

FATE AND TRANSPORT OF CONTAMINANTS IN THE HYPORHEIC ZONE

Daniel O'Rourke

Department of Geosciences
State University of New York at Stony Brook
Stony Brook, NY 11794-2100

Ronald J. Paulsen

Suffolk County Department of Health Services
Bureau of Water Resources
220 Rabro Drive East Hauppauge, NY 11788

Teng-fong Wong

Department of Geosciences
State University of New York at Stony Brook
Stony Brook, NY 11794-2100

Abstract

The fate and transport of metals and volatile organic compounds at two field sites were observed and characterized at the coastline and the hyporheic zone. Metal concentrations were determined at West Neck Bay, both at the coastline and up to 90 ft offshore. Qualitatively, it appears that the groundwater discharging into West Neck Bay is composed of three components. These components result from groundwater originating near the coast, at a landfill approximately 1200 ft upgradient, and from residential areas further inland on Shelter Island. Comparison with an analytical flow net indicates that these observations cannot be explained by advective transport alone, and it is likely that colloidal transport plays a major role in the study area. Naphthalene concentrations entering Lawrence Creek in Bayshore, NY were also determined and a methodology is introduced at that site for determining contaminant or nutrient fluxes into a coastal environment.

Introduction

A fundamental understanding of groundwater discharge into a coastal environment has become increasingly important in recent years due to its potential effects on marine biota and the chemical balance of a coastal body (Moore, 1996; Montlucon et al, 2000; Li et al, 1999). Constituents, both dissolved and colloidal, enter a coastal body through the hyporheic zone which provides a direct route for groundwater and its constituents to impact the water chemistry. Metal analyses conducted on water samples taken from nested piezometers at the coastline and the hyporheic zone of West Neck Bay show characteristics that reflect varying land uses. A similar sampling approach has also been used in Bayshore, NY and concentrations of naphthalene were discovered entering Lawrence Creek.

The hyporheic zone varies in spatial extent and may be quite complex, especially if dredging has been done in the area. Complex zones such as these may distort flow paths due to the high degree of anisotropy and sampling methods need to consider this.

The site at Lawrence Creek reflects these complications. The West Neck Bay site is relatively undisturbed.

This paper outlines the field methods used at both sites and introduces a technique to obtain contaminant loading in the field by utilizing an ultrasonic seepage meter used by Paulsen et al (2000). Although the majority of this study involves West Neck Bay, the Lawrence Creek site is discussed as it was used to test the new technique. A preliminary analysis is given describing the likely origins of contaminants and their discharge into coastal environments.

Study Sites

West Neck Bay is located on Shelter Island, NY and is shown in Figure 1. What is unique about West Neck Bay is that with the exception of runoff, no surface waters discharge into the bay. Therefore, recharge to the bay is through precipitation and groundwater discharge. Since groundwater is a major recharge component, it plays a large role in controlling the chemistry of the bay. Since 1985, West Neck Bay has experienced blooms of the algal species *Aureococcus anophagefferens* (locally referred to as Brown Tide). It has been suggested (LaRoche et al, 1997) that groundwater is a controlling factor responsible for the blooms. Approximately 1000 - 1200 ft inland from the coastline of the study area is a landfill that is no longer active, but remains a waste depository. Along the coastline, the bay is relatively undisturbed from anthropogenic activities such as dredging.

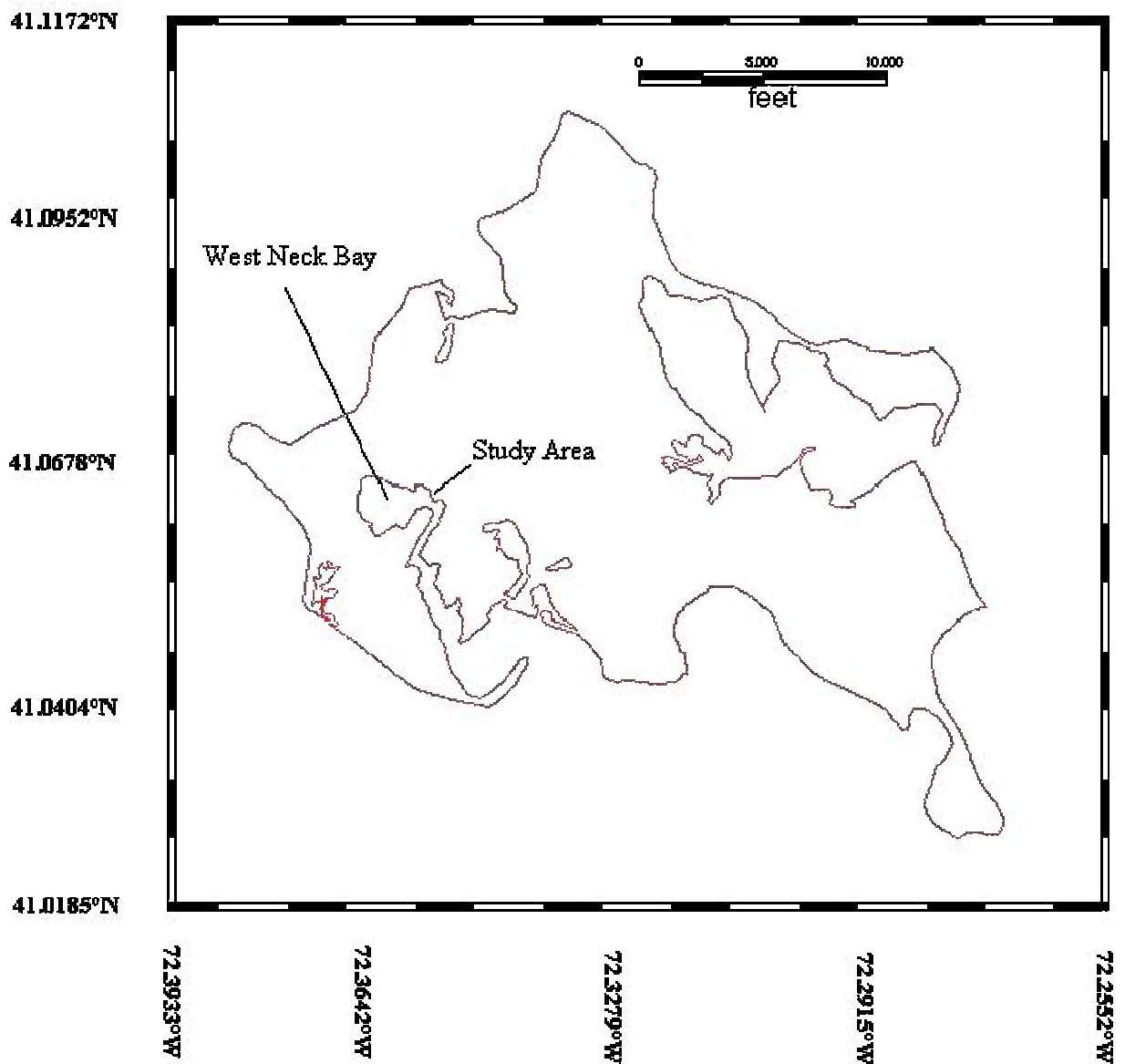


Figure 1 Location map for West Neck Bay study site.

