

INORGANIC AND ORGANIC CHARACTERIZATION OF  
DREDGED SEDIMENTS FROM THE PROPOSED  
QUONSET POINT CHANNEL IN NARRAGANSETT BAY

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16. Abstract The purpose of this study is to provide a preliminary analysis of organic and inorganic contaminants in sediments from the Quonset Point and Davisville areas in Narragansett Bay, Rhode Island. Of particular interest is whether the level of contamination could affect disposal options and proposed "beneficial uses" of the dredged sediments. To address these issues, five sediment cores were taken from the Quonset Point/Davisville area, and analyzed for organic and inorganic contaminants. Concentrations of mercury, PCBs, and DDTs exceeded NOAA ER-M values in subsurface sediments near the Davisville and Quonset piers. Contaminant concentrations were used to classify the sediment according to a modification of the EPA National Sediment Inventory Data Evaluation Approach. This approach would result in a Tier 1 classification with probable associated adverse effects to aquatic or human health. The sediments dredged near the piers will probably require more expensive disposal options for dredged material. Elevated levels of contaminants and the fine grain size of the majority of the sediments may limit the potential beneficial uses of proposed dredged materials.			
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**Note:**

**The Appendices of the report exist only in hardcopy.**

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## INTRODUCTION

The Rhode Island Economic Development Corporation (RIEDC) is proposing to develop a major cargo/passenger port at Quonset Point, North Kingstown, Rhode Island. The dredging of deep-water access to the existing carrier piers is one part of the overall proposal that is being investigated. Sediment samples from the potential dredged areas are to be assessed for their usefulness as building materials for intermodal components such as port structures and roads. This assessment is based primarily on the physical properties of the sediment, (Silva 1999). However, given the long industrial history of many areas around Narragansett Bay, there is a strong possibility that the dredged sediments could contain toxic organic and inorganic constituents. These contaminants could be resuspended into the water column by dredging operations, creating an environmental threat. In addition, dredged sediments that are contaminated may not be appropriate for proposed "beneficial uses." The University of Rhode Island was commissioned by the Rhode Island Department of Transportation to analyze the extent of the chemical contamination in the sediments immediately off the Quonset Point/Davisville area. The results of this study provide baseline chemical data and preliminary classification of sediments in the area proposed for dredging.

## MATERIALS AND METHODS

### Collection of Sediment Cores

Figure 1 illustrates the Davisville/Quonset Point area within Narragansett Bay. Five sediment cores between 170 - 424 cm in length were taken from this area, and the specific sites are illustrated in Figures 1 and 2. Two cores were

taken from the Davisville area, and three from the Quonset Point area. Cores VC-08 and VC-6B are three inch diameter vibracores, whereas core LGC-21 is a four inch diameter gravity core. These three cores were obtained on the Ocean Engineering research vessel CT-1 by Armand Silva and Chis Baxter of the Marine Geomechanics Laboratory. Cores QP-1, 3, and 5 were obtained with a three inch diameter piston corer on the research vessel Capt'n Bert by John King. Subsamples were taken from each core, distributed approximately evenly down the length of the cores, and these subsamples were then analyzed for inorganic and organic contaminants. Inorganic analyses included Simultaneously Extracted Metals - Acid Volatile Sulfide (SEM - AVS) and trace metals, in addition to grain size, and total organic carbon. Organic analyses included Benzotriazoles (BZTs), Polychlorinated Biphenyls (PCBs), Polycyclic Aromatic Hydrocarbons (PAHs), and organo-chloride pesticides (OCPs), specifically Dichlorodiphenyl trichloroethanes (DDTs).

## **Laboratory Analyses**

### ***Organic Contaminants:***

The organic contaminants measured in this study include:

Benzotriazoles (BZTs): Synthetic chemicals used as ultraviolet light absorbers. They were produced by a chemical plant on the Pawtuxet River during 1963 to 1972 for the chloro-BZT and 1970 to 1985 for the C10-BZT.

Dichlorodiphenyl trichloroethanes (DDTs): Synthetic organochlorine pesticides that were produced from 1940 to 1972. In addition to the parent p,p' and o,p'-DDT compounds, the four DDD and DDE metabolites are also found in the environment.

Polychlorinated Biphenyls (PCBs): Synthetic chemicals produced from 1929 to 1977 as complex mixtures for a variety of commercial uses including dielectric fluids.

Polycyclic Aromatic Hydrocarbons (PAHs): Two to six ring aromatic compounds found in petroleum and petroleum products produced from about 1880 to present as well as PAHs formed in combustion processes.

Total Petroleum Hydrocarbons (TPHs): Aliphatic and aromatic hydrocarbons from petroleum and petroleum products

The organic contaminants measured in this investigation included most of the PCBs, PAHs and OCPs recommended by the NOAA Status and Trends Program for Estuarine and Coastal Monitoring (Appendix II). In addition, total petroleum hydrocarbons (TPHs: boiling range of nC12 to nC34) and two substituted benzotriazoles (BZTs: C10 BZT and chloro-BZT) were also measured. The sum of the 27 PCB congeners multiplied by two is approximately equal to the total PCBs ( $\Sigma$ PCBs; Latimer and Quinn, 1996). This value is similar to the total Aroclors such as the sum of Ar 1242, Ar 1254, and Ar 1260. The sum of the 23 PAHs is the total PAHs ( $\Sigma$ PAHs). In addition, the sum of the 6 DDT compounds is reported as total DDTs ( $\Sigma$ DDTs).

Samples were extracted with organic solvents, the extract fractionated by silica gel column chromatography, and the fractions analyzed by capillary column gas chromatography for PCBs/OCPs, TPHs/PAHs and BZTs using a mass selective detector (MSD). Details of the analytical procedures are available in Latimer and Quinn (1996) and Reddy and Quinn (1999), as well as in Appendix II. Sediment organic carbon (OC) values were determined using a CHN analyzer. All values are reported on an average dry weight basis or carbon



normalized basis. Information on the % moisture and % organic carbon is given in Appendix I. A detailed description of the quality control (QC) procedures is contained in Appendix II and results of the QC samples (blanks, duplicates, spikes and standard reference materials) are shown with the field data in Appendix III.

### ***Inorganic Contaminants***

Wet sediment from each station was homogenized, then subsampled for four types of analyses: 1) total trace metals; 2) grain size; 3) total organic carbon, and 4) Simultaneously Extracted Metals - Acid Volatile Sulfide (SEM - AVS). Details about the Quality Assurance/Quality Control (QA/QC) procedures for each of these analyses are found in Appendix II, and summary data tables are found in Appendix III.

