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Current Report

The Narragansett Bay Project

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The Narragansett Bay Project is sponsored by
the U.S. Environmental Protection Agency and
the R.I. Department of Environmental Management.



DEVELOPMENT OF A ONE DIMENSIONAL
WATER QUALITY MODEL
FOR THE BLACKSTONE RIVER;
PART 1: CHEMICAL MONITORING
OF POLLUTANTS IN THE BLACKSTONE RIVER

Quinn JG et al.
NBP-88-03

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Final Report for the
Narragansett Bay Project
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FOREWORD

The United States Congress created the National Estuary Program in 1984, citing its concern for the "health and ecological integrity" of the nation's estuaries and estuarine resources. Narragansett Bay was selected for inclusion in the National Estuary Program in 1985 and the Narragansett Bay Project (NBP), a multi-year study of the Bay and its resources, was established. Under the joint sponsorship of the U.S. Environmental Protection Agency and the Rhode Island Department of Environmental Management, the NBP has involved participation by local, state, and federal agencies, the academic community, and local interest and user groups. The purpose of the Narragansett Bay Project is first to identify and evaluate pollution problems and causes in the Bay through a five-year plan of scientific research. Based on the results, the NBP will then develop a comprehensive management plan by December, 1990, which will recommend actions to improve and protect the Bay from further degradation.

In March, 1988, the Administrator of EPA and the Governor of Rhode Island signed an agreement officially designating Narragansett Bay as an "estuary of national significance". The State of Rhode Island pledged to make a good faith effort to institute whatever corrective actions are recommended by the management plan as necessary to protect the Bay. The EPA will continue to support the NBP through 1995 for the express purpose of overseeing implementation of the recommended actions and monitoring their effectiveness. After 1995, the State of Rhode Island will assume responsibility for implementation of the management plan to protect the Bay and its resources for future generations.

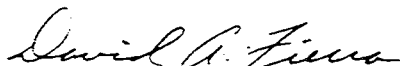
The NBP has established the following seven priority issues for Narragansett Bay:

- * management of fisheries
- * nutrients and potential for eutrophication
- * impacts of toxic contaminants
- * health and abundance of living resources
- * health risk to consumers of contaminated seafood
- * land-based impacts on water quality
- * recreational uses

The NBP is taking an ecosystem approach to address these problems and has funded research that will help to improve our understanding of various aspects of these priority problems. The Project is also working to expand and coordinate existing programs among state agencies, governmental institutions, and academic researchers in order to apply research findings to the practical needs of managing the Bay and improving the environmental quality of its watershed.

This report represents the technical results of an investigation performed for the Narragansett Bay Project. The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under assistance agreement #CX812768 to the Rhode Island Department of Environmental Management. It has been subject to the Agency's and the Narragansett Bay Project's peer and administrative review and has been accepted for publication by the Management Committee of the Narragansett Bay Project. The results and conclusions contained herein are those of the author(s) and do not necessarily represent the views or recommendations of the NBP. Final recommendations for management actions will be based upon the results of this and other investigations.

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SUMMARY

Water samples were collected from nine stations on the Blackstone River and effluent samples were collected from four major point sources on the river. The samples were collected on three dates during the summer/fall of 1985 and analyzed for a variety of organic and metal pollutants.

In most cases, the organic pollutants were strongly associated with the particulate phase of the samples. The average concentrations of hydrocarbons, phthalates, coprostanol, and hexachlorocyclohexanes (HCHs) were highest in the Woonsocket Wastewater Treatment Plant effluent. Corning/G.T.E. Products usually had the highest levels of suspended solids, total polycyclic aromatic hydrocarbons (PAHs), and total polychlorinated biphenyls (PCBs) in its effluent. The Okonite Company effluent generally had low concentrations of all components measured. The S.A.B. Nife Inc. effluent, on the one date it was sampled, showed low concentrations for most species; however, it did contain high amounts of HCHs and PAHs.

All of the monitored point source effluents showed relatively similar concentrations of cadmium and lead; the former was usually in the dissolved fraction and the latter tended to be in the particulate phase of the samples. The G.T.E. effluent had the highest levels of chromium and silver (both were mostly dissolved) and it was similar to the Woonsocket Plant, in that it had relatively high levels of dissolved copper and nickel. Based on the one date it was sampled, Nife had low levels of all six metals analyzed in this study.

Generally, the point source effluents were higher than the river in their concentrations of suspended solids, coprostanol, and

phthalates; however, the levels of hydrocarbons, PAHs, and PCBs in the river were frequently comparable or higher than the values detected in the point sources. River stations directly downstream of point sources usually did not show elevated concentrations of organic compounds associated with the input; in the case of the HCHs, however, the Woonsocket Plant apparently influenced the next two downstream stations.

The concentrations of organic components in the river did not show any prominent trends with distance. However, the first station (on the Branch River) usually had the lowest concentration of all components, and the second station (Massachusetts-Rhode Island line) generally had the highest levels of these components.

The last survey (October) had the highest average river concentration of suspended solids, hydrocarbons, PAHs, PCBs, and coprostanol. Since the effluent concentrations from the point sources were higher during this survey, this may account for the higher river pollutant values on this date. In addition, the flow rate of the river was twice as high as the other two surveys, perhaps causing resuspension of sediment containing these organic contaminants.

The average river concentrations of the metals varied somewhat for the three dates. In the case of particulate copper and lead, the variability correlated with the flow rates of the river such that higher rates may have caused resuspension and remobilization of metals associated with the bottom sediments. For many of the other metals, the changes over the three dates were not large. Cadmium, copper, and nickel were mostly in the dissolved phase in the river samples; while chromium, lead and silver were associated with the suspended load of

the river. For most of the metals, the point source discharges into the river had no observable affect on either the concentration or the fractionation of the metals in the receiving water.

In general, the concentration of metals either remained constant or decreased slightly from station 2 through station 9. Station 1 showed substantially reduced metal concentrations to the point where most samples had levels at or near the detection limits of the methods employed. For the remainder of the river, most stations had metal concentrations greater than the fresh water chronic criteria; however, the concentrations of chromium (presumably Cr (III)) and nickel were found to be less than this criteria. In addition, generally all of the stations had levels significantly less than the acute criteria designation except in the case of copper, where the concentrations exceeded the criteria by 50% on average. Finally, for chromium, copper, and silver, the point sources tended to have higher concentrations than the river; for cadmium, the river had higher concentrations; and for nickel and lead, the concentrations were variable.

The largest amount of most of the organics discharged from point sources to the Blackstone River was from the Woonsocket Wastewater Treatment Plant. Compared to the municipalities previously studied on the Pawtuxet River, the Woonsocket Plant had smaller or comparable mass loadings of hydrocarbons, PAHs, coprostanol, and phthalates, but larger loads of suspended solids. Overall, Woonsocket, like the municipalities on the Pawtuxet, had much lower loads of suspended solids and all organic compounds than the Fields Point plant in Providence.