The second site is located in Bayshore, NY near the upper reaches of the intertidal zone of Lawrence Creek (Fig. 2). The site is located down gradient of what was once the Bayshore Manufactured Gas Plant. Recently, Suffolk County Department of Health

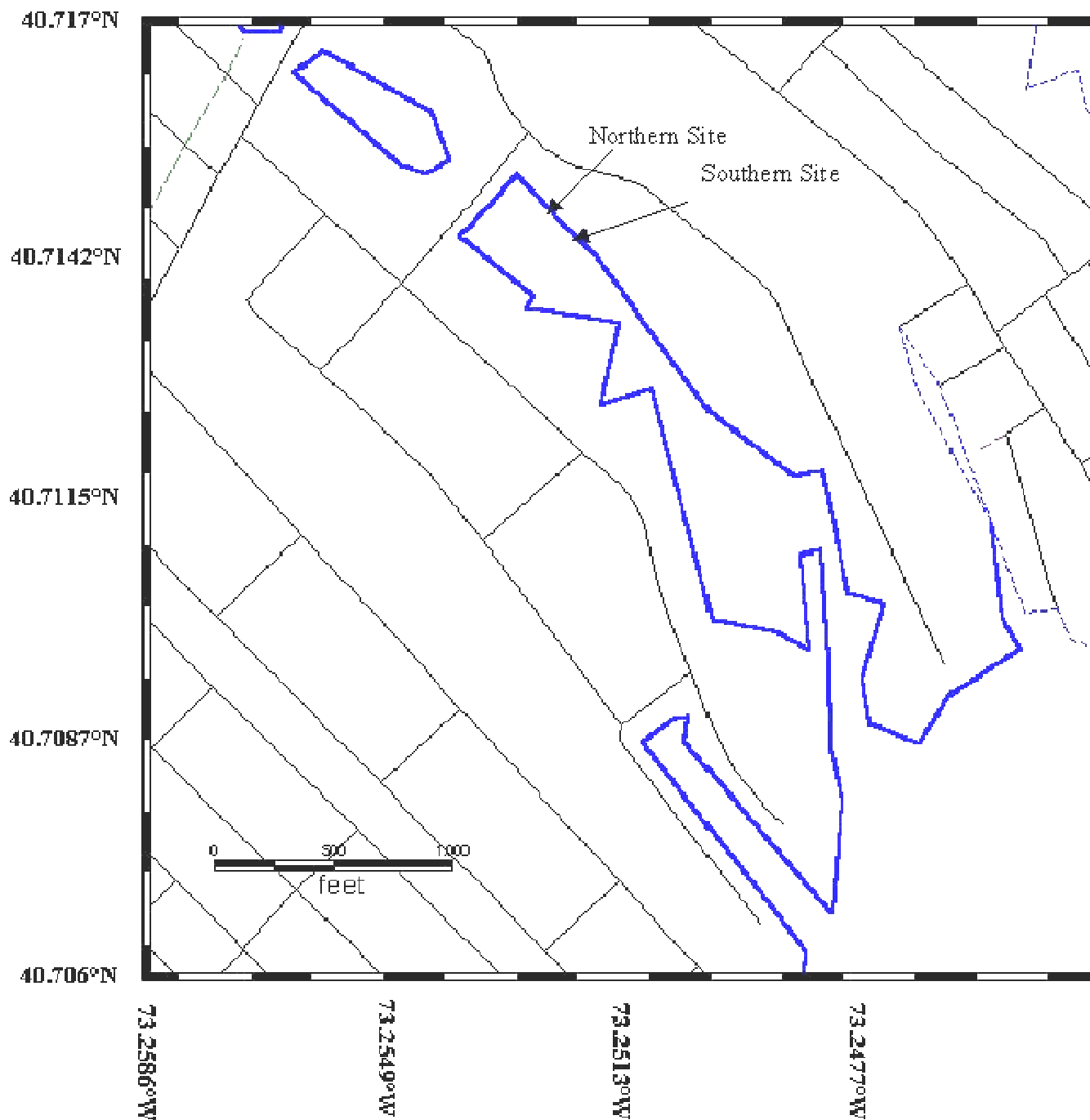


Figure 2 *Lawrence Creek location map.*

Services have been tracking the migration of a naphthalene plume that resulted from the former plant. The hyporheic zone in Lawrence Creek is more heterogeneous than that in West Neck Bay due to dredging activities involved in the installation of bulkheads along the banks of the creek.

Methods

During the early summer of 1999, three nested $\frac{3}{4}$ " PVC piezometers were installed at the coastline of West Neck Bay (Fig.1). The piezometers have screen intervals at depths of 8-12', 26-31', and 45-50', respectively, and were sampled throughout the summer in two to three week intervals. Unfiltered samples were collected following the protocol outlined by Suffolk County Department of Health Services that involves three evacuations of the water volume in the piezometer. Samples were collected using a peristaltic pump at rates ranging from 500-650 ml/min.

In addition to sampling the piezometers at the coastline, sampling was extended offshore using manually driven piezometers which have shown to be effective in collecting groundwater samples offshore (Norrstrom and Jacks, 1996; Welch and Lee, 1989). In this study, $\frac{3}{4}$ " piezometers were installed perpendicular from the coastline at distances 0, 20, 50, 90 ft. The piezometers were driven into the bottom sediments using a rubber mallet, with screen intervals approximately 1-2 ft below the sediment-water interface. The piezometer 90 ft offshore was driven an additional foot below the sediment-water interface due to a silty layer overlying coarser sediment. Pumping rates had to be sufficiently low to ensure that surface water would not intrude into the sample. Therefore, rates were approximately 100 ml/min. To further protect the sample from intruding salt water, the piezometers were modified such that a 15" diameter PVC disk was added which provided a seal at the sediment-water interface (Fig. 3). Samples collected were placed in a cooler and taken to the EPA certified laboratory of Suffolk County Department of Health Services to be analyzed for metal concentrations following EPA method 200.8.

