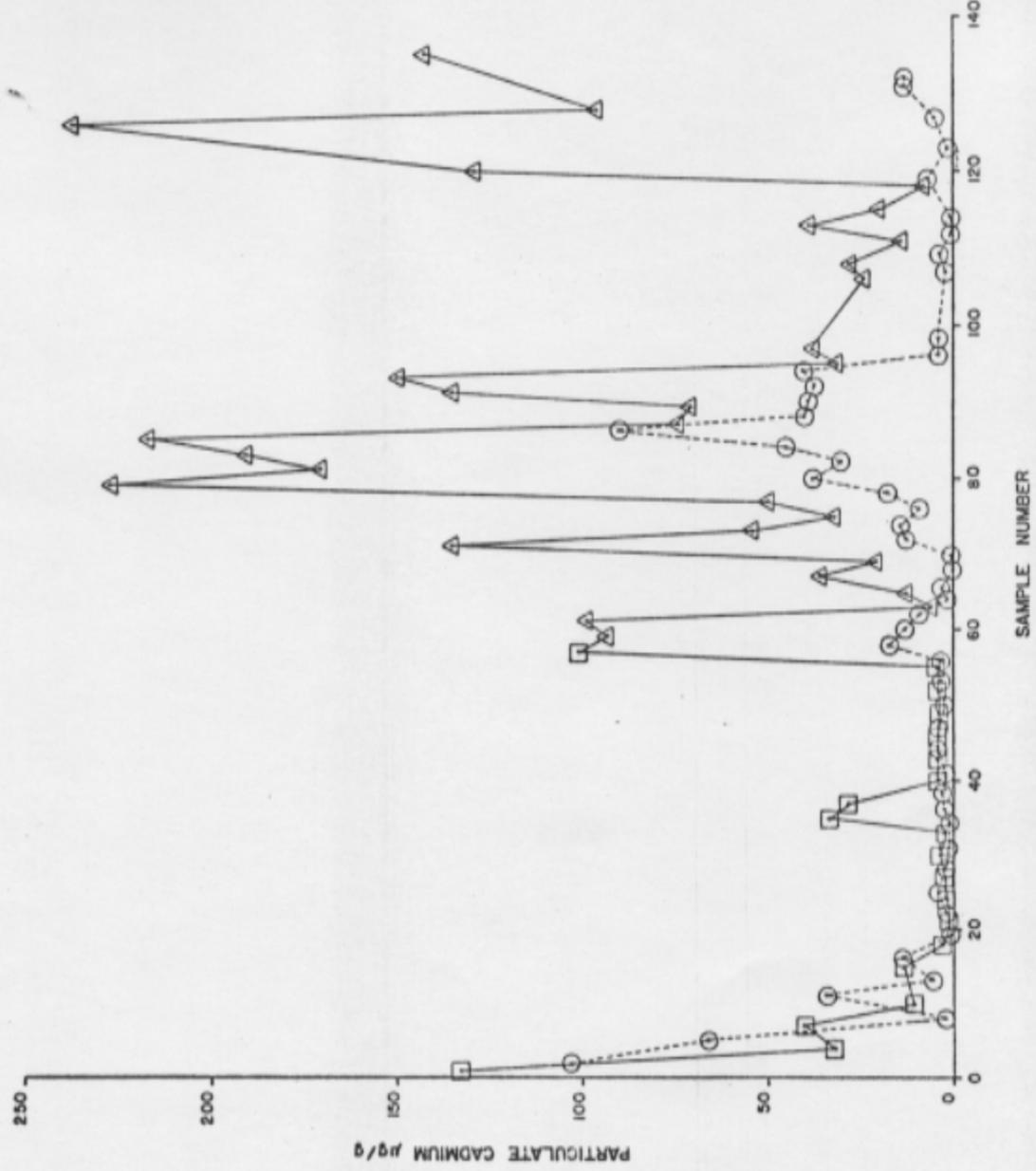


Figure 17. Particulate cadmium ($\mu\text{g/g}$) at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from December 1973 to February 1975; \square = middle spillway, \triangle = No. 1 spillway, \odot = northeast open water.

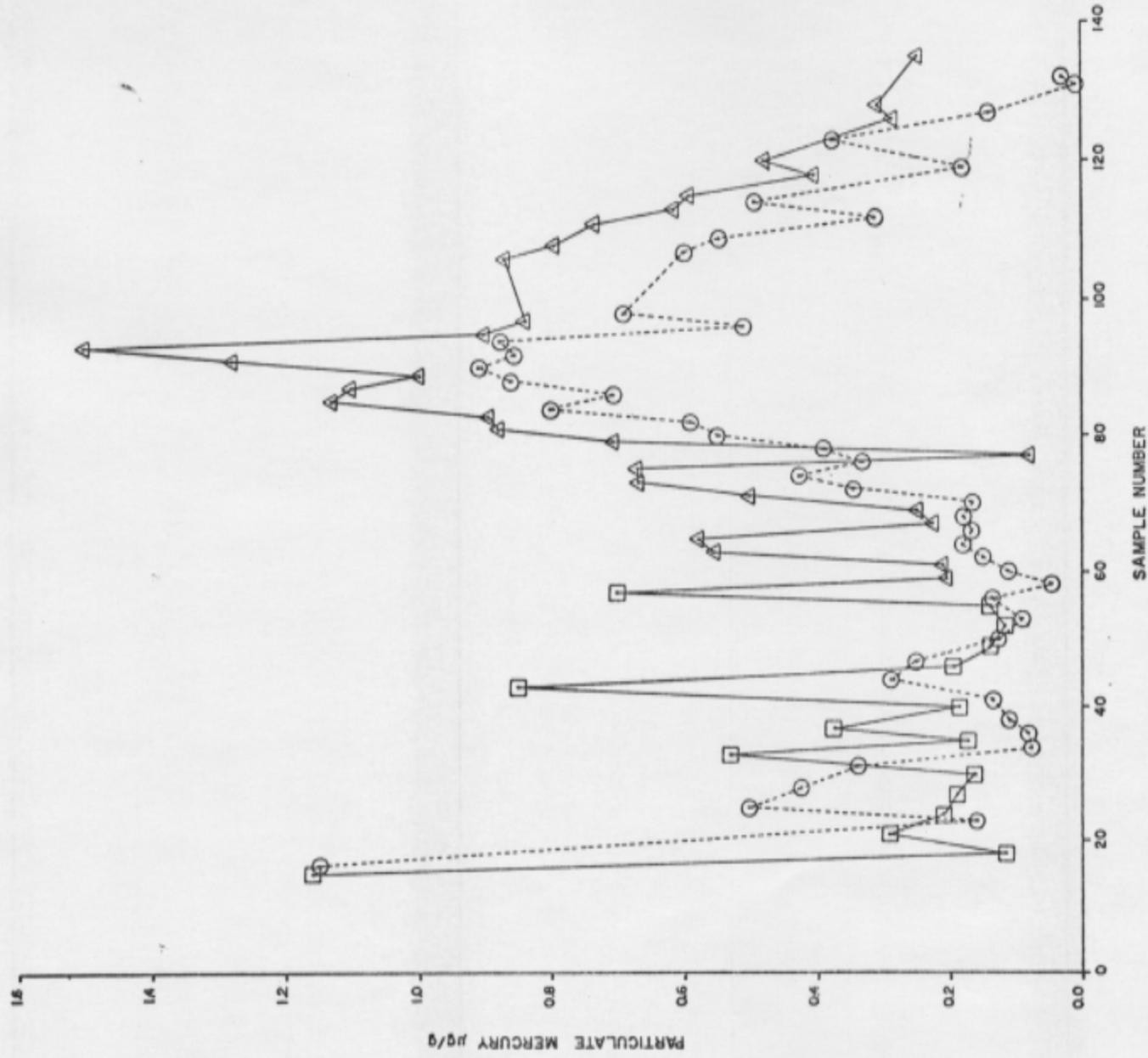
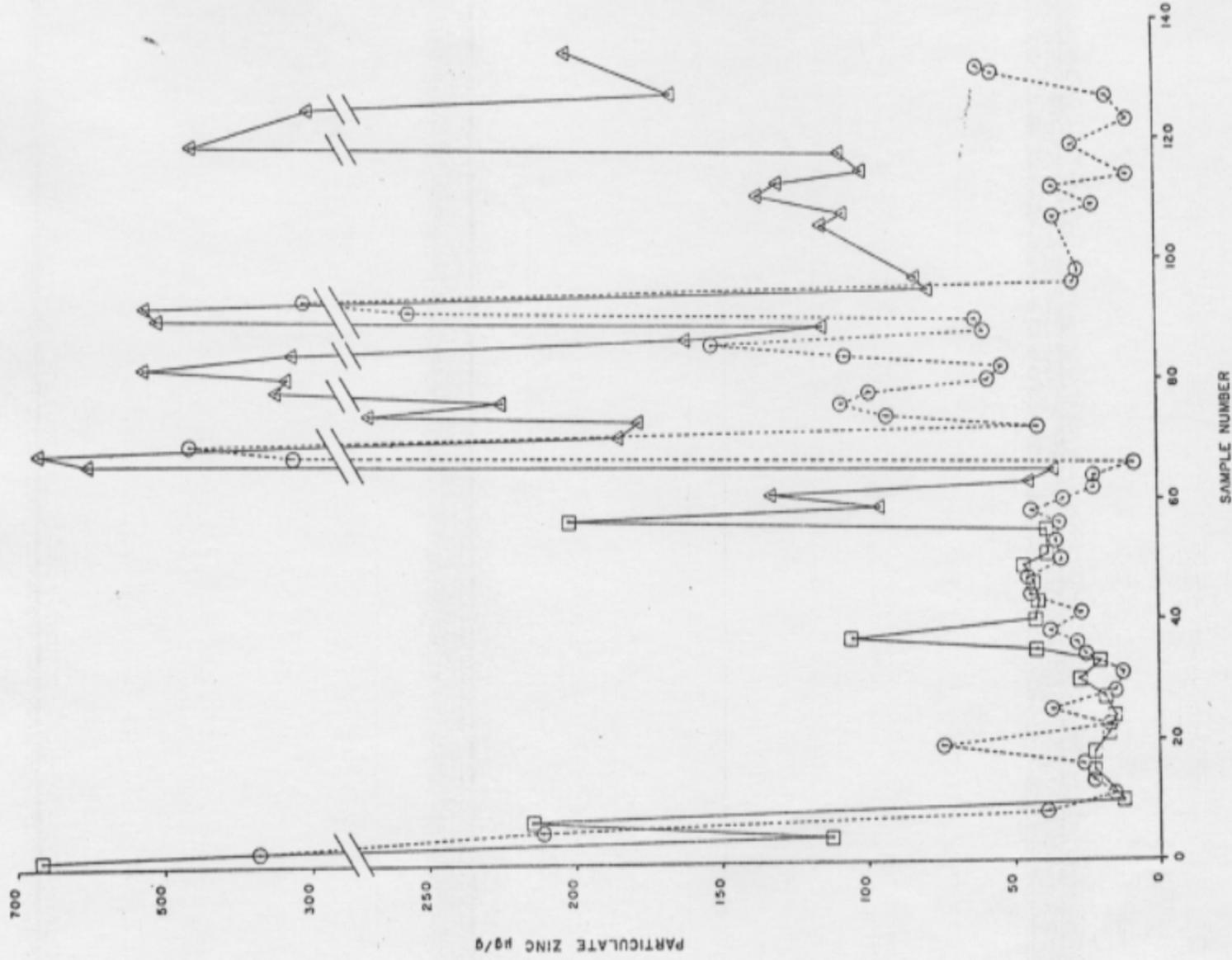


Figure 18. Particulate mercury ($\mu\text{g/g}$) at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from December 1973 to February 1975; \square = middle spillway, Δ = No. 1 spillway, \circ = northeast open water.

while the NE Open water site was $0.429 \pm 0.539 \mu\text{g/g}$. The relative standard deviation for measurements of particulate mercury at the spillways changed from 173 to 106 percent during the two different portions of the monitoring program, while values from the NE Open water site improved from 208 to 126 percent. During the first period from December 1973 until June 1974, particulate zinc (Figure 19) ranged from 12.3 to $667 \mu\text{g/g}$ (mean of $87.3 \pm 289 \mu\text{g/g}$) at the middle spillway, while the NE Open water site was 12.9 to $374 \mu\text{g/g}$ (mean of $57.2 \pm 163 \mu\text{g/g}$). From August 1974 to February 1975, ranges were similar, however the averages were higher. This could occur if filter pads lost weight during filtration, a phenomenon common to some types of membrane filters (especially Millipore, which were not used for particulate metal analyses). The range for the No. 1 spillway from August 1974 to February 1975 was 35.8 to $664 \mu\text{g/g}$ (mean of $239 \pm 347 \mu\text{g/g}$), while at the NE Open, values ranged from 8.62 to $462 \mu\text{g/g}$ (mean of $87.8 \pm 213 \mu\text{g/g}$). Variability in the measurements of particulate zinc from the same site at different times also changed, with the relative standard deviation in the measurements at the No. 1 spillway improving from 331 percent (during the first portion) to 145 percent (second portion). The relative standard deviation at the NE Open water site changed from 284 percent (first portion) to 242 percent (second portion). Because of improved analytical techniques, it would be best to regard the concentrations of particulate metals during the second part of the program as being somewhat more representative.



SAMPLE NUMBER

Figure 19. Particulate zinc ($\mu\text{g/g}$) at the middle and No. 1 spillway and northeast open water (see Figure 2 for locations) from December 1973 to February 1975; \square = middle spillway, Δ = No. 1 spillway, \circ = northeast open water. Note the scale break and scale change above 275 $\mu\text{g/g}$.

DISCUSSION

Since the purpose of this sampling program was to describe the various water quality parameters of the Craney Island Disposal area effluents and relate them to those observed in the harbor of Hampton Roads (as described by the NE Open water site), the data will be examined under these guidelines. Additionally, further observations will be provided concerning the impact or influence of the effluent waters to the Port of Hampton Roads. Due to the natural variability of these parameters in an estuarine environment, which was observed at the NE Open water site, and the fluctuations of the dredge material entering the disposal area, an analysis of variance between the two locations (spillways and NE Open) was considered and found to be significant for some of the parameters. Because the differences in concentrations of specific constituents between the two locations were of greater importance, concentration ratios (spillway versus NE Open values) were calculated. With this information, meaningful relationships could be ascertained. It was possible to quantify the differences between the two locations, both with respect to the concentration of any specific water quality parameter and with respect to time. Statistics of the ratios from each sampling period and for the total program, where applicable, are provided in Tables 5 and 6. Standard deviations in the tables and text are presented as two sigma, or the 95% confidence limit. The analysis of variance is discussed later.

Temperature

Warming and cooling trends within the Craney Island Disposal area were generally observed to be more sensitive to the immediate local weather conditions than was the NE Open water site, as would be expected from the relative volumes of the two areas. The fact that water depths adjacent to the weirs at the disposal area sampling sites are considerably less (approximately 0.3 m versus 2-3 m at the NE Open site) also tends to substantiate the observed statistics. With the exception of the maximum for the No. 1 spillway on 18 September 1974, when the temperature at the NE Open water site (24.80°C) was higher than the No. 1 spillway (24.12°C), maxima and minima for the spillways during the entire sampling program were greater than or less than, respectively, the NE Open values taken concurrently. An example for a relatively warm day would be 16 October 1974, when the average daily temperature was nearly six degrees centigrade higher than the

Table 5. Parameter comparisons (Spillway Concentration) from 28 December 1973 to 20 February 1975 at the Craney Island Disposal area, Port of Hampton Roads, Virginia.

Parameter	Middle Spillway December 1973 to August 1974				No. 1 Spillway September 1974 to February 1975							
	Range	Mean	Number of Comparisons	Percent Greater Than	Percent Less Than	Percent Equal	Range	Mean	Number of Comparisons	Percent Greater Than	Percent Less Than	Percent Equal
	pH	0.97 to 1.15	1.05	20	80	10	10	1.04 to 1.26	1.10	29	100	0
Dissolved Oxygen (mg/l)	0.69 to 1.38	0.99	20	40	50	10	0.80 to 1.49	1.10	29	66	24	10
Oxygen Saturation (%)	0.69 to 1.43	1.00	20	45	45	10	0.78 to 1.34	1.07	29	55	21	24
Fecal Coliforms Bacteria (Colonies/100 ml)	0	0	20	20	5	75	3.17 to 78.00	27.67	29	93	7	0
Dissolved Orthophosphate (mg/l)	0.00 to 15.29	2.82	18	71	24	6	0.54 to 3.20	1.55	29	62	14	24
Total Phosphorus (mg/l)	0.97 to 14.26	3.16	20	95	5	0	0.75 to 3.54	2.44	23	96	4	0
Dissolved Nitrate (mg/l)	0.29 to 85.75	6.04	19	32	58	11	0.02 to 5.60	0.85	27	19	81	0
Dissolved Nitrite (mg/l)	0.02 to 68.75	7.79	20	55	40	5	0.20 to 2.53	1.32	24	48	45	7
Ammonia (mg/l)	0.15 to 26.54	5.70	20	80	20	0	0.37 to 21.19	3.06	29	59	24	17
Total Kjeldahl Nitrogen (mg/l)	NA ²	NA	NA	NA	NA	NA	1.72 to 27.35	6.27	21	100	0	0
Total Suspended Solids (mg/l)	0.79 to 94.00	20.32	20	95	5	0	1.14 to 13.83	3.46	29	100	0	0
Dissolved Cadmium (mg/l)	0.09 to 1.80	0.96 ³	19	37	53	11	0.17 to 19.53	1.97 ⁴	29	59	38	3
Dissolved Mercury (mg/l)	0.91 to 1.67	1.22	12	40	5	55	1.00 to 4.33	1.90	29	69	0	31
Dissolved Zinc (mg/l)	0.50 to 3.24	1.19 ³	18	56	44	0	0.39 to 13.29	2.29 ⁴	29	59	31	10
Particulate Cadmium (µg/g)	0.41 to 29.41	4.19	20	50	20	30	1.82 to 260	20.62	28	100	0	0
Particulate Mercury (µg/g)	0.41 to 6.84	1.80	15	73	27	0	1.10 to 41.00	3.27	29	100	0	0
Particulate Zinc (µg/g)	0.50 to 5.49	1.56	20	50	30	20	1.44 to 47.20	5.58	29	100	0	0

¹ A comparison which is equal would be defined as less than plus or minus the standard deviation of the method.

² NA = not applicable.

³ Determined by ASV as reactive concentration.

⁴ Determined by GFAA as total concentration.

Table 6. Parameter comparisons ($\frac{\text{Spillway Concentration}}{\text{NE Open Concentration}}$) from

28 December 1973 to 20 February 1975 at the Craney Island Disposal area, Port of Hampton Roads, Virginia (ratios of both middle and No. 1 spillways were combined when appropriate).

Parameter	Entire Period (where appropriate)					
	Range	Mean	Number of Comparisons	Percent Greater Than	Percent Less Than	Percent Equal
pH	0.97 to 1.26	1.08	49	92	4	4
Dissolved Oxygen (mg/l)	0.69 to 1.49	1.05	49	55	35	10
Oxygen Saturation (%)	0.69 to 1.43	1.04	49	51	31	18
Fecal Coliform Bacteria (colonies/100 ml)	NA ²	NA	NA	NA	NA	NA
Dissolved Orthophosphate (mg/l)	0.24 to 15.29	2.04	47	66	17	17
Total Phosphorus (mg/l)	0.75 to 14.26	2.78	43	95	2	2
Dissolved Nitrate (mg/l)	0.02 to 83.75	2.99	46	24	72	4
Dissolved Nitrite (mg/l)	0.02 to 68.75	4.26	44	51	43	6
Ammonia (mg/l)	0.15 to 21.19	4.14	49	67	22	10
Total Kjeldahl Nitrogen (mg/l)	NA	NA	NA	NA	NA	NA
Total Suspended Solids (mg/l)	0.79 to 94.00	10.34	49	98	2	0
Dissolved Cadmium (mg/l)	NA	NA	NA	NA	NA	NA
Dissolved Mercury (mg/l)	0.91 to 4.33	1.70	41	75	2	23
Dissolved Zinc (mg/l)	NA	NA	NA	NA	NA	NA
Particulate Cadmium (µg/g)	0.41 to 260	13.78	48	79	8	13
Particulate Mercury (µg/g)	0.41 to 41.00	2.77	44	91	9	0
Particulate Zinc (µg/g)	0.30 to 47.20	3.94	49	80	12	8

¹ A comparison which is equal would be defined as less than plus or minus the standard deviation of the method.