In order to determine the mass balance of organics in the Blackstone River, it was necessary to include station 2 as part of the point source summation because of the high values (apparently derived from upstream in Massachusetts) detected at this location. The calculation of the mass balance showed that suspended solids, PAHs and PCBs were in balance with what could be accounted for by the combined sources. Most of the other organic contaminants showed that less was transported out of the river than could be accounted for by the point sources suggesting deposition to the river sediments. In the case of g-HCH, the values indicated that about 20% more was transported out of the river than could be accounted for by the mass balance; resuspension of river sediments containing this compound may be responsible for the observed values.

The Woonsocket Municipal Treatment Plant was the major point source of metals to the river, contributing significant amounts of all the metals when compared to the industrial discharges. However, except for silver, this source was relatively insignificant compared to the metal loadings coming from the Massachusetts portion of the river. Within the variability of the data, it appears that most of the lead that entered the river was transported the length of the river and then discharged into the Seekonk River. As for the other metals, about 50% were transported into the Seekonk River and the remaining 50% were probably sedimented out in the Blackstone River. In addition, the Seekonk River, because it is an estuary itself, may be a major sink for the metals (and organics) that are discharged into it and further investigation of this "river" would need to be undertaken in order to

determine the extent of the pollutants that actually enter the Providence River and Upper Narragansett Bay from the Seekonk.

Compared to previous mass discharge estimates of other municipal facilities, the Woonsocket Treatment Plant had generally greater metal discharges than those on the Pawtuxet, yet substantially less than the Fields Point discharge. On the basis of the mass of metals discharged, the Blackstone River tended to be less than the Pawtuxet River, except in the case of chromium where it had higher mass loadings than the Pawtuxet.

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I. INTRODUCTION

In April 1985, the Narragansett Bay Project Office issued an RFP to develop a water quality model for the Blackstone River. A proposal responding to this RFP was submitted by James G. Quinn, Professor of Oceanography and Raymond M. Wright, Assistant Professor of Civil Engineering, both at the University of Rhode Island. Based on our previous experience with the Pawtuxet River (Quinn et al. 1985; Wright et al. 1985), we proposed to develop a steady-state one dimensional model that describes the transport and fate of selected organic and metal pollutants in the Blackstone River. The model would be applicable to well-mixed systems with major transport mechanisms of longitudinal advection and dispersion. It would be capable of simulating a maximum of three conservative parameters, total suspended solids, and five non-conservative pollutants at one time. The information obtained from this model could be used, in conjunction with other ongoing Bay Project studies, to provide information on the sources and amounts of pollutants discharged to Narragansett Bay from the Blackstone-Seekonk rivers.

The pollutants were chosen based on a number of factors including: 1) our previous experience with other river systems in the state; 2) the EPA Priority Pollutant Classification; and 3) the possibility of using various pollutants to provide information on the sources of these components in the Blackstone River and Narragansett Bay (e.g., sewage [coprostanol and low molecular weight polycyclic aromatic hydrocarbons,

(PAHs)], urban runoff [high molecular weight PAHs and lead], and industrial discharges [specific organic compounds and trace metals].

The major objectives of the study were: 1) to monitor selected organic and metal pollutants in the river; 2) to investigate the hydraulic characteristics of the river; and 3) to use these data to develop, calibrate and verify a steady-state one dimensional model that describes the transport and fate of pollutants in the Blackstone River.

The proposal was approved and work on the chemical monitoring phase of the study was started in July, 1985 and completed in August, 1986.

II. SAMPLING

A. SAMPLING LOCATIONS (Refer to Figure II-1.)

Blackstone River

Samples were collected from nine river stations ranging from station 1 on the Branch River to station 9 on the Blackstone at the Main Street Bridge in Pawtucket. The locations of the stations are shown in Figure II-1 and a brief description is as follows:

Station 1: Branch River at the Route 146A bridge in North Smithfield;

Station 2: Blackstone River at the Main Street Bridge in Blackstone, MA;

Station 3: Blackstone River at the Route 122 Bridge in Woonsocket;

Station 4: Blackstone River at the Manville Dam;

Station 5: Blackstone River at the Albion Dam;

Station 6: Blackstone River at the Martin Street Bridge in Ashton;

Station 7: Blackstone River at the Route 122 Bridge in Lonsdale;

Station 8: Blackstone River at the Route 114 Bridge in Pawtucket;

Station 9: Blackstone River at the Main Street Bridge in Pawtucket.

Point Sources

Effluent samples were collected from the following point sources on the Blackstone River:

- 1) Woonsocket Wastewater Treatment Facility which serves the city of Woonsocket;
- 2) S.A.B. Nife, Inc. which manufactures nickel-cadmium batteries;
- 3) Okonite Co. which manufactures insulated wire and cable;
- 4) Corning/G.T.E. Products which manufactures blown glassware, lamp envelopes, vacuum bottle liners and decorating fixtures.

B. SAMPLING DATES

The river water samples were collected on three dates, each representing different river flow conditions. The collection dates were: July 8, 1985, August 20, 1985 and October 8, 1985.

C. SAMPLING METHODOLOGY

Blackstone River

Samples of surface river water (top 30 cm) were collected using a 2-liter Teflon container, which had been acid-leached and rinsed with distilled water and methanol prior to its use in the field. The samples were taken from the center of the upstream side of the bridge spans. All river samples were collected by URI personnel. Before each sample was collected, the Teflon "bucket" was rinsed with river water at each station. Then, river samples were collected and 4-liters were transferred to a solvent rinsed amber glass bottle for transportation back to the laboratory. Another portion of the river sample was transferred from the bucket to a water-rinsed Teflon beaker (acid cleaned) to be used for metal determinations; the water (100-200 ml) was filtered in the field using acid-washed Millipore filters (0.45 um). The filters were stored in plastic filter vials and the filtrate in acid-cleaned polyethylene bottles. Nitric acid (3N) was added to

each filtrate to obtain a pH of less than 2 for preservation of these samples. A third portion of some of the samples was transferred to other containers for additional analysis by the R. I. Department of Health (RIDOH) Laboratory. These samples were analyzed for various water quality parameters and the data is presented in Appendix C. Samples were collected at each river station four times each sampling day, about six hours apart. The four daily samples for organics from each station were composited to give one sample per station for eight of the stations; however, the metal samples were individually analyzed. In the case of the remaining station (#4), the four individual samples were analyzed for both organics and metals.

Point sources

Industrial samples were collected by R.I. Department of Environmental Management (DEM) personnel during the river sampling period, and were 24 hour composite samples. These samples were stored in glass and polyethylene containers like those of the river samples.