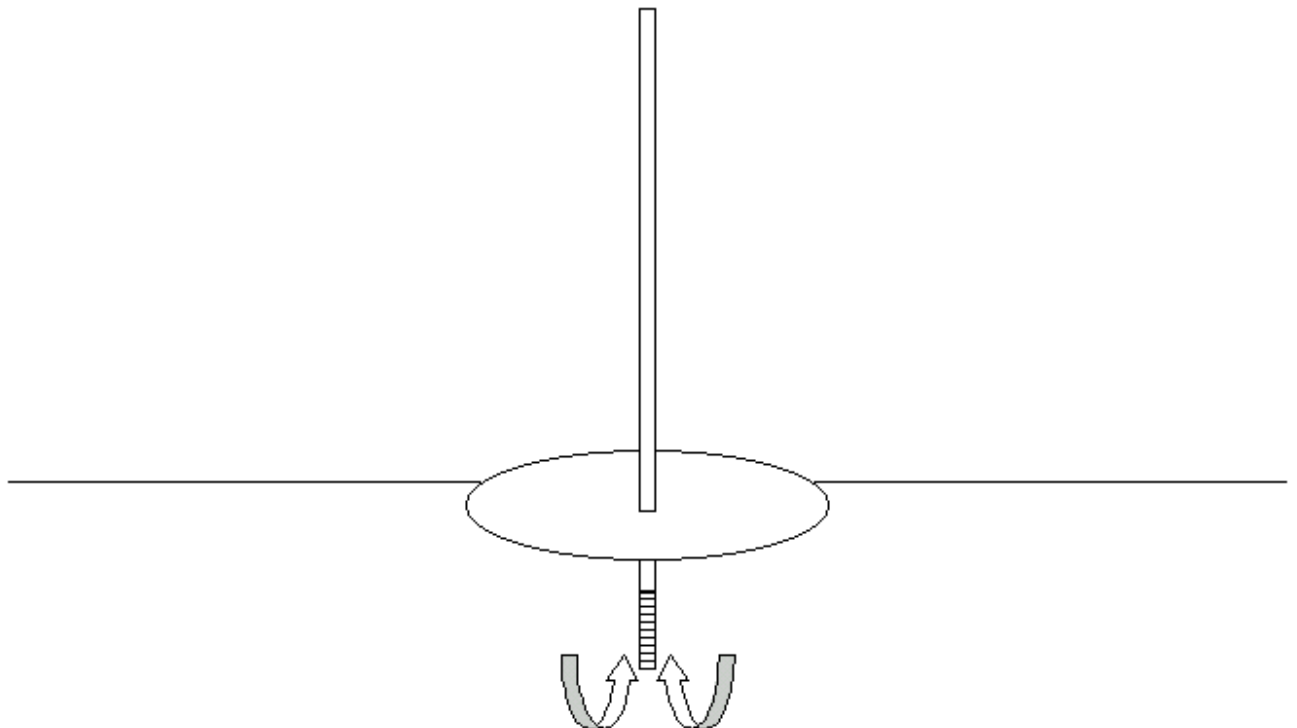


Figure 3 *Modified piezometer for offshore sampling in the hyporheic zone.*

Groundwater sampling at the Lawrence Creek site was conducted following a similar approach as West Neck Bay with the exception that water was only sampled approximately 2 ft offshore, primarily due to the lack of accessibility at further distances. However, preliminary specific discharge measurements show a very strong seepage face (inversely correlated to tide stage) close to shore (Fig. 4). Using the modified piezometers described above, porewater was sampled 1-2 ft below the sediment-water interface and along the creek bottom. Again, pumping rates were very low (approx. 90-100 ml/min) below the sediment-water interface to minimize salt water contamination. To delineate contaminant discharge areas, initial sampling was conducted at northern and southern sites along Lawrence Creek (Fig. 2).

The ultrasonic seepage meter utilized by Paulsen et al (2000) was modified in this study so that groundwater could be sampled directly from the collection device (Fig. 5). The collection funnel was lined with high-density polyethylene and stainless steel so that the funnel would not contaminate the sample. Through the top of the funnel, a polyethylene nozzle was tapped and connected to tygon tubing that allowed for sampling of the collected seepage. A valve was attached to the nozzle of the funnel and was connected via tygon tubing to the flow tube used in calculating the specific discharge (Paulsen et al, 2000). Prior to sampling, the valve was closed and the sample was then collected. To ensure that samples were not contaminated by salt water, conductivity measurements were taken in the field. Upon completion of the sample collection, the valve was reopened so that continuous measurements of specific discharge could resume. Again, samples were analyzed by Suffolk County Department of Health Services for concentrations of naphthalene following EPA method 524.2/624 for volatile organics.

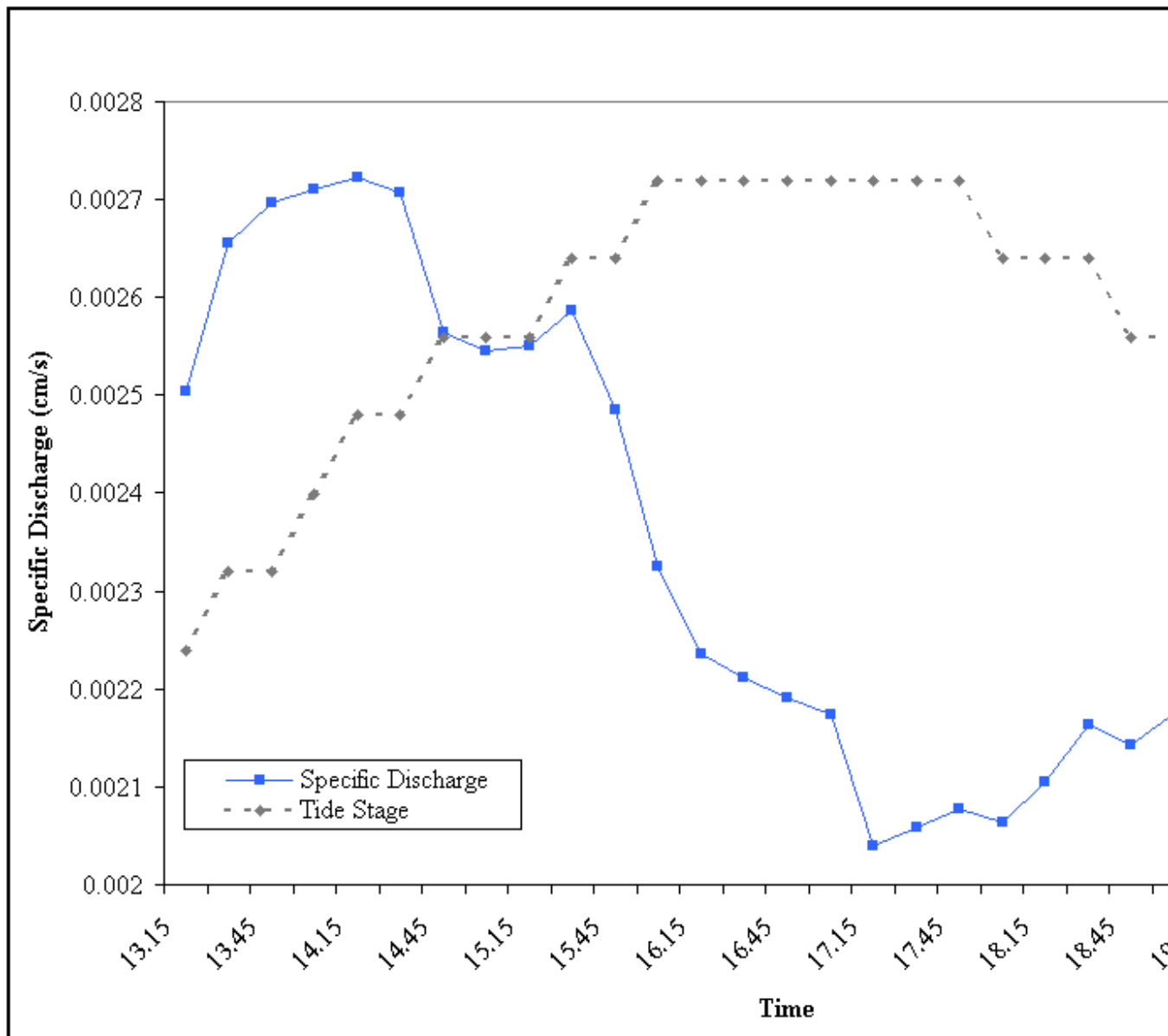


Figure 4 Specific discharge into Lawrence Creek 12/1/99. MSL = mean sea level.