### ***Total Trace Metals:***

Approximately 5 grams of wet sediment from each station was transferred to sterile centrifuge tubes and freeze-dried for 48 hours. After freeze-drying, approximately 0.2 grams dry sediment was weighed into acid-washed Teflon centrifuge tubes, and the weights were recorded. 5 ml of concentrated Nitric Acid ( $\text{HNO}_3$ ), 1 ml of concentrated Hydrochloric Acid (HCl), and 4 mls of Hydrofluoric Acid (HF) were then added to each sample. Samples were swirled, capped tightly, and placed in a heated sonicator for 48 hours for sediment digestion. At the end of 48 hours, the samples were removed from the sonicator, left tightly closed, and allowed to cool and stabilize for approximately 48 hours. 30 ml of 5% Boric Acid was then added to neutralize the HF, and 10

mls of deionized water was added to reduce viscosity and bring the finished sample volume to 50 mls. Samples were then transferred to acid-washed plastic storage jars, and were ready for analysis.

Digested samples were analyzed with three instruments: 1) Graphite Furnace Atomic Absorption Spectrometer (GFAA), 2) Inductively Coupled Plasma/Atomic Emission Spectrometer (ICP/AES), and 3) Cold Vapor Atomic Absorption Spectrometer (CVAA) for mercury only. The expected concentration of samples and instrument sensitivities dictated which instrument was used for each analyte. Strict quality assurance/quality control (QA/QC) procedures were adhered to throughout the process of analyzing trace metals. Standard reference materials (SRMs) with certified concentrations, as well as blanks and replicates were analyzed with each batch of sediment samples, and the results compared to target concentrations. In addition, reagent blanks and/or mid-range check standards were analyzed every 10 samples during the GFAA, CVAA, and ICP/AES runs to insure accurate results throughout the course of the runs. All samples were analyzed in duplicate, and the final concentrations are reported as the average of two duplicates.

***Grain Size:***

Approximately 4 grams of wet sediment was added to a 50ml centrifuge tube, and covered with 1N acetic acid to remove carbonates. Samples were shaken, and allowed to react for 24 hours. DI was then added, and samples were centrifuged for 10 minutes at 2300 rpm. The supernatant was decanted, and an additional 50ml of DI was added to rinse away any remaining acetic acid. Samples were centrifuged and decanted again, then transferred to 250ml

beakers. 10 ml of 30% hydrogen peroxide was added to each sample to begin removal of organics. Samples were swirled, covered loosely and allowed to react and evaporate for 24 hours. Ten ml of hydrogen peroxide was added every 24 hours, for a total of 50 mls. Once the reaction had stopped, samples were allowed to evaporate to approximately 20 mls, then transferred back to centrifuge tubes. 50 mls of DI was added to rinse away the hydrogen peroxide, and samples were centrifuged under the conditions above. The supernatant was decanted, an additional 50 ml of DI was added, and the samples were centrifuged and decanted again. Once the samples were thoroughly rinsed, they were sieved through a 63  $\mu\text{m}$  sieve. The  $>63 \mu\text{m}$  fraction was collected in a pre-weighed beaker, dried at 50°C, weighed again, and the dry weights recorded. The  $<63 \mu\text{m}$  fraction was collected in a pre-weighed beaker, and analyzed with an Elzone Particle Size Analyzer. The Elzone determines the volume of each sample  $> 3.9 \mu\text{m}$ , and  $> 15.6 \mu\text{m}$ . After analysis on the Elzone, the samples were dried, and the dry weights recorded. The % sand, % silt, and % clay was then calculated for each sample.

***Total Organic Carbon:***

Total organic carbon was calculated for each sample using the loss-on-ignition method. Exactly 1cc of wet sediment was transferred to a pre-weighed crucible, and dried at 100°C for 24 hours. The sample was then weighed, and returned to the oven at 500°C for 1 hour. The sample was weighed again. "Total % Organic" and "% Organic Carbon" was then calculated using the relationship between the weight of the sediment wet, after 100°C drying, and after 500°C heating.

### **SEM-AVS:**

SEM-AVS analysis was performed with the purge and trap technique detailed in the USEPA Environmental Monitoring and Assessment Program Laboratory Methods manual (1991). The AVS was measured using a sulfide-selective electrode. SEM concentrations were determined for cadmium, copper, nickel, lead, and zinc using GFAA and ICP-AES. For each sample, total SEMs were compared to AVS to predict potential bioavailability of metals.

## **RESULTS AND DISCUSSION**

### **Introduction**

Sediment chemistry results were compared to the established NOAA ER-L (“Effects Range-Low”) and ER-M (“Effects Range-Median”) values for each analyte. The ER-L and ER-M are sediment quality guidelines established by *Long, et al.* (1995) to predict the extent of adverse biological effects produced by chemical contaminants in sediments. Contaminant concentrations below the ER-L are expected to have minimal biological effects, concentrations between the ER-L and ER-M will possibly have biological effects, and concentrations above the ER-M are likely to have biological effects. Sediments from the Quonset Point/Davisville area are compared to established ER-L and ER-M values, and then classified using a modification of the EPA National Sediment Inventory Data Evaluation approach (USEPA, 1997).

### **Organic Analyses and Contaminants**

The distributions of major organic contaminants with depth in the cores

are shown in Figures 3 through 7, and the values for TPHs are given in Appendix III. At station VC-6B (Figure 3), there was a subsurface concentration maxima at approximately 15 to 70 cm for all contaminants. Only the PCBs exceeded the ERM guidelines at 25 to 70 cm; however, concentrations of both DDTs and PAHs were close to ERM values at these depths. Station QP-1,3 (Figure 4) had a deeper and stronger subsurface concentration maxima (about 110 cm to the bottom of the core at 242 cm) than the previous site. The DDTs and PCBs were over the ERM guidelines at several depths in the maxima, while the PAHs were closest to this value at 150 to 160 cm.

Concentrations of contaminants were generally low at station LGC-21 (Figure 5) with the DDTs and PCBs exceeding the ERL guidelines from the surface to about 94 cm for the former contaminant and surface to 34 cm for the latter. In addition, the DDTs were greater than the ERL at 210 to 214 cm. Station QP-5 (Figure 6) had a subsurface maxima for all contaminants starting at approximately 25 cm. In most cases, the concentrations decreased slowly with depth after the maxima and the PCBs and PAHs had relatively high values at the core bottom (220 cm). Both the DDTs and PCBs exceeded the ERM values at the maxima and the latter also exceeded this value at 185 to 195 cm. The final core (VC-08; Figure 7) again had a subsurface concentration maxima at 40 to 90 cm for the BZTs and about 20-110 cm for the other contaminants. Only the PCBs were over the ERM guideline at the maxima.

Based on the distribution of unique chemical markers for Narragansett Bay (C10-BZT, introduced in 1970 and chloro-BZT, introduced in 1963), station LGC-21 had the slowest sedimentation rate and station QP-1,3 had the highest rate (the last two sections of this core had very high levels of the older chloro-

BZT). In addition, the highest concentrations of most contaminants were generally found at station QP-1,3. Since the core sections analyzed were not continuous, it was not possible to estimate the sedimentation rate using the dates of introduction of the various organic contaminants.