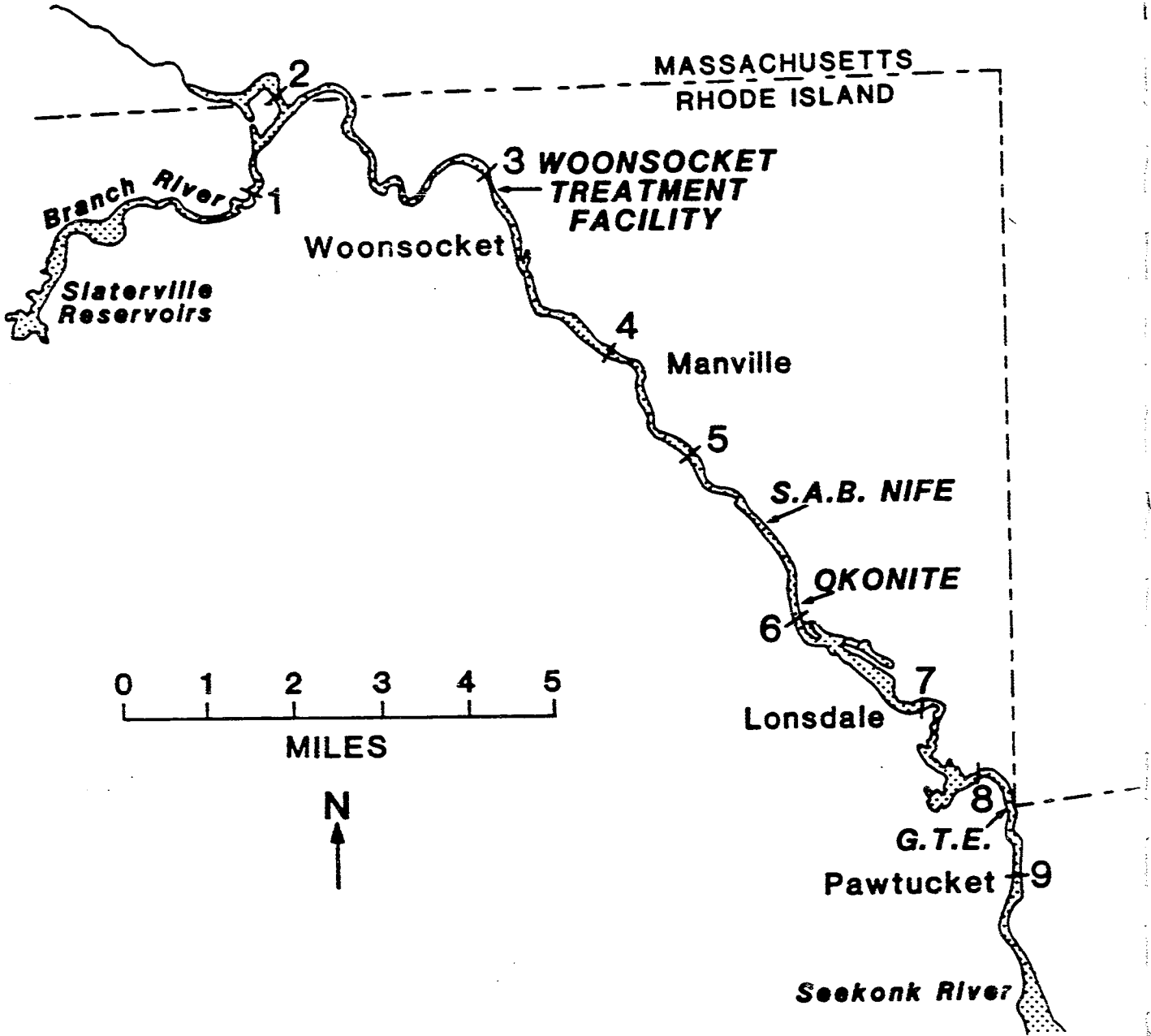


Figure II-1. Sampling locations on the Blackstone River.

III. METHODS

A. ORGANICS (see Figure III-1)

Filtration and extraction

Shortly upon return to the laboratory, the water samples were filtered through precombusted and preweighed glass fiber filters (Whatman GF/C, particle size retention of 1.2 μm). In the case of municipal and industrial samples, the amount was about 4 liters and ca 4 filters were used; for the river samples, the volume was usually 12 liters and this also required ca 4 filters. After drying to constant weight at room temperature, the filters were reweighed to determine the amount of suspended solids (SS) in each sample and then stored at -20°C .

Internal standards were added to each filtrate (dissolved-soluble components) and these solutions were extracted once with a 10% volume of dichloromethane in the original glass sample container. The organic extracts were then isolated, solvent exchanged with hexane and reduced in volume on a rotary evaporator under reduced pressure at $<30^{\circ}\text{C}$, and stored at room temperature.

The filters for each sample were shredded and transferred to a round bottom flask. Internal standards were then added followed by 50 to 200 ml of methanol, depending on the type and size of the sample. This mixture was refluxed for 2 hrs, cooled, and decanted into a separatory funnel. The sample was rinsed with petroleum ether and the rinse was combined with the filtrate in the separatory funnel which also contained distilled water in a volume equal to or greater than that of the methanol added to the sample. The water-methanol mixture was extracted 3 times with petroleum ether and the extracts were

combined and reduced to ca 15 ml using rotary evaporation and stored at room temperature.

Separation

All extracts were separated into three fractions by silica gel chromatography using a method modified from Pruell and Quinn (1985). According to this procedure, the sample was reduced in volume to ca 2 ml and charged to a 0.5 cm x 10 cm column of fully activated silica gel (Grace Grade 922) using nitrogen to produce a flow rate of ca 5 ml/minute. The first fraction (f_1) was eluted with 15 ml of petroleum ether and contains saturated petroleum hydrocarbons. The second fraction (f_2) was then eluted with 15 ml of 80:20 petroleum ether:dichloromethane. This fraction contains unsaturated petroleum hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) with 2-6 fused rings. Phthalic acid esters and coprostanol were eluted into the third fraction (f_3) using 15 ml of 80:20, dichloromethane:ethyl acetate. In addition, the polychlorinated biphenyls (PCBs) and hexachlorocyclohexanes (HCHs) were obtained by charging a known amount of sample to a silica gel column and eluting with 80:20 petroleum ether:dichloromethane. In some cases, a second silica gel column (98:2; petroleum ether; dichloromethane) was required to clean up the PCB fraction.