² NA = not applicable.

average daily temperature for the month (20.6°C versus 14.8°C ; NOAA data). On this day the No. 1 spillway temperature (average of two samples) was 23.77°C , while the average of two samples from the NE Open water site was 20.75°C . The daily average temperature exceeded the monthly daily average for the four days preceding 16 October 1974; however, as shown by the temperature data for the four samples, the disposal area indicated a quicker response to the change than was evident at the NE Open water site. On a relatively cold day, 27 November 1974, temperatures at the No. 1 spillway (mean of two samples) measured 3.86°C , while the average of two samples from the NE Open water site was 9.17°C . This day had the coldest daily minimum (-1.7°C) and the coldest average daily temperature (3.3°C) for the month. The average daily temperature for that day was 8.6°C lower than the average daily temperature for the month of November 1974. Temperature data are presented graphically in Figure 3. Observations at station eight (Adams et al. 1975; see Figure 2 for location) provided a mean temperature of 15.51°C ($n = 19$, two sigma = 14.16°C) with a range from 6.09°C to 28.48°C during the period from October 1973 to April 1975. The range at the NE Open water site was 4.18°C to 24.80°C from December 1973 to February 1974.

The abrupt temperature fluctuations at the spillways might be important in causing thermal shock to certain temperature-sensitive biota within the Craney Island Disposal area. Also, the higher temperatures during warmer periods, and the higher levels of orthophosphate within the disposal area, might explain the apparently higher productivity within the area, as noted by the green coloration of the water and higher values for pH, total phosphorus, and total Kjeldahl nitrogen (see discussion on these parameters).

Salinity

Salinity in the lower Chesapeake Bay, as measured at three stations on a transect from Little Creek Harbor to the mouth of Hampton Roads Harbor during the period from October 1973 to April 1975 averaged $19.680 \pm 6.698^{\circ}/\text{oo}$ ($n = 57$) and ranged from $10.210^{\circ}/\text{oo}$ to $25.204^{\circ}/\text{oo}$, while salinities at stations within Hampton Roads Harbor (Adams et al. 1975) ranged from $5.591^{\circ}/\text{oo}$ to $24.320^{\circ}/\text{oo}$ and averaged $17.141 \pm 9.318^{\circ}/\text{oo}$ ($n = 76$) during a similar time period. Data from station eight (Adams et al. op. cit.; see Figure 2), which was nearest to the NE Open water site, ranged from $6.090^{\circ}/\text{oo}$ to $24.480^{\circ}/\text{oo}$ and averaged $15.513 \pm 14.164^{\circ}/\text{oo}$ ($n = 19$) during the period from October 1973 to April 1975. Salinities measured at the NE Open water site showed a smaller

range (9.408°/oo to 21.939°/oo) than those at station eight; however, averages were similar. From December 1973 to February 1974, the mean salinity at the NE Open water site was $15.144 \pm 5.568^{\circ}/\text{oo}$ (n = 21), and from 18 September 1974 to 20 February 1975 the average was $17.100 \pm 5.620^{\circ}/\text{oo}$ (n = 29).

The salinities within the Harbor of Hampton Roads are a function of the tidal stage, local river discharge, and the presence or lack of precipitation. Several rivers, including the James, Lafayette, Elizabeth, Nansemond, and Pagan, empty into Hampton Roads Harbor, thus local precipitation may strongly affect the salinities measured within the Harbor. However, within the Craney Island Disposal area the salinities are mainly affected by the amount and source of dredge material as well as precipitation and desiccation. Since the dredge spoil contained considerable water (maximum suspended solid data for dredge effluent was 4.6×10^5 mg/liter solids = ca. 46% solids), salinity within Craney Island is a function of this source (salt, brackish, or fresh). It would also be changed by local precipitation or extensive warm periods with no rainfall. Temperatures and salinities were measured during this program primarily for the calculation of dissolved oxygen saturation, and thus were not subjected to an intensive analysis.

pH

The pH ratio of the middle spillway relative to the NE Open water site from December 1973 to August 1974 ranged from 0.97 to 1.15 (average of 1.05, n = 20). Of 20 comparison samples, 16 were greater (80%), two were lower (10%), and two were equal (10%). This means that on the average (n = 20), pH values were approximately 0.40 units greater at the spillway. This might be expected if phytoplankton activity was high, resulting in an increase in the basicity of the Craney Island waters due to the utilization of carbon dioxide. From September 1974 to February 1975, the pH ratio of the No. 1 spillway to the NE Open ranged from 1.04 to 1.26 (averaged 1.10). pH values were similar between both portions of the sampling program, but somewhat higher during the second portion. Of 29 comparison samples, 29 (100%) were higher at the No. 1 spillway. The total yearly means of pH at both spillways (middle spillway plus No. 1 spillway) and the NE Open water site yielded 8.57 and 7.95, respectively, with a mean ratio of 1.08 (equal to 0.62 pH units greater at the spillways). The mean for pH at station eight (Adams et al. 1975; see Figure 2) was 7.72 ± 0.62 (n = 19) with a range from 6.80 to 8.11 pH units (from October 1973 to April 1975).

That this difference between the spillways and the NE Open water site might be due to carbon dioxide utilization by the phytoplankton within Craney Island was indicated by other parameters which measure the organic material in the waters. Total phosphorus and total Kjeldahl nitrogen were nearly always higher at the spillways (see Figures 8 and 12). Chlorophyll measurements would be quite useful; however, these were not conducted during this period of the monitoring program.¹ Photosynthesis will usually increase both the pH and the dissolved oxygen concentration of the waters, and thus a positive relationship should exist. Linear correlation coefficients for pH versus dissolved oxygen saturation for the first portion of the sampling program for the middle spillway and the NE Open were 0.39 and 0.17, respectively, while for the second sampling period these were -0.03 (No. 1 spillway) and -0.40 (NE Open water). One possible explanation for the poor correlation would be the random collection times, which were generally in the morning (ca. 10 a.m.). If an intensive sampling of the spillways for pH and dissolved oxygen were conducted, a diurnal sinusoidal curve would probably be seen. Maxima would correspond to the afternoon (daylight) periods when photosynthetic processes would have utilized carbon dioxide (increase the pH) and produced oxygen. Minima in both dissolved oxygen and pH would be expected in the early morning (dark) hours, when respiratory processes were active, yet little or no oxygen was being produced. This has been observed in other embayments (Riley and Chester 1971) and could result in oxygen-deficient waters being discharged after sunlight hours. Effluent waters might also tend to be super-saturated during periods of high photosynthetic activity.

In shallow biologically-active waters (such as the enclosed portion of the Craney Island Disposal area), large diurnal pH variations are common, where values ranging from 9.5 in the daytime to 7.3 at night or in early morning have been reported (EPA 1973). Measurements at the middle spillway ranged from 7.82 to 9.24, and those from the No. 1 spillway varied from 8.28 to 9.08 during the sampling program. The degree of dissociation of various toxic metals is related to the pH of the solution, so that this variable, plus other abiotic factors (such as temperature, salinity, dissolved oxygen, various cations and anions), will influence the overall quality of the impounded waters within Craney Island. Fish are less sensitive to changes in pH than are the plankton and benthic invertebrates, while oyster larvae are impaired at a pH of 9.0 and die within a few hours at a pH of 9.1 (EPA op. cit.). Recommendations for pH fluctuations are (EPA op. cit.):

¹ Chlorophyll concentrations are presently being measured during the second year of the monitoring program (April 1975 to March 1976).

Changes in sea water pH should be avoided. The effects of pH alteration depend on the specific conditions. In any case, the normal range of pH in either direction should not be extended by more than 0.2 units Addition of foreign material should not drop the pH below 6.5 or raise it above 8.5.

Since the plume at each spillway was not sampled during this period, the effect of the effluent water on the pH of the receiving waters could not be ascertained. Since April 1975, samples from the plumes are collected and analyzed on a monthly basis, and these data will be discussed in a subsequent report for the period between April 1975 to March 1976.

Dissolved Oxygen

Dissolved oxygen (DO) ratios of the middle spillway to NE Open from December 1973 to August 1974 ranged from 0.69 to 1.38, and averaged 0.99 (ratio of means = 0.97). Of 20 comparison samples, eight (40%) were higher at the spillway, ten (50%) were lower, and two (10%) were equal within the accuracy and precision of the method (ca. 10%). As mentioned earlier, oxygen analysis during this period was done with a polarographic probe, which was calibrated against standard Winkler titrations. During the second time period (September 1974 to February 1975), a calibration of the probe was conducted by measuring DO in the field and concurrently preserving samples for laboratory titrations. Duplicates showed poor precision and accuracy with the probe. This was most likely due to improper field calibration of the probe. All oxygen analyses since September 1974 were done with Winkler titrations. Ratios of DO for this second period of the monitoring program ranged from 0.80 to 1.49 (averaged 1.10). Of 29 comparison samples, 19 were higher at the spillway (66%), seven were lower (24%), and three were equal within the accuracy and precision of the method ($\pm 5\%$). Yearly averages of DO concentrations (mg/l) for the spillways (middle spillway plus No. 1 spillway) and NE Open were 9.18 and 8.90, respectively (ratio of means was 1.05). For the period from September 1974 to February 1975, the respective means were 9.49 and 8.14 (the ratio of means was 1.08). The latter data may be more representative; however, it is possible that seasonal trends might account for the differences between the two sampling periods. The mean for DO at station eight (Adams et al. 1975; see Figure 2) was 7.95 ± 4.84 mg/liter ($n = 19$), with a range from 3.33 to 11.48 mg/liter, during the period from October 1973 to April 1975.

Dissolved oxygen saturation percentage ratios from December 1973 to August 1974 at the middle spillway versus NE Open ranged from 0.69 to 1.43 (averaged 1.01). Of 20 comparison samples, nine (45%) were greater at the spillway, nine (45%) were lower, and two (10%) were equal. Means of the saturation percentages were 98% and 99% for the two locations. From September 1974 to February 1975, the No. 1 spillway to NE Open ratios ranged from 0.78 to 1.34 (averaged 1.07). Of 29 comparison samples, 16 (55%) were greater, six (21%) were less, and seven (24%) were equal. Individual means of percent saturation were 99% (No. 1 spillway) and 94% (NE Open). Yearly DO saturation percentages for both spillways and NE Open sites were 99% and 97%, respectively. Oxygen saturation at station eight (Adams et al. op. cit.; see Figure 2) averaged $87.45 \pm 40.82\%$ (n = 19) with a range from 40.80 to 131.10 percent saturation (from October 1973 to April 1975).

Guidelines for dissolved oxygen concentrations are listed in EPA (1973):

Each proposed change in the dissolved oxygen concentration in estuaries and coastal waters should be reviewed for risk or damage to aquatic life. The limited laboratory data and field observations on marine organisms suggest that easily observed effects, which are in many cases deleterious, occur with dissolved oxygen concentrations of 4 to 5 mg/liter as daily minimum values for periods of several days. As a guideline, therefore, reduction of the dissolved oxygen concentration to values below 4 mg/liter can be expected to change the kinds and abundances of the aquatic organisms in the affected volume of water and area of bottom. Particular attention should be directed toward identifying species with restricted spawning and nursery areas and conservatism should be used in applying guidelines to these areas.

Inspection of the dissolved oxygen data indicates that depletion at the spillways, and the subsequent effect on the receiving waters of Hampton Roads, was not a problem. However, the organic load (phytoplankton and dissolved organic carbon) could not be evaluated, and therefore, these parameters are presently under investigation. Also, samples were not collected during the night or early morning hours when oxygen concentrations would be lower.

Fecal Coliform Bacteria

Measurements of fecal coliform (*Escherichia coli*.) at the middle spillway from December 1973 to August 1974 ranged from 0 to 200 colonies/100 ml (average of 17 ± 95 , n = 20), while at the NE Open the counts ranged from 0 to 1 colony/100 ml. During the second portion of the monitoring program, larger water volumes (10 to 100 ml versus one ml) were processed through the filter pads in

order to obtain more accurate counts for bacteria. This generally resulted in higher values than those reported during the first part of the program. Therefore, fecal coliform colonies from September 1974 to February 1975 ranged from 0 to 217 colonies/100 ml (average of 64 ± 118 , $n = 30$) at the No. 1 spillway and from 0 to 20 colonies/100 ml (mean of 3 ± 8 colonies/100 ml, $n = 29$) at the NE Open water site. The ratios of the concentrations of fecal coliforms at the No. 1 spillway to those at the NE Open ranged from 3.17 to 78.00 (mean of 27.67 ± 49.52 , $n = 29$) from September 1974 to February 1975. Because of measurements of zero fecal coliforms from December 1973 to August 1974, ratios could not be calculated. During this period, however, four measurements (20%) were greater at the spillway, one (5%) was lower, and 15 (75%) were equal. From September 1974 to February 1975, when more accurate measurements were undertaken, 27 (93%) of the water samples were higher at the spillway and two (7%) were lower.

Frequently, bird populations, which were primarily ducks, were evident within the disposal area during the second portion of the program. *Escherichia coli*. are common to the intestinal tracts and feces of most warmblooded animals. Geldreich et al. (1962) have shown that more than 96% of the coliform in human feces provided a positive test when the Millipore membrane filter procedure was used. At least 93 percent of the total coliform in other warmblooded animals, including livestock, poultry, cats, dogs, and rodents, were also detected by this test. At least one pathogen, Salmonella, provided a positive linear relationship with *Escherichia coli*. (Geldreich 1970, Geldreich and Bordner 1971), with an abrupt increase in the frequency of Salmonella detection when fecal coliform densities were present at greater than 200 colonies/100 ml (Table 7).

Table 7. Fecal coliform counts (*Escherichia coli*.) and detection of Salmonella in natural waters (from EPA 1973).

<i>Escherichia coli</i> . (Colonies/100 ml)	Percent Positive		Number of Determinations
	Salmonella Detection		
1 - 200	31.7		41
200 - 1000	83		50
1000 - 2000	88.5		17
>2000	97.6		123

Any occurrence of fecal coliform in water is prime evidence of contamination by wastes of some warmblooded animals, and as the fecal coliform densities increase, potential health hazards become greater . . . (EPA 1973).

Virginia water quality parameters for public or municipal water supplies are divided into two categories for the basis of setting standards for permissible fecal coliform levels. These are primary contact waters (class A) where there is "prolonged intimate contact and considerable risk of ingestion, and the propagation of fish, shellfish, and other aquatic life" (Pheiffer, Donnelly, and Possehl 1972), and secondary contact waters (class B) for recreation, and the propagation of fish, shellfish, and aquatic life.

The James River estuary, defined as beginning at the transect between Old Point Comfort and Fort Wool (see Figure 2) and ending at the fall line in Richmond, is classified as Class IIB water by Virginia water quality guidelines. The bacteriological standards for these waters are: fecal coliform within a 30-day period should not exceed a mean of 200 colonies per 100 ml and not more than ten percent of the samples in a 30-day period may be greater than 400 colonies per 100 ml. The fecal coliform concentrations at the Craney Island spillways were greater than or equal to 200 colonies per 100 ml on two occasions from December 1973 to February 1975. None of the fifty samples taken at the NE Open water site were greater than or equal to 200 colonies per 100 ml. For ~~Class A~~ ^{specific shellfish} waters (shellfish waters), the median density of fecal coliform bacteria shall not exceed 70 colonies/100 ml, and not more than 10% of the samples should be greater than 230 colonies/100 ml in the areas where fecal contamination is most likely during the worst possible conditions. These are the water quality parameters applied to the shellfish areas of Hampton Roads Harbor (Pheiffer, Donnelly, and Possehl 1972).

On two occasions from December 1973 to August 1974, the spillway effluent concentration (middle spillway) was equal to or exceeded 70 colonies/100 ml, and on 11 occasions from September 1974 to February 1975 concentrations at the No. 1 spillway were in excess of 70 colonies/100 ml. At no time during the entire sample period did the concentrations at the NE Open water site exceed or equal 70 colonies/100 ml. Neither sample area during the entire time period showed coliform concentrations greater than 230 colonies/100 ml.

Total Phosphorus and Dissolved Orthophosphate-Phosphorus

During the first portion of the program from December 1973 until June 1974, dissolved inorganic orthophosphate (DIP) ranged from less than detection (0.001 mg/liter) to 0.264 mg/liter (mean of 0.065 ± 0.134 mg/liter; $n = 20$) at the middle spillway, while the range was much less at the NE Open water site (0.000 to 0.090 mg/liter) and the mean was half the average value (0.032 ± 0.048 mg/liter; $n = 21$) determined for the spillway. The ratio of DIP at the middle spillway as compared to the NE Open water site varied from 0 to 15.29 (mean of 2.82; $n = 18$). From a total of 18 comparison samples, 71 percent were higher at the middle spillway, while 24 percent were lower, and six percent were equal (within the accuracy of the analysis). The range (0.013 to 0.340 mg/liter) and average (0.085 ± 0.130 mg/liter; $n = 30$) at the No. 1 spillway during the second portion of the monitoring program (September 1974 to February 1975) were only slightly greater than the first seven months. This slight shift could have been caused by a change in sampling locations (from the middle spillway to the No. 1 spillway; however, examination of the January and February 1975 data indicated that there were no significant differences between the two spillways as was evident in the dissolved metal data) or a seasonal phenomena. DIP at the NE Open water site also exhibited an overall increase in the range (0.023 to 0.262 mg/liter) and a doubling of the mean (0.064 ± 0.110 mg/liter; $n = 29$) over the first seven months; however, these statistics were biased by five data points during the period from 18 September to 16 October 1974, when DIP values were greater than 0.100 mg/liter. The ratio of the No. 1 spillway to the NE Open water site ranged from 0.54 to 3.20, and averaged 1.55 ($n = 29$). From a total of 29 comparison samples, 62 percent were higher at the No. 1 spillway, while 14 percent were lower and 24 percent were equal. The combined ratios for the entire monitoring program from December 1973 until February 1975 provided a range of 0.24 to 15.29 when the spillway concentrations were compared to the NE Open water site (see Table 6). From 47 comparison samples, DIP was higher 66 percent of the time at the spillways, while the rest of the water samples were divided evenly between either the same or less concentration at the spillways when values were compared to the NE Open water site.

Dissolved inorganic orthophosphate at station eight (see Figure 2 for station location) ranged from 0.023 to 0.100 mg/liter, with a mean of 0.042 ± 0.041 mg/liter ($n = 19$) during the period from October 1973 until April 1975. The mean at the NE Open water site during the entire sampling program (0.050 mg/liter) was only slightly greater (19 percent) than the average concentration at station eight, even

though the variation at the 95% level of confidence was double (0.095 vs. 0.041 mg/liter, as listed above). This wider scatter in the values at the NE Open water site, which has been seen for many of the other parameters, could have been caused by the shallower water depth, whereby wind-mixing would suspend particulate material from nearby bottom sediments and release dissolved components. Also, rainwater runoff and underground seepage from the Craney Island Disposal area could alter many of the chemical constituents. The mean at the spillways (0.076 mg/liter) for the entire sampling program was 81 percent greater than the average for station eight, 130 percent greater than the average concentration of DIP at three surface stations in the lower Chesapeake Bay (mean of 0.033 ± 0.042 mg/liter; $n = 57$), and 105 percent greater than the mean of four surface stations in Hampton Roads Harbor (mean of 0.037 ± 0.035 ; $n = 76$) during the same time period (Adams et al. 1975). It is interesting to note that both the range (0.000 to 0.941 mg/liter) and mean (0.091 ± 0.226 mg/liter; $n = 66$) for water samples collected from four stations (October 1973 to April 1975) in the Elizabeth River were greater than the spillway effluent from Craney Island, and in fact, the spillway waters were on the average 20 percent less concentrated in DIP than the waters of the Elizabeth River. It should be pointed out that the Elizabeth River is known to be eutrophic, and high chlorophyll concentrations (mean of 25.9 ± 40.3 $\mu\text{g/liter}$; $n = 16$) have been measured during the summer of 1974 (Adams et al. op. cit.); therefore, it would be prudent to compare spillway concentrations with those waters contiguous to Craney Island, i.e., open waters of the Hampton Roads Harbor, which are not subject to intense urbanization (for example, approximately 50 million gallons of treated sewage wastes, which have an average DIP concentration of 7 mg/liter, are pumped into the Elizabeth River on a daily basis).

Ketchum (1969) proposed concentrations for phosphorus enrichment of 0.08 mg/liter in the winter and 0.05 mg/liter in the summer before an estuary could reach a possible dangerous level of eutrophication. However, it is presently difficult to assess problems related to nutrients at the Craney Island spillways, especially if these are not phyto-toxic. The greatest understanding that could be derived from excessive nutrient concentrations would be an examination of ecological trends in the biota inhabiting the adjacent waters. For example, massive and persistent blue-green algae blooms have been related to nutrient enrichment of the upper Potomac tidal river system (Jaworski, Lear, and Villa 1972). Even though there are known correlations between nutrient enrichment and excessive algal growth, EPA (1973) has not been able to provide recommendations because of the complexity

of the relationships between phosphate concentrations and biological productivity, yet it is suggested that 0.05 mg/liter of phosphorus is clearly excessive (see the next section for further discussion).