The following conclusions can be drawn from the organic analyses conducted for this study: 1) the concentration of organic contaminants showed subsurface maxima in all of the cores and decreased to trace levels at various depths, depending on the station location; 2) most of the cores had PCB and DDT subsurface concentrations that exceeded established sediment quality guidelines (>ERM, Long et al., 1995) that are frequently associated with adverse biological effects. Two of the stations exceeded the guidelines at the bottom of the cores (> 2 meters depth), and 3) based on the distribution of chemical markers (C10 -BZT introduced in 1970 and Chloro-BZT introduced in 1963) in the cores, station LGC-21 had the slowest sedimentation rate and station QP-1,3 had the highest rate of sedimentation.

## **Inorganic Analyses and Contaminants**

### ***Trace metals:***

Samples from each of the five stations were analyzed for 12 metals: aluminum, arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel, silver, and zinc. All results are summarized in table-form in Appendix 3. It should be noted that silver data is reported only for stations QP-5 and VC-08. Unfortunately, we experienced difficulties with our laboratory reagents during the analyses of samples from the additional three sites, and are unable to provide accurate silver concentrations from these areas.

Results for arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc are also summarized graphically in Figures 8A-E. (Aluminum, iron, and manganese are not included in the graphical plots because these metals tend to occur naturally in high concentrations, and generally are not considered to be contaminants of concern.) The ER-L and ER-M ranges for each analyte are shown by areas of light and dark orange shading on each graph.

The following conclusions can be made from the trace metal data:

1) The highest concentrations of trace metals occur at varying depths within the cores, not in the sediment surface. Concentration maxima usually occur at or below 25-50 cm depth.

2) At all stations, trace metal concentrations frequently exceed the ER-L. However the ER-M for any analyte is only exceeded at station QP-1/3, from Davisville. The major contaminant of concern at this site is mercury.

3) Sediments from station QP-1/3 at Davisville are the most contaminated with trace metals, with 76% percent of the samples analyzed exceeding the ER-L, and 2 samples exceeding the ER-M. The second-most contaminated site occurs in the Quonset Point area at station QP-5, where 49% of the samples analyzed exceed the ER-L. However, unlike station QP-1/3, no analytes exceed the ER-M at this site. At all other stations, 31-41% of the samples analyzed exceed the ER-L, with none exceeding the ER-M. These data seem to suggest that, in general, the Davisville area is more highly contaminated than the Quonset Point area. However, the large percentage of samples exceeding the ER-L at station QP-5 suggests that this could be an additional area of concern, although the lateral extent of the contamination could not be determined from this study.

***SEM - AVS:***

The results of the SEM - AVS analyses are summarized in table form in Appendix III. The relationship between SEM and AVS is used to predict the extent to which trace metals are bioavailable. For each sample, the AVS concentration ( $\mu\text{mole/gram dry weight}$ ) is subtracted from the SEM concentration. If the resulting difference is greater than 1, then trace metals are considered to be potentially bioavailable for the sample in question. In this study only one sample, taken at 155-165 cm depth at station QP-5, produces an SEM-AVS difference of greater than 1. Therefore, trace metals do not appear to be readily bioavailable at either the Davisville, or Quonset Point core locations.

***Grain Size:***

The percentages of sand, silt, and clay at each station are depicted in Figure 9. The majority of sediment samples collected for this study consist primarily of silt, with smaller percentages of clay and sand. One station, VC-6B in the Quonset Point area, was characterized by sandy sediment, only the lower one-half of the core was largely sand. The fine-grained nature of the majority of samples suggests that material dredged from the study area is not the ideal grain size for proposed beneficial uses.

***Total Organic Carbon:***

The percent water, total percent organic, and percent organic carbon was calculated for each sample. Results are summarized in table-form in Appendix III. Samples from station QP-1/3 exhibit the highest average percent water, total percent organic, and percent organic carbon. At all stations, average percent



water ranged from 39 - 56%; average total percent organic ranged from 4 - 8%, and average percent organic carbon ranged from 2-4%.

### Classification of Sediments from Quonset Point and Davisville

We have used the following table as a preliminary screening tool for classifying Quonset/Davisville sediment:

Sediment Classification	Associated Adverse Effects To Aquatic or Human Health?	Sediment Chemistry
Modified Tier 1:	Probable	1. Sediment chemistry values exceed the ER-M for any one chemical, OR 2. SEM - AVS > 5
Modified Tier 2:	Possible but Infrequent	1. Sediment chemistry values exceed the ER-L for any one chemical, OR 2. SEM - AVS = 0-5
Modified Tier 3:	None	Any station not defined as Tier 1 or Tier 2

This table is a simplified version of EPA National Sediment Inventory Data Evaluation Approach. Based on this approach, we classify sediment from Davisville sites QP-1/3 and VC-6B, and Quonset Point site QP-5 as “Modified Tier 1”, probably producing potential aquatic and/or human health effects. This conclusion is based on the fact that the ER-M is exceeded for one or more analytes at multiple depths. Sediment from the other sites studied is classified as “Modified Tier 2”, possibly but infrequently producing risks to aquatic life and/or human health. This classification is based on the large majority of analytes that exceed the ER-L. Note that at site VC-08, one sample also exceeds the the ER-M for  $\Sigma$ PCBs at one depth, but in general is "Modified Tier 2."

## CONCLUSIONS

Sediments from the Quonset Point/Davisville area are not pristine. The majority of sediment samples studied exhibit elevated concentrations of organic and inorganic contaminants, with the highest concentrations occurring below the sediment surface. Elevated contaminant concentrations at LGC-21, and VC-08 (both at Quonset Point) could possibly cause adverse effects to aquatic life and/or human health, but these effects are expected to be infrequent. However, at sites VC-6B and QP-1/3 (Davisville), and at QP-5 (Quonset Point), adverse effects to aquatic life and/or human health are probable due to the high concentrations of mercury,  $\Sigma$ DDTs, and/or  $\Sigma$ PCBs.

The results of this preliminary study indicate that the majority of sediments that would be removed by dredging would not require expensive disposal options. However, sediments located near the Davisville piers, and in the area of site QP-5 at Quonset Point are likely to require a more expensive disposal option. Resuspension of contaminated sediments during dredging operations is a potential concern and should guide the selection of dredging methods. Additional study in the QP-5 area is required to document the lateral extent of the contamination seen in this study.

Sediments from the Quonset Point/Davisville area are primarily silt. The fine grain size, combined with elevated contaminant concentrations negatively impact the potential beneficial uses of proposed dredged materials. Further study of the stability of chemical contaminants contained within Quonset Point/Davisville sediments in potential beneficial use scenarios is warranted.