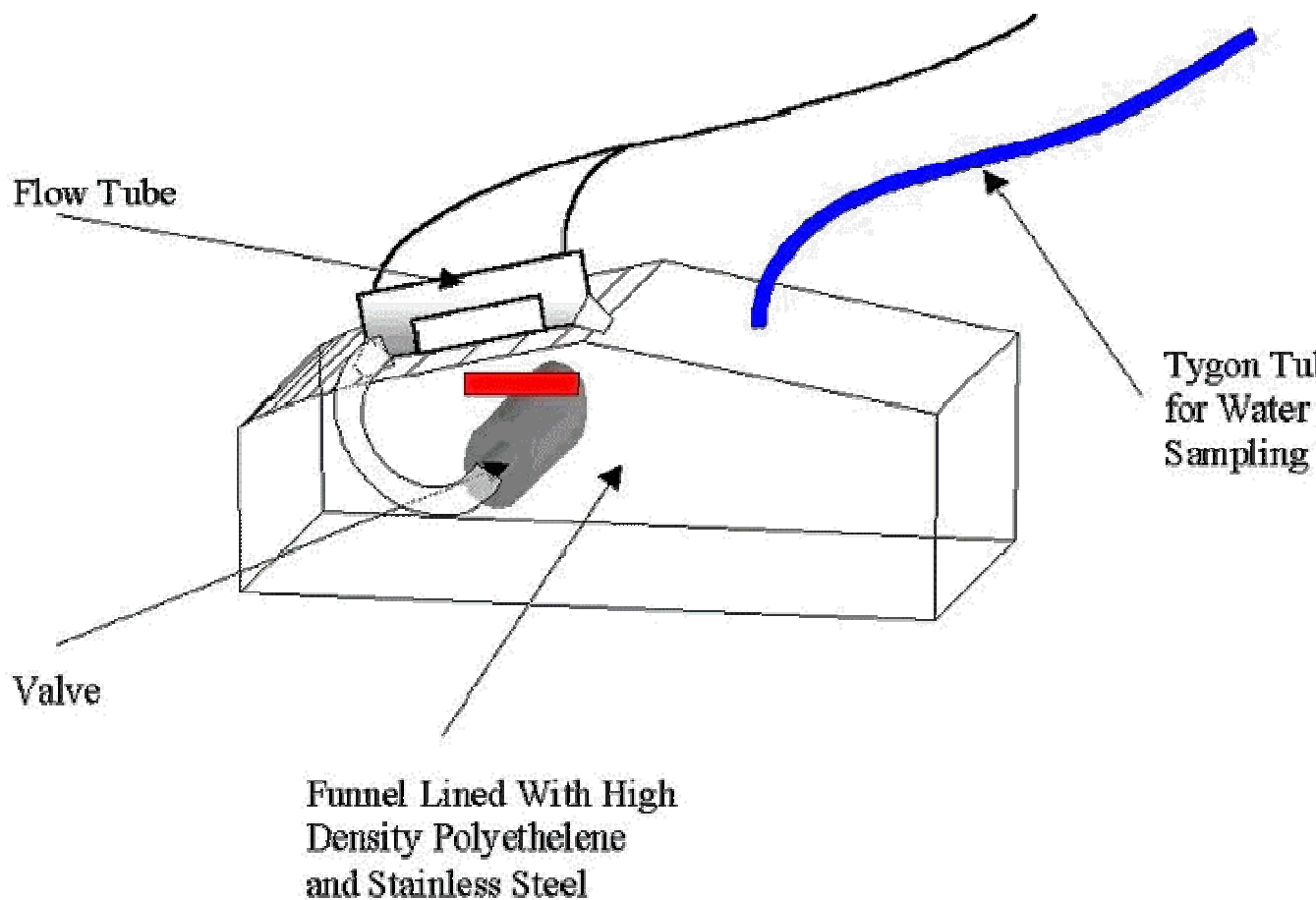


Figure 5 Modified funnel used to collect water samples while determining specific Discharge (not to scale).

Results

Iron concentrations from West Neck Bay are shown in Table 1 and graphically in Figure 6 for the three nested piezometers at the coastline. From Table 1 and Figure 6, it is clear that concentrations found in the piezometer screened 26-31' below the surface shows substantially higher iron concentrations than the other two piezometers. This relative increase is shown throughout the sampling period and therefore is not an isolated occurrence. What is also interesting to note is the potential relationship between the samples collected from the 26-31' piezometer and concentrations 90' offshore. Although offshore data are sparse and concentrations are not identical to the 26-31' piezometer, the relative concentrations are similar (ie. the 26-31' piezometer shows consistently higher concentrations than the deep or shallow piezometers and the samples collected 90' offshore show higher concentrations than the other offshore samples).

Date	Upgradient (Landfill)	8-12'	26-31'	45-50'	Shoreline	20' Offshore	50' Offshore	90' Offshore
5/26/99	46.1	0.234	10.5	5.24	<u>N/A</u>	<u>N/A</u>	<u>N/A</u>	<u>N/A</u>
6/9/99	N/A	ND	0.147	ND	<u>N/A</u>	ND	ND	<u>N/A</u>
6/22/99	N/A	ND	1.17	0.179	ND	ND	0.107	0.549
7/12/99	N/A	ND	0.993	ND	0.119	ND	0.629	2.18
8/9/99	N/A	ND	10.3	0.293	ND	ND	0.374	
8/25/99	N/A	0.138	1.87	0.307	0.439	1.8		3.37

Table 1 Iron concentrations (mg/l) at West Neck Bay . Dotted line at 50' sample indicates salt water contamination.
ND = below detection limit (< 0.1 mg/l)