As well as the measurements of DIP, total phosphorus (TP) was analyzed at the spillways and NE Open water site. During the first portion of the program from December 1973 to June 1974, TP ranged from 0.058 to 1.369 mg/liter at the middle spillway, and averaged 0.287 ± 0.558 ($n = 20$). The range at the NE Open water site during the same time was 0.014 to 0.169 mg/liter, while the concentrations averaged 0.094 ± 0.070 mg/liter ($n = 21$) and were about 33 percent of the spillway values. The ratio of TP at the middle spillway as compared to the NE Open water site ranged from 0.97 to 14.26, with a mean of 3.16 ($n = 20$). From a total of 20 comparison samples, TP was greater 95 percent of the time at the middle spillway, while the NE Open water site had a larger concentration for the remainder of the period. The range of TP at the NE Open water site was slightly greater (0.049 to 0.243 mg/liter) during the second portion (September 1974 to February 1975) even though the average (0.103 ± 0.100 mg/liter; $n = 23$) was about the same as the previous seven months. While the average (0.235 ± 0.190 mg/liter; $n = 24$) at the No. 1 spillway during the second portion of the monitoring program was similar to the first period, the range (0.095 to 0.445 mg/liter) was less. The ranges (0.095 to 0.445 at the No. 1 spillway vs. 0.058 to 0.444 mg/liter at the middle spillway) and averages (0.235 at the No. 1 spillway vs. 0.227 mg/liter at the middle spillway) for both periods would be almost identical if one value (1.369 mg/liter on 18 January 1974) were excluded from the data; however, both the high suspended load (2535 mg/liter) and large ammonia concentration (5.3 mg/liter) at the middle spillway (see Figures 11 and 16), coupled with active dredging at the NW corner of Crane Island (see Tables A9 and A10), has led to the speculation that some of the dredged spoils did not settle before reaching the spillway. The ratio of TP at the No. 1 spillway as compared to the NE Open water site varied from 0.75 to 3.54 (mean of 2.44; $n = 23$). Therefore, these abnormally high data could not be discarded as analytical error. From a total of 23 comparison samples, 96 percent were higher at the spillway, while the rest (four percent) were lower. These values were identical to the calculations for the first seven months of the program; therefore, during the entire monitoring program from December 1973 until February 1975, TP was greater 95 percent of the time at the spillways as compared to the NE Open water site.

There was little information for comparing total phosphorus values collected during this program with data from local waters. The average for station eight (see Figure 2) from February to April 1975 was 0.077 mg/liter (n = 3), while values for three stations in Chesapeake Bay were 0.074 mg/liter (n = 9), four stations in Hampton Roads Harbor averaged 0.075 mg/liter (n = 12), and four stations in the Elizabeth River (February to April 1975, n = 12) provided a higher value of 0.131 mg/liter (Adams et al. 1975). Values for Delaware Bay ranged from 1.3 to 2.7 mg/liter (Polis, Kupferman, and Szekielda 1973). The average for TP at the spillways (0.256 mg/liter) during the entire period from December 1973 until February 1975 was twice as high as those from the Elizabeth River, but further relationships should not be drawn because it would not be valid to compare a winter sampling time (February to April 1975) for local waters with annual data from the Craney Island spillways. The NE Open water average for the entire monitoring program (0.099 mg/liter) was only slightly higher than station eight and Hampton Roads Harbor (during the period from February to April 1975; consult Adams et al. op. cit.).

Total phosphorus in bottom sediments ranged from 4 to 359 ppm in the channel of the Elizabeth River (VIMS 1971), while dredge spoil entering Craney Island ranged from 0.043 to 4.133 mg/liter (mean of 0.893 ± 1.974 mg/liter; n = 31). It was surprising that TP values at the dredge pipes were much lower than measured in sediments from local areas. It is possible that the processing of sediment samples, where analyses were performed on solids, would provide somewhat different values than dredge pipe effluent samples which consisted of a mixture of bottom sediments and overlying waters.

Total phosphorus is a measurement of the different forms of combined- and uncombined-phosphorus liberated to solution through acid digestion. This would include particulate and dissolved inorganic and organic phosphorus, polyphosphates, and dissolved inorganic orthophosphate (DIP). The difference between total phosphorus and DIP would mostly represent particulate material, which is composed of both inorganic sediment particles and organic material (living and dead plankton as well as organic detritus). The difference between TP and DIP ranged from a low of 0.005 to 0.177 mg/liter at the NE Open water site to a level of 0.047 to 0.359 mg/liter at the No. 1 spillway, and was as high as 0.02 to 1.27 mg/liter at the middle spillway. Measurements of total phosphorus at the beginning of the program were generally related to high concentrations of suspended solids, while higher TP values occurred again during the latter part of June (sample nos. 46 to 55) and continued until August 1974 (sample no. 57), at which time high levels of

dissolved nitrates and ammonia were present in the spillway waters. These high values might be related to an increased productivity within the diked area. Another peak in TP appeared in October and November 1974, which closely followed a large maximum in DIP in September 1974 at the No. 1 spillway. Therefore, it seemed that the concentrations of TP could be related to both the inorganic and organic fractions of the suspended material, and further indicators of plankton populations would be needed before these processes could be elucidated. The measurements of chlorophyll are presently being conducted during the second year of the monitoring program (1975 - 1976).

Dissolved Inorganic Nitrate and Nitrite

Inorganic nitrate ranged from 0.018 to 0.465 mg/liter during December 1973 to June 1974 at the middle spillway, and averaged 0.130 ± 0.234 mg/liter ($n = 20$). During the same time period, concentrations were lower at the NE Open water site, with a range of 0.004 to 0.263 mg/liter and a mean of 0.101 ± 0.144 mg/liter ($n = 21$). The ratio of concentrations at the middle spillway as compared to the NE Open water site ranged from 0.29 to 83.75, with a mean of 6.04 ($n = 19$). From a total of 19 comparison samples, 32 percent of the values were greater at the spillway, while 58 percent were less and 11 percent were the same. Starting in August 1974 and continuing to the end of the second portion of the monitoring program, high transient levels of nitrates were measured at both the NE Open water site (ranged from 0.073 to 3.801 mg/liter) and the No. 1 spillway (ranged from 0.007 to 2.832 mg/liter). The average for this time period at the No. 1 spillway (mean of 0.440 ± 1.620 mg/liter; $n = 28$) was 240 percent above the previous seven months at the middle spillway, while the NE Open water site (mean of 0.567 ± 1.564 mg/liter; $n = 28$) was 460 percent higher. The ratio of the No. 1 spillway to the NE Open water site ranged from 0.02 to 5.60 (mean of 0.85; $n = 27$), while these comparisons show that nitrates were higher 81 percent of the time at the NE Open water site. The No. 1 spillway samples were greater in concentration only 19 percent of the time. Comparison samples ($n = 46$) for the entire period from December 1973 to February 1975 substantiated that nitrates were higher at the NE Open water site 72 percent of the time, while 24 percent of the values were higher at the spillways, and two percent were equal. This was the only parameter measured during this program which was usually higher at the NE Open water site, and when the 17 constituents listed in Table 6 are examined, dissolved nitrates and nitrites were consistently higher in the background waters as compared to the spillways. This was not as noticeable for nitrites (43%) as nitrates (72%), as shown

above); however, differences are striking when these two parameters are compared to the others listed in Table 6.

Dissolved nitrate at station eight (see Figure 2) ranged from 0.074 to 0.441 mg/liter during the period from October 1973 until April 1975, with an average of 0.197 ± 0.193 mg/liter ($n = 19$). The mean of the entire monitoring program at the NE Open water site (0.376 mg/liter) was 91 percent greater than station eight; yet it was 12 percent less than the average (0.422 ± 0.451 mg/liter; $n = 104$) for dissolved nitrate at five stations on the James River, which had a range from 0.027 to 1.293 mg/liter, during the same period of time (October 1973 to April 1975). In comparing the NE Open water site with other local bodies of water, nitrates were 146 percent higher than the average of three stations in the lower Chesapeake Bay (mean of 0.153 ± 0.228 mg/liter; $n = 57$), 113 percent higher than the average of four stations in Hampton Roads Harbor (mean of 0.176 ± 0.192 mg/liter; $n = 76$), and 64 percent greater than the mean of four stations in the Elizabeth River (average of 0.229 ± 0.230 mg/liter; $n = 66$) during the same time (Adams et al. 1975). It was recommended by EPA (1973) that public water supplies not exceed 10 mg/liter. Even though none of the water samples measured during this monitoring program were above this concentration for dissolved nitrate, it should be emphasized that this level has been established for drinking water and not for estuarine systems.

With the exception of three occasions, dissolved nitrite in the spillway samples were less than 0.100 mg/liter. During the first portion of the program from December 1973 to June 1974, nitrite ranged from 0.001 to 0.280 mg/liter at the middle spillway, with an average of 0.049 ± 0.164 mg/liter ($n = 20$). The range at the NE Open water site was 0.001 to 0.063 mg/liter, where the average (0.013 ± 0.029 mg/liter; $n = 21$) was 277 percent less than the mean concentration of nitrites in the spillway during the same period of time. The ratio of nitrites in the middle spillway as compared to the NE Open water site ranged from 0.02 to 68.75, with a mean of 7.79 ($n = 20$). From a total of 20 comparison samples, 55 percent of the values were higher at the middle spillway, 40 percent were lower, and five percent were equal. During the second portion of the program from September 1974 to February 1975, dissolved nitrites were usually lower at the No. 1 spillway, with a range from less than detection (<0.006 mg/liter) to 0.089 mg/liter. The average was 0.028 ± 0.050 mg/liter ($n = 30$), which was 75 percent less than the average of the first seven months. With the exception of two values in September 1974, concentrations were less than 0.100 mg/liter at the NE Open water site during

the same period of time. The range was <0.006 to 0.141 mg/liter, with a mean of 0.027 ± 0.068 mg/liter ($n = 29$), which was more than double the average for the first part of the monitoring program at the background site. The ratio of nitrites at the No. 1 spillway as compared to the NE Open water site ranged from 0.20 to 2.53 , with a mean of 1.32 ($n = 24$). From a total of 24 comparison samples, the concentration ratios were divided about evenly between the No. 1 spillway and the NE Open water site, where 48 percent of the samples were greater in nitrite concentration at the spillway, 45 percent were greater at the background site, and seven percent of the water samples collected at the two locations were equal. For the entire monitoring program from December 1973 to February 1975, 49 comparison samples were evaluated and provided a ratio ranging from 0.02 to 68.75 (mean of 4.26). Dissolved nitrite was higher 51 percent of the time at the spillways, while the NE Open water site exhibited a greater concentration 43 percent of the time. The means of the NE Open water site (0.020 mg/liter) and spillways (0.033 mg/liter) for the entire period were slightly higher than the average at station eight (0.015 ± 0.029 mg/liter; $n = 19$) during the period from October 1973 to April 1975. These were also higher than the average of four stations in the Harbor of Hampton Roads (0.019 ± 0.073 mg/liter; $n = 76$), three stations in the lower Chesapeake Bay (mean of 0.014 ± 0.035 mg/liter; $n = 57$), five stations in the James River (mean of 0.017 ± 0.041 mg/liter; $n = 103$), and four stations in the Elizabeth River (mean of 0.017 ± 0.021 mg/liter; $n = 66$) during the same time period (Adams et al. 1975).

Even though criteria have been established by EPA (1973) for specific levels of nitrates (10 mg/liter) and nitrites (1 mg/liter) in public water supplies, the problems associated with excessive levels of these two nutrients in estuarine waters have not been satisfactorily addressed. Some thirty years ago, Sawyer (1947) suggested that 0.3 mg/liter of inorganic nitrogen at the spring maximum would be a critical level for some Wisconsin lakes, where algal blooms would be expected to ensue. Brezonik (1972) related the trophic level of 55 Florida lakes to critical loading rates of nitrogen (and phosphorus) from the surrounding watersheds and derived a dangerous loading level of $3.4 \text{ g m}^{-2} \text{ yr}^{-1}$ for nitrogen (which was double the permissible level of $1.9 \text{ g m}^{-2} \text{ yr}^{-1}$). It is difficult to assess the environmental problems associated with dissolved inorganic nitrogen at the spillways, because quantitative information concerning the phytotoxicity or phyto-stimulatory nature of the spillway waters is not available and concentrations were at times (73 percent for nitrates and 43 percent for nitrites) higher at the background NE Open water site.

EPA (op. cit.) has recommended that:

If the maximum amounts of available nitrogen and phosphorus in domestic wastes increase the concentration in receiving waters to levels of 0.05 mg/liter of phosphorus and 0.36 mg/liter of nitrogen, enough organic matter would be produced to exhaust the oxygen content of the water, at the warmest time of the year under conditions of poor circulation, to levels below those recommended. These concentrations of nutrients are clearly excessive.

Even though the total available inorganic nitrogen (nitrate, nitrite, and ammonia) components were higher at the spillways (averaged 2.39 mg/liter during the first portion of the program during active dredging at the NW Corner, with discharge through the middle spillway; and 0.89 mg/liter during the second portion of the monitoring program at the No. 1 spillway), the levels at the NE Corner background site (averaged 0.65 mg/liter) exceeded the recommended concentrations. Dissolved inorganic orthophosphate data were not as excessive as nitrogen, where the spillways averaged 0.076 mg/liter (compared to the NE Open water values of 0.050 mg/liter and station 8 of 0.042 mg/liter).

Dissolved Ammonia Nitrogen and Total Kjeldahl Nitrogen

During the first portion of the program from December 1973 to June 1974, dissolved ammonia ranged from 0.011 to 13.76 mg/liter at the middle spillway (averaged 2.208 ± 7.109 mg/liter; $n = 20$), while the range at the NE Open water site was about one-third (0.011 to 4.532 mg/liter) and the average was one-fifth (0.488 ± 1.938 mg/liter; $n = 21$) of the spillway values. The ratios of dissolved ammonia at the middle spillway as compared to the NE Open water site ranged from 0.15 to 26.54, with an average of 5.70 ($n = 20$). From a total of 20 comparison samples taken this period, 80 percent of the values were higher at the spillway while the rest were lower at the NE Open water site. Starting in August 1974 and continuing until February 1975, the overall range (0.007 to 2.679 mg/liter) and mean (0.419 ± 1.242 mg/liter; $n = 30$) for the No. 1 spillway decreased substantially from the previous seven months. As illustrated in Figure 11, transient high-level concentrations of ammonia were still in evidence at the spillways (on 20 December 1974, and again on 20 February 1975), but the frequency of these occurrences was less than in the previous seven months. Values at the NE Open water site exhibited both a diminished range (0.019 to 0.214 mg/liter) and an eighty percent reduction in the average concentration (0.108 ± 0.088 mg/liter; $n = 29$). Variability in the data for the NE Open water site was also

substantially reduced from a relative standard deviation of 397 percent, at the 95 percent level of confidence, during the first portion of the program to 81 percent during the last six months. The decrease in scatter could have been caused by changes in biological activity during the winter months, which would have normally produced both higher values and greater fluctuations in the ammonia content of the water column, or the cessation of active dredging and disposal within Craney Island during these months as compared to the previous seven months. The ratio of the concentration of ammonia at the No. 1 spillway as compared to the NE Open water site ranged from 0.37 to 21.19 (mean of 3.06; n = 29) during the second portion of the program. Of the 29 comparison samples, 59 percent were greater at the No. 1 spillway, while 24 percent were less and 17 percent were equal in concentration during this time period. During the entire period from December 1973 to February 1975, the ratios of dissolved ammonia at the spillways as compared to the NE Open water site ranged from 0.15 to 21.19 (mean of 4.14; n = 49). From a total of 49 comparison samples, 67 percent of the ammonia values were greater at the spillways, while 22 percent were higher in concentration at the NE Open water site (10 percent were equal, within the accuracy of the method).

During the period from December 1973 to February 1975, ammonia exceeded one mg/liter on 12 different occasions at the spillways, and a third of these were greater than five mg/liter. These high concentrations at the spillways accounted for 20 percent of the sample collections during the entire monitoring period; however, 100 percent of the abnormally high values (>5 mg/liter) and eight of the 12 samples listed above occurred at the middle spillway during the period of active disposal at the NW corner of Craney Island. During this period of dredge operation at the NW corner, dissolved ammonia at the NE Open water site was also greater than one mg/liter on two occasions. Whether or not the high values at the NE Open water site were related to these dredging operations would be a matter of conjecture. The average of dissolved ammonia at the spillways (0.422 mg/liter) and the NE Open water site (0.180 mg/liter) were compared to concentrations of local waters. Dissolved ammonia averaged 0.126 ± 0.176 mg/liter (n = 12), with a range from 0.000 to 0.301 mg/liter, at station eight (see Figure 2) during the period from May 1974 to April 1975 (Adams et al. 1975). During the same time, the average for three surface stations in the lower Chesapeake Bay was 0.121 ± 0.204 mg/liter (n = 36), while surface values from four stations in Hampton Roads Harbor measured 0.129 ± 0.187 mg/liter (n = 48). The average for the NE Open water site was 40

percent higher than Hampton Roads, while the average concentration of dissolved ammonia at the spillways was 227 percent greater. However, spillway concentrations were less than double the values measured at four surface stations in the Elizabeth River (mean of 0.274 ± 0.364 mg/liter; $n = 44$) during the period from May 1974 to April 1973 (Adams et al. op. cit.).

During the bacterial oxidation of ammonia to nitrate, dissolved nitrite would be one of the intermediate products (Keeney 1972). A comparison of Figures 10 and 11 suggested that this was occurring within the Craney Island Disposal area, where the high levels of ammonia were becoming oxidized to nitrites and nitrates. A simple linear least squares regression of nitrites with ammonia at the middle spillway resulted in a correlation coefficient of $r = 0.55$ ($n = 19$), while at the No. 1 spillway r was 0.62 ($n = 24$). Nitrates were poorly correlated with ammonia ($r = 0.17$ for $n = 20$ at the middle spillway; $r = 0.07$ for $n = 30$ at the No. 1 spillway), which suggested that the oxidation of the abnormally high levels of ammonia was not complete. This was further substantiated by the fact that nitrates were higher 72 percent of the time at the NE Open water site when values were compared to the spillways. If the ammonia entering Craney Island had oxidized completely, nitrate concentrations would have definitely been higher at the spillways as compared to the NE Open background site. The poor correlation between ammonia and nitrate could have resulted from a short residence time for dredge effluent within Craney Island, especially in the case of the NW Dredge effluent leaving through the middle spillway, or due to the production and escape of ammonia from anaerobic sediments near the weirs. Sedimentary production and release of ammonia would probably not be related to dredging activity but to wind-mixing of the shallow sediments; seasonal temperature changes, bacterial activity, and bioturbation.

With a thermodynamic equilibrium constant of $pK_1 = 9.2$ for the ionization of NH_4^+ in water (Gieskes and Rogers 1973), at a pH of 9.2 the concentration of un-ionized ammonia (NH_3) and ammonium ion (NH_4^+) would be equal. The equilibrium of these two species in water would be a function of pH, and the ammonium ion would predominate in most natural waters (pH from 7 to 8). At a pH of 7.95 (mean of the NE Open water site), only six percent of the total concentration of ammonia would be present as the un-ionized species. Since the toxic component of ammonia is the un-ionized species (EPA 1973), the toxicity would increase as the waters become more basic (as pH increased). At the mean pH for the spillways (pH = 8.57), the concentration of un-ionized ammonia would be approximately 23

percent of the total concentration of ammonia present, while it was as high as 57 percent on 31 January 1975 when a pH of 9.44 was measured. Sublethal and acutely toxic concentrations of un-ionized ammonia for various fish species range from an LC₅₀ of 0.29 mg/liter for perch to as high as 2.8 mg/liter for striped bass (EPA op. cit.). At the highest total ammonia concentration of 13.76 mg/liter on 25 January 1974 at the middle spillway, the concentration of NH₃ was 1.7 mg/liter (pH = 8.28), while the maximum concentration of un-ionized ammonia was 4.2 mg/liter on 22 February 1974 (pH = 9.24).

It has been advised by EPA (op. cit.) for freshwater aquatic life:

Once a 96-hour LC50 has been determined using the receiving water in question and the most sensitive important species in the locality as the test organism, a concentration of un-ionized ammonia (NH₃) safe to aquatic life in that water can be estimated by multiplying the 96-hr LC50 by an application factor of 0.05; but no concentration greater than 0.02 mg/liter is recommended at any time or place.

Furthermore, in the marine section of the EPA (op. cit.) guidelines, it is recommended that:

On the basis of freshwater data available at this time, it is suggested that concentrations of un-ionized ammonia equal to or exceeding 0.4 mg/liter constitute a hazard to the marine biota, and levels less than 0.01 mg/liter present minimal risk of deleterious effects.