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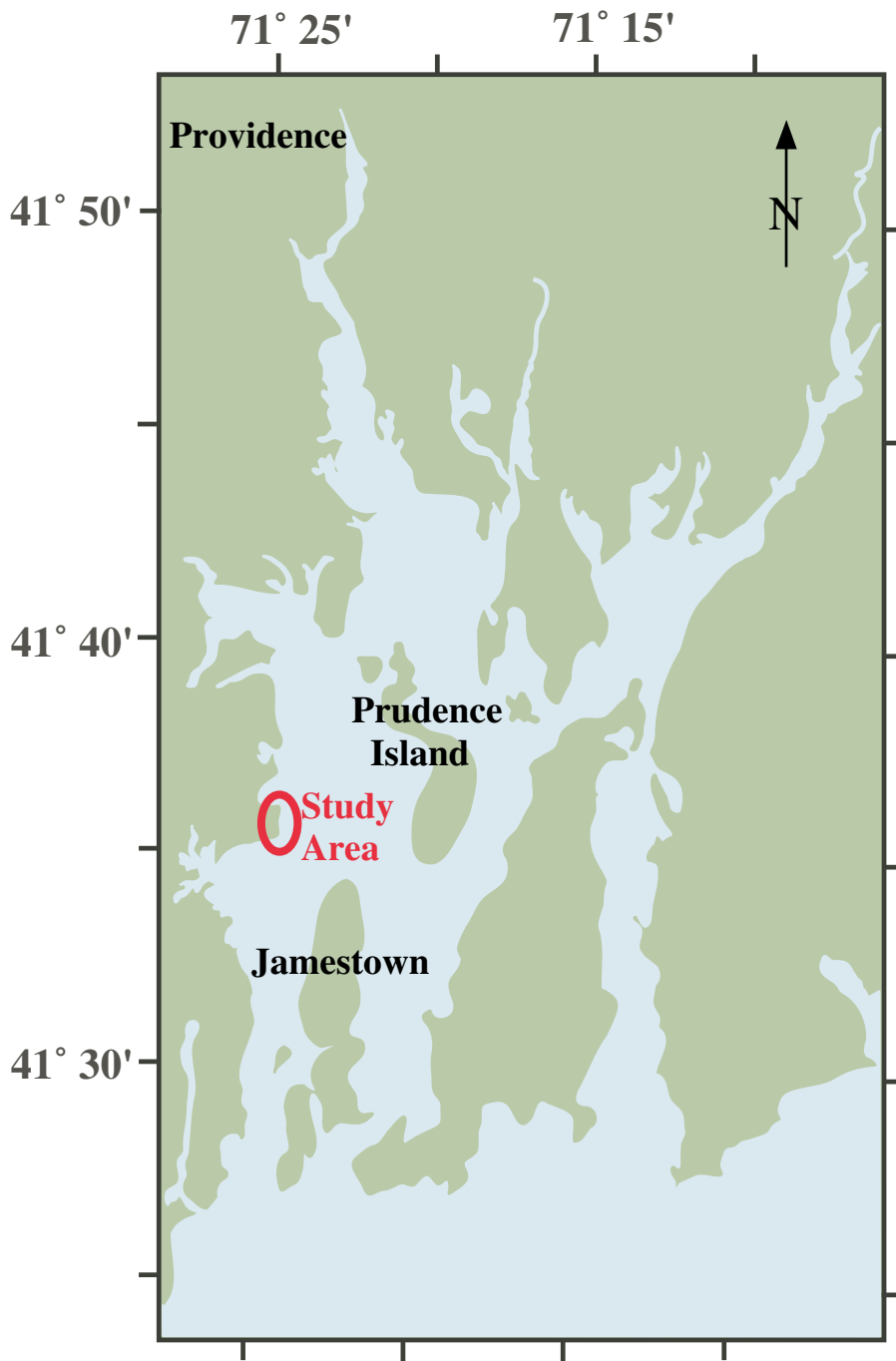


Figure 1. Location of Davisville/Quonset Point areas in Narragansett Bay, shown in red.

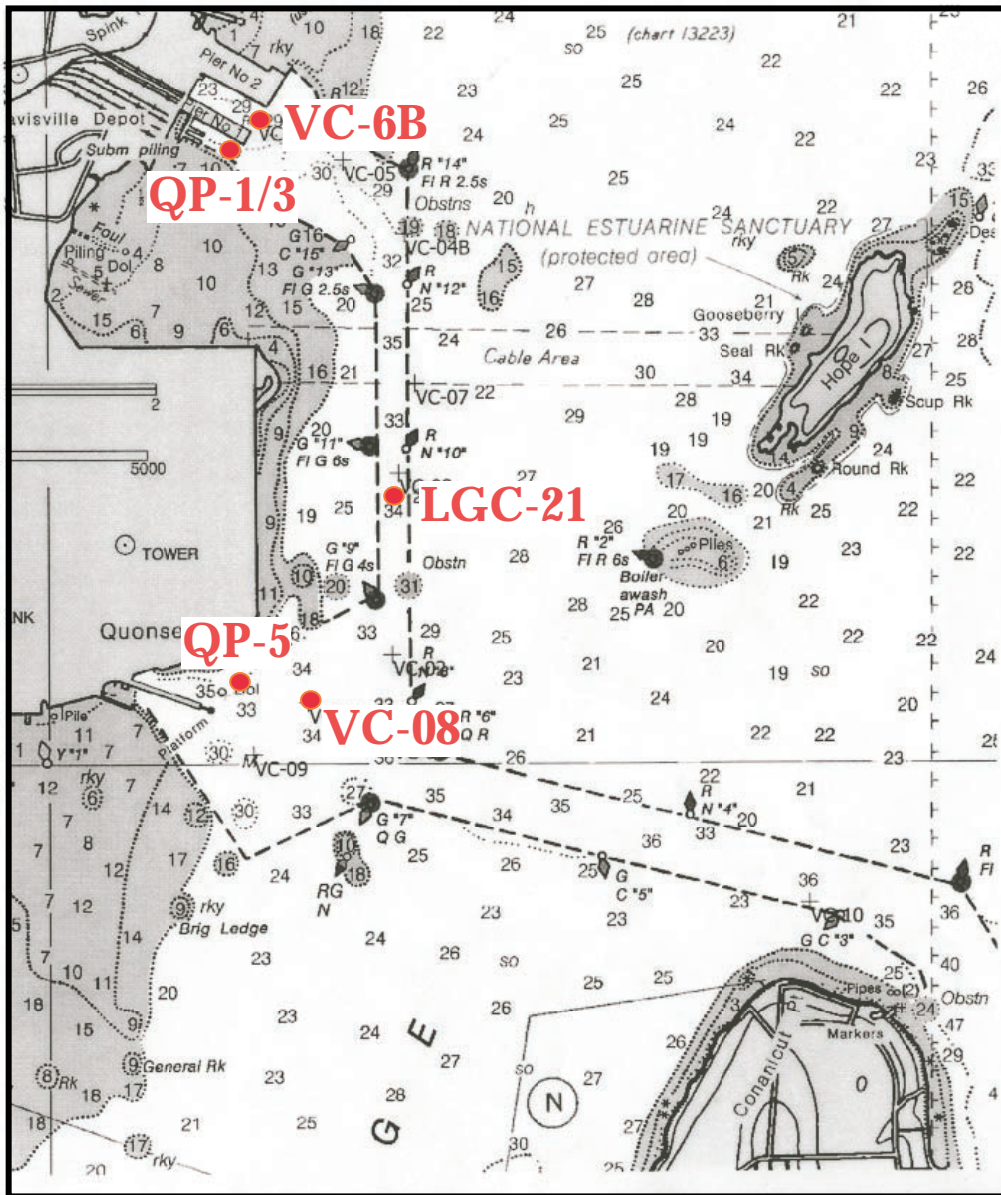


Figure 2. Location of sediment cores taken from the Davisville and Quonset Point areas.