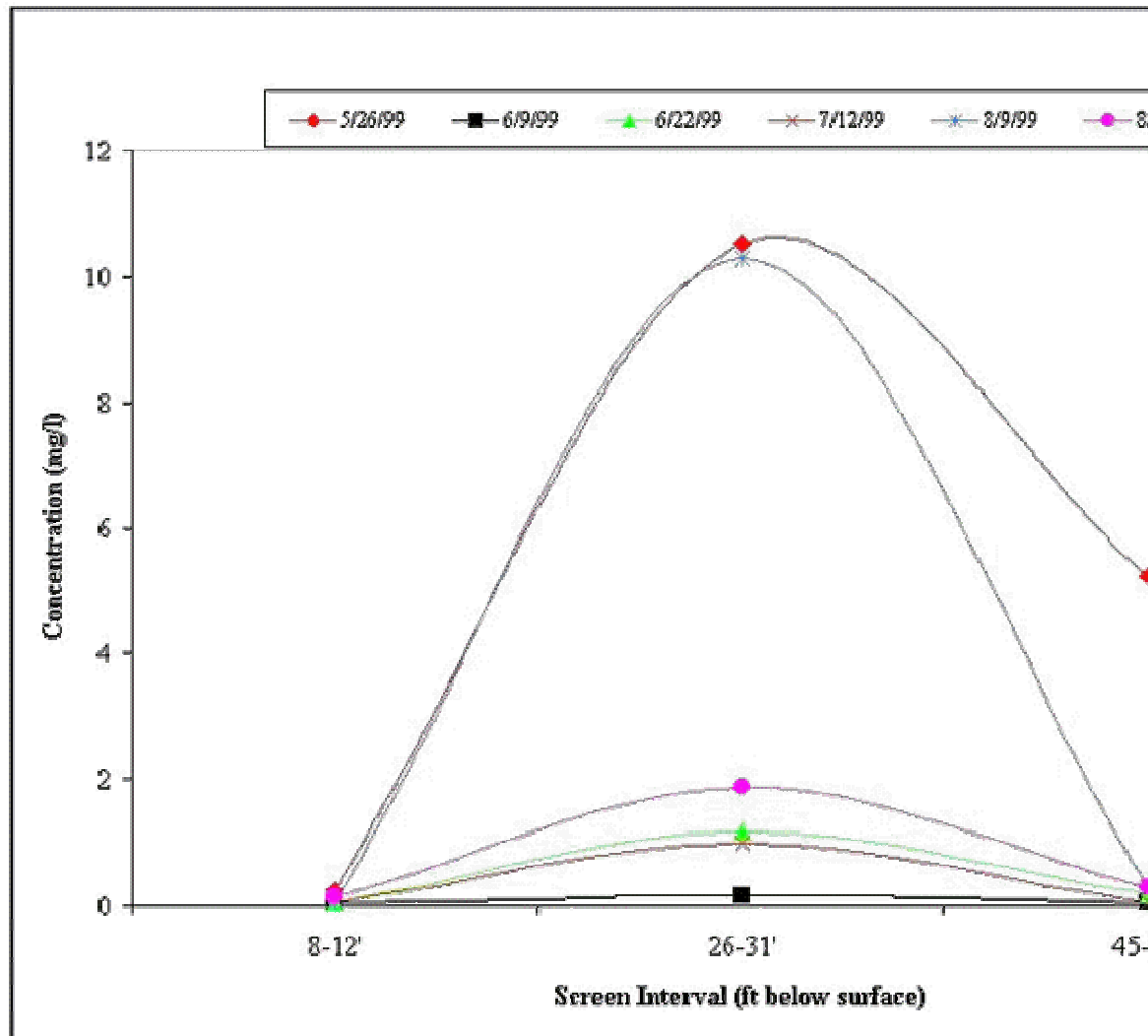


Figure 6 Iron concentrations (mg/l) for three nested piezometers along the coastline of West Neck Bay. Concentrations < 0.1 mg/l are undetectable by the lab.

To emphasize that the high iron concentrations found are not likely resulting from natural phenomena, copper is shown in Table 2 and Figure 7. Copper appears to show a similar trend with highest concentrations found in the 26-31' piezometer. Relative offshore concentrations are also highest 90' offshore. Other metals analyzed during these sampling intervals show similar trends as well (Fig. 8).

Water quality results for Lawrence Creek are shown in Table 3. Much higher concentrations of naphthalene are found in the porewater than along the creek bottom. Specific discharge collected was averaged over 12/1-12/6/99 and was $6.56 \text{ cm}^3/\text{s}$ ($3.22 \times 10^{-3} \text{ cm}^3/\text{s}$). Therefore, using concentrations in the funnel the flux of naphthalene to Lawrence Creek is approximately 43.08 mg/day. This estimate is through 2.5 ft^2 , the area of the hyporheic zone covered by the funnel.

Date	8-12'	26-31'	45-50'	Shoreline	20' Offshore	50' Offshore	90' Offshore
5/26/99	ND	16.5	7.62	N/A	N/A	N/A	N/A
6/9/99	ND	ND	ND	N/A	ND	ND	N/A
6/22/99	ND	4.62	ND	ND	ND	ND	ND
7/12/99	ND	1.05	ND	ND	ND	2.09	4.04
8/9/99	ND	10.8	ND	ND	ND	1.18	
8/25/99	1.25	4.85	ND	6.68	2.24		6.81

Table 2 Copper concentrations ($\mu\text{g/l}$) at West Neck Bay. Dotted line at 50' sample indicates salt water contamination. ND = below detection limit ($< 1 \mu\text{g/l}$).