Analyses

Each fraction was concentrated on a rotary evaporator and analyzed on one of several different Hewlett-Packard gas chromatographs (GC). The f_1 was processed using a 5840A GC (FID) equipped with a 0.25mm i.d. x 15 m DB-5 (0.25 μ m; J & W, Inc.) fused silica capillary column with helium as the carrier gas (ca 1 ml/min) and temperature programmed from 35 to 290°C at 8°C/min. Second fractions (f_2) were

analyzed under similar conditions on a 5890 GC. The f_3 was measured on a 5710A GC (FID) using a 30 m DB-1701 (J & W, Inc.) column which was programmed from 150 to 290°C at 4°C/min with a helium flow of ca 1 ml/min. PCBs were analyzed on a 5710A GC (ECD) using a 30 m DB-5 column programmed from 100-290°C at 8°C/min with a helium flow of 1 ml/min.

Resolved peaks were quantified against the internal standards using Hewlett Packard integrators (3388A and 3390A). The unresolved complex mixture (UCM) in f_1 and f_2 was measured by planimetry and its area compared to that of the *n*-docosane (*n*-C₂₂) and *m*-terphenyl internal standards, respectively. Total petroleum hydrocarbons (HC) include the resolved and unresolved components in both fraction 1 (saturated hydrocarbons) and fraction 2 (unsaturated hydrocarbons). The 16 priority pollutant PAHs in f_2 were also quantified against *m*-terphenyl. Those components in f_3 were measured using the *n*-tricosanol (*n*-C_{23OH}) internal standard; they included three priority pollutant phthalates, (butyl benzyl-, bis(2-ethylhexyl-), and di-*n*-octyl-), and coprostanol. The PCBs were quantified against octachloronaphthalene internal standard using 4 peaks from each Aroclor mixture (i.e. 1248, 1254 and 1260). The organochlorine pesticides (HCHs - 3 isomers) were also quantified using this internal standard. For purposes of discussion, the saturated and unsaturated HC are summed and called total HC; the 16 PAHs are summed and called total PAHs; the three phthalates are summed and called total phthalates; and the PCB mixtures are summed and called total PCBs.

Several samples were initially analyzed without the addition of internal standards in order to assess the background levels of these compounds. In all cases the background levels were insignificant when

compared with the amount of internal standard added. Authentic standards were obtained for all of the individual compounds analyzed. Peak identification by retention time was confirmed by gas chromatography-mass spectrometry for selected samples. This instrumentation included a Finnigan 4531 GC-MS with a Nova 3 computer and a 30 m DB-5 fused silica capillary column (J & W, Inc.) and it was located at the Environmental Research Laboratory, EPA/Narragansett.

B. METALS (refer to Figure III-2)

Analyses

A known volume of 5% HNO₃ (Baker-Ultrex) was added to the filters, containing the particulate components of the river samples, to leach the metals (one week) from the particulate substrate. Cadmium, chromium, copper, lead, nickel, and silver were analyzed directly by flameless atomic absorption spectrophotometry (AAS). Metals dissolved in the acidified filtrate were analyzed directly by AAS.

Analyses were performed on a Perkin Elmer model 603 atomic absorption spectrophotometer equipped with a model 400 heated graphite atomizer and an As-40 auto injector, utilizing D₂ arc background correction in order to minimize spectral interferences. Instrument parameters depended upon the specific metal being analyzed as well as the analyte concentration, but were in accordance with the manufacturer's guidelines.

Quantification was based upon calibration curves of standard solutions of metals made up in the approximate acid proportion as the samples. These calibration curves were determined several times daily during the period of analyses.

C. QUALITY ASSURANCE

Detailed information on the work/quality assurance plan for this project has been submitted to the Narragansett Bay Project Monitor, EPA Project Officer and EPA QA Coordinator on March 18, 1986. A copy of this plan is included in Appendix D of this report.

The data used in the preparation of this plan was obtained from a large data base obtained in our laboratory over the past 10 years. During the course of the work on the Blackstone River project, additional studies were undertaken to update the work/quality assurance plans for our laboratory. The results of these investigations were in good agreement with previously reported values that are cited in Appendix D.

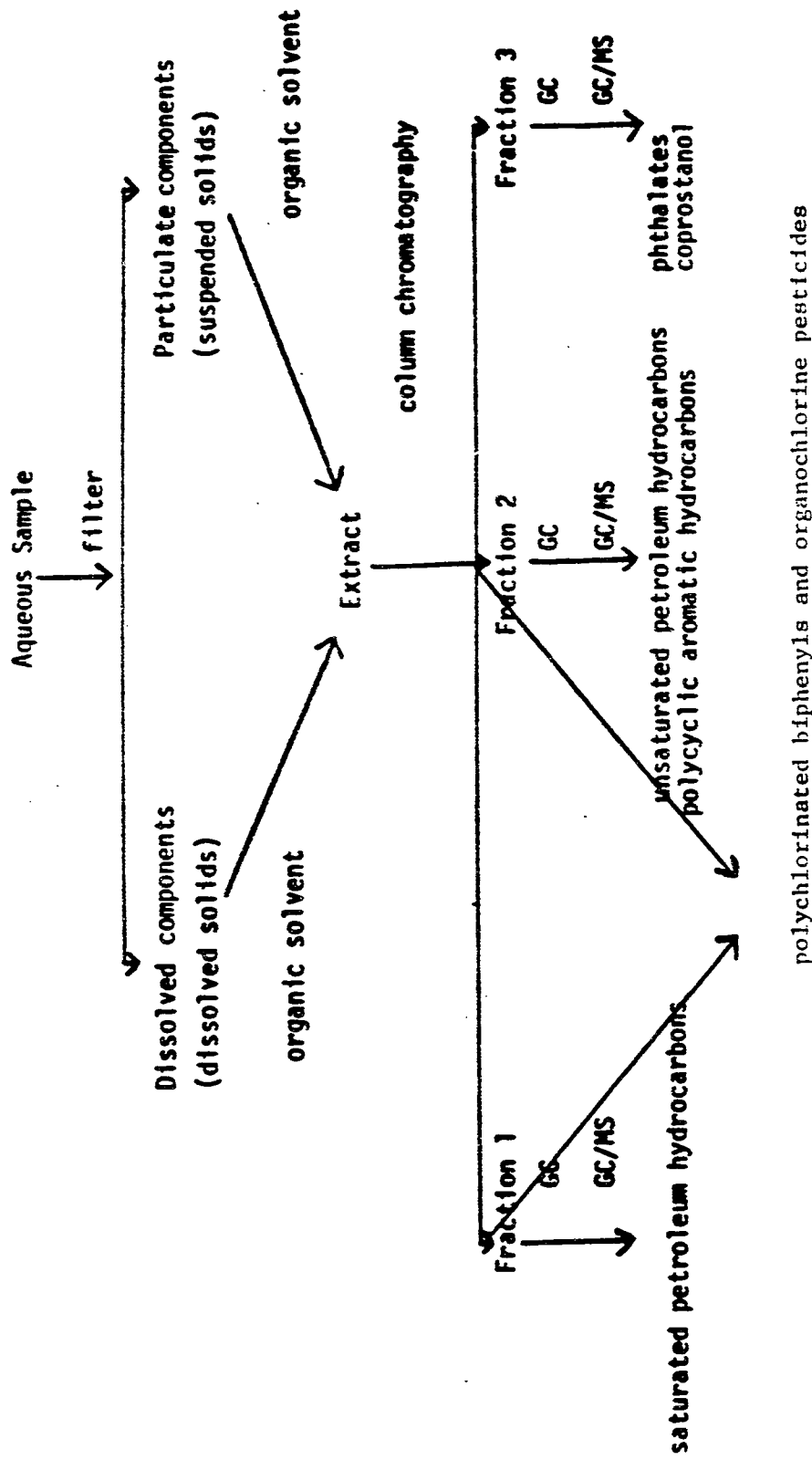
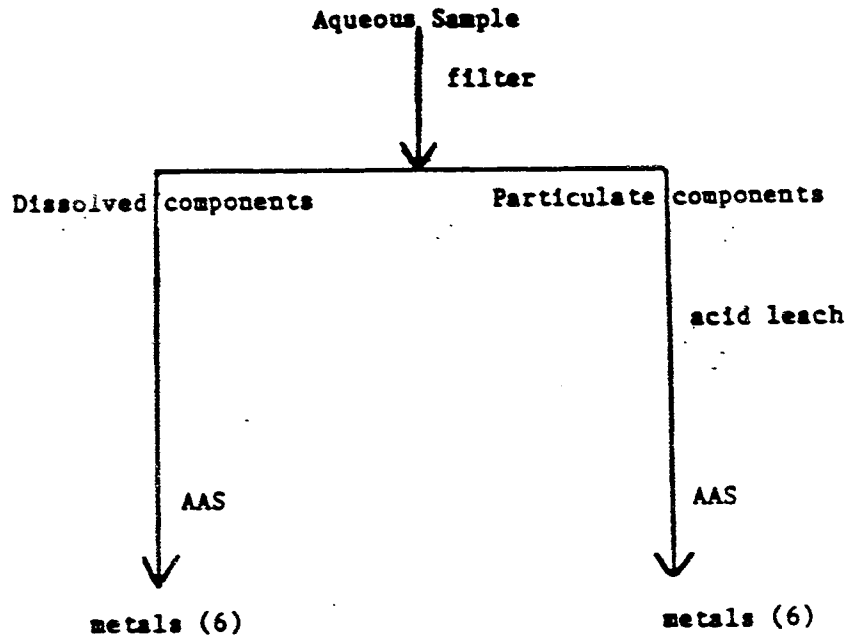