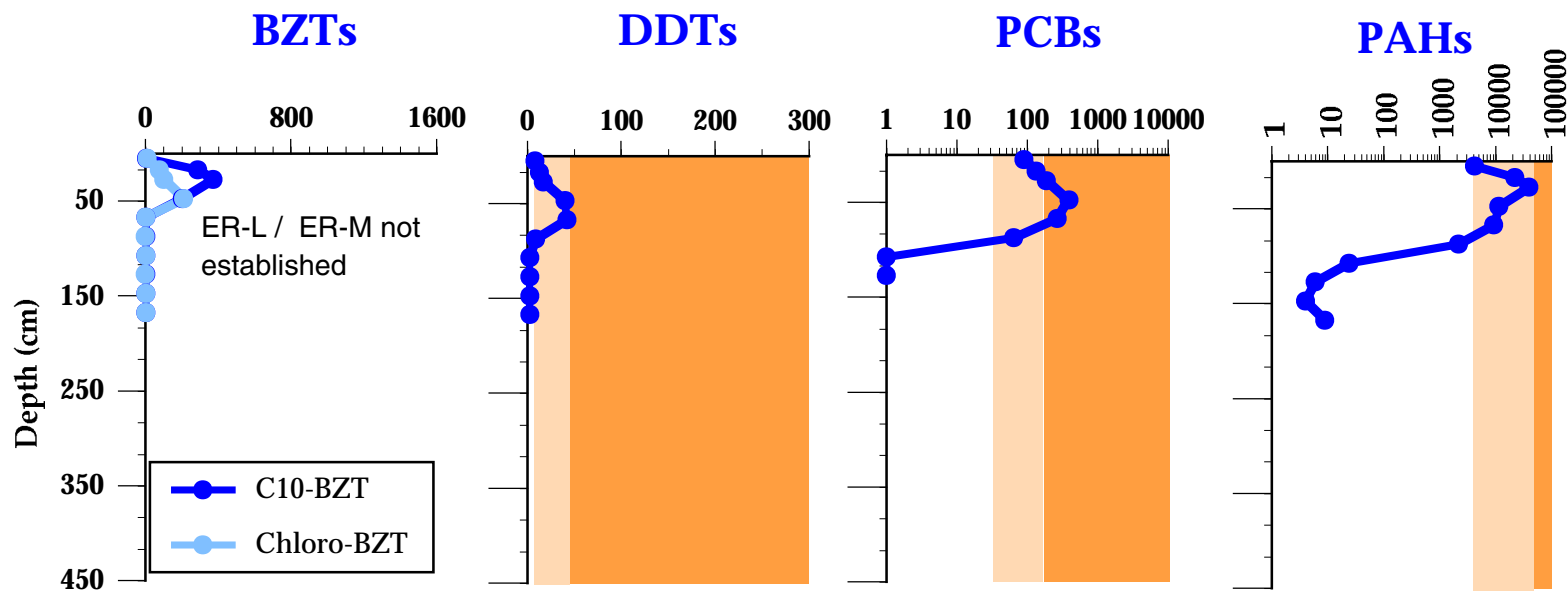


Figure 3. Concentration (ng/g dry weight sediment) of organic contaminants in the Davisville sediment core, VC-6B. Light orange bars indicate the ER-L range; dark orange bars designate the ER-M range.

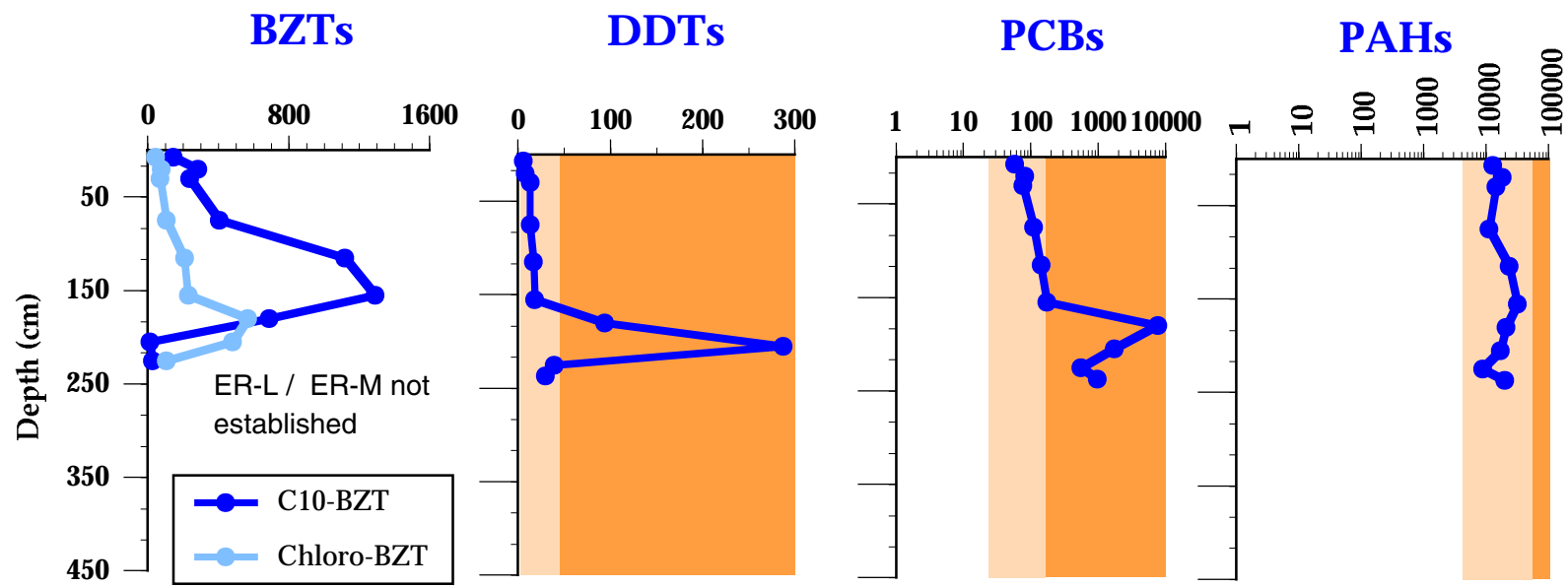


Figure 4. Concentration (ng/g dry weight sediment) of organic contaminants in the Davidville sediment core, QP-1/3. Light orange bars indicate the ER-L range; dark orange bars designate the ER-M range.