Because of the lower salinities at the Craney Island spillways (10.1 to 20.2 ‰), it would be prudent to apply the freshwater criteria, especially in the case of dissolved ammonia, to the results of the monitoring program. It is assumed that the 0.02 mg/liter level for freshwater refers to the un-ionized species of ammonia. Using the thermodynamic ionization constant of $pK_1 = 9.2$ and the pH measurement of each water sample, the concentration of the un-ionized species was calculated at the spillways and the NE Open water site. During the entire monitoring program, only four samples (7 percent) contained less NH₃ at the spillways than the recommended level of 0.02 mg/liter, which meant that 93 percent of the water samples were greater in un-ionized ammonia concentration than has been suggested by EPA (op. cit.) for freshwater systems. This was not the case for the NE Open water site, where the un-ionized portion of ammonia was greater than 0.02 mg/liter only 16 percent (n = 8) of the time, and 84 percent of the water samples contained less than the recommended level. Of the eight high values at the NE Open water site, 75 percent of these were collected between 18 January and 10 April 1974 (sample nos. 8 to 22) which was one of the times that total suspended solids were the highest (see Figure 16) at the middle spillway and

dredging was active at the NW corner of Craney Island. If the data are examined in light of the criteria for marine waters (0.4 mg/liter of un-ionized ammonia), only 32 percent (6 out of 19) of the middle spillway samples were above the recommended levels, while this was the case for 15 percent (6 out of 41) of the water samples collected at the No. 1 spillway. None of the samples from the NE Open water site were above the recommended level of 0.4 mg/liter.

During a period of time when dredging activity was at a minimum (January and February 1975), water samples were collected at each of the three spillways at approximately the same time. These concentrations were compared to the NE Open water site and are presented in Table 8. As in the case of the dissolved metals, the No. 1 spillway effluent contained the greatest concentration of ammonia, and there was a noticeable decrease proceeding towards the No. 3 spillway (see Figure 2). Since the No. 1 spillway is furthest from the source of dredge material discharge, the sediments near the weir would probably be the finest. Because of the sedimentary texture, anaerobic conditions would possibly be greatest at the No. 1 spillway. Therefore, this source of ammonia (from the sediments as opposed to dredge effluent pipes) would be expected to increase as one moves away from the source of dredged material (from the No. 3 towards the No. 1 spillway) during periods of little dredging activity.

Table 8. Total dissolved ammonia at the Craney Island Disposal area spillways and NE Open water site during January and February 1975.

Date	Spillways			Ratios			
	No. 1	Middle	No. 3	No. 1:	Middle:	No. 3:	
	mg/l	mg/l	mg/l	NE Open	NE Open	NE Open	
31 Jan	3.40	2.55	3.35	1.31	2.59	1.95	2.56
	3.97	--	--	--	--	--	--
14 Feb	4.65	4.99	3.35	0.17	27.4	29.4	19.7
	4.88	4.42	4.03	0.23	21.2	19.2	17.5
20 Feb	4.93	3.97	4.31	0.46	10.7	8.63	9.37
	5.16	4.37	4.82	0.28	18.4	15.6	17.2
Mean	4.50	4.06	3.97	0.49	16.1	15.0	13.3

The analysis of total Kjeldahl nitrogen (TKN) was not started until 30 October 1974 (sample no. 75) but continued until 20 February 1975 (see Figure 12). The range of TKN at the No. 1 spillway was 2.15 to 9.92 mg/liter (mean of 4.95 ± 3.68 mg/liter; n = 22), while values for the NE Open water site averaged

less than 30 percent (mean of 1.42 ± 1.46 mg/liter; $n = 21$) of the spillway concentrations. The range at the background site was 0.17 to 2.43 mg/liter, which was 75 to 90 percent less than the spillways. The ratio of spillway concentrations compared to the NE Open water site ranged from 1.72 to 27.35, with a mean of 6.27 ($n = 21$). All (100 percent) of the samples collected during this time period were higher at the spillways when concentrations were compared to the NE Open water site.

As with the measurements of total phosphorus in the water column, there are few values from local waters with which to compare this monitoring program. Water samples were collected at station eight (see Figure 2) from January to April 1975 for TKN measurements, which provided a range from 0.522 to 1.050 mg/liter with a mean of 0.738 mg/liter ($n = 4$). During the same period of time, the mean for TKN at three surface stations in the lower Chesapeake Bay was 0.834 ± 0.497 mg/liter ($n = 12$), while Hampton Roads Harbor values averaged 0.930 ± 0.603 mg/liter ($n = 16$) at four surface stations, with a range from 0.522 to 1.358 mg/liter. Concentrations of TKN, during the same time period, were almost double at six surface stations on the James River (mean of 1.744 ± 5.125 mg/liter, $n = 22$; with a range from 0.275 to 11.28 mg/liter) and at four surface stations in the Elizabeth River (mean of 1.704 ± 4.047 mg/liter, $n = 16$; with a range from 0.360 to 8.860 mg/liter).

EPA (1973) has not addressed the problem of TKN with respect to water quality, yet it has recommended that sediments which contain 1000 ppm (dry weight basis) or greater of nitrogen should not be disposed of in open waters. Considering the concentrations of TKN in the sediments, which range from 1000 ppm near Craney Island to nearly 35,000 ppm (3.5 percent) in the Elizabeth River near the Intracoastal Waterway (Pheiffer, Donnelly, and Possehl 1972), the Craney Island Disposal area has been effective in retaining a considerable proportion of this component; since under normal conditions, all but the finest sediments would be retained within the disposal area. The retention of dredged spoil could be related to the retention or removal of residual nitrogenous material, which would be measured as total Kjeldahl nitrogen. Further information concerning TKN, where 23 sediment samples from the mouth of the James River to river mile six ranged from 100 to 1500 ppm (Pheiffer, Donnelly, and Possehl op. cit.), Newport News surface sediments averaged 600 ± 558 ppm ($n = 6$), and 12 sediment samples from Norfolk Harbor provided a mean of 1685 ± 1328 ppm (VIMS 1972), suggests that most of the contiguous sediments are either close to or above the EPA criteria for open water disposal, and therefore should be deposited in disposal areas during dredging operations.

Dissolved Cadmium, Mercury, and Zinc

During the first seven months of the program (December 1973 to June 1974), dissolved cadmium measurements by anodic stripping voltammetry (ASV) indicated a reactive concentration ranging from 0.001 to 0.019 mg/liter at the middle spillway (mean of 0.005 ± 0.010 mg/liter) and from 0.001 to 0.056 mg/liter at the NE Open water site (mean of 0.010 ± 0.026 mg/liter). The ratio of dissolved cadmium concentrations at the spillway to those measured at the NE Open water site ranged from 0.09 to 1.80 and averaged 0.96 ($n = 19$). Of the 19 comparison samples taken during this period, seven (37%) were greater at the spillway, ten (53%) were lower, and two (11%) were equal. The number of ratios calculated was not equal to the number of comparisons due to measurements of zero for the NE Open site. There was a noticeable difference in the concentration of dissolved cadmium between the first and second portions of the monitoring program. Starting in September 1974, dissolved cadmium was determined by graphite furnace atomic absorption (GFAA), while before this (from December 1973 to June 1974), concentrations were determined with a PAR model 174 Polarographic Analyzer (Princeton Applied Research, Princeton, NJ). This method (anodic stripping voltammetry - ASV) provides a measurement of the reactive or free ion concentration in solution. Fitzgerald (1970) defined this free metal concentration as the sum of any and all forms of the particular metal which are reactive to and detected by the analytical method. In the case of anodic stripping voltammetry, these forms would include hydrated metal ions and readily reactive organic and inorganically sequestered ligands (labile fraction). The amount of metal in this fraction would hardly ever be equal to the total dissolved metal concentration of natural waters. Zirino and Yamamoto (1972) reported the percent of free ions in sea water (pH 8.1) as follows: Cu (1%), Cd (2.5%), and Zn (17%). These values agree reasonably well with the results of this study, where total dissolved metal concentrations were determined by graphite furnace atomic absorption (GFAA) on a Perkin-Elmer model 303 atomic absorption spectrophotometer equipped with a Perkin-Elmer model HGA 2100 graphite furnace accessory (Perkin-Elmer Corp., Norwalk, CT). The GFAA measurements included an oxidation procedure with perchloric acid in the graphite furnace at temperatures ranging from 200°C to 500°C, depending on the particular metal. This insured that organically and inorganically sequestered species of the metal would be in the same oxidation state, thus equally reactive, immediately prior to atomization (when the signal was measured). Continuous monitoring of the recorder trace during the analysis indicated that metal ions were not volatilized prior to atomization. At the present time it is difficult

to state which of the two methods of analysis (ASV or GFAA) is better, since current literature reflects the controversy as to the mechanisms(s) of trace metal uptake by organisms. Often, the addition of a complexing agent (which generally sequesters most of the free ion in solution) will stimulate growth under experimental culture conditions. Thus, it is not clear as to which species -- free ion or complexed metal -- is most likely to be utilized by, or dangerous to, the biota.

From September 1973 to February 1975, total dissolved cadmium at the No. 1 spillway (as measured by GFAA) ranged from 0.005 to 0.254 mg/liter, and averaged 0.051 ± 0.096 mg/liter ($n = 30$), a mean value of nearly ten times the average reactive concentration measured by ASV. At the NE Open site for the same time period, concentrations ranged from 0.013 to 0.076 mg/liter, and averaged 0.036 ± 0.029 mg/liter ($n = 29$), which was approximately 3.5 times greater than the mean reactive value measured by ASV. Ratios of total dissolved cadmium at the No. 1 spillway with respect to the NE Open water site (GFAA) ranged from 0.17 to 19.53 (see Table 5), and averaged 1.97 ($n = 29$). This was approximately two times greater than the average ratio of spillway to NE Open as measured by ASV. Of 29 comparison samples by GFAA, 17 (59%) were greater at the spillway, 11 (38%) were lower, and one (3%) was equal.

An interesting phenomenon was observed during the second sampling period. When more than one spillway was sampled at approximately the same time (January and February 1975), concentrations at the middle spillway were frequently lower than at the No. 1 spillway (Table 9). This was also the case with ammonia and dissolved mercury and zinc. If this trend were consistent throughout the entire monitoring program, it would aid in explaining the difference between the two time periods, where total dissolved metal concentrations at the No. 1 spillway were usually greater than reactive concentrations at the middle spillway. There were, of course, insufficient data to support such a contention, and the methodology was different (middle spillway samples during the first time period were done by ASV, while the No. 1 spillway samples during the second time period were analyzed by GFAA). The only obvious physical differences between the two sites were the water depth and the apparent sediment composition adjacent to the weirs. The sediments seemed to be coarser, and the water was deeper, near the middle spillway. If the complexing agents, such as various organic ligands, and the associated bound metals were released from fine-grained, anoxic sediments, then higher metal concentrations would be expected at the No. 1 spillway.

Table 9. Dissolved cadmium at the Craney Island Disposal area spillways and NE Open water site during January and February 1975. Analyses were done by graphite furnace atomic absorption (GFAA).

Date	Spillways			Ratios		
	No. 1	Middle	No. 3	No. 1:	Middle:	No. 3:
	mg/l	mg/l	mg/l	NE Open	NE Open	NE Open
31 Jan	0.027	0.019	0.025	0.024	0.79	1.04
	0.023	--	--	--	--	--
14 Feb	0.053	0.019	0.031	0.038	0.50	0.82
	0.099	0.071	0.071	0.023	3.09	3.09
20 Feb	0.076	0.071	0.065	0.036	1.97	1.81
	0.069	0.061	0.055	0.042	1.45	1.31
Mean	0.069	0.048	0.049	0.033	1.56	1.61

If, for purposes of comparison, the ASV data were assumed to be typical of the reactive concentration of the dissolved metal, and the GFAA data were considered as the total concentration, then the complexed or non-reactive portion (sequestered by inorganic or organic ligands) of dissolved cadmium was calculated as 90 percent of the total dissolved cadmium present in the spillway effluent and 73 percent at the NE Open water site. In other words, ten percent of the dissolved cadmium existed as an ionic or reactive form in the spillway effluent, and this portion was detected by ASV. Jernelöv (1974) reported that coastal seawater contains 0.00005 to 0.001 mg/liter dissolved cadmium (ca. 0.05 to 1 ppb). That the average (0.010 mg/liter reactive or 0.036 mg/liter total) for the NE Open water site was approximately 10 to 700 times higher than coastal values may not be unusual, for the port of Hampton Roads is a center of shipbuilding and various shipping and Naval operations. Cadmium in the sediments has been reported as high as 62 µg/g near the Naval Air Station (see Figure 2). Cadmium binds strongly to organic substances, especially those found in plants containing chlorophyll (Jernelöv op. cit.). These compounds could also be associated with phytoplankton, which have been observed at the spillway as green coloration on the filter pads and in the water samples. The organically-complexed (non-reactive to ASV) dissolved fraction of these metals would be expected to be high. If the organic composition of the sediments of dredge-spoil were investigated, humic acids would be present in reasonable concentrations. Humic compounds are also capable of binding or complexing trace metals, for benzoquinone, which is thought to be one of the components of humic substances, was experimentally used to solubilize from 8 to 119 mg

(per gram of benzoquinone) of copper, zinc, cobalt, manganese, and nickel (Rashid 1972). This might account for approximately two to nine percent of the total metal-solubilizing or complexing capacity of humic acids (Rashid op. cit.). Quinones are present in many naturally occurring pigments associated with green plants. Other porphyrin-type compounds may produce quinones upon oxidation, or through other reactions which take place after sedimentation and early diagenesis (Flaig 1960, 1966). Such oxidation-reduction processes, followed by a subsequent complexation of metals, could serve to mobilize these trace metals from the sediments. Holmes, Slade, and McLerran (1974) found that sediments from Corpus Christi Bay can be leached of up to 30 percent of the total sedimentary cadmium merely by agitation in an 0.5 M NaCl matrix (a salt content closely approximating that of sea water). These complexed or leached compounds could be desorbed from solid particles by dredging and the associated turbulence, and thus would be released from the sediments to the dissolved phase during pumping and deposition within the Craney Island Disposal area.

Cadmium is a biologically nonessential and nonbeneficial element (EPA 1973), and it has been shown to be highly toxic. Shuster and Pringle (1969) reported that 0.1 to 0.2 $\mu\text{g/g}$ cadmium (solution concentration) prevents shell growth and causes lost pigmentation in the mantle of *Crassostrea virginica* (common Virginia oyster). Shaw and Lowrance (1956) suggested that 0.056 mg/liter cadmium was the LC₅₀ dose for guppies. For *Salmo gairdneri* (rainbow trout), LC₅₀ was 0.008 to 0.01 $\mu\text{g/g}$ (solution concentration) for a seven-day test period (Ball 1967). Many, if not most trace metals, are concentrated in body tissues of various marine species. The concentration factors of cadmium, mercury, and zinc in some organisms are listed in Table 10. By these means, even small dissolved concentrations can lead to extremely high relative concentrations in local biota, which could eventually reach toxic levels.

Table 10. Biological concentration factors for trace metals in body tissues ($\mu\text{g/g}$) versus the concentration (mg/liter) of the supportive media.

<u>Element</u>	<u>Concentration Factor</u>	<u>Species</u>	<u>Body Part</u>	<u>Reference</u>
Cadmium	>4500	Marine organisms		Noddack and Noddack (1939)
	>250	<i>Leander</i> sp.	Viscera	Hiyama and Shimizu (1964)
	>10	<i>Chasmochthys gulosus</i>	Viscera	Hiyama and Shimizu (1964)
	100 - 1000	Marine organisms		Jernölov (1974)
Mercury	3670	Cod	Gills	Hannerz (1968)
	112	Cod	Fins	Hannerz (1968)
	1258	Pike	Liver	Hannerz (1968)
	650	Zooplankton	Whole body	Rubin (1974)
Zinc	32500	Marine organisms		Noddack and Noddack (1939)
	1800	<i>Laminaria digitata</i>	Whole plant	Bryan (1969)
	1.2×10^5	<i>Crassostrea virginica</i>	Soft tissue	Wolfe (1970)
	5500	Phytoplankton	Whole body	Rubin (1974)
	533	Fish	Whole body	Rubin (1974)

It is stated in EPA Water Quality Criteria (1973) that

. . . on the basis of data available at this time, it is suggested that concentration of cadmium equal to or exceeding 0.010 mg/l constitutes a hazard in the marine environment as well as to human populations In the presence of copper and/or zinc at one mg/l or more, there is evidence that the application factor for cadmium should be lower by at least one order of magnitude.

Of the samples analyzed by ASV at the middle spillway, two (11%) of 19 samples were greater than EPA guidelines, while of 20 samples at the NE Open water site, five (25%) were in violation of this level. Cadmium concentrations determined by GFAA at the No. 1 Spillway were greater than 0.010 mg/liter for 28 (93%) of 30 samples, while 100 percent of the samples (29) at the NE Open water site were in excess of EPA guidelines. It appears then that the concentrations of dissolved cadmium measured at the Craney Island effluent and NE Open water sites, as determined by GFAA, are in excess of latest EPA guidelines.

From December 1973 to August 1974, dissolved mercury ranged from 0.000 to 0.021 mg/liter (average of 0.006 ± 0.021 mg/liter, $n = 19$) at the middle spillway and from 0.000 to 0.023 mg/liter at the NE Open water site (mean of 0.006 ± 0.014 mg/liter, $n = 20$). Of 20 comparison samples, eight (40%) were higher at the spillway, one (5%) was lower, and 11 (55%) were equal (eight of the samples which were reported as equal were less than the detection limit of 0.0001 mg/liter). From September 1974 to February 1975, dissolved mercury values ranged from 0.001 to 0.014 mg/liter (mean of 0.005 ± 0.007 mg/liter, $n = 30$) at the No. 1 spillway, and from 0.001 to 0.005 (mean of 0.003 ± 0.003 mg/liter, $n = 29$) at the NE Open water site. Of 29 comparison samples, 20 (69%) were higher at the spillways than at the NE Open, and nine (31%) were equal (all samples were >0.0001 mg/liter mercury). Ratios of the concentrations of dissolved mercury at the middle spillway to those measured at the NE Open water site ranged from 0.91 to 1.67 (December 1973 to August 1974) and averaged 1.22, while ratios of concentrations at the No. 1 spillway as compared to the NE Open water site for the period from September 1974 to February 1975 ranged from 1.00 to 4.33, and averaged 1.90 ($n = 29$). Mercury concentrations taken at each of the three spillways and the NE Open site in January and February 1975 are compared in Table 11. At no time were mercury concentrations at the middle or No. 3 spillways greater than those measured at the No. 1 spillway. Thus, there appears to be some process(es) which allows for higher levels of dissolved mercury at the No. 1 spillway than was observed at the others. This was also evident for dissolved cadmium and zinc. Such a phenomenon may be related to chemical processes taking place in the sediments adjacent to these sampling sites. The No. 1 spillway is most distant from the major input sources of dredge spoil, and thus the surrounding sediments would be expected to have the smallest grain size. Fine-grained sediments are more likely to be reducing in that they allow less exchange of oxygen with the overlying water. A high organic load in the sediments, derived from the phytoplankton within the disposal area, could contribute to the oxygen demand of the sediment, thus increasing its reducing potential. The reducing sediments could be a source of active biomethylation of mercury and the production of other organic ligands, such as humic compounds, which would sequester the metals in the sediments and release these to the overlying water column.

Table 11. Dissolved mercury at the three spillways and NE Open water site during January and February 1975.

Date	Spillways				Ratios		
	No. 1 mg/l	Middle mg/l	No. 3 mg/l	NE Open mg/l	No. 1: NE Open	Middle: NE Open	No. 3: NE Open
31 Jan	0.005	0.004	0.003	0.003	1.67	1.33	1.00
	0.004	--	--	--	--	--	--
14 Feb	0.004	0.004	0.003	0.003	1.33	1.33	1.00
	0.004	0.002	0.002	0.004	1.00	0.50	0.50
20 Feb	0.002	0.002	0.002	0.002	1.00	1.00	1.00
	0.003	0.003	0.003	0.001	3.00	3.00	3.00
Mean	0.005	0.003	0.003	0.003	1.60	1.43	1.30

Mercury levels may be locally intensified through industrial and agricultural usages (Wallace et al. 1971), such as vermilion (a red pigment of HgS), which was formerly used as an antifouling paint, and organo-mercurial fungicides. Also, mercury is reportedly liberated from the burning of fossil fuels (Bertine and Goldberg 1971, and Joensuu 1971). According to EPA Water Quality Criteria (1973):

On the basis of data available at this time, it is suggested that concentrations of mercury equal to or exceeding 0.0001 mg/l (ca. 0.1 ppb) constitute a hazard in the marine environment.

Since the method (Hatch and Ott 1968) employed during this sampling program is considered a measurement of total dissolved mercury, which incorporates most of the organically associated forms of mercury, it is difficult to assess the possible impact of these mercury levels (mean at middle spillway was 0.006 ± 0.016 mg/liter, while the No. 1 spillway was 0.005 ± 0.007 mg/liter) on local biota and water quality. During the entire sampling program for dissolved mercury, 84 percent (42 of 50) of the water samples at the NE Open water site violated the total mercury value of 0.0001 mg/liter established by EPA (1973), while 16 percent ($n = 8$) were less than this standard. If the combined percentages for all three spillways were included, then 87 percent (52 of 60) were greater than 0.0001 mg/liter and 13 percent (8 of 60) were lower. Of 30 samples taken at the No. 1 spillway, 100 percent exceeded the standard. In the case of the middle ($n = 25$) and No. 3 spillways ($n = 5$), 68 percent were greater (32% lower) at the middle spillway while 100 percent were greater at the No. 3 spillway than the recommended standard.