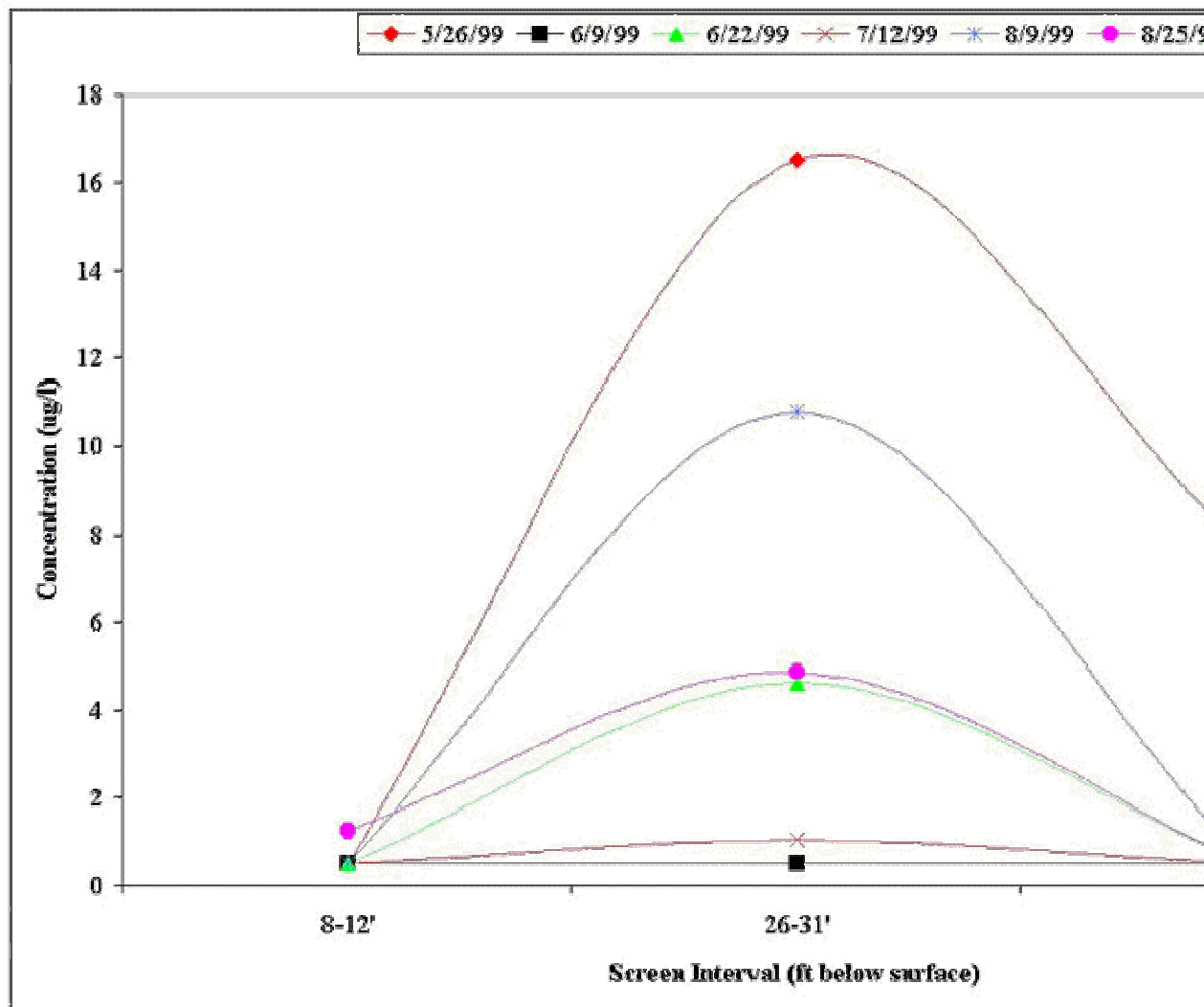
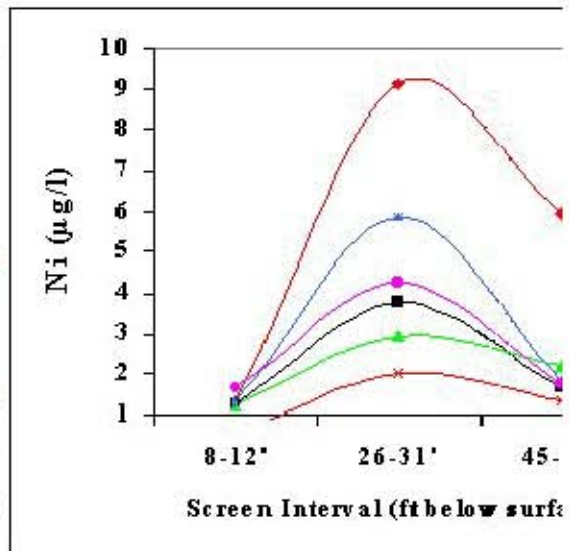
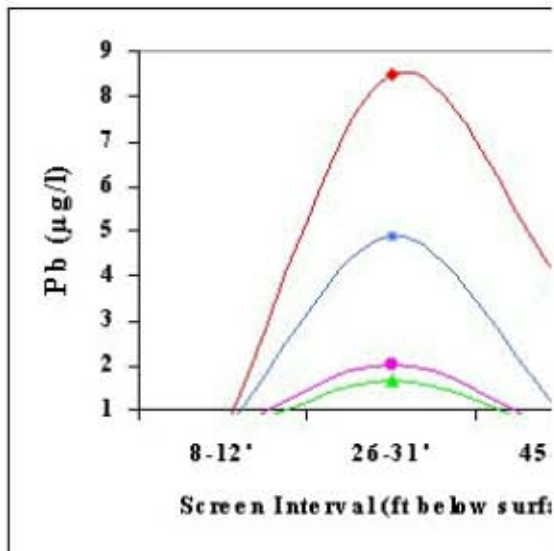
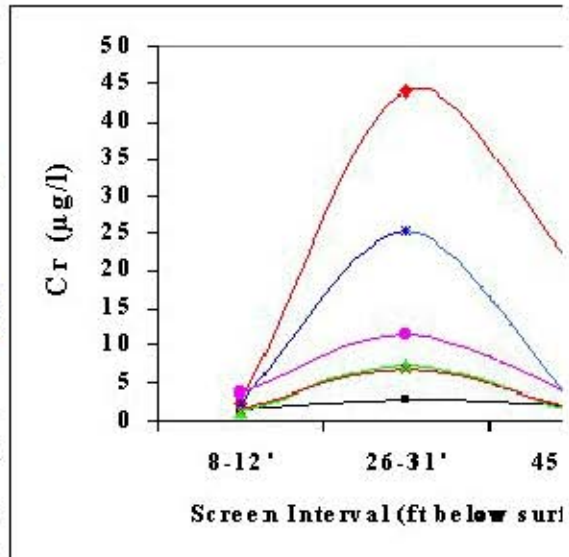
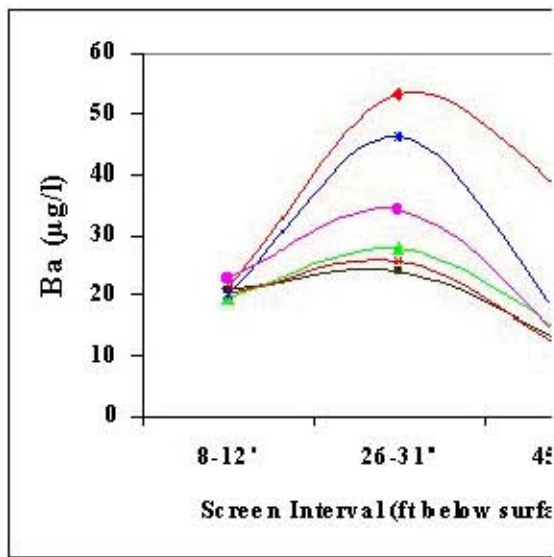


Figure 7 Copper concentrations for three nested piezometers along the coastline of West Neck Bay.

Concentrations < 1 $\mu\text{g/l}$ are not detected by the lab.

<i>Date</i>	<i>Porewater S ($\mu\text{g/l}$)</i>	<i>Sediment-Water Interface S ($\mu\text{g/l}$)</i>	<i>Funnel ($\mu\text{g/l}$)</i>
10/22/99	2200	140	N/A
12/2/99	1200	25	76

Table 3 Naphthalene concentrations from Lawrence Creek (southern site) Bayshore, NY.