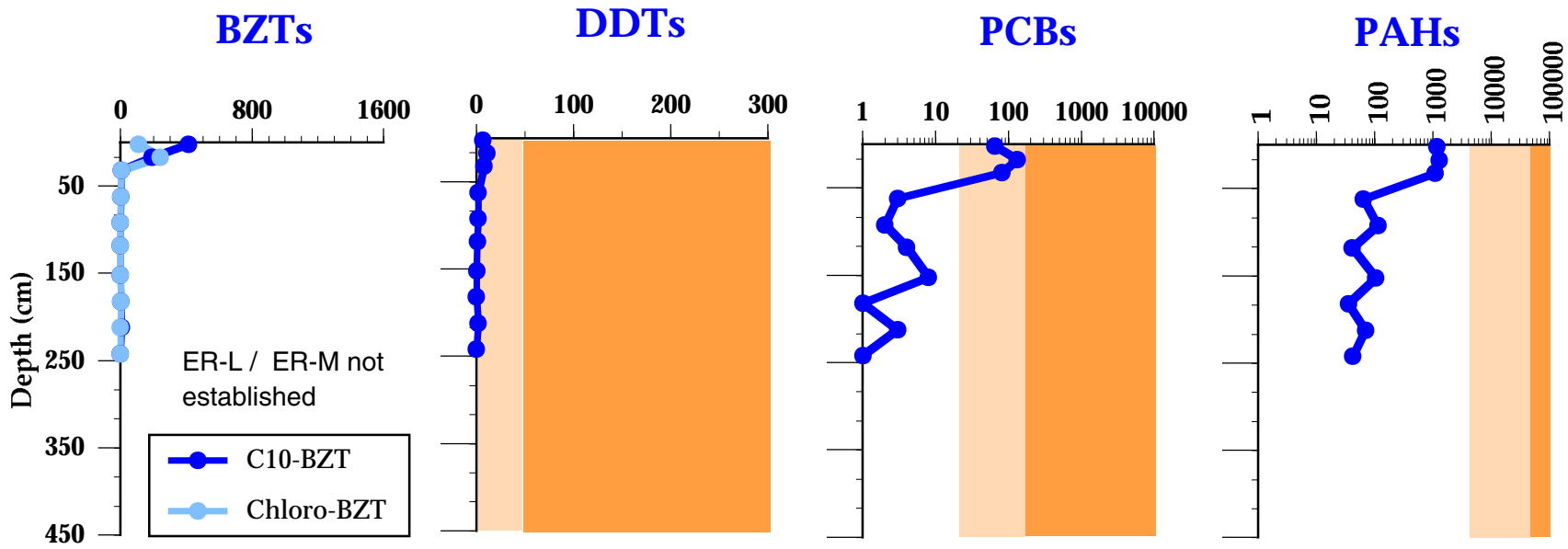


Figure 5. Concentration (ng/g dry weight sediment) of organic contaminants in the Quonset Point sediment core, LGC-21. Light orange bars indicate the ER-L range; dark orange bars designate the ER-M range.



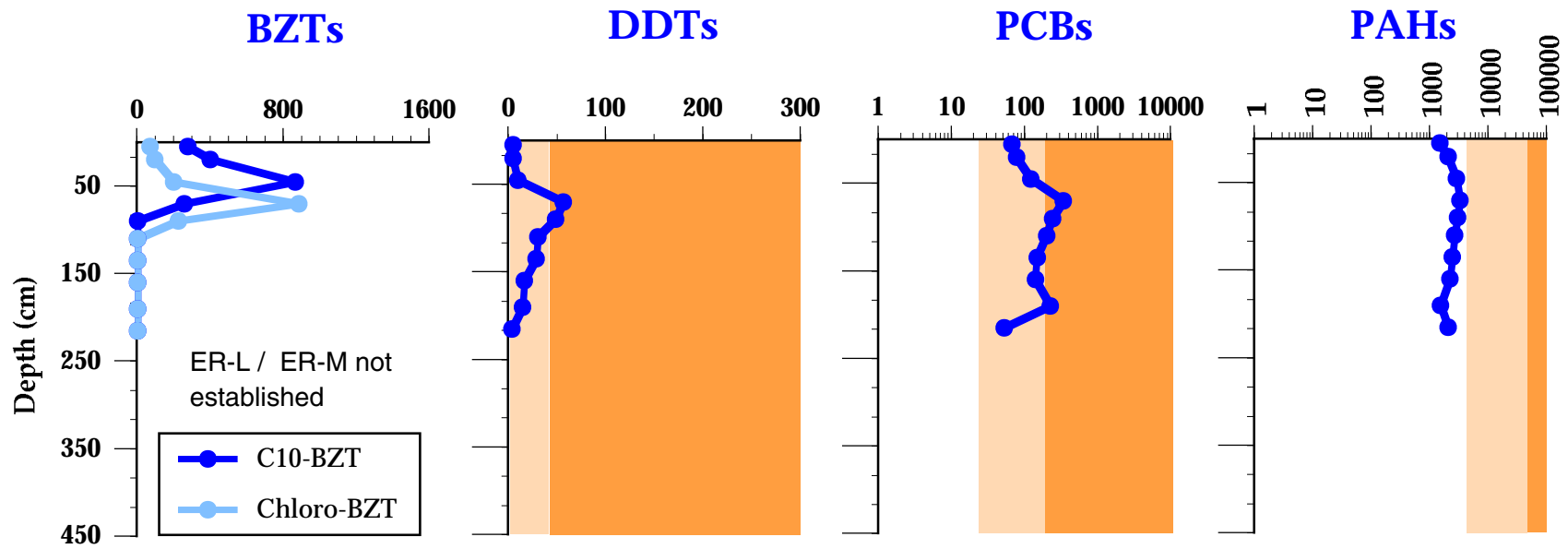


Figure 6. Concentration (ng/g dry weight sediment) of organic contaminants in the Quonset Point sediment core, QP-5. Light orange bars indicate the ER-L range; dark orange bars designate the ER-M range.