From December 1973 to June 1974, dissolved zinc measurements (by ASV) showed a reactive concentration at the middle spillway ranging from 0.010 to 0.149 mg/liter (mean of 0.054 ± 0.072 mg/liter), and from 0.012 to 0.116 mg/liter (average of 0.047 ± 0.059 mg/liter) at the NE Open water site. Of 18 comparison samples, ten (56%) were higher at the spillway and eight (44%) were lower. Ratios of concentrations of dissolved zinc at the spillway to those measured at the NE Open water site ranged from 0.30 to 3.24, and averaged 1.19 ($n = 18$).

During the second portion of the sampling program, when dissolved zinc was measured by graphite furnace atomic absorption (GFAA), values were generally higher than those determined by the ASV method for the first period (although not to the extent that cadmium was higher). Concentrations at the No. 1 spillway ranged from 0.035 to 0.586 mg/liter (mean of 0.175 ± 0.256 mg/liter), and from 0.028 to 0.282 mg/liter (mean of 0.109 ± 0.116 mg/liter) at the NE Open water site. For the spillways, the mean of these values was approximately 3.3 times greater during this portion of the sampling program than the mean of the first period, while at the NE Open water site the ratio of the means was 2.4 times greater for the second portion of the sampling period. Of 29 comparison samples from September 1974 to February 1975, 17 (59%) were greater at the No. 1 spillway than at the NE Open water site, nine (31%) were lower, and three (10%) were equal.

As was noted for dissolved cadmium and mercury, dissolved zinc levels for five comparison samples taken on three days in January and February 1975 were lower at the middle spillway than at the No. 1 spillway. Values at the No. 3 spillway were, on an average basis, approximately equal to those at the No. 1 spillway; however, as shown in Table 12, there seemed to be no evident trend in zinc concentrations between these two discharge points.

Table 12. Dissolved zinc concentrations for five comparison samples taken during January and February 1975 at three Craney Island Disposal area spillways. Analyses were done by graphite furnace atomic absorption.

Date	Spillways					Ratios		
	No. 1	Middle	No. 3	NE Open	No. 1:	Middle:	No. 3:	
	mg/l	mg/l	mg/l	mg/l	NE Open	NE Open	NE Open	
31 Jan	0.163	0.110	0.145	0.028	5.82	3.93	5.18	
	0.211	--	--	--	--	--	--	
14 Feb	0.252	0.008	0.145	0.120	2.10	0.07	1.21	
	0.435	0.004	0.039	0.055	7.91	0.07	0.71	
20 Feb	0.136	0.034	0.223	0.083	1.64	0.41	2.69	
	0.133	0.134	0.434	0.207	0.64	0.65	2.10	
Mean	0.202	0.058	0.197	0.099	3.62	1.03	2.38	

In addition to the fact that the values of dissolved zinc were higher at both the No. 1 and No. 3 spillways when concentrations were determined by GFAA, the ratios of concentrations at the spillways to those measured at the NE Open water site were approximately 1.61 times greater (mean of 2.29 vs. 1.19 for the first period) during the second period. This indicated that there was a higher percentage of non-reactive or complexed zinc in the spillway effluent than at the NE Open water site. For the sake of comparison, if the GFAA data were assumed to be an appropriate measure of the total concentration of dissolved zinc which was both discharged from the Craney Island Disposal area and was present in the waters of the NE Open site, and the ASV data were representative of the reactive portion, then the percentage of dissolved zinc which was complexed (non-reactive) was 70 percent at the spillways and 42 percent at the NE Open water site. These fractions are lower than those calculated by Zirino and Yamamoto (1972), but are the same order of magnitude.

Many marine plants require zinc as a micronutrient for growth. Among these are other metallic micronutrients, such as copper, cobalt, iron, manganese, molybdenum and vanadium (Riley and Chester 1971). Most aquatic or marine organisms are capable of tolerating zinc in relatively high concentrations. For example the 96-hour LC₅₀ dosage for *Lepomis macrochirus* (blue-gill fish) was 12.5 mg/liter in hard water at 20°C (Academy of Natural Sciences 1960). Mount (1966) listed the acute dose for *Pimephales promelas* (fat-head minnows) as 4.9 µg/g (solution concentration). Other acute dosages ranged from slightly less than 1 µg/g (0.88 mg/liter) to 105 µg/g (solution concentration) for various species in different media (EPA 1973).

It is recommended in EPA (op. cit.) Water Quality Criteria:

On the basis of data available at this time, it is suggested that concentrations of zinc equal to or exceeding 0.1 mg/liter constitute a hazard in the marine environment It should be noted that there is a synergistic effect when zinc is present with other heavy metals, e.g. copper and cadmium, in which case the application factor may have to be lowered by an order of magnitude.

Of the samples analyzed for dissolved zinc by ASV from December 1973 to June 1974, 11 percent (two of 19) were greater than 0.1 mg/liter at the middle spillway, while 10 percent (two of 20) exceeded this standard at the NE Open water site. Using the GFAA data from August 1974 to February 1975, 70 percent (21 of

30), 33 percent (two of six), and 80 percent (four of five) of the samples taken at the No. 1, middle, and No. 3 spillways, respectively, exceeded 0.1 mg/liter. Fifty percent (15 of 30) of the samples were in violation of the EPA standard at the NE Open water site during the same period (using GFAA).

Dissolved trace metal concentrations from various coastal and estuarine waters are listed in Table 13. Values cited in this report are higher than other coastal areas; however, concentration levels for dissolved zinc in the contiguous waters of Hampton Roads and Chesapeake Bay approximate those presented here. The authors feel that because of the extent of industrialization in the Hampton Roads Harbor area and the large volume of sediments (dredge spoil) of varying degrees of contamination deposited within the Craney Island disposal area, the higher levels of dissolved metal concentrations reported for these areas were both reasonable and valid, when the method of analysis is taken into consideration. With the exception of reactive cadmium at the middle spillway, where it was apparently sequestered by various complexing agents so that this metal was not detectable by ASV, dissolved trace metal concentrations within the Craney Island Disposal area were generally higher than at the NE Open water site, and this was especially true for the complexed, non-reactive fraction of cadmium and zinc.

Total Suspended Solids

Suspended solids measured at the middle spillway from December 1973 to August 1974 ranged from 49 to 3430 mg/liter. With the exception of two samples, January 18 (2535 mg/liter) and February 22 (3430 mg/liter) 1974, suspended solids were less than 600 mg/liter. These two samples were taken on days when the NW dredge was discharging sediment in the vicinity of the middle spillway (see Figure 2). Field observations confirmed that extension of the dredge discharge pipe caused only a slight dilution and settling of the dredge material before exiting the middle spillway. This was also reflected in the ammonia data, which measured 5.27 and 7.72 mg/liter at the spillway, and 4.53 and 1.55 mg/liter at the NE Open water site for these two days, respectively. Thus, it seemed that on these two days, both dissolved and particulate materials from the NW dredge were leaving the disposal area at the middle spillway before extensive settling occurred, and some of these components were observed as far away as the NE Open water site. Ammonia values for the NW dredge on these two dates were 3.33 and 2.17 mg/liter, respectively, while concentrations of suspended solids at the dredge pipe effluent were 2.68×10^4 and 8.7×10^4 mg/liter. Maximum values measured during the

Table 13. Concentrations (mg/liter) of dissolved cadmium, mercury, and zinc for coastal and estuarine waters.

<u>Element</u>	<u>Range (mg/l)</u>	<u>Location</u>	<u>References</u>
Cadmium	0.00005 - 0.001	Coastal waters	Jernelöv (1974)
	0.00015 - 0.00023	E. Long Island Sound	Dehlinger, et al. (1973) ¹
	0.00002 - 0.00023	Coastal GA and SC	Windom and Smith (1972)
	0.000 - 0.019	Craney Island middle spillway	(This report) ¹
	0.005 - 0.254	Craney Island No. 1 spillway	(This report) ²
	0.001 - 0.056	NE Open water, Hampton Roads	(This report) ¹
	0.013 - 0.076	NE Open water, Hampton Roads	(This report) ²
	0.000006 ± 0.000002	Coastal waters	Fitzgerald and Lyons (1975)
	0.000030	S. California Bight	Young et al. (1975)
	0.000008 - 0.000068	Lake Washington, Seattle, WA	Rubin (1974)
0.000003 - 0.000010	Puget Sound, WA	Rubin (1974)	
0.000010 - 0.00021	English Channel	Rubin (1974)	
<0.0005 - 0.0076	James River, VA	Pheiffer, Donnelly, and Possehl (1972)	
<0.0005 - 0.0014	York River, VA	Pheiffer, Donnelly, and Possehl (1972)	
0.000 - 0.021	Craney Island middle spillway	(This report)	
0.000 - 0.023	NE Open water, Hampton Roads	(This report)	
Zinc	0.0008 - 0.0095	E. Long Island Sound	Dehlinger, et al. (1973)
	0.0005 - 0.017	Coastal GA and SC	Windom and Smith (1972)
	<0.010 - 0.080	James River, VA	Pheiffer, Donnelly, and Possehl (1972)
	0.001 - 0.299	Choptank River, MD	Pheiffer, Donnelly, and Possehl (1972)
	0.010 - 0.030	Pamunkey River, VA	Pheiffer, Donnelly, and Possehl (1972)
	0.004 - 0.359	Hampton Roads Harbor, VA	Adams et al. (1975)
	0.004 - 0.122	Chesapeake Bay, VA	Adams et al. (1975)
	0.005 - 0.337	James River, VA	Adams et al. (1975)
	0.001 - 0.622	Elizabeth River, VA	Adams et al. (1975)
	0.010 - 0.149	Craney Island middle spillway	(This report) ¹
	0.012 - 0.116	NE Open water, Hampton Roads, VA	(This report) ¹
	0.035 - 0.586	No. 1 spillway, Craney Island, VA	(This report) ²
	0.028 - 0.282	NE Open water, Hampton Roads, VA	(This report) ²

¹ Measured by anodic stripping voltammetry (ASV).

² Measured by graphite furnace atomic absorption (GFAA).

program for dredge pipe effluent were 59.94 mg/liter for ammonia, and 4.6×10^5 mg/liter for suspended solids. The fact that the NW dredge was operating on those two days, plus the visual observations taken in the field and the extremely high ammonia and suspended solids measurements at the middle spillway confirmed that the dredge pipe effluent was leaving the middle spillway before particulates had settled and ammonia had been utilized.

Including the two high suspended solids concentrations on January 18 and February 22, 1974, the average value for suspended solids at the middle spillway from December 1973 to August 1974 was 461 ± 1728 mg/liter ($n = 20$). At the NE Open site for the same period, concentrations ranged from 4 to 92 mg/liter, and averaged 32 ± 48 mg/liter ($n = 21$). The ratio of suspended solids at the spillway to the NE Open water site ranged from 0.79 to 94.00, and averaged 20.32 ± 27.39 ($n = 20$). Of twenty comparison samples, 19 (95%) were higher at the spillway, and one (5%) was lower.

From September 1974 to February 1975, suspended solid determinations at the No. 1 spillway did not reproduce the maximum levels (ca. 2500 and 3400 mg/liter) noticed during the first portion of the program. Little dredging had occurred during this time, and resumption did not take place until mid-December 1974. The NW dredge did not operate during the second portion of the sampling program. The NE Open water site did exhibit a suspended solid maximum in February 1975 (see Figure 16), which was probably due to rough water conditions resuspending the bottom material. Values taken concurrently at the No. 1 spillway were also relatively high during February 1975. The range for total suspended solids at the No. 1 spillway from September 1974 to February 1975 was 54 to 660 mg/liter (mean of 254 ± 364 mg/liter; $n = 30$), and from 14 to 345 at the NE Open water site (average of 95 ± 202 mg/liter; $n = 29$). The ratio of No. 1 spillway solids to NE Open water samples ranged from 1.14 to 13.83, and averaged 3.46 ± 5.54 ($n = 29$). Of 29 comparison samples, 100 percent were higher at the spillway. Combined means for both the middle and No. 1 spillways and NE Open water site total suspended solids, and the combined average ratio of each spillway to NE Open were 337 and 68 mg/liter, and 10.34, respectively.

Seston concentrations can more than double during a tidal cycle (EPA 1973). During a 24-hour period in the upper Chesapeake Bay, the suspended solids concentrations ranged from 20 to 100 mg/liter (Biggs 1970). Particle concentrations in coastal waters generally range from 1 to 30 mg/liter, with higher concentrations near the bottom (Biggs op. cit.). Manheim, Meade, and Bond (1970) and Biggs (op. cit.) reported that organic matter fragments composed 20 to 40 percent of the suspended particles in coastal waters.

Under conditions when wave and wind action did not contribute to resuspension of bottom sediments in the two areas, the measurements of total suspended solids usually reflected productivity, since the material retained on the filter pads at the spillways was usually green. At the NE Open water site, the suspended material tended to be a mixture of both organic and inorganic detrital material.

Particulate Cadmium, Mercury, and Zinc

Particulate cadmium from December 1973 to August 1974 at the middle spillway ranged from 0.75 to 133 $\mu\text{g/g}$ (mean of $21.46 \pm 68.84 \mu\text{g/g}$; $n = 20$), and from 0.47 to 103 $\mu\text{g/g}$ (average of $13.22 \pm 50.11 \mu\text{g/g}$; $n = 21$) at the NE Open water site. From September 1974 to February 1975, particulate cadmium ranged from 6.82 to 237 $\mu\text{g/g}$ (mean of $107 \pm 263 \mu\text{g/g}$; $n = 30$) at the No. 1 spillway, and from <0.5 to $90.3 \mu\text{g/g}$ (average of $17.2 \pm 40.3 \mu\text{g/g}$; $n = 29$) at the NE Open water site. The yearly mean at the spillways was $60.2 \pm 66.3 \mu\text{g/g}$ ($n = 50$) and $15.5 \pm 44.8 \mu\text{g/g}$ ($n = 50$) at the NE Open water site. The ratios of values at the spillways to the NE Open water concentrations differed widely during the first and second portions of the program. From December 1973 to August 1974, ratios ranged from 0.41 to 29.41 (mean of 4.19 ± 13.91 ; $n = 20$), while from September 1974 to February 1975, ratios ranged from 1.82 to 260 (average of 20.62 ± 97.40 ; $n = 28$). The total yearly mean of the ratio was 13.78 ± 38.38 ($n = 48$). Of 48 comparison samples during the entire program, 79 percent were greater at the spillway, eight percent were lower, and 13 percent were equal (within the standard deviation of the method). For the first period, the respective percentages were 50 (greater), 20 (less), and 30 (equal); while for the second period, particulate cadmium was greater at the spillway 100 percent of the time.

Riley and Chester (1971) reported that phytoplankton can readily assimilate chelated (organically- and inorganically-complexed) forms of many elements. Many culturing techniques are aided by the addition of chelated trace metals, while other studies (Johnson 1963) have shown that the addition of EDTA (ethylene diamine tetraacetic acid - a strong metal-complexing agent) to sea water was as beneficial to phytoplankton production as addition of chelated trace metals. This appears not to be a detoxification reaction, but rather one which stimulates growth by making micro-elements available to the organisms. This assimilation, then, of chelated trace metals from solution would tend to elevate the concentration of metals in the biota versus that of the supportive media. This could partially explain the higher concentrations of metals in the suspended matter.

Recent marine sediments in Santa Barbara basin contain about 2 $\mu\text{g/g}$ cadmium (Young 1974), while natural nearshore marine sediments contain on the order of 0.4 $\mu\text{g/g}$ cadmium. Municipal effluents in the Southern California Bight have been reported to contain 65 to 245 $\mu\text{g/g}$ cadmium (Young 1974). Sediments near the Norfolk Naval Shipyard (Elizabeth River, VA) had cadmium levels as high as 24 $\mu\text{g/g}$, while 62 $\mu\text{g/g}$ was reported for bottom sediments near the Norfolk Naval Air station, which is in the proximity of Craney Island (see Figure 2). Cadmium can be concentrated in marine organisms as high as 4500 times the values for the supportive media (see Table 10). Approximately 90 percent of the total dissolved cadmium was calculated as the sequestered, or complexed form, which averaged 0.049 mg/liter for the No. 1 spillway (see dissolved cadmium section of this report). Thus the chelated trace metal fraction would equal approximately 0.045 mg/liter. The overall average for particulate cadmium was 60.2 $\mu\text{g/g}$, which would result in an average concentration factor of 1300 X. This is somewhat high in view of reported values, but it is not totally unsubstantiated in the literature. Both the suspended matter leaving the disposal area and that recovered from the NE Open water site were composed of organic and inorganic particulate material, so the metal contribution of each fraction should be considered. In addition to the fact that living phytoplankton, which represents a portion of the organic suspended material, may concentrate metals from solution, the inorganic fraction of the suspended matter may be more concentrated in metals than the sediments from which they were derived. The smaller particles in suspension would have a much greater surface area for adsorption of metals. As an example, Anderson (1974) reported that an unsieved sediment sample analyzed for zinc (a group II B element, as are cadmium and mercury) had a concentration of 199 $\mu\text{g/g}$, whereas a subsample of the sediment retained on a No. 18 (U. S. Standard Sieve = 1.001 mm) sieve provided a value of 146 ppm, while another subsample retained on a No. 200 (0.074 mm) sieve measured 462 ppm. Another sample, which was processed in the same manner, gave 135 $\mu\text{g/g}$, 35 $\mu\text{g/g}$, and 367 $\mu\text{g/g}$, respectively. Thus, for an approximate 14-fold (1.001/0.072 mm) size difference, zinc concentrations changed by a factor of 3.2 and 10.5, respectively. The size fraction represented by the suspended load would be considerably smaller, ranging from 0.45 microns (filter size) to perhaps five to ten microns. This could account for the one to two orders of magnitude increase in the values measured during this monitoring program from those usually reported for sediments. This would be especially true for samples collected at a time when the suspended solid concentrations were low (i.e., lower current velocities and, therefore, a smaller size

fraction would be present in suspension), for the concentration of metals would then be expected to be higher in the inorganic fraction.

Another important factor to consider in the evaluation of high metal values for suspended matter would be the analytical error. This would include loss or gain of weight by the filters during filtration and drying, inaccuracy of the balances in relation to the weight of sediment digested (ca. 0.1 g), and the recording of extremely low absorbances during the analysis of the digested sample. If a sample absorbance, which was in many instances only slightly higher than the filter and acid blank, were converted to an element mass (μg), and then calculated for a concentration (expressed as $\mu\text{g/g}$ of sediment) when suspended sediments were low, the reported result could be excessively high. This would be the case of interpreting the difference between instrumental noise and baseline fluctuations to a signal exhibited for a sample. Since February 1975, and employing similar methods but with better analytical quality control, values for particulate metals have not, as yet, yielded such high values for particulate cadmium. Therefore, it is possible that analytical problems could be one of the sources of error for the excessively high concentrations of particulate cadmium reported during the first year (December 1973 to February 1975) of this monitoring program.

Concentrations of particulate mercury from December 1973 to August 1974 at the middle spillway ranged from 0.115 to 1.16 $\mu\text{g/g}$ (mean of $0.345 \pm 0.597 \mu\text{g/g}$, $n = 16$), and from 0.045 to 1.15 $\mu\text{g/g}$ (mean of $0.261 \pm 0.543 \mu\text{g/g}$; $n = 15$) at the NE Open water site. Ratios of concentrations at the spillway to those from the NE Open water site ranged from 0.41 to 6.84, and averaged 1.80 ($n = 15$). Of the 15 comparison samples taken, 73 percent were greater at the spillway, and 27 percent were lower. Values of particulate mercury for the second portion of the period, September 1974 to February 1975, exhibited a similar range for both locations, but higher average values. Reported concentrations at the No. 1 spillway for the latter period ranged from 0.082 to 1.50 $\mu\text{g/g}$, and averaged $0.650 \pm 0.689 \mu\text{g/g}$ ($n = 30$), while the range at the NE Open water site was 0.008 to 0.908 $\mu\text{g/g}$, with a mean of $0.429 \pm 0.539 \mu\text{g/g}$ ($n = 29$). The ratio of the No. 1 spillway mercury concentrations to those at the NE Open water site (generally taken ca. 30 minutes apart) ranged from 1.10 to 41.00 and averaged 3.27 ± 14.51 ($n = 29$). Of 29 comparison samples analyzed, 100 percent had higher mercury concentrations at the No. 1 spillway. The total yearly means for both spillway locations, all of the NE Open water samples, and the combined ratios (spillways vs. NE Open) for both sampling periods were $0.544 \pm 0.720 \mu\text{g/g}$ ($n = 46$), $0.372 \pm 0.563 \mu\text{g/g}$ ($n = 44$), and 277 ± 12.01 ($n = 44$), respectively. For

a total of 44 comparison samples, 91 percent were greater at the spillways and nine percent were lower during the entire sampling period.