Figure III-1. Flow chart for the analyses of organic compounds.



- Cadmium
- Chromium
- Copper
- Lead
- Nickel
- silver

Figure III-2. Flow chart for the analyses of metals.

IV. POINT SOURCES

A. ORGANICS (combined soluble and particulate fractions).

The results for the effluent analyses of the four point sources sampled in this study are given in Table IV-1 and the complete data for the three sampling dates are in Appendix A, Tables 1-16.

Woonsocket Wastewater Treatment Facility

Suspended solids (SS) values for the Woonsocket plant tripled from the first to the third survey even though flow was relatively constant (see A-19 for flow data). The average ss concentration was 38.4 ± 17.6 mg/l (RSD = 46%).

The concentrations of total hydrocarbons (HCs) detected in the Woonsocket effluent were relatively high on all three sampling dates; the majority of these HCs were associated with the particulate fraction and were similar to fuel oils. Woonsocket had the highest levels of total HCs on all three sampling dates. The average HC concentration (769 ± 231 ug/l) was determined to be statistically higher ($P < 0.05$) than the average concentrations observed in any of the other point source effluents.

The total PAH values detected in the Woonsocket effluent were relatively low and followed a similar trend as HCs, with the highest concentration, observed on the second sampling date, being just over 1 ug/l. The average concentration of total PAHs was 0.59 ± 0.44 ug/l.

The concentrations of coprostanol in the Woonsocket effluent were the largest of any of the point sources sampled; however, it was low relative to other treatment plants that have been previously monitored (Quinn et al., 1985). The values decreased by a factor of

3.5 from the first to the last sampling date and the average concentration of coprostanol was 8.72 ± 5.26 ug/l.

The Woonsocket plant had the highest concentration of total phthalates on all three sampling dates. The average concentration (197 ± 46 ug/l) was determined to be statistically higher ($P < 0.05$) than the average concentrations detected in all the other point source effluents.

Throughout the study, no polychlorinated biphenyls (PCBs) could be positively determined; however, in some of the samples there were a significant number of interfering compounds which precluded the determination of PCBs.

Of the point sources sampled, the highest concentrations of hexachlorocyclohexanes (HCHs) were observed at the Woonsocket facility. Lindate (g-HCH) was the major isomer detected on all three dates. The other two HCH isomers (a and b) usually followed a concentration trend similar to that of g-HCH over the three dates. All HCHs were found to be exclusively in the dissolved fraction of the samples.

Okonite

The Okonite effluent had the lowest point source concentration of SS on all three sampling dates. The highest value observed was 1.79 mg/l on the third survey and the mean value was 0.91 ± 0.76 mg/l.

The Okonite plant had small concentrations of total HCs (average concentration of 13.0 ± 3.9 ug/l). These HCs appeared to consist of petroleum products, including fuel oils.

The concentrations of total PAHs detected in the Okonite effluent were very low on all three sampling dates. The average concentration of total PAHs (0.26 ± 0.19 ug/l) was the lowest of all the point sources.

Coprostanol was not detected in any of the effluent samples from Okonite.

The levels of phthalates detected in the Okonite effluent ranged from 64 to 106 ug/l throughout the study. The average concentration was 81 ± 22 ug/l.

PCBs were detected only in the sampling of 8/20/86 with a total value of 7.55 ng/l; on all the other dates, no PCBs were observed. The PCBs detected were about evenly split between the particulate and dissolved fraction of the sample. In the soluble fraction, Ar 1248 and 1254 made up most of the PCBs present, while in the particulate fraction, they were evenly distributed between Ar 1254 and 1260. This is a consequence of the decreasing water solubility of the compounds as the number of chlorine atoms are added to the molecule.

The concentration of the HCHs were less than 1 ng/l with g-HCH being slightly higher than the other two isomers. Only minor changes in the concentrations could be seen over the sampling dates.

Corning/G.T.E.

This plant was on vacation during the first sampling and thus had only a small effluent discharge at that time. Therefore, compared to the other dates the concentration of SS was low (13.2 mg/l). The concentrations rose dramatically during the second and third surveys (293 and 635 mg/l, respectively), giving the GTE effluent the highest concentration of suspended solids on those two dates.