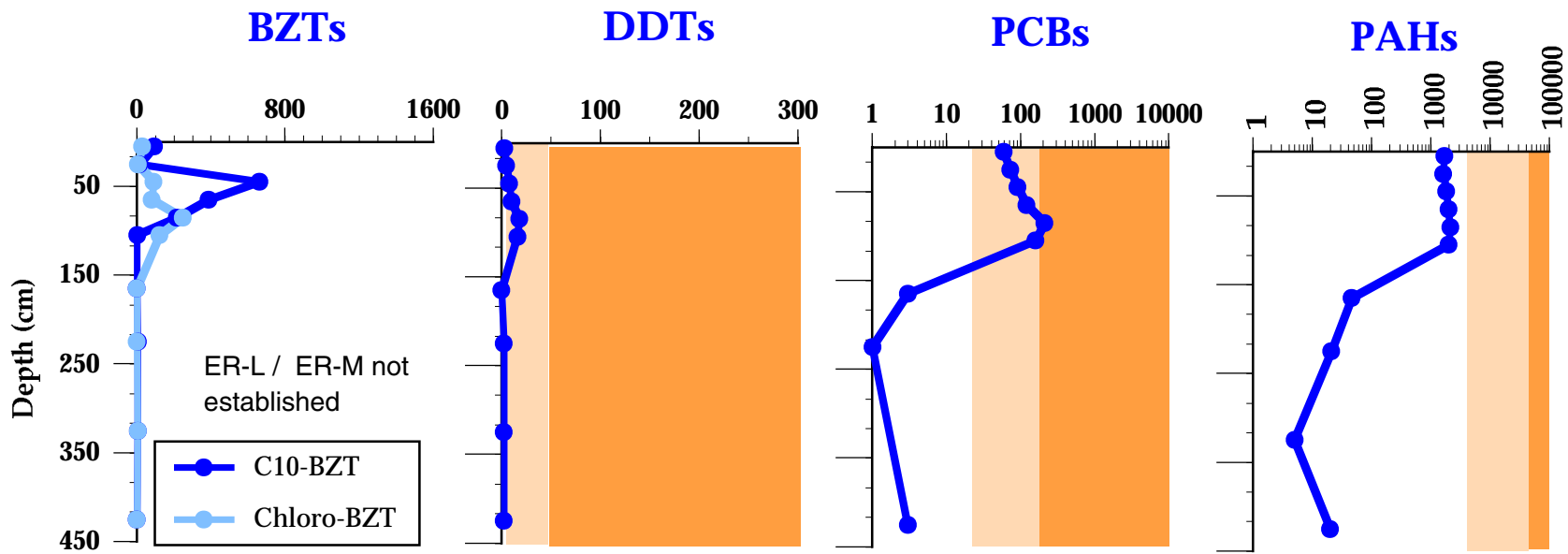


Figure 7. Concentration (ng/g dry weight sediment) of organic contaminants in the Quonset Point sediment core, VC-08. Light orange bars indicate the ER-L range; dark orange bars designate the ER-M range.

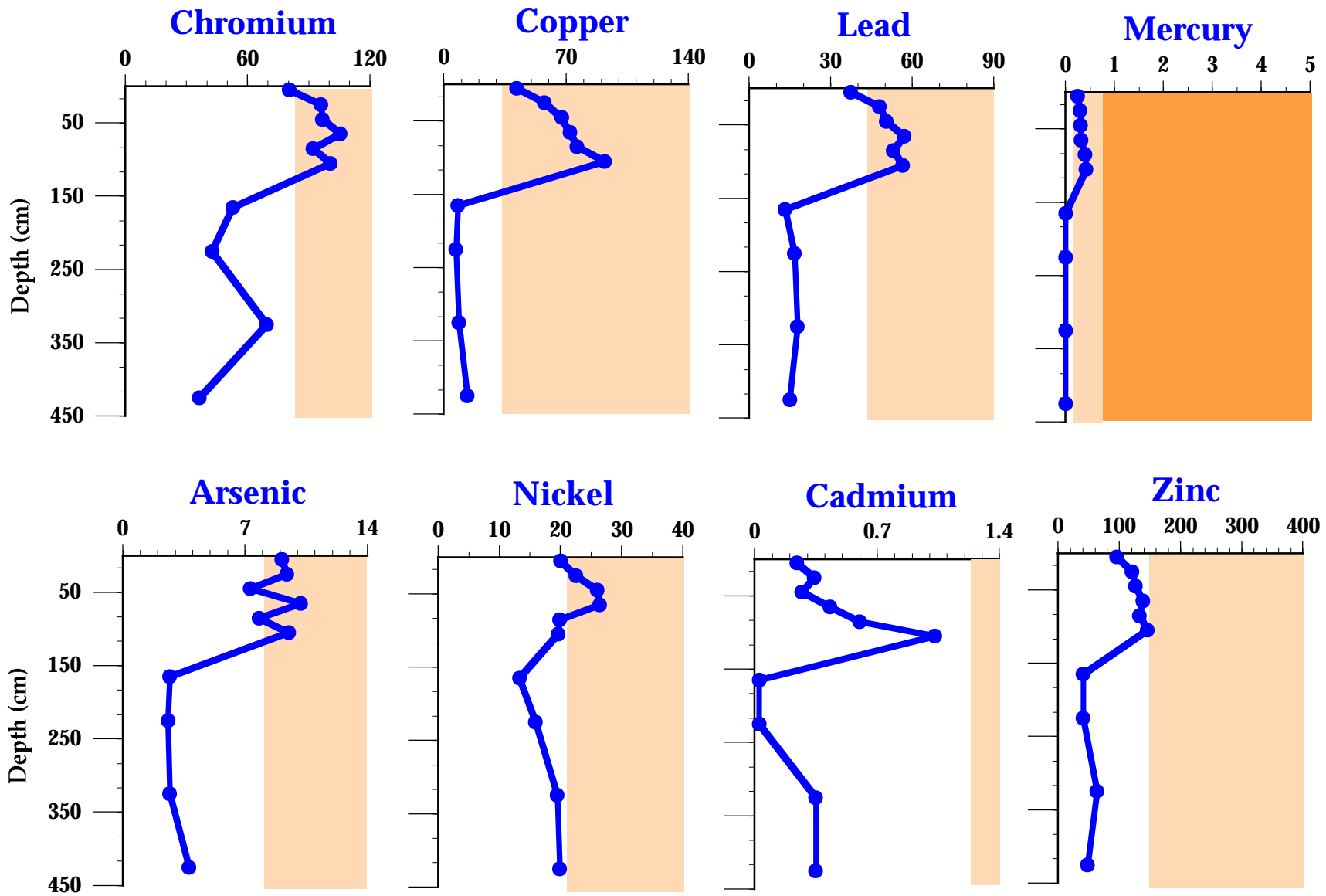


Figure 8A: Concentrations ( $\mu\text{g/g}$ ) of trace metals at site VC-08, in the Quonset Point area. Light orange bars indicate the ER-L range; dark orange bars designate the ER-M range.