Particulate mercury concentrations reported for this area are not unreasonable, especially if the sediments are contaminated with a sizeable addition of heavy metal pollutants from anthropogenic sources. Pristine sites may show sediment mercury concentrations ranging from 0.01 to 0.02 $\mu\text{g/g}$, whereas sediments in locales subjected to industrial and commercial activity may have mercury concentrations of 0.5 to 0.8 $\mu\text{g/g}$ (Brinckman and Iverson 1975). In an idealized water column, consisting of sediment, water, and plankton (using actual data from Baltimore Harbor), the concentration of mercury in each compartment was $0.26 \pm 0.01 \mu\text{g/g}$, $0.37 \pm 0.01 \text{ ppb}$, and $1.65 \pm 0.19 \mu\text{g/g}$, respectively (Brinckman and Iverson op. cit.).

The average concentration of total dissolved mercury at the spillways was 0.006 mg/liter, whereas the average suspended solid concentration of mercury was 0.544 $\mu\text{g/g}$. This would require a bioaccumulation factor (if the suspended solids were primarily organic) of approximately 90 X, which is within the values illustrated in Table 10. The average concentration was similar to other values for mercury in local sedimentary environments. James River sediments have been collected from Richmond, Virginia, to the mouth at Hampton Roads, and the concentrations of mercury ranged from approximately 0.05 to 0.8 $\mu\text{g/g}$ (Pheiffer, Donnelly and Possehl, 1972).

Standards for open water disposal of spoil material have been set by EPA to limit the concentration of mercury at 1 $\mu\text{g/g}$. Five (11%) of the 46 samples analyzed for particulate mercury at the spillways exceeded the maximum permissible level of 1 $\mu\text{g/g}$, while only one (2%) at the NE Open water site was higher than this level.

Considering the mixed composition of the suspended particulate matter in the disposal area effluent and the background waters of Hampton Roads Harbor, the concentrations of particulate mercury found during this study were comparable to what could be expected for an area impacted by industrial activity. It should be emphasized, however, that these values are in excess of those which would be found in an area not contaminated with industrial and municipal wastes, and shipping activity.

The species should be considered when mercury is investigated. The method employed during these measurements cannot differentiate methyl mercury from less

toxic species, such as insoluble mercurous salts. It was apparent, however, that there was a concentration process occurring within the Craney Island Disposal area which could transfer heavy metal pollutants from the sediments to the suspended matter, and this might be present both as organic and inorganic particulates. This could be biological (especially bacterial) methylation, particularly in the case of mercury. Other metals such as selenium, tellurium, arsenic, and tin might also be affected by such biotransformations. Research on the methylation of cadmium and zinc is presently underway at the National Bureau of Standards (Brinckman, personal communication).

Particulate zinc at the middle spillway ranged from 12.3 to 667 $\mu\text{g/g}$ (mean of $87.3 \pm 289 \mu\text{g/g}$; $n = 20$) from December 1973 to August 1974, and from 12.9 to 374 $\mu\text{g/g}$ (averaged $57.2 \pm 163 \mu\text{g/g}$; $n = 21$) at the NE Open water site for the same period. Ratios of particulate zinc at the spillway to that of the NE Open water site ranged from 0.30 to 5.49, and averaged 1.56 ± 2.62 ($n = 20$). Of 20 comparison samples, 50 percent were higher at the spillway, 30 percent were lower, and 20 percent were equal within the accuracy of the method. As with particulate cadmium and mercury, particulate zinc exhibited a similar range during the two portions of the sampling period; however, average values were higher during the second period. The range of reported values at the No. 1 spillway during the latter period was 35.8 to 664 $\mu\text{g/g}$ zinc (mean of $239 \pm 347 \mu\text{g/g}$; $n = 30$) and from 8.62 to 462 $\mu\text{g/g}$ (averaged $87.8 \pm 213 \mu\text{g/g}$; $n = 29$) at the NE Open water site during the same period. The ratio of zinc in the suspended matter at the No. 1 spillway as compared to the NE Open water site ranged from 1.44 to 47.20, and averaged 5.58 ± 17.17 ($n = 29$). During the second portion of the program for 29 comparison samples, 100 percent of the values for particulate zinc were higher at the No. 1 spillway versus the NE Open water site. Combined ratios for the entire sampling program ranged from 0.30 to 47.20, and averaged 3.94 ± 13.90 ($n = 49$). Over the entire time period, 80 percent of the samples had higher particulate zinc concentrations at the spillways, 12 percent were lower, and eight percent were equal within the accuracy of the method.

The concentration of dissolved complexed zinc at the spillways has been estimated at 70 percent of the mean value of 0.175 mg/liter; therefore, approximately 0.12 mg/liter dissolved zinc at the No. 1 spillway was in a form which can be readily assimilated by marine plants, according to Riley and Chester (1971). Thus, to account for the average concentration of particulate zinc (239 $\mu\text{g/g}$), the concentration factor necessary for organic material would be about 1900 X. This is well within the range of bioaccumulation factors presented in Table 10.

Zinc concentrations in the sediments of the James River have been reported as ranging from about 20 to greater than 700 $\mu\text{g/g}$ (Pheiffer, Donnelly, and Possehl 1972). EPA has set limits of 50 $\mu\text{g/g}$ zinc for open water disposal of spoil materials. Thirty-three (66%) of the 50 samples analyzed for particulate zinc at the spillways exceeded this recommendation, while 17 (34%) of the samples at the NE Open site were greater than 50 $\mu\text{g/g}$.

SUMMARY AND CONCLUSIONS

Effluent from three spillways at the Norfolk District of the U.S. Army Corps of Engineers' Craney Island dredged disposal area in the Port of Hampton Roads, Virginia, was monitored from December 1973 to February 1975. A background site at the NE corner of the disposal area on the open water side of the levee was also sampled for comparative purposes. During the first nine months of the program, dredged material entering Craney Island was also collected to assess its composition.

Tests were conducted for 18 different parameters, which were temperature, salinity, pH, dissolved oxygen, dissolved inorganic orthophosphate, total phosphorus, nitrate, nitrite, ammonia, total nitrogen (TKN), fecal coliform, and total suspended solids, as well as dissolved and particulate cadmium, mercury, and zinc. The concentration of each specific parameter at the spillway was compared to its value at the background site, and these in turn were related to the composition of contiguous waters. In an effort to assess the water quality of the spillways, these data were compared to the most recent criteria, if available, recommended by the Environmental Protection Agency and the State of Virginia.

The data were further evaluated by an F-test, which is a one-way classification of variance between the spillway(s) and background concentrations. The hypothesis that the variances of two populations are equal is evaluated by the F-test. If the computed F ratio (estimated variance between locations/estimated variance within locations) is greater than $F_{0.05}$, the conclusion is that at a 5 percent significance level the variance between populations is greater than that within. The 5 percent significance level means that 5 percent of all possible sets of values will give calculated F ratios greater than $F_{0.05}$. These sets, then, would indicate that the variances are not equal, when in fact they are (rejection of a true hypothesis). As sample number increases, the rejection of a false hypothesis becomes more certain. From 40 to 50 samples, usually 50, were taken for all parameters (except dissolved zinc and cadmium) at both locations (20 by ASV, 30 by GFAA). It is assumed that there was a significant difference between the two sampling locations if the calculated F ratio was greater than a critical $F_{0.05}$ value. Under these guidelines, it was found that the concentrations of the following parameters at the spillways were not statistically significantly different from their levels at the NE Open water background site: dissolved oxygen, nitrate, nitrite, dissolved cadmium by ASV, dissolved cadmium by GFAA, and dissolved zinc by ASV.

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There was a significant difference between the spillways and background site for fecal coliform concentrations, yet it was felt that because of the low levels, these should not pose any problems. Dissolved oxygen concentrations did not drop below specified criteria; however, it should be remembered that water samples were collected during the mid-morning or early afternoon, when oxygen concentrations would usually be higher, rather than at night or during the early morning hours when eutrophic conditions might deplete dissolved oxygen.

During the monitoring program, pH values were significantly different at the spillways. These concentrations were higher 92 percent of the time when compared to the background waters. Both the average (8.58, which was 0.64 units greater at the spillways than the NE Open water site) and range (7.82 to 9.24) suggested that this parameter could be deleterious to organisms (EPA 1973). It should be emphasized that the higher pH conditions at the spillways were probably a result of excessive plankton growth within the relatively shallow, nutrient rich, waters of the diked area. These conditions would also have increased pH, dissolved oxygen, suspended solids, total phosphorus, and total nitrogen (TKN) during the daylight hours.

Dissolved phosphate (averaged 0.076 mg/liter) was above recommended criteria (0.05 mg/liter) and was significantly different at the spillways than measurements at the background site. EPA (op. cit.) suggested that the organic load produced by these higher concentrations of nutrients could lower the oxygen content of the water under conditions of poor circulation; such nutrient levels have created eutrophic conditions in the Elizabeth River during the summer months. It is not presently known if such problems exist in the waters to the west of Craney Island; however, because of the improved tidal circulation (as compared to the Elizabeth River) and better oxygen ventilation of the shallow waters eutrophication is not likely. It should be pointed out that the concentrations of dissolved phosphate at the NE Open water site were 35 percent less than at the spillways, while those from station 8 (see Figure 2 for location) were close to 50 percent of values measured at the spillways.

There were transient spikes in the concentrations of most of the nutrients, especially the dissolved nitrogen compounds. With the exception of the high values of ammonia at the middle spillway during dredge disposal at the NW corner of Craney Island (averaged 2.34 mg/liter ammonia), total dissolved inorganic nitrogen (ammonia, plus nitrate and nitrite) averaged 0.89 mg/liter for the

entire program at the No. 1 spillway. Concentrations at the NE Open water site were 0.65 mg/liter, which was almost double EPA (op. cit.) criteria of 0.36 mg/liter. Examination of data for total dissolved inorganic nitrogen from the James River (averaged 0.56 mg/liter for five stations sampled monthly from October 1973 to April 1975), the Elizabeth River (averaged 0.51 mg/liter for four stations during the same time period), and Hampton Roads Harbor (averaged 0.31 mg/liter for four stations) suggests that the recommended criteria are not realistic for local water conditions. The values for total dissolved inorganic nitrogen at the No. 1 spillway were 34 percent greater than background (NE Open water site) and 59 percent greater than the James River. Even though it would be considered excessive by EPA criteria, concentrations were not much greater at the spillways (during normal operation) than in contiguous waters.

Dissolved ammonia was clearly at levels which should have been deleterious to biota inhabiting the spillway waters, yet this did not seem to be the case. Even though the benthos or pelagic organisms were not sampled or studied to ascertain ammonia toxicity, it appeared that the spillway waters contained a normal and, at times, somewhat abundant biota. The worst conditions for dissolved ammonia occurred at the middle spillway during periods of active dredging operations at the NW corner of the disposal area. During the entire program, the average concentration of dissolved ammonia was 230 percent greater at the spillways than at the NE Open background site. There was a significant difference between the two sampling locations. These concentrations, coupled with the abnormally high levels of pH, would have created excessive concentrations of un-ionized ammonia (NH₃) according to equilibrium calculations. The calculated values for un-ionized ammonia exceeded EPA (1973) recommendations of 0.4 mg/liter for marine waters 32 percent of the time at the middle spillway and 15 percent at the No. 1 spillway. Because of the lower values for pH at the background site, none of the water samples were above the specified criteria with respect to calculated values for un-ionized ammonia. According to EPA (op. cit.) and other literature, the levels of un-ionized ammonia at the spillways should be toxic. ^{also} It is possible that either rapid dilution or utilization by the phytoplankton ^{or} have depressed the concentrations of ammonia so that the effects are not readily apparent; however, these observations should not dismiss the possibility of long-term sublethal toxicity to organisms indigenous to the spillways.

Values for suspended solids, total nitrogen, and total phosphorus at the spillways clearly illustrated that the major proportion of the dredged material remained within Craney Island. Considering the concentration of nitrogen and phosphorus in the sediments of contiguous waters, the disposal area has been very effective in retaining a considerable proportion of these components.

When samples were analyzed by graphite furnace atomic absorption, concentrations of total dissolved cadmium exceeded EPA recommended levels (0.01 mg/liter) almost 100 percent of the time at both the No. 1 spillway and NE Open water site. As stated earlier, there were no significant differences between the spillway and NE Open water sites with respect to dissolved cadmium. The concentrations of dissolved mercury were usually in excess of recommended levels (0.001 mg/liter) at both the NE Open water site (84%) and at all three spillways (87%). Concentrations of dissolved mercury at the spillways were greater than those measured in background samples 75 percent of the time. There was a significant difference between the two sampling locations during the entire monitoring program. Since the method for measuring dissolved mercury detects the concentrations of both inorganic and organic fractions, i.e. total mercury, it is difficult to assess the impact on local biota. From the calculations of sequestered (non-reactive) dissolved cadmium (90%) and zinc (70%), it is possible that a considerable fraction of dissolved mercury would be organically complexed. Dissolved zinc concentrations (by graphite furnace atomic absorption) exceeded EPA recommended levels (0.1 mg/liter) 68 percent of the time at the spillways, while this was the case 50 percent of the time at the NE Open water site. As with dissolved cadmium, 59 percent of the spillway samples had greater concentrations of dissolved zinc than were measured at the background site. There was a significant difference between the two sampling locations when dissolved zinc was measured by graphite furnace atomic absorption.

Even though the concentrations of dissolved metals exceeded EPA criteria at the spillways (from a maximum of 100 percent of the time for cadmium to 68 percent of the time for zinc), the fact that this was also evident (to a lesser extent) at the NE Open water site suggests that either the NE Open water site was not a good choice for the background site, or that the concentrations of dissolved metals are excessively high in the waters of Hampton Roads. Because of the industrial and shipping activity, the latter possibility is probable. It is also possible that the graphite furnace data and the EPA recommended criteria should

be evaluated in greater detail. In any case, these problems should be addressed in future studies.

Concentrations of particulate metals were also noticeably higher at the spillways than those at the NE Open water site. In the case of particulate cadmium, 79 percent of the samples were greater in concentration at the spillways, while for particulate mercury and particulate zinc, these values were 91 and 80 percent, respectively. The differences between spillway and NE Open water concentrations for particulate metals were all statistically significant. However, the concentration of particulate mercury was only 44 percent greater at the spillways than at the NE Open. Because of this and the natural variability of the data, it would be difficult to assess the effects of this parameter. This was not the case for particulate cadmium (the concentration was 323 percent higher at the spillways than at the NE Open water site) and particulate zinc (averaged 125 percent greater), where concentrations were high enough at the spillways to suggest that these two metals could be concentrated by organisms inhabiting the waters to the west of Craney Island. It is obvious that the fate of particulate cadmium and zinc should be investigated to ascertain whether or not rapid sedimentation occurs in the waters contiguous to the spillways or if biological uptake is occurring.

Because of the high values of pH and the concentrations of specific parameters (especially ammonia, phosphate, dissolved and particulate metals) at the spillways, it became apparent that the monitoring program should be modified to measure their spatial limits, i.e., their subsequent dilution by or removal from the waters to the west of Craney Island. Of additional concern was the concentration of organic material (both dissolved and particulate, living and detrital) leaving the disposal area, and the oxygen demand which this organic matter would impose upon the receiving waters. Beginning in April 1975, a series of five stations located in the plume, at approximately 160 m intervals, have been sampled monthly. This program, which is presently in effect, should provide information concerning the concentration and lateral extent of each of the 18 parameters in the surface waters near the spillways. In order that the concentration of living phytoplankton might be related to suspended material and detrital carbon, measurements of chlorophyll and particulate organic carbon were added to the program. Dissolved organic carbon was also included to evaluate possible relationships between the dissolved metals and organic material. In addition, measurements of particulate and dissolved lead have been included to assess the levels and the potential impact of this metal at the spillway and NE Open water (background) site.

RECOMMENDATIONS

Changes in operations at Craney Island should be implemented to insure that the middle (No. 2) and No. 3 spillways are closed during dredging operations at the NW corner. As indicated in this report, high levels of ammonia and suspended solids were measured at the middle spillway when dredge disposal occurred simultaneously at the NW corner of Craney Island. If only the No. 1 spillway were open during this time period, the quality of the effluent would probably improve by allowing the suspended material to settle before discharge.

Recommendations for further studies at the Craney Island disposal area are outlined as follows:

1. Diurnal sampling for temperature, salinity, dissolved oxygen (and oxygen saturation calculations), pH, and chlorophyll at two-hour intervals should be initiated. During the monitoring program reported here (Dec 1973 to Feb 1975), water samples were collected in either the morning or early afternoon when oxygen and pH conditions would probably be highest. During or following bloom conditions in the spring and summer, it would be interesting to know whether or not the effluent waters had excessively depressed oxygen concentrations due to the increased organic load within the diked area. The time of day would also affect the pH conditions of the effluent.

2. From the analysis of dissolved ammonia and metals at the different spillways during this program, there seemed to be a relationship between the quality of the effluent and the sediment texture near the sampling location at the weirs (from a visual estimation of texture). Dissolved ammonia and metals were highest (during periods of no dredging activity) at the No. 1 spillway where the sediments would probably be finest. Short cores or grab samples should be collected within Craney Island near the spillways, and these could be used to define the sediment texture as well as the interstitial and leachable nutrients and metals. This would provide information concerning the potential release of various components to the overlying waters near the spillways. In addition, cores or grab samples should be collected in the vicinity of the spillway plume(s) to assess the deposition of metals and nutrients as the effluent enters the Hampton Roads Harbor to the west of Craney Island.

3. Large samples (at least 20 liters) should be collected at each site for separation of suspended materials. The particulates could then be measured by

spectrographic emission techniques for trace metal components. Present analyses by this method include Ag, Al, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Si, Sr, Ti, V, and Zn. These analyses would provide useful information concerning the presence or absence of other trace metals.

4. There was, as would be expected, a difference between the measurements of both cadmium and zinc due to the methodology associated with different analytical techniques. Dissolved cadmium and zinc were both abnormally high when analyses were conducted by graphite furnace atomic absorption, using procedures developed at the Institute of Oceanography, Old Dominion University. There has been a noticeable difference between graphite furnace data and concentrations determined through APDC-MIBK extraction techniques, which are presently used during the second year of the monitoring program (April 1975 to March 1976). The previous data by GFAA should therefore be assessed as to its accurate description of the total dissolved concentrations of cadmium and zinc by intercalibration of the methods with standard reference materials.

5. The discharge of effluent from one spillway should be measured during a specified period of time which would be described as both active dredging (with and without rain) and a period of no dredging activity (with and without rain). From these data and with the previous concentrations of various parameters, mass emission rates from the disposal area could be calculated.

6. The biostimulatory potential of the effluent from the spillways on Hampton Roads Harbor water should be investigated. Macronutrients such as nitrogen and phosphorus and micronutrients such as iron, manganese, and cobalt are the main constituents of the effluent which should be assayed to determine the potential for algal growth. The recommended bioassay procedure is the standardized EPA Marine Algal Assay Bottle Test (EPA 1974). This bioassay should determine the nutrient which is limiting algal productivity in the spillway waters and will provide information concerning availability of various forms of this limiting nutrient.

7. The biotoxicity potential, both acute and chronic, of the effluent from the spillways should also be investigated. Acute toxicity of the effluent could be monitored by using the Oyster Embryo Bioassay (Woelke 1967). This would be accomplished by placing trays of oysters at various distances from the spillway and at suitable background stations. Measurements would include growth rate, mortality, viability of offspring, bioaccumulation of toxic trace metals, and

physiological measurements such as oxygen consumption and apparent pumping rate. Substantial uptake of cadmium, copper, mercury, manganese, nickel, and zinc has been noted in oysters at control stations in Long Island Sound (Dehlingef, et al. 1973). The Marine Algal Assay Procedure listed above could also be used to test the biotoxicity potential of the spillway effluent on the phytoplankton community as well.

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APPENDIX A

COLLECTION TIMES

AND

DATA TABULATION

Table A1. Collection times at the Craney Island Disposal area, Port of Hampton Roads, Virginia for the period 28 December 1973 to 28 June 1974 (with exception of dredge pipe collection on 6 August 1974). See Figure 2 for location of sampling sites.

Date	Middle Spillway		Northeast Open Water		Dredge Pipes		No. of dredges in operation
	Sample No.	Time	Sample No.	Time	Sample No.	Time ¹	
<u>1973</u>							
28 Dec	1	1000	2	1107	3	1130	3
<u>1974</u>							
11 Jan	4	1105	5	1025	6	1055	2
18 Jan	7	0940	8	1030	9	1030	3
25 Jan	10	1145	11	1105	12	1115	2
8 Feb			13	1030	14	1020	1
22 Feb	15	1030	16	1115	17	1110	2
22 Mar	18	0950	19	1050	20	1020	2
10 Apr	21	1110	22	1145	23	1130	1
11 Apr	24	1205	25	1235	26	1235	1
26 Apr	27	1125	28	1135	29	1120	1
10 May	30	1010	31	1030	32	1045	1
17 May	33	1000	34	1015			
24 May	35	1105	36	1120			
14 Jun	37	1035	38	1045	39	1050	1
27 Jun	40	0930	41	0945	42	0950	2
	43	1130	44	1145	45	1200	2
	46	1330	47	1340	48	1340	1
28 Jun	49	0930	50	1015	51	1000	2
	52	1130	53	1210	54	1200	2
	55	1330	56a	1410	56b	1400	2
6 Aug					56c	1120	1

¹ Times of dredge sampling are median times in the case of multiple sample collections on a single day.