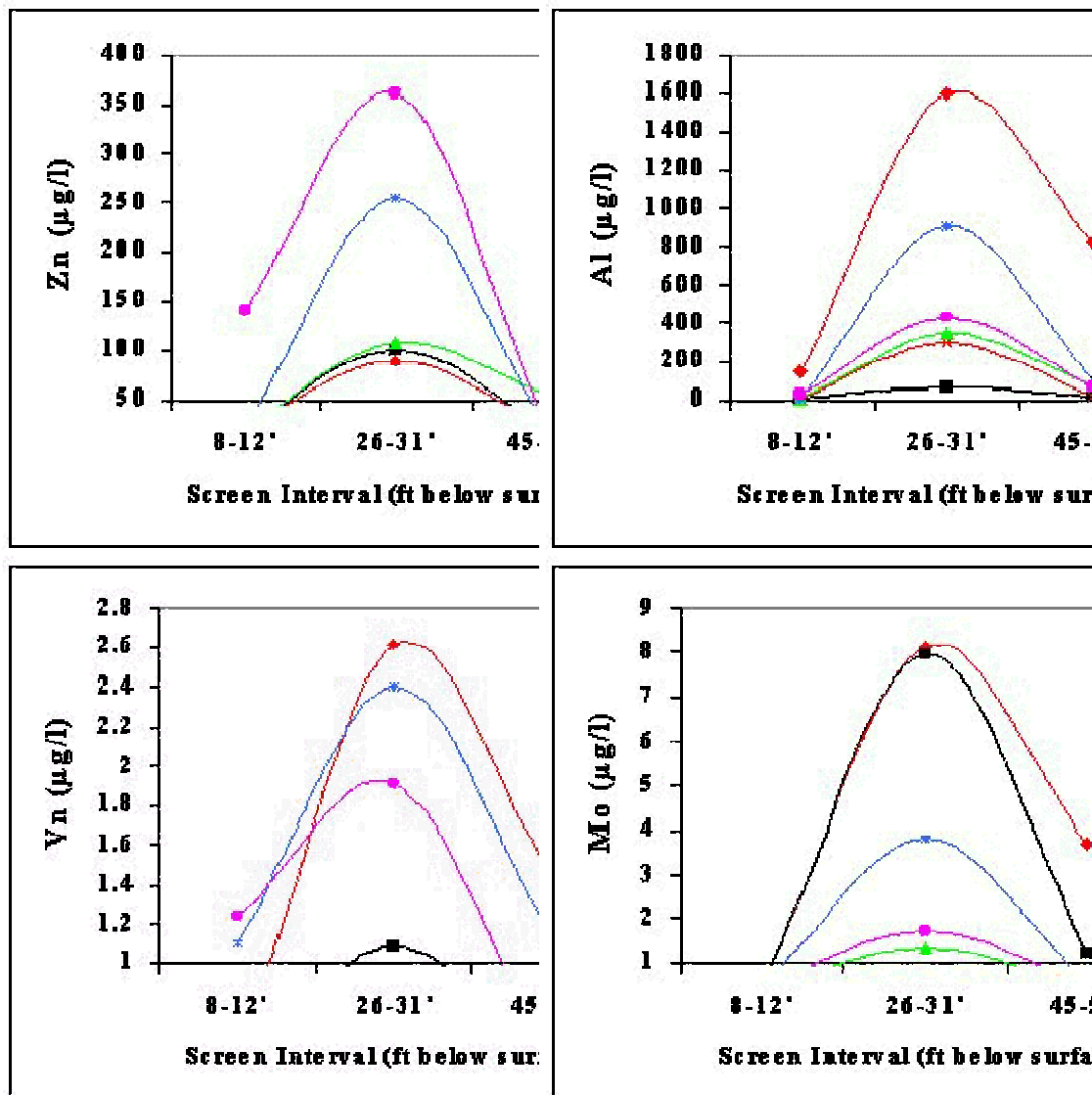


Figure 8 Metal concentrations sampled from West Neck Bay. Y axis – concentration ($\mu\text{g/l}$); x-axis – screen interval (ft below surface).
 Dates equivalent to Figs 6&7. A) Ba; B) Cr; C) Pb; D) Ni; E) Zn; F) Al; G) Vn; H) Mo.

Discussion

West Neck Bay

As shown above, metal concentrations in the middle piezometer are much greater than in the deep and shallow piezometers. This characteristic should be related to land use and local hydrogeology.

Figure 9 is an aerial photograph that shows three distinct land uses relevant to the water quality. Near shore, the water is considered "pristine" in that it is quite young and most likely originated only a few hundred feet inland. This water is represented by the shallow piezometer at the coastline. The elevated concentrations of iron and other metals present in the samples collected from the 26-31' piezometer are most likely water that originated at or near the landfill. This water carries higher metal concentrations than near shore areas or areas further inland. Supporting this notion, a well located just downgradient of the landfill was sampled and found to contain iron concentrations of 46.1 mg/l (SCDHS unpublished data; Table 1). Finally, the third area is mildly residential and mildly developed. Results indicate that the concentrations found in the deep piezometer represent background concentrations of Shelter Island (SCDHS unpublished data). These three distinct flow paths are illustrated schematically by the thick lines in Figure 10.



Figure 9 Aerial photograph of West Neck Bay site illustrating three distinct land uses

These flow paths can be traced offshore and it would be expected that the relative water quality would be similar to the corresponding flow path. From Figure 10, the flow path that intersects the 8-12' piezometer should discharge approximately 50 ft offshore. This is what is relatively observed in the water samples collected (Tables 1, 2). The flow path

that intersects the 26-31' piezometer should discharge further offshore, approximately 100-120 ft. Water sampled from the piezometer 90 ft offshore