The concentrations of total HCs also reflected the fact that the plant was on vacation during the first survey. The levels detected increased on the second and third dates by factors of 5.7 and 7.2, respectively, over those observed in the first survey (HCs = 19.2

ug/l). The HCs appeared to consist of petroleum products, especially fuel oils.

The levels of total PAHs detected in GTEs effluent increased by a factor of 7.8 from the first to the third survey. This plant had the highest levels of PAHs; however, the highest concentration observed was only 4.54 ug/l.

Coprostanol was detected only in the second survey at a concentration of 1.16 ug/l.

The concentrations of total phthalates in GTE's effluent were quite variable with the highest concentration observed on the second sampling date.

No PCBs were detected in the sample collected on the 7/8/85 survey. There were, however, PCBs observed on the last two surveys and the concentration was much higher on 8/20/85 than on 10/8/85. On both of these dates, the PCBs were found to be exclusively in the particulate fraction. On 8/20/85, Aroclor 1248, 1254 and 1260 were present in about equal concentrations in the sample; however, on 10/8/85, only Ar 1254 was detected. Because of the particularly high value on the 8/20/85 sampling date (37 ng/l) the overall average of the concentrations makes G.T.E. the largest contributor of PCBs to the Blackstone River.

Only the 7/8/85 sample contained HCHs. In this sample, the major component was b-HCH with g-HCH at a much lower level.

S.A.B. Nife

The S. A. B. Nife company was on vacation during the first two sampling surveys and effluents were not collected on those two dates.

The concentration of SS observed in the Nife effluent on the third sampling date (25.9 mg/l) was relatively small.

The Nife plant had a low concentration of total HCs on the third survey. The HCs detected were associated with the soluble fraction and appeared to consist of petroleum products, especially fuel oils.

The PAHs detected in the Nife effluent were also associated with the soluble fraction. The concentration of total PAHs was a relatively high level of 3.20 ug/l, compared with the other point sources.

Coprostanol was not detected in the Nife effluent.

The concentration of total phthalates detected in the Nife effluent (4.51 ug/l) was the lowest of all the point sources on the third sampling date.

No PCBs were detected in this effluent.

Three HCHs were detected in the sample with g-HCH having the highest concentration (5.79 ng/l).

Summary

The average concentrations of total HCs and total phthalates were statistically higher in the Woonsocket effluent than the other point sources. The Woonsocket plant also had the highest concentrations of coprostanol and HCHs in its effluent. G.T.E. had the overall highest levels of suspended solids, total PAHs and total PCBs in its effluent. The Okonite effluent generally showed low concentrations of all components. The Nife effluent had low levels of most organic compounds except for the HCHs. Nife and the Woonsocket treatment facility had the highest levels of HCHs, and the municipality also had the highest levels of PAHs.

B. METALS

The results for metals in both the dissolved and particulate fractions of the effluent samples are given in tables IV-2 through IV-5 and the complete data for the three sampling dates are in Appendix B, tables 1-18.

Woonsocket Wastewater Treatment Facility (Table IV-2).

The concentrations of total cadmium were similar in the samples collected on the first two dates but increased by about a factor of two on 10/8/85; the range was from 0.29 to 0.58 ug Cd/l with an average of 0.40 ug Cd/l. Most of this metal was found in the dissolved fraction ($x = 83\%$). No previous data on cadmium, above the analytical detection limits, could be found.

Chromium was observed to be highest on 8/20/85 and lowest on the 7/8/85 survey with the average concentration being 13.3 ug Cr/l. For the first and the last sampling dates, chromium was strongly associated with the particulate phase while on 8/20/85 it was more associated with the dissolved fraction. Overall, the dissolved fraction had 40% of the total. The concentration values obtained in this study were slightly lower than had been observed in the past (DEM, 1983, 21 ugCr/l).

The concentrations of copper were similar on the three sampling dates with an average of 77.8 ug Cu/l and a variation of 14%. Copper was found to be mostly associated with the dissolved fraction ($x = 80\%$).

The concentration of lead at this facility was extremely variable ranging from 1.11 to 21.1 ug Pb/l; an average of 10.6 ug Pb/l was obtained with a variation of 94%. The variation was observed to be mostly related to the dissolved concentration which contained from 0 to

63% of the observed metal and averaged 41%. The values obtained in the present study were similar to those determined in a 1983 study by DEM (i.e. 7 ug Pb/l).

Greater than 90% of the nickel detected in the samples was found in the dissolved fraction ($x = 93\%$) and the concentration ranged from 16.6 to 40.2 ug Ni/l, with an average of 25.4 ug Ni/l. These values were slightly lower than those previously observed for the facility (i.e. 40 to 87 ug Ni/l; DEM, 1983).

The silver concentration ranged from 0.67 to 1.78 ug Ag/l for the samples with an average of 1.18 ug Ag/l. These values were similar to previous data which indicated concentrations of from 1 to 3 ug Ag/l in a study in 1980 (DEM, 1980). The silver was found to be detected mostly in the particulate fraction with an average of only 16% in the dissolved phase.

The metal concentrations and fractionations determined in the present study at the Woonsocket plant were comparable with data from the Pawtuxet River treatment facilities as well as other secondary facilities in this country and Canada (Hoffman et al., 1986; Quinn et al., 1985; Nielsen and Hrudý, 1983; and Rossin et al., 1983).

Okonite (Table IV-3)

The cadmium data from Okonite exhibited considerable variation over the three sampling dates with an overall variation of 94%. The average concentration was 0.27 ug Cd/l with most of the cadmium being found in the dissolved phase of the samples ($x = 88\%$). As with the Woonsocket Wastewater Treatment Facility, no previous data was found that was above the detection limits and there is no limitation for cadmium in this effluent.

The data for chromium were also variable ranging from none detected (<0.1 ugCr/l) to 1.5 ug Cr/l ($\bar{x} = 0.70$ ug/l). The partitioning also showed variability; in the 8/20/85 sample, essentially all of the chromium that was detected was in the particulate fraction while in the 10/8/85 sample, it was exclusively in the dissolved fraction.

The concentrations of copper in the effluent were similar on all three dates, exhibiting a coefficient of variation of only 14% and the dissolved fraction contained 92% of the copper determined in the samples. Although no previous data could be cited for copper analysis, Okonite is limited to a daily maximum of 100 ug Cu/l by a RIPDES permit (Table IV-6). The observed data ($\bar{x} = 41$ ugCu/l) was well below this level.

There was considerable variation in the concentrations and in the fractionation of lead in the samples taken at the Okonite site (1.17 - 17.8 ug Pb/l). The variation was observed to be due to the dissolved levels of the metal. The first and last samples showed lead to be highly associated with the particulate fraction of the sample; while in the 8/20/85 sample, the lead was strictly found in the dissolved fraction. The average concentration of lead was 7.1 ug Pb/l.