Table A2. Collection times at the Craney Island Disposal area, Port of Hampton Roads, Virginia for the period August 6, 1974 to February 20, 1975. See Figure 2 for location of sample sites.

Date	No. 1 Spillway		Middle Spillway		No. 3 Spillway		Northeast Open Water	
	Sample No.	Time	Sample No.	Time	Sample No.	Time	Sample No.	Time
<u>1974</u>								
6 Aug			57	1045			58	1110
18 Sep	59	1025					60	1121
	61	1152					62	1220
25 Sep	63	1115					64	1142
	65	1212					66	1238
16 Oct	67	1122					68	1200
	69	1220					70	1245
25 Oct	71	1205					72	1232
	73	1253					74	1514
30 Oct	75	1025					76	1045
	77	1105					78	1125
6 Nov	79	1025					80	1051
	81	1110					82	1152
20 Nov	83	1000					84	1025
	85	1045					86	1110
27 Nov	87	1020					88	1045
	89	1110					90	1135
4 Dec	91	1125					92	1155
	93	1225					94	1245
20 Dec	95	1040					96	1110
	97	1150					98	1208
27 Dec	106	1123					107	1203
	108	1218					109	1240
<u>1975</u>								
22 Jan	111	1057					112	1152
	113	1200					114	1225
31 Jan	115	1445	116	1500	117	1510		
	118	1520					119	1545
14 Feb	120	1100	121	1130	122	1145	123	1210
	126	1315	125	1300	124	1240	127	1345
20 Feb	128	0850	129	0905	130	0915	131	0930
	135	1020	134	1010	133	1000	132	0945

Table A3. Data from the Craney Island Disposal area, Port of Hampton Roads Virginia, from 28 December 1973 until 28 June 1974. Parameters are dissolved oxygen, oxygen saturation, orthophosphate, total phosphorus, nitrate, nitrite, and ammonia.

Date	Location ¹	Sample No.	Sample Time	Diss. O ₂ mg/l	O ₂ - Sat %	PO ₄ - P mg/l	Tot. P mg/l	NO ₃ - N mg/l	NO ₂ - N mg/l	NH ₄ - N mg/l
<u>1973</u>										
28 Dec	M Spill	1	1000	9.60	96	0.025	0.107	0.465	0.086	3.677
	NE Open	2	1107	9.12	83	0.045	0.063	0.263	0.011	0.168
<u>1974</u>										
11 Jan	M Spill	4	1105	8.10	85	0.074	0.336	0.185	0.070	7.229
	NE Open	5	1025	8.60	83	0.047	0.072	0.248	0.009	0.275
18 Jan	M Spill	7	0940	8.20	71	0.095	1.369	0.064	0.105	5.268
	NE Open	8	1030	11.80	104	0.061	0.096	0.133	0.012	4.532
25 Jan	M Spill	10	1145	10.70	95	0.105	0.366	0.190	0.280	13.76
	NE Open	11	1105	10.40	69	0.069	0.169	0.018	0.013	0.939
8 Feb	NE Open	13	1030	10.80	106	0.023	0.092	0.014	0.018	0.441
	M Spill	15	1030	8.20	83	0.214	0.246	0.052	0.011	7.715
22 Feb	NE Open	16	1115	10.60	108	0.014	0.113	0.011	0.001	1.551
	M Spill	18	0950	9.20	95	0.052	0.152	0.335	0.063	0.373
22 Mar	NE Open	19	1050	11.40	96	0.023	0.127	0.004	0.004	0.233
	M Spill	21	1110	10.00	95	0.034	0.069	0.170	0.011	1.250
10 Apr	NE Open	22	1145	9.80	94	0.055	0.071	0.049	0.004	0.496
	M Spill	24	1205	6.80	64	0.264	0.283	0.018	0.003	1.421
11 Apr	NE Open	25	1235	9.40	98	0.047	0.071	0.043	0.003	0.109
	M Spill	27	1125	11.50	124	0.010	0.174	0.308	0.275	0.103
26 Apr	NE Open	28	1135	10.80	116	0.005	0.058	0.160	0.004	0.052
	M Spill	30	1010	9.80	115	0.109	0.184	0.069	0.015	0.062
10 May	NE Open	31	1030	10.20	119	0.012	0.139	0.111	0.037	0.033
	M Spill	33	1000	8.40	112	0.042	0.105	0.057	0.018	0.377
17 May	NE Open	34	1015	9.00	118	0.047	0.052	0.200	0.005	0.123
	M Spill	35	1105	7.60	97	0.040	0.176	0.065	0.008	0.108
24 May	NE Open	36	1120	7.00	89	0.025	0.122	0.078	0.003	0.065
	M Spill	37	1035	7.40	96	0.009	0.058	0.055	0.004	0.040
14 Jun	NE Open	38	1045	7.40	89	0.009	0.014	0.063	0.005	0.011
	M Spill	40	0930	7.60	105	0.030	0.176	0.043	0.003	0.306
27 Jun	NE Open	41	0945	6.20	125	0.000	0.115	0.106	0.016	0.188
	M Spill	43	1130	9.60	120	0.000	0.181	0.046	0.004	1.505
	NE Open	44	1145	8.20	103	0.090	0.095	0.104	0.005	0.149
	M Spill	46	1330	9.40	118	0.025	0.274	0.099	0.002	0.738
28 Jun	NE Open	47	1340	6.80	82	0.010	0.088	0.096	0.014	0.334
	M Spill	49	0930	9.00	113	0.051	0.444	0.102	0.002	0.043
	NE Open	50	1015	7.80	99	0.049	0.110	0.107	0.010	0.291
	M Spill	52	1130	9.30	109	0.022	0.442	0.071	0.001	0.063
	NE Open	53	1210	9.80	121	0.024	0.128	0.098	0.063	0.144
	M Spill	55	1330	8.40	100	0.036	0.316	0.083	0.008	0.043
	NE Open	56a	1410	8.80	106	0.013	0.082	0.111	0.005	0.117

¹ M Spill is middle spillway and NE Open is northeast open water sample (see Figure 2 for station locations).

Table A4. Continuation of Table A3 for the same time period. Parameters are temperature, salinity, pH, fecal coliform, total suspended solids, cadmium, mercury, and zinc.

Date	Location	Sample No.	Sample Time	Temp °C	Sal ‰	pH	Fecal Coliform Colonies per 100 ml	Total Susp. Solids mg/l	Cadmium		Mercury		Zinc	
									Diss. ¹ mg/l	Part. µg/g	Diss. mg/l	Part. µg/g	Diss. ¹ mg/l	Part. µg/g
1973														
28 Dec	M Spill	1	1000	12.80	15.769	7.82	0	65	0.004	133	0.003	---	0.014	667
	NE Open	2	1107	8.35	11.423	7.96	0	34	0.003	103	0.003	---	0.015	374
1974														
11 Jan	M Spill	4	1105	15.05	11.896	7.95	0	376	0.009	32.3	0.003	---	0.149	112
	NE Open	5	1025	10.90	12.686	7.74	0	4	0.005	66.7	0.002	---	0.046	211
18 Jan	M Spill	7	0940	5.50	15.981	8.15	100	2535	0.001	40.3	0.003	---	0.010	214
	NE Open	8	1030	7.00	13.799	7.71	0	37	0.009	1.37	0.002	---	0.033	39.0
25 Jan	M Spill	10	1145	6.94	12.555	8.28	20	202	0.019	10.7	0.003	---	0.087	12.3
	NE Open	11	1105	7.62	13.075	7.78	0	17	0.013	34.2	0.003	---	0.093	16.3
8 Feb	NE Open	13	1030	6.70	14.751	7.99	0	29	0.006	5.14	0.002	---	0.035	23.4
22 Feb	M Spill	15	1030	17.05	16.520	9.24	20	3430	0.017	13.5	0.002	1.16	0.037	22.8
	NE Open	16	1115	12.52	15.094	8.02	0	55	0.011	13.3	0.002	1.15	0.029	26.9
22 Mar	M Spill	18	0950	10.45	14.783	8.09	0	212	0.005	2.44	0.021	0.115	0.047	22.1
	NE Open	19	1050	7.05	17.579	8.32	0	17	0.005	0.47	0.023	---	0.040	74.3
10 Apr	M Spill	21	1110	9.90	12.055	8.10	200	578	0.003	0.75	0.018	0.290	0.024	17.6
	NE Open	22	1145	10.55	11.708	8.10	0	83	0.006	1.56	0.014	0.161	0.019	17.8
11 Apr	M Spill	24	1205	19.50	10.076	8.51	0	487	0.005	1.71	0.018	0.208	0.016	15.3
	NE Open	25	1235	12.80	9.408	8.19	0	8	0.006	4.14	0.013	0.503	0.012	37.0
26 Apr	M Spill	27	1125	15.20	14.308	8.71	0	83	0.009	2.09	0.018	0.188	0.047	18.7
	NE Open	28	1135	15.05	14.772	8.34	0	34	0.034	2.14	0.016	0.423	0.072	15.5
10 May	M Spill	30	1010	20.60	14.595	8.83	0	189	0.006	3.59	0.021	0.163	0.039	27.6
	NE Open	31	1030	18.60	16.068	8.18	0	5	0.009	1.03	0.018	0.342	0.041	12.9
17 May	M Spill	33	1000	26.20	16.156	8.87	0	192	0.005	2.18	0.013	0.527	0.114	20.0
	NE Open	34	1015	22.90	15.661	8.13	0	18	0.056	1.10	0.012	0.077	0.108	25.2
24 May	M Spill	35	1105	26.40	17.926	8.53	0	87	0.006	33.6	<0.001	0.172	0.039	41.5
	NE Open	36	1120	23.80	15.739	8.18	0	54	0.004	1.98	<0.001	0.083	0.033	28.6
14 Jun	M Spill	37	1035	24.20	20.174	8.73	0	211	0.003	28.2	<0.001	0.373	0.071	105
	NE Open	38	1045	23.83	15.931	8.73	0	21	0.002	3.24	<0.001	0.108	0.029	37.6
27 Jun	M Spill	40	0930	20.50	15.639	8.55	0	49	0.004	4.35	<0.001	0.187	0.076	42.4
	NE Open	41	0945	21.80	17.752	8.15	0	62	0.004	2.33	<0.001	0.136	0.029	27.0
	M Spill	43	1130	20.20	12.285	8.85	0	79	0.004	4.16	<0.001	0.850	0.029	40.9
	NE Open	44	1145	21.80	18.447	8.20	0	16	0.003	4.21	<0.001	0.288	0.045	43.9
	M Spill	46	1330	20.20	14.972	8.95	0	138	0.002	4.17	<0.001	0.193	0.030	42.8
	NE Open	47	1340	21.30	14.467	8.40	0	18	0.005	4.18	<0.001	0.252	0.026	44.7
28 Jun	M Spill	49	0930	19.90	14.037	8.58	0	66	<0.001	3.59	<0.001	0.137	0.087	46.0
	NE Open	50	1015	21.50	20.475	8.10	0	16	0.021	2.52	<0.001	0.125	---	33.4
	M Spill	52	1130	19.90	13.102	8.60	0	75	<0.001	3.77	<0.001	0.115	0.024	38.0
	NE Open	53	1210	20.90	18.640	8.11	0	26	0.001	3.86	<0.001	0.092	0.066	35.8
	M Spill	55	1330	20.70	12.406	8.45	0	50	<0.001	3.84	<0.001	0.138	0.078	38.9
	NE Open	56a	1410	21.60	13.077	8.01	0	20	0.001	3.83	<0.001	0.135	0.116	34.3

¹ Measured as reactive concentration by anodic stripping voltammetry (ASV).

² Data were inaccurate because of instrumental problems.

Table A5. Data from the Craney Island Disposal area, Port of Hampton Roads, Virginia, from 6 August 1974 until 4 December 1974. Parameters are dissolved oxygen, oxygen saturation, orthophosphate, total phosphorus, nitrate, nitrite, ammonia, and total Kjeldahl nitrogen.

Date	Location ¹	Sample No.	Sample Time	Diss. O ₂ mg/l	O ₂ - Sat %	PO ₄ - P mg/l	Tot. P mg/l	NO ₃ - N mg/l	NO ₂ - N mg/l	NH ₄ - N mg/l	TKN mg/l
1974											
6 Aug	M Spill	57	1045	5.40	71	0.008	0.245	---	0.006	0.011	-- ²
	NE Open	58	1110	6.40	87	0.000	0.108	0.508	0.030	0.021	--
18 Sep	#1 Spill	59	1025	6.14	80	0.340	---	2.071	0.039	0.274	--
	NE Open	60	1121	7.57	103	0.112	---	1.039	0.141	0.109	--
	#1 Spill	61	1152	8.81	116	0.192	---	1.979	0.027	0.190	--
	NE Open	62	1220	7.24	98	0.262	---	0.404	0.134	0.177	--
25 Sep	#1 Spill	63	1115	9.75	112	0.163	---	---	<0.006	0.048	--
	NE Open	64	1142	11.30	137	0.196	---	2.288	<0.006	0.101	--
	#1 Spill	65	1212	10.69	126	0.212	---	---	<0.006	0.071	--
	NE Open	66	1238	9.71	118	0.161	---	---	<0.006	0.072	--
16 Oct	#1 Spill	67	1122	10.10	134	0.067	---	0.030	0.008	0.088	--
	NE Open	68	1200	11.30	146	0.106	---	0.211	0.007	0.123	--
	#1 Spill	69	1220	9.04	120	0.069	---	0.010	0.002	0.079	--
	NE Open	70	1245	11.36	147	0.077	---	0.392	0.029	0.124	--
25 Oct	#1 Spill	71	1205	12.18	145	0.058	0.257	0.072	0.012	0.110	--
	NE Open	72	1232	9.24	108	0.059	0.214	0.295	0.015	0.101	--
	#1 Spill	73	1253	10.04	120	0.048	0.095	0.047	0.007	0.136	--
	NE Open	74	1314	9.02	108	0.053	0.126	0.256	0.013	0.119	--
30 Oct	#1 Spill	75	1025	8.60	108	0.052	0.367	0.019	0.006	0.032	2.34
	NE Open	76	1045	8.72	107	0.056	0.243	0.131	0.009	0.073	1.16
	#1 Spill	77	1105	11.00	138	0.047	0.369	0.017	0.003	0.035	3.49
	NE Open	78	1125	12.08	149	0.047	0.179	0.124	0.009	0.095	1.22
6 Nov	#1 Spill	79	1025	7.95	91	0.086	0.445	0.409	0.011	0.025	3.80
	NE Open	80	1051	7.95	94	0.070	0.145	0.073	0.007	0.024	1.92
	#1 Spill	81	1110	7.46	84	0.080	0.428	0.094	0.007	0.007	3.25
	NE Open	82	1132	7.54	90	0.030	0.128	0.162	0.008	0.019	1.94
20 Nov	#1 Spill	83	1000	11.90	126	0.049	0.126	0.060	0.006	0.128	4.84
	NE Open	84	1025	8.86	94	0.023	0.049	0.192	0.013	0.068	2.42
	#1 Spill	85	1045	10.47	112	0.040	0.112	0.018	0.016	0.070	4.38
	NE Open	86	1110	8.86	95	0.024	0.056	0.191	0.010	0.082	2.27
27 Nov	#1 Spill	87	1020	10.36	88	0.032	0.179	0.089	0.010	0.127	5.82
	NE Open	88	1045	6.95	69	0.029	0.088	0.228	0.007	0.057	1.98
	#1 Spill	89	1110	10.06	86	0.031	0.218	0.091	0.007	0.080	4.20
	NE Open	90	1135	7.13	70	0.029	0.094	0.238	0.010	0.077	1.28
4 Dec	#1 Spill	91	1125	8.82	77	0.035	0.170	0.057	0.005	0.377	6.13
	NE Open	92	1155	8.03	76	0.026	0.048	0.190	0.010	0.110	1.22
	#1 Spill	93	1225	8.96	79	0.013	0.110	0.051	0.007	0.262	5.45
	NE Open	94	1245	7.91	74	0.024	0.052	0.179	0.012	0.089	1.86

¹ M Spill is middle spillway, #1 Spill is No. 1 spillway, while NE Open is northeast open water sample (see Figure 2 for station locations).

² Instrumental breakdown.

Table A6. Continuation of Table A5 for the same time period. Parameters are temperature, salinity, pH, fecal coliform, total suspended solids, cadmium, mercury, and zinc.

Date	Location ¹	Sample No.	Sample Time	Temp. °C	Sal ‰	pH	Fecal Coliform Colonies per 100 ml	Total Susp. Solids mg/l	Cadmium	Mercury	Zinc			
									Diss. ² mg/l	Part. µg/g	Diss. ² mg/l	Part. µg/g		
6 Aug	M Spill	57	1045	24.02	15.284	8.28	0	117	0.113	98.9	0.698	0.071	181	
	NE Open	58	1110	24.21	19.475	7.79	1	92	0.020	16.9	0.045	0.056	27.7	
18 Sep	#1 Spill	59	1025	23.10	15.675	8.40	10	75	0.045	93.1	0.203	0.586	95.1	
	NE Open	60	1121	24.45	19.559	7.96	0	59	0.025	13.2	0.003	0.113	32.5	
	#1 Spill	61	1152	24.12	15.643	8.45	55	83	0.016	99.1	0.005	0.210	0.076	132
	NE Open	62	1220	24.80	17.294	8.01	0	68	0.047	9.38	0.005	0.150	0.158	22.4
25 Sep	#1 Spill	63	1115	16.44	14.513	8.35	6	90	0.031	6.82	0.555	0.245	44.3	
	NE Open	64	1142	19.35	14.782	7.52	0	51	0.053	1.58	0.180	0.214	22.4	
	#1 Spill	65	1212	17.79	14.548	8.38	13	54	0.006	13.0	0.007	0.578	0.063	35.8
	NE Open	66	1238	19.35	15.069	7.84	2	26	0.056	3.30	0.004	0.165	0.152	8.62
16 Oct	#1 Spill	67	1122	23.89	16.907	8.53	11	88	0.016	36.4	0.225	0.262	602	
	NE Open	68	1200	20.70	20.718	8.02	3	40	0.021	<0.5	0.180	0.067	321	
	#1 Spill	69	1220	23.65	17.667	8.49	19	92	0.023	20.9	0.008	0.248	0.402	664
	NE Open	70	1245	20.75	20.737	8.05	6	56	0.015	0.60	0.003	0.165	0.030	462
25 Oct	#1 Spill	71	1205	17.60	16.883	8.54	75	185	0.083	135	0.002	0.503	0.148	184
	NE Open	72	1232	15.78	19.787	8.13	2	60	0.040	12.8	0.002	0.345	0.163	42.0
	#1 Spill	73	1253	17.95	16.760	8.75	13	135	0.057	54.4	0.002	0.668	0.056	177
	NE Open	74	1314	17.21	19.847	8.12	0	43	0.029	14.0	0.001	0.428	0.051	92.6
30 Oct	#1 Spill	75	1025	20.25	17.284	8.91	4	90	0.017	31.9	0.002	0.668	0.110	269
	NE Open	76	1045	17.39	21.800	8.19	0	79	0.076	8.70	0.001	0.330	0.282	108
	#1 Spill	77	1105	20.31	17.894	8.87	0	110	0.020	50.0	0.002	0.082	0.124	224
	NE Open	78	1125	17.85	21.939	8.18	1	66	0.059	18.2	0.001	0.390	0.056	98.2
6 Nov	#1 Spill	79	1025	17.19	12.34	8.62	39	173	0.012	227	0.002	0.705	0.089	343
	NE Open	80	1051	16.84	17.60	8.13	5	70	0.033	38.4	0.001	0.548	0.070	58.1
	#1 Spill	81	1110	16.50	12.01	8.63	100	135	0.026	170	0.002	0.878	0.045	288
	NE Open	82	1132	16.99	19.13	8.10	14	68	0.026	30.2	0.001	0.592	0.049	53.6
20 Nov	#1 Spill	83	1000	12.82	13.65	8.59	8	62	0.077	190	0.002	0.893	0.193	522
	NE Open	84	1025	12.64	14.92	7.23	2	29	0.030	45.2	0.002	0.802	0.123	107
	#1 Spill	85	1045	13.39	13.26	9.08	38	132	0.047	216	0.002	1.13	0.120	321
	NE Open	86	1110	12.61	16.16	7.18	1	42	0.035	90.3	0.002	0.705	0.156	152
27 Nov	#1 Spill	87	1020	3.64	14.25	8.73	78	130	0.005	75.4	0.002	1.10	0.100	160
	NE Open	88	1045	9.19	17.91	7.88	1	45	0.024	39.8	0.002	0.862	0.080	59.4
	#1 Spill	89	1110	4.08	14.00	8.98	158	144	0.077	70.8	0.002	0.998	0.138	114
	NE Open	90	1135	9.15	15.82	7.69	4	14	0.034	38.9	0.002	0.908	0.113	62.2
4 Dec	#1 Spill	91	1125	5.40	10.24	8.39	120	392	0.013	134	0.001	1.28	0.093	503
	NE Open	92	1155	6.60	18.65	6.78	3	70	0.056	37.9	0.001	0.855	0.153	256
	#1 Spill	93	1225	5.95	11.03	8.49	145	406	0.048	150	0.002	1.50	0.398	518
	NE Open	94	1245	6.22	19.14	7.58	2	72	0.065	40.4	0.001	0.878	0.137	303

¹ M Spill is middle spillway, #1 Spill is No. 1 spillway, while NE Open is northeast open water sample (see Figure 2 for station locations).