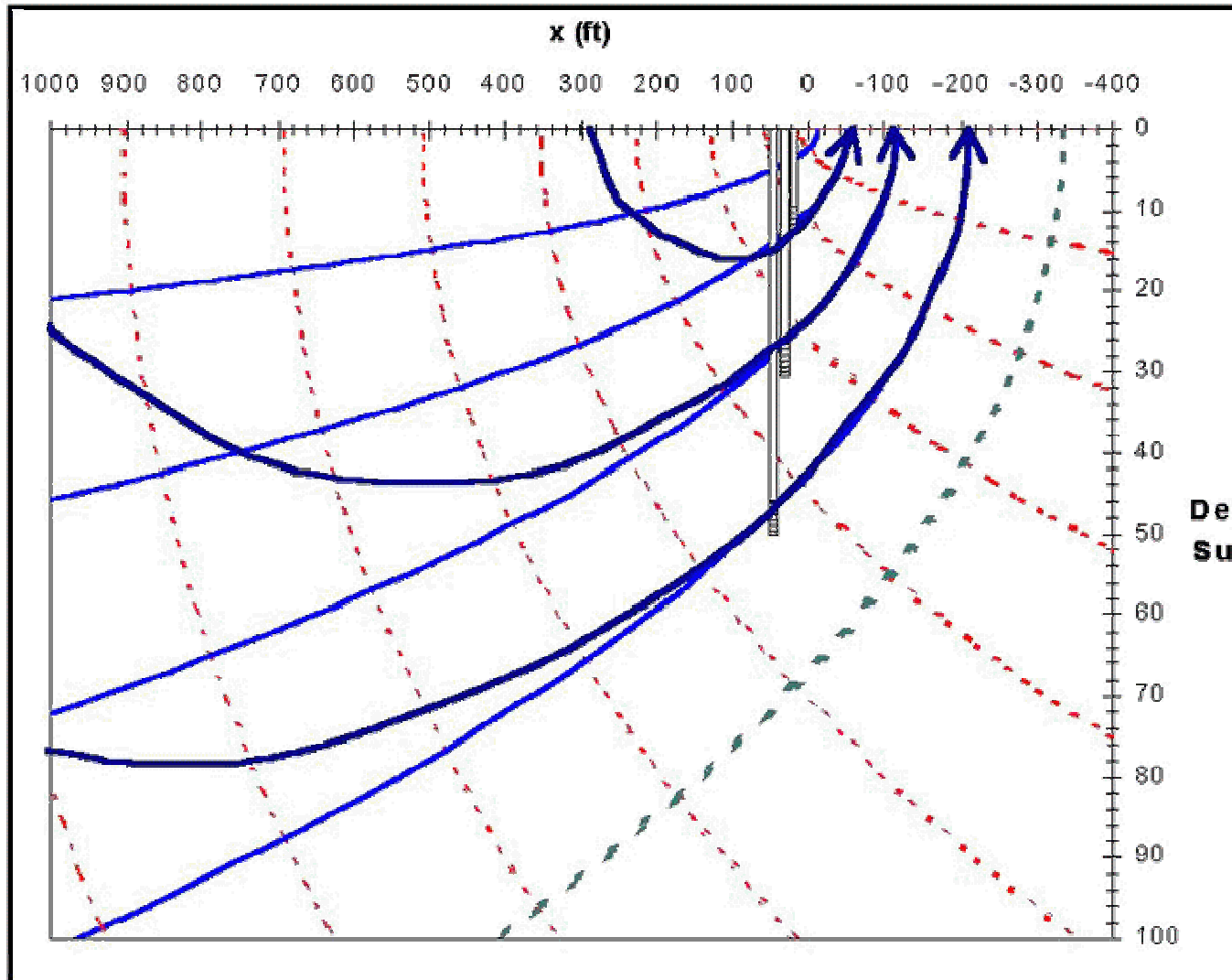


Figure 10 Modified flow net for West Neck Bay site showing the nested piezometers and possible mechanisms for flow. The x-axis represents distance away from shore. The green dotted line represents the salt-water interface (after Paulsen et al, 1997). Vectors for illustrative purpose only.

shows much higher metal concentrations than near shore samples. This is most likely representative of the water sampled from the 26-31' piezometer. There is a time lag (Table 1), but that is expected since it would take approximately 2 weeks for the water to discharge from the coastline to a distance 90 ft offshore (using an average specific discharge of 0.0002 cm/s measured 6/9/99-6/22/99). The flow path that intersects the 45-50' piezometer represents "background levels" and should discharge approximately 200 ft

offshore. Unfortunately, sampling at that distance could not be accomplished since the dock that was used for sampling only extended 90 ft.

Several coupled mechanisms are responsible for contaminant transport. If we first focus on advection, its contributions can be constrained reasonably well by the piezometric data. Water table data in the study area indicate that the horizontal gradient is 0.0028 in the Upper Glacial. In comparison, the inland vertical gradient is relatively small. Hence the advective transport is expected to be sub-horizontal, as illustrated by a flow net calculated using complex variable methods for an anisotropic, unconfined aquifer (Paulsen et al, 1997; Figure 10). For this setting, we have used the following parameters to obtain the flow net:

K_x	232 ft/day
K_z	2.32 ft/day
$Q/(K_x K_z)^{1/2}$	0.172 ft

where K_x and K_z are the hydraulic conductivities in the x and z directions, respectively. The total discharge is denoted by Q (ft^2/s). The parameter $Q/(K_x K_z)^{1/2}$ controls the location of the water table and salt water interface and is derived using water table data for three wells ranging 5 - 950' inland from mean tide mark (see Paulsen et al, 1997 for further details regarding construction of the flow net). Similar flow path results were also obtained by Schubert (1999) using a numerical scheme (MODFLOW).

It is clear that the vertical stratification of contamination we observed in the nested piezometers cannot be explained solely by advective transport. Other mechanisms including dispersion, colloidal transport, and sorption can play significant roles. Sorption processes, however, are not likely responsible for the patterns observed here since the relative concentrations for all the metals studied are similar (Figs. 6, 7 and 8). If sorption processes were dominant, it would be expected that each metal would respond differently. Colloidal transport is a likely mechanism and relative percentages of dissolved and colloidal constituents are currently under investigation. If colloidal transport is dominant in the area, the pumping rate at which the nested piezometers were sampled (500-650 ml/min) causes concern. When sampling groundwater for metals (that may be attached to colloids), turbidity causes problems and therefore "micropurging" (≤ 100 ml/min) is preferred (Fetter, 1999). However, pumping rates did not vary much for the three piezometers on any given sampling date and the relative concentrations are observed regardless. In addition, Kearl et al (1994) concluded that there was no major statistical difference in results for waters sampled using the micropurging technique or purging at higher rates as with normal purging techniques.

Data in Table 3 show that the naphthalene plume is entering Lawrence Creek at the southern site of the sampling station. Data also show that porewater samples contain concentrations an order of magnitude higher than samples collected along the creek bottom. This observation is in general agreement with Trichloroethene data in San Diego Bay obtained by Chadwick et al (1999), who attributed the difference in concentrations found at the sediment-water interface and the porewater to the high solubility of TCE and its byproducts. It was concluded that the VOCs entering the inlet were being flushed quickly by San Diego Bay. In the study outlined here, a similar mechanism is likely due to the close proximity of Lawrence Creek to Great South Bay. However, as mentioned above, the hyporheic zone in Lawrence Creek has been disturbed by dredging for the addition of bulk heads. Therefore, the migration pattern and spatial distribution of the naphthalene into the creek are more complicated due to several local anisotropies and further investigation is needed.

The collection funnel used in determining specific discharge measurements has been modified to allow for sampling directly at a location where seepage is quantified. Similar work has been conducted by Chadwick et al (1999) to accurately determine fluxes into a coastal environment. However, the seepage device used by Chadwick et al (1999) is not capable of continuous measurements in that it involves the installation and removal of plastic collection bags as used by Lee (1977).

The estimated flux of naphthalene to Lawrence Creek has a high uncertainty since it is based on specific discharge measurements over several days. Ideally, concentrations should be coupled with discharge measurements at the time of sampling to calculate instantaneous flux rates. Unfortunately, minor equipment problems and available laboratory resources prevented specific discharge measurements on the day of groundwater sampling (12/2/99). However, the funnel concentrations and a flux estimate are given here as a pilot study of the methodology to be utilized in a comprehensive investigation of real time contaminant (or nutrient) flux into a body of water.

Conclusion and Future Work

Preliminary results show that water discharging into West Neck Bay varies in quality with a distinct zone of relatively high metal concentrations. The water quality data show that the waters sampled are of different origins corresponding to three distinct land uses. Comparison with flow paths of conventional flow nets imply that advection alone cannot explain the vertical stratification of contaminants. Other transport mechanisms such as dispersion, nonlinear sorption processes, and colloidal transport also play important roles. Further investigation of colloidal transport at West Neck Bay is underway.

Thorough sampling is needed if sampling in or near the hyporheic zone. If only a few samples are collected during a single sampling time, it will most likely be unrepresentative of the time and spatial dependency of contaminant discharge. This holds true in Lawrence Creek as well as West Neck Bay, although far less disturbed. If only one sampling event was conducted, the concentrations may be unrepresentative of the

long term conditions. For example, if the only sample taken from West Neck Bay was on 5/26/99, when highest concentrations were observed, this would be unrepresentative since concentrations decreased drastically less than two weeks later.

Further study in greater detail is planned for Lawrence Creek as well as West Neck Bay using the modified funnels shown in Figure 5 to determine real time load estimates. The complexity of the hyporheic zone in Lawrence Creek needs to be further evaluated using other constituents due to the high solubility of VOCs. Continuous sampling over a time period equivalent to at least ½ of a tide cycle is planned to provide greater insight into possible tidal influences on contaminant fluxes into coastal surface waters.

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