The concentrations of nickel in the first two samples were very similar with none detected in the dissolved fractions. In contrast, the concentration in the last sample was about ten times greater than the first two with most of the nickel detected in the dissolved phase.

All of the silver detected in the samples was found to be in the particulate fraction and none of the concentrations were above 0.03 ug Ag/l. The data was also relatively constant with only a 41% variation over the three dates.

G.T.E. (Table IV-4)

The cadmium concentration in the discharge from G.T.E. ranged from 0.05 to 1.06 ug Cd/l with an average of 0.57 ug Cd/l. There was a substantial variation in the fractionation pattern for cadmium although in all the samples at least 60% of the metal was in the dissolved fraction ($x = 82\%$). All previous data were consistent with the results of the present study, and in these analyses the concentration of cadmium at G.T.E. was found to be less than a 5 ug Cd/l detection limit.

The results for chromium show a wide range in the concentration over the three sampling dates; the values increased by a factor of over 7 in comparison with that of the first date. There was also a change in the partitioning of the metal in which the concentration shifted from being mostly in the particulate phase on the second date (8/20/85) to the dissolved phase in the 7/8/85 and 10/8/85 samples. The chromium concentration on the last two dates exceeded the allowed level for the daily maximum as set by the RIPDES, of 100 ug Cr/l (for CR-VI, see Table IV-6) and previous data for chromium determined by DEM (1983 i.e. 110-310 ugCr/l) were similar to the values observed in the present study.

The concentration of copper was somewhat variable with an average value of 81.5 ug Cu/l and a variation of 95%. These values agree reasonably well with a DEM analysis done in 1983 in which the concentration was found to be 70 ug Cu/l. In the present study, copper was found to be mostly (88%) associated with the dissolved fraction of the samples.

Lead concentrations were somewhat variable over the sampling period and ranged from none detected (<0.1 ugPb/l) to 5.9 ug Pb/l. The percent of the metal in each fraction was very different with most of the lead determined in the particulate fraction in the 8/20 sample, while most of it was found in the dissolved in the 10/8 sample. The concentrations observed in the present study were consistent with those of a sample taken in 1983 in which 5 ug Pb/l was detected. Furthermore, the concentrations of lead determined in the samples were well below the limit of 100 ug Pb/l set by the RIPDES permit (Table IV-6).

The concentrations of nickel were relatively constant over the study period; the average concentration was 22.9 ug Ni/l with a variation of 48% for the three samples, and most of the nickel was detected in the dissolved fraction of the sample (\bar{x} = 94%). Previous data indicated that the concentration of the effluent was less than 20 ug Ni/l (DEM, 1983).

Silver showed substantial variability in both concentration and partitioning for the three samples. The partitioning ranged from 40 to 94% in the dissolved fraction (\bar{x} = 63%). The average silver concentration was 13.8 ug Ag/l with a relative standard deviation of over 107%. None of the samples exceeded the RIPDES level of 100 ug Ag/l (daily maximum, Table IV-6); furthermore, the values were consistent with previous data which indicated concentrations of from 1 to less than 25 ug Ag/l (DEM, 1983).

S.A.B. Nife (Table IV-5)

Only one sample was collected at the Nife site because the company was on vacation and clearly one sample was not adequate to characterize the effluent. It was observed, however, that the

concentrations of all the metals were far below those determined previously by DEM in 1983. For example, the sample collected on 10/8/85 showed only a concentration of 3.8 ug Ni/l, which was considerably lower than the concentration of 420 ug Ni/l determined by DEM on 10/7/83; furthermore, this was well below the limit set by the RIPDES of 500 ug Ni/l (daily maximum, Table IV-6). The reasons for the discrepancies are unknown.

Summary

All of the monitored point sources along the Blackstone River showed relatively similar concentrations of cadmium and lead over the course of the study (excluding Nife, which had no lead detected in the only sample collected). The majority of the cadmium was in the dissolved fraction and the lead tended to be in the particulate phase of the samples. It appears that G.T.E. had significantly higher levels of chromium and silver (both were mostly dissolved) than the other sources along the river, and together with the Woonsocket Waste Water Treatment Facility, G.T.E. had somewhat higher levels of copper and nickel (both mostly dissolved) than the other sources. Based on a single sample, Nife had surprisingly low levels of all the metals relative to RIPDES values.

Table IV-1. Average concentrations of organic compounds in the point source effluents on the three sampling dates.

I. Woonsocket STP

Date	Suspended solids (mg/l)	HC (ug/l)	PAH (ug/l)	Coprostanol (ug/l)	Phthalates (ug/l)	PCB (ng/l)	HCHs (ng/l)		
							a	b	g
7/8/85	18.6	504	0.20	14.5	250	ND	2.04	5.92	19.0
8/20/85	44.2	932	1.07	7.46	169	ND	9.45	9.11	14.8
10/8/85	52.3	870	0.51	4.20	173	ND	1.58	0.59	4.24
x+s.d.	38.4+17.6	769+231	0.59+0.44	8.72+5.26	197+46	ND	4.36	5.21	12.7
							+4.42	+4.30	+7.60

II. Okonite

Date	Suspended solids (mg/l)	HC (ug/l)	PAH (ug/l)	Coprostanol (ug/l)	Phthalates (ug/l)	PCB (ng/l)	HCHs (ng/l)		
							a	b	g
7/8/85	0.40	14.2	0.33	ND	106	ND	0.39	ND	0.56
8/20/85	0.54	16.2	0.40	ND	64.1	7.55	0.38	0.34	0.71
10/8/85	1.79	8.63	0.04	ND	72.9	ND	0.61	ND	0.77
x+s.d.	0.91+1.76	13+3.9	0.26+1.19	ND	81+22	2.52+4.36	0.46	0.11	0.68
							+0.13	+0.20	+0.11

III. G. T. E.

Date	Suspended solids (mg/l)	HC (ug/l)	PAH (ug/l)	Coprostanol (ug/l)	Phthalates (ug/l)	PCB (ng/l)	HCHs (ng/l)		
							a	b	g
7/8/85	13.2	19.2	0.58	ND	2.12	ND	ND	3.26	0.14
8/20/85	293	109	1.12	1.16	97.6	37.0	ND	ND	ND
10/8/85	635	138	4.54	ND	36.7	5.94	ND	ND	ND
x+s.d.	314+311	88.7+62	2.08+2.15	0.39+1.67	45.5+48	14.3+19.9	ND	1.09	0.05
							+1.88	+0.08	

IV. Nife

Date	Suspended solids (mg/l)	HC (ug/l)	PAH (ug/l)	Coprostanol (ug/l)	Phthalates (ug/l)	PCB (ng/l)	HCHs (ng/l)		
							a	b	g
7/8/85	NC	NC	NC	NC	NC	NC	NC	NC	NC
8/20/85	NC	NC	NC	NC	NC	NC	NC	NC	NC
10/8/85	25.9	5.05	3.02	ND	4.51	ND	0.49	1.81	5.79
x+s.d.	25.9	5.05	3.02	ND	4.51	NC	0.49	1.81	5.79

ND = None detected;

NC = not collected.