² Measured as total dissolved metal by graphite furnace atomic absorption.

Table A7. Data from the Craney Island Disposal area, Port of Hampton Roads, Virginia, from 20 December 1974 until 20 February 1975. Para-meters are dissolved oxygen, oxygen saturation, orthophosphate, total phosphorus, nitrate, nitrite, ammonia, and total Kjeldahl nitrogen.

Date	Location ¹	Sample No.	Sample Time	Diss. O ₂ mg/l	O ₂ - Sat %	PO ₄ - P mg/l	Tot. P mg/l	NO ₃ - N mg/l	NO ₂ - N mg/l	NH ₄ - N mg/l	TKN mg/l	
1974												
20 Dec	#1 Spill	95	1040	9.65	86	0.067	0.326	1.902	0.024	1.549	6.36	
	NE Open	96	1110	9.10	85	0.053	0.108	0.577	0.010	0.100	2.43	
	#1 Spill	97	1150	10.10	92	0.067	0.246	0.348	0.027	1.695	7.92	
	NE Open	98	1208	8.77	83	0.048	0.100	1.201	0.011	0.080	2.29	
27 Dec	NE Open ²	102	1205	8.95	83	0.147	0.198	---	0.012	0.076	1.85	
	#1 Spill	106	1123	9.42	87	0.101	0.185	1.924	0.038	0.368	7.45	
	NE Open	107	1203	7.91	75	0.040	0.070	3.801	0.015	0.116	1.61	
	#1 Spill	108	1218	9.06	84	0.084	0.216	2.832	0.016	0.401	9.92	
1975	NE Open	109	1240	8.09	76	0.066	0.099	1.071	0.012	0.094	2.07	
	22 Jan											
	#1 Spill ³	110	1053	10.34	89	0.069	0.260	0.034	0.053	0.401	--	
	#1 Spill	111	1057	10.11	86	0.060	0.249	0.028	0.059	0.364	3.35	
31 Jan	NE Open	112	1132	9.12	81	0.043	0.130	0.414	0.029	0.142	3.45	
	#1 Spill	113	1200	10.03	86	0.069	0.256	0.036	0.053	0.319	2.15	
	NE Open	114	1225	9.65	83	0.054	0.092	0.560	0.025	0.143	1.25	
	#1 Spill	115	1445	10.00	97	0.096	0.185	0.007	0.048	0.217	3.40	
14 Feb	M Spill	116	1500	8.76	84	0.125	0.221	0.031	0.017	0.127	2.55	
	#3 Spill	117	1510	8.59	83	0.094	0.195	0.027	0.014	0.115	3.35	
	#1 Spill	118	1520	9.75	94	0.110	0.180	0.020	0.014	0.291	3.97	
	NE Open	119	1545	7.62	74	0.030	0.058	0.308	0.030	0.185	1.31	
20 Feb	#1 Spill	120	1100	8.02	71	0.072	0.186	0.022	0.064	0.329	4.65	
	M Spill	121	1150	7.69	69	0.104	0.160	0.032	0.066	0.932	4.99	
	#3 Spill	122	1145	7.31	67	0.099	0.126	0.048	0.069	0.514	3.35	
	NE Open	123	1210	7.22	66	0.037	0.065	0.351	0.037	0.109	0.17	
20 Feb	#3 Spill	124	1240	7.50	69	0.069	0.147	0.038	0.071	0.699	4.03	
	M Spill	125	1300	7.31	67	0.089	0.169	0.034	0.071	0.161	4.42	
	#1 Spill	126	1315	8.23	72	0.072	0.172	0.027	0.014	0.491	4.88	
	NE Open	127	1345	7.41	67	0.024	0.066	0.356	0.033	0.136	0.23	
20 Feb	#1 Spill	128	0850	9.03	85	0.074	0.262	0.031	0.089	1.713	4.93	
	M Spill	129	0905	8.62	81	0.074	0.173	0.033	0.093	1.469	3.97	
	#3 Spill	130	0915	9.19	85	0.084	0.169	0.061	0.093	1.956	4.31	
	NE Open	131	0930	9.36	85	0.029	0.086	0.371	0.042	0.214	0.46	
20 Feb	NE Open	132	0945	9.50	86	0.036	0.082	0.383	0.040	0.181	0.28	
	#3 Spill	133	1000	8.79	83	0.089	0.154	0.031	0.097	1.776	4.82	
	M Spill	134	1010	8.60	81	0.094	0.208	0.015	0.083	1.157	4.37	
	#1 Spill	135	1020	9.09	85	0.075	0.240	0.027	0.083	2.679	5.16	

¹ M Spill is middle spillway, #1 Spill is No. 1 spillway, #3 Spill is No. 3 spillway, while NE Open is northeast open water sample (see Figure 2 for station locations).

² Sample taken ca. 50 m off levee at NE Open site from small fiberglass boat.

³ Spillway samples were normally collected inside the levee at the weir. These specific samples were collected from both inside at the usual site and outside the levee. The #1 Spill taken on 22 Jan 1975, designated with footnote 3, was collected outside the levee.

Table A8. Continuation of Table A7 for the same time period. Parameters are temperature, salinity, pH, fecal coliform, total suspended solids, cadmium, mercury, and zinc.

Date	Location ¹	Sample No.	Sample Time	Temp °C	Sal ‰	pH	Fecal Coliform Colonies per 100 ml	Total Susp. Solids mg/l	Cadmium		Mercury		Zinc	
									Diss. ² mg/l	Part. µg/g	Diss. mg/l	Part. µg/g	Diss. ² mg/l	Part. µg/g
1974														
20 Dec	#1 Spill	95	1040	6.18	12.25	8.28	145	212	0.113	31.3	.012	0.900	0.266	78.8
	NE Open	96	1110	6.63	16.38	7.81	2	53	0.030	4.05	.005	0.510	0.092	28.9
	#1 Spill	97	1150	6.62	12.69	8.81	35	364	0.254	38.6	.014	0.840	0.151	82.0
	NE Open	98	1208	7.20	17.82	7.72	0	73	0.013	3.98	.004	0.690	0.056	26.9
	NE Open ³	102	1205	6.64	16.45	7.92	4	54	0.007	1.80	.007	0.720	0.079	47.0
27 Dec	#1 Spill	106	1123	6.61	14.85	8.42	90	196	0.047	23.7	.013	0.870	0.136	114
	NE Open	107	1203	7.72	15.14	7.95	6	63	0.041	1.88	.004	0.600	0.063	35.1
	#1 Spill	108	1218	6.76	15.02	8.47	129	234	0.044	28.3	.013	0.795	0.099	107
	NE Open	109	1240	7.60	13.93	7.96	2	71	0.038	3.68	.003	0.548	0.146	21.8
1975														
22 Jan	#1 Spill ⁴	110	1053	4.00	15.06	8.28	76	325	0.065	10.1	.002	0.855	0.110	97.1
	#1 Spill	111	1057	3.20	15.31	8.28	70	281	0.017	13.8	.003	0.735	0.068	136
	NE Open	112	1132	5.05	14.20	7.90	4	58	0.023	0.60	.003	0.308	0.128	35.8
	#1 Spill	113	1200	3.35	16.10	8.28	85	484	0.021	39.1	.004	0.615	0.035	129
	NE Open	114	1225	4.18	14.39	7.98	5	35	0.032	0.15	.003	0.495	0.087	9.60
31 Jan	#1 Spill	115	1445	9.40	12.65	8.94	20	468	0.027	20.2	.005	0.592	0.163	100
	M Spill	116	1500	8.85	13.01	9.19	260	244	0.019	26.0	.004	0.508	0.110	129
	#3 Spill	117	1510	9.09	13.22	9.44	300	368	0.025	0.975	.003	0.233	0.145	40.7
	#1 Spill	118	1520	9.20	13.00	8.93	36	544	0.023	8.02	.004	0.465	0.211	108
	NE Open	119	1545	8.58	15.16	7.86	2	76	0.024	6.98	.003	0.180	0.028	28.7
	#1 Spill	120	1100	5.00	13.84	8.96	11	500	0.053	129	.004	0.480	0.252	457
14 Feb	M Spill	121	1130	6.01	14.01	8.90	3	285	0.019	122	.004	0.225	0.008	443
	#3 Spill	122	1145	6.52	14.09	9.00	2	405	0.031	194	.003	0.263	0.145	360
	NE Open	123	1210	6.10	15.63	8.01	2	340	0.038	1.72	.003	0.375	0.120	9.68
	#3 Spill	124	1240	6.58	14.13	8.95	0	420	0.071	68.3	.002	0.240	0.039	414
	M Spill	125	1300	6.58	14.00	8.94	0	95	0.071	147	.002	0.240	0.004	476
	#1 Spill	126	1315	4.95	13.93	9.04	0	505	0.099	237	.004	0.285	0.435	294
	NE Open	127	1345	6.14	15.04	8.00	3	340	0.023	4.72	.004	0.142	0.055	16.4
	#1 Spill	128	0850	7.58	15.12	8.73	217	660	0.076	96.1	.002	0.508	0.136	165
	M Spill	129	0905	7.45	15.25	8.81	47	570	0.071	73.1	.002	0.278	0.034	158
	#3 Spill	130	0915	6.63	15.31	8.74	237	360	0.065	57.4	.002	0.195	0.233	137
	NE Open	131	0930	6.35	13.63	7.66	20	340	0.036	13.4	.002	0.008	0.083	55.9
	NE Open	132	0945	6.34	13.72	7.73	5	345	0.042	13.4	.001	0.030	0.207	60.8
	#3 Spill	133	1000	7.30	15.40	8.78	81	535	0.055	72.2	.003	0.248	0.434	200
M Spill	134	1010	7.58	15.30	8.77	7	580	0.061	108	.003	0.218	0.134	166	
#1 Spill	135	1020	7.22	15.19	8.63	152	595	0.069	142	.003	0.203	0.133	201	

¹ M Spill is middle spillway, #1 Spill is No. 1 spillway, #3 Spill is No. 3 spillway, while NE Open is northeast open water sample (see Figure 2 for station locations).

² Measured as "total" dissolved metal by graphite furnace atomic absorption.

³ Sample taken ca. 50 m off levee at NE Open site from small fiberglass boat.

⁴ Spillway samples were normally collected inside the levee at the weir. These specific samples were collected from both inside at the usual site and outside the levee. The #1 Spill taken on 22 Jan 1975, designated with footnote 4, was collected outside the levee.

Table A9. Dredge pipe effluent data from the Craney Island Disposal area, Port of Hampton Roads, Virginia, from 28 December 1973 to 6 August 1974. Parameters are dissolved oxygen, oxygen-saturation, orthophosphate, total phosphorus, nitrate, nitrite, and ammonia.

Date	Location ¹	Sample Time	Sample No.	Diss. O ₂ mg/l	O ₂ - Sat %	PO ₄ - P mg/l	Tot. P mg/l	NO ₃ - N mg/l	NO ₂ - N mg/l	NH ₄ - N mg/l
1973										
28 Dec	NW Dredge	1040	3	8.10	74	0.348	0.649	0.242	0.013	4.069
	NE Dredge	1118		0.00	0	0.103	0.138	0.296	0.017	8.157
	G Dredge	1300		7.86	76	0.013	0.254	0.869	0.010	0.971
1974										
11 Jan	NW Dredge	1045	6	9.20	93	0.046	0.156	0.616	0.010	6.832
	G Dredge	1125		7.90	82	0.539	0.867	0.189	0.010	8.419
18 Jan	NW Dredge	0930	9	9.50	95	0.011	0.196	0.108	0.008	3.333
	NE Dredge	1010		2.80	27	0.046	0.066	0.024	0.002	14.55
25 Jan	G Dredge	1130	12	10.40	96	0.181	0.190	0.067	0.019	2.148
	NW Dredge	1045		3.40	33	0.578	1.521	0.017	0.021	25.84
	NE Dredge	1125		6.30	59	0.221	1.110	0.015	0.013	59.94
8 Feb	NE Dredge	1010	14	2.20	35	0.105	4.133	0.072	0.062	4.520
22 Feb	NW Dredge	1105	17	3.60	74	0.010	0.126	0.055	0.010	2.171
	NE Dredge	1130		4.20	31	0.051	0.140	0.040	0.002	0.594
22 Mar	NW Dredge	1010	20	4.40	37	0.404	1.245	0.138	0.213	0.560
	NE Dredge	1035		10.90	105	0.000	0.019	0.261	0.005	0.280
10 Apr	NW Dredge	1128	23	8.80	85	0.465	0.494	0.003	0.005	0.819
11 Apr	NW Dredge	1300	26	6.80	69	0.357	2.593	0.412	0.015	1.445
26 Apr	NW Dredge	1100	29	3.60	39	0.016	0.165	0.164	0.073	4.596
10 May	NW Dredge	1115	32	1.80	21	0.012	0.139	0.111	0.037	1.990
14 Jun	S Dredge	1110	39	4.80	62	0.016	0.081	0.126	0.002	0.060
27 Jun	NE Dredge	0955	42	1.00	12	0.033	0.043	0.054	0.023	2.951
	S Dredge	1010		2.00	26	0.091	1.286	0.115	0.003	1.551
	S Dredge	1300		2.20	28	0.024	0.399	0.067	-0.007	1.825
	NE Dredge	1230		1.20	16	0.030	0.054	0.059	0.016	2.435
28 Jun	S Dredge	1355	48	5.40	68	0.071	0.083	0.127	0.020	1.556
	NE Dredge	1000		1.40	17	0.823	2.360	0.058	0.003	4.130
	S Dredge	1030		1.80	22	1.025	1.917	0.097	0.016	2.446
	NE Dredge	1200		1.40	17	0.741	2.054	0.053	0.005	2.962
6 Aug	S Dredge	1230	54	2.20	27	1.091	1.812	0.085	0.012	2.364
	NE Dredge	1400		1.40	17	0.022	1.738	0.071	0.003	4.464
	S Dredge	1430		1.40	17	0.700	1.654	0.094	0.005	1.180
6 Aug	NE Dredge	1120	56c	0.50	7	0.002	0.087	0.727	0.013	0.067

¹ NW Dredge, NE Dredge, and S Dredge designate the compass locations of the dredge pipes, i.e., northwest, northeast, and south. G Dredge is the USCE GOETHALS hopper dredge (see Figure 2 for locations).

Table A10. Continuation of Table A9 for the same time period. Parameters are water temperature, salinity, pH, fecal coliform, total suspended solids, cadmium, mercury, and zinc.

Date	Location ¹	Sample Time	Sample No.	Temp °C	Sal ‰	pH	Fecal Coliform Colonies per 100 ml	Total Susp Solids mg/l	Cadmium		Mercury		Zinc	
									Diss. mg/l	Part. µg/g	Diss. mg/l	Part. µg/g	Diss. mg/l	Part. µg/g
1973														
28 Dec	NW Dredge	1040		9.30	14.246	8.06	0	1.91 × 10 ⁵	0.002	11.0	0.003	---	---	56.4
	NE Dredge	1118	3	8.50	19.053	7.59	150	1.96 × 10 ⁴	0.002	153	0.003	---	0.015	447
	G Dredge	1300		9.80	15.838	7.51	250	3000	0.003	426	0.002	---	0.017	745
1974														
11 Jan	NW Dredge	1045		13.50	12.323	8.33	0	8.6 × 10 ⁴	0.008	6.78	0.005	---	0.052	26.4
	G Dredge	1125	6	13.45	13.847	7.50	200	1.56 × 10 ⁴	0.006	49.4	0.003	---	0.012	86.4
18 Jan	NW Dredge	0930		12.20	14.370	8.26	0	2.68 × 10 ⁴	0.009	103	0.002	---	0.007	114
	NE Dredge	1010	9	7.40	25.484	7.58	100	4.35 × 10 ⁴	0.001	77.8	0.002	---	0.007	209
	G Dredge	1130		7.50	20.192	7.69	0	4.58 × 10 ⁴	0.009	60.0	0.003	---	0.019	262
25 Jan	G Dredge	1045		9.95	15.959	7.98	100	5.8 × 10 ⁴	0.001	11.6	0.003	1.060	0.034	157
	NW Dredge	1125	12	8.70	14.277	8.22	100	3.58 × 10 ⁴	0.007	9.29	0.003	0.750	0.045	48.2
8 Feb	NE Dredge	1010	14	7.05	18.265	7.68	240	6.79 × 10 ⁴	0.008	12.5	0.002	1.050	0.058	111
22 Feb	NW Dredge	1105	17	13.65	12.860	8.36	0	8.7 × 10 ⁴	0.005	14.0	0.003	1.020	0.136	46.2
	NE Dredge	1130		12.80	20.816	7.84	0	6.88 × 10 ⁴	0.004	196	0.002	4.180	0.035	94.7
22 Mar	NW Dredge	1010	20	8.40	15.814	8.33	0	8.5 × 10 ⁴	0.007	0.55	0.027	0.154	0.034	36.6
	NE Dredge	1035		8.05	19.892	8.32	0	43.3	0.005	3.50	0.020	0.137	0.073	27.0
10 Apr	NW Dredge	1128	23	10.75	10.850	8.22	0	3190	0.004	0.40	0.016	0.177	0.043	30.7
11 Apr	NW Dredge	1300	26	13.00	11.425	8.49	100	1.4 × 10 ⁵	0.008	0.59	0.014	0.062	0.064	26.2
26 Apr	NW Dredge	1100	29	16.00	14.250	8.54	0	5.3 × 10 ⁴	0.007	0.52	0.021	0.202	0.030	30.7
10 May	NW Dredge	1115	32	20.00	15.431	7.89	0	3.6 × 10 ⁴	0.006	0.84	0.018	0.081	0.051	94.5
14 Jun	S Dredge	1110	39	23.80	18.504	7.84	0	1.4 × 10 ³	0.004	28.9	0.000	0.555	0.076	190
27 Jun	NE Dredge	0955		21.60	16.659	8.00	100	9.5 × 10 ⁴	0.001	25.0	0.000	0.462	0.034	83.3
	S Dredge	1010		22.40	14.088	8.15	100	4.3 × 10 ⁵	0.001	13.8	0.000	0.025	0.102	41.0
	S Dredge	1300		21.80	17.824	7.51	0	3.8 × 10 ⁵	0.001	13.8	0.000	0.094	0.214	38.5
	NE Dredge	1230		21.80	15.987	8.07	0	1.1 × 10 ⁵	0.001	26.3	0.000	0.611	0.029	72.5
	S Dredge	1355		21.70	18.565	7.79	200	9.2 × 10 ⁴	0.002	13.8	0.000	0.136	0.155	56.7
28 Jun	NE Dredge	1000	51	21.20	17.519	7.50	100	2.3 × 10 ⁵	0.001	22.9	0.000	0.455	0.008	63.7
	S Dredge	1030		20.60	18.197	7.85	200	4.6 × 10 ⁵	0.000	11.1	0.000	0.961	0.022	22.3
	NE Dredge	1200	54	21.20	18.009	7.50	100	9.0 × 10 ⁴	0.000	16.6	0.000	0.607	0.112	74.9
	S Dredge	1230		20.80	18.124	7.78	200	4.6 × 10 ⁵	0.000	14.5	0.000	1.016	0.025	29.0
	NE Dredge	1400		20.50	17.099	7.49	100	9.4 × 10 ⁴	0.000	18.3	0.000	0.574	0.011	86.6
	S Dredge	1430	56b	20.80	17.288	7.45	100	4.2 × 10 ⁵	0.000	25.6	0.000	0.293	0.052	51.4
6 Aug	NE Dredge	1120	56c	25.23	21.116	7.89	0	1.23 × 10 ⁵	0.263 ^b	163	0.006	1.163	0.399 ⁴	738

¹ NW Dredge, NE Dredge, and S Dredge designate the compass locations of the dredge pipes, i.e., northwest, northeast, and south. G Dredge is the USCE GOETHALS hopper dredge (see Figure 2 for locations).

² Measured as reactive concentration by anodic stripping voltammetry (ASV).

³ Data rejected due to possible error in procedure.

⁴ Done by graphite furnace atomic absorption, which should measure total dissolved metal.