Table IV-2. Trace metal data for the Woonsocket Wastewater Treatment Facility (ug/l)

Date	Cadmium				Chromium			
	Dissolved	Particulate	Total	% D	Dissolved	Particulate	Total	% D
7-8-85	0.24	0.05	0.29	83	1.65	4.47	6.12	27
8-20-85	0.27	0.05	0.32	84	13.8	8.72	22.5	61
10-8-85	0.48	0.10	0.58	83	3.64	7.72	11.4	32
Average	0.33	0.07	0.40	83	6.36	6.97	13.3	40
Std. Dev.	0.13	0.03	0.16	1	6.52	2.22	8.4	19
RSD %	39.4	42.0	39.8	1	102	31.9	62.8	46
	Copper				Lead			
	Dissolved	Particulate	Total	% D	Dissolved	Particulate	Total	% D
7-8-85	67.3	10.5	77.8	87	N.D.	1.11	1.11	
8-20-85	78.6	10.0	88.6	89	13.4	7.75	21.2	63
10-8-85	44.3	22.9	67.1	66	5.67	4.00	9.67	59
Average	63.4	14.5	77.8	80	6.36	4.29	10.6	41
Std. Dev.	17.50	7.31	10.71	13	6.73	3.33	10.1	35
RSD %	27.6	50.6	13.8	16	106	77.7	94.5	87
	Nickel				Silver			
	Dissolved	Particulate	Total	% D	Dissolved	Particulate	Total	% D
7-8-85	15.6	0.96	16.6	94	0.60	1.18	1.78	34
8-20-85	38.6	1.55	40.2	96	N.D.	1.09	1.09	
10-8-85	17.49	2.00	19.5	90	0.10	0.57	0.67	15
Average	23.9	1.50	25.4	93	0.23	0.95	1.18	16
Std. Dev.	12.8	0.52	12.9	3	0.32	0.33	0.56	17
RSD %	53.4	34.6	50.6	4	138	34.9	47.5	104

N.D. = None detected

Table IV-3. Trace metal data for Okonite Co. (ug/l)

Date	Cadmium				Chromium			
	Dissolved	Particulate	Total	% D	Dissolved	Particulate	Total	% D
7-8-85	0.05	0.02	0.07	71	N.D.	N.D.	N.D.	
8-20-85	0.51	0.04	0.55	93	N.D.	0.60	0.60	
10-8-85	0.18	0.00	0.18	100	1.50	0.00	1.50	100
Average	0.25	0.02	0.27	88	0.50	0.20	0.70	29
Std. Dev.	0.24	0.02	0.25	15	0.87	0.35	0.75	46
RSD %	95.4	100	94	17	0.76	173	108	161
Date	Copper				Lead			
	Dissolved	Particulate	Total	% D	Dissolved	Particulate	Total	% D
7-8-85	44.5	3.22	47.7	93	0.68	1.51	2.19	31
8-20-85	33.2	3.03	36.2	92	17.0	0.80	17.8	96
10-8-85	35.9	3.51	39.4	91	0.38	0.79	1.17	33
Average	37.9	3.25	41.1	92	6.02	1.03	7.05	53
Std. Dev.	5.90	0.24	5.93	1	9.51	0.41	9.32	37
RSD %	15.6	7.37	14.4	1	158	40	132	69
Date	Nickel				Silver			
	Dissolved	Particulate	Total	% D	Dissolved	Particulate	Total	% D
7-8-85	N.D.	0.77	0.77		N.D.	0.02	0.02	
8-20-85	N.D.	0.80	0.80		N.D.	0.03	0.03	
10-8-85	7.24	0.25	7.49	97	N.D.	0.01	0.01	
Average	2.41	0.61	3.02	32	N.D.	0.02	0.02	
Std. Dev.	4.18	0.31	3.87	56	N.D.	0.01	0.01	
RSD %	3.41	51.1	128.2	173	N.D.	40.7	40.7	

N.D. = None detected

Table IV-4. Trace metal data for GTE Co. (ug/l)

Date	Cadmium				Chromium			
	Dissolved	Particulate	Total	% D	Dissolved	Particulate	Total	% D
7-8-85	0.03	0.02	0.05	60	52.7	6.52	59.2	89
8-20-85	0.93	0.13	1.06	88	36.5	114	151	24
10-8-85	0.59	0.02	0.61	97	388	46.8	435	89
Average	0.52	0.06	0.57	82	159	55.8	215	67
Std. Dev.	0.45	0.06	0.51	19	198	54.3	196	38
RSD %	86.5	100	89.5	23	125	97.3	91.2	57
Date	Copper				Lead			
	Dissolved	Particulate	Total	% D	Dissolved	Particulate	Total	% D
7-8-85	22.2	1.31	23.5	94	N.D.	N.D.	N.D.	
8-20-85	121	48.3	169	72	N.D.	5.90	5.90	
10-8-85	50.5	1.37	51.9	97	2.31	0.30	2.61	89
Average	64.6	17.0	81.5	88	0.77	2.07	2.84	45
Std. Dev.	50.9	27.1	77.1	14	1.33	3.32	2.96	63
RSD %	78.8	159	94.6	16	173	160	104	140
Date	Nickel				Silver			
	Dissolved	Particulate	Total	% D	Dissolved	Particulate	Total	% D
7-8-85	9.77	0.79	10.6	92	10.1	0.72	10.8	94
8-20-85	24.1	2.57	26.7	90	16.5	13.4	29.9	55
10-8-85	31.1	0.19	31.3	99	0.32	0.49	0.81	40
Average	21.7	1.18	22.9	94	8.97	4.87	13.8	63
Std. Dev.	10.9	1.24	10.9	5	8.15	7.39	14.8	28
RSD %	50.2	105	47.6	5	90.9	152	107	44

N.D. = None detected

Table IV-5. Trace metal data for Nife Co. (ug/l)

Date	Cadmium				Chromium			
	Dissolved	Particulate	Total	% D	Dissolved	Particulate	Total	% D
7-8-85					<i>NOT COLLECTED</i>			
8-20-85					<i>NOT COLLECTED</i>			
10-8-85	0.27	0.02	0.29	93	N.D.	N.D.	N.D.	
Date	Copper				Lead			
	Dissolved	Particulate	Total	% D	Dissolved	Particulate	Total	% D
7-8-85					<i>NOT COLLECTED</i>			
8-20-85					<i>NOT COLLECTED</i>			

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Blackstone River 181 pp.

Quinn, Latimer, Carey, Ellis, & Zheng (URI)

Narragansett Bay Estuary Program