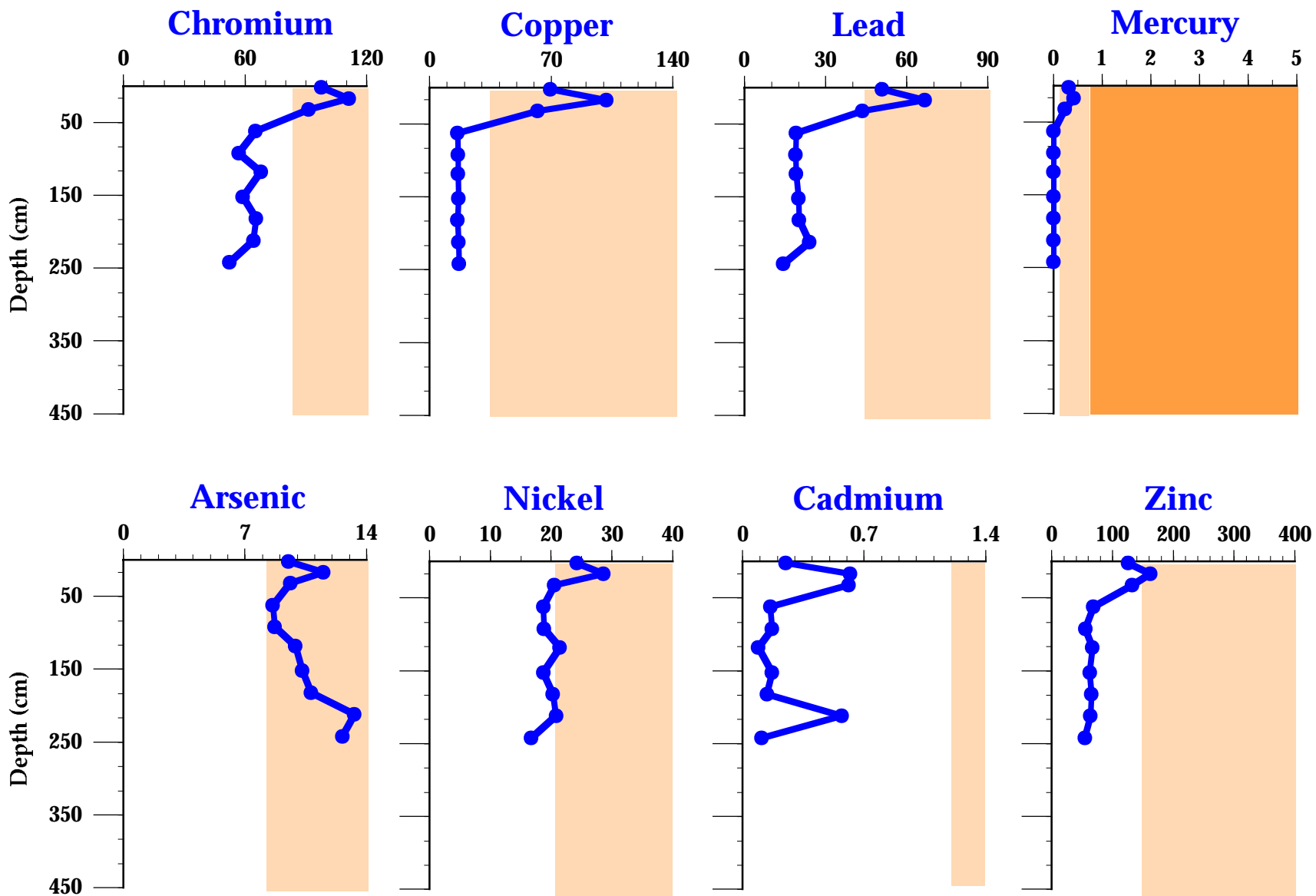


Figure 8B: Concentrations ( $\mu\text{g/g}$ ) of trace metals at site LGC-21, in the Quonset Point area. Light orange bars indicate the ER-L range; dark orange bars designate the ER-M range.

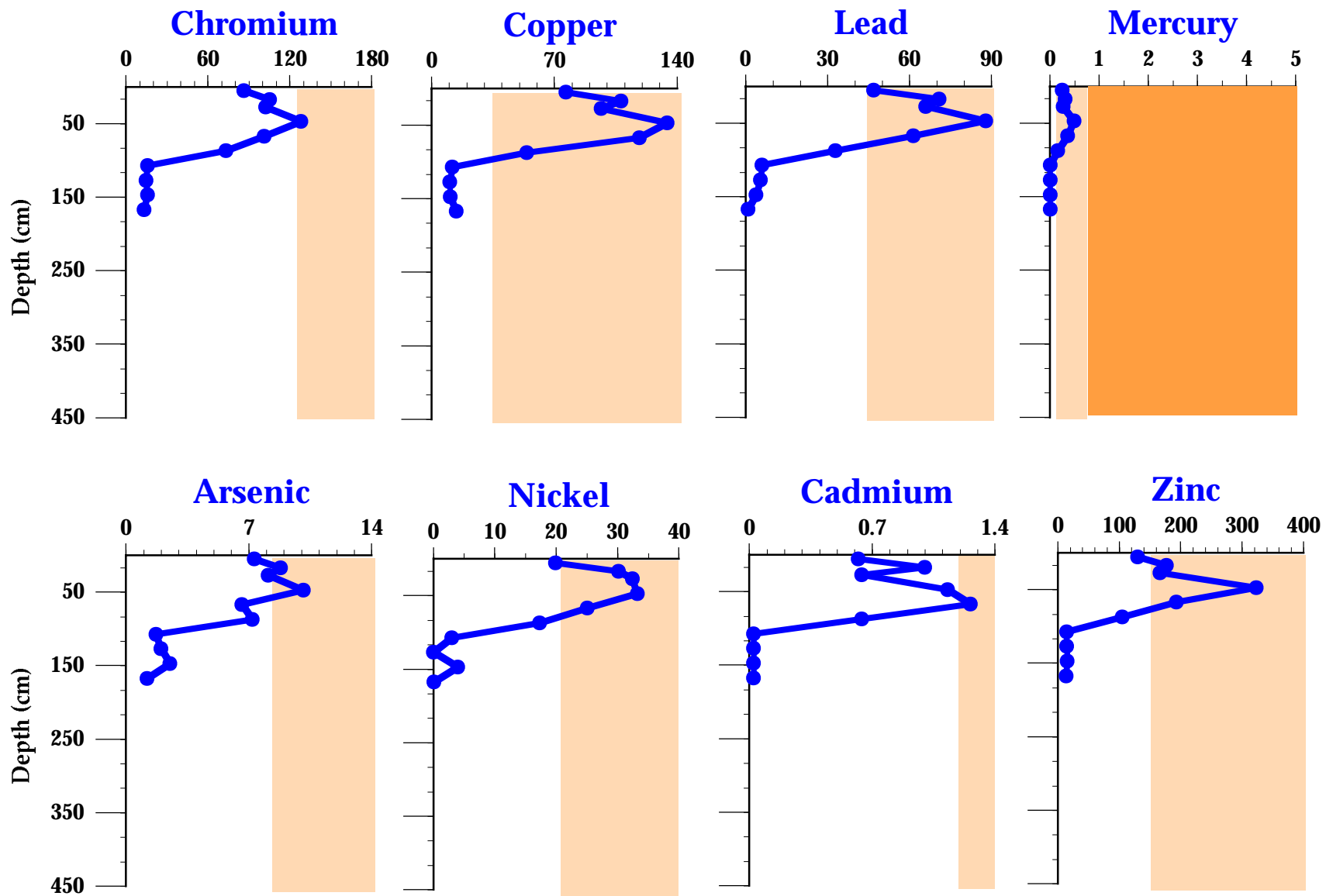


Figure 8C: Concentrations ( $\mu\text{g/g}$ ) of trace metals at site VC-6B, in the Davisville area. Light orange bars indicate the ER-L range; dark orange bars designate the ER-M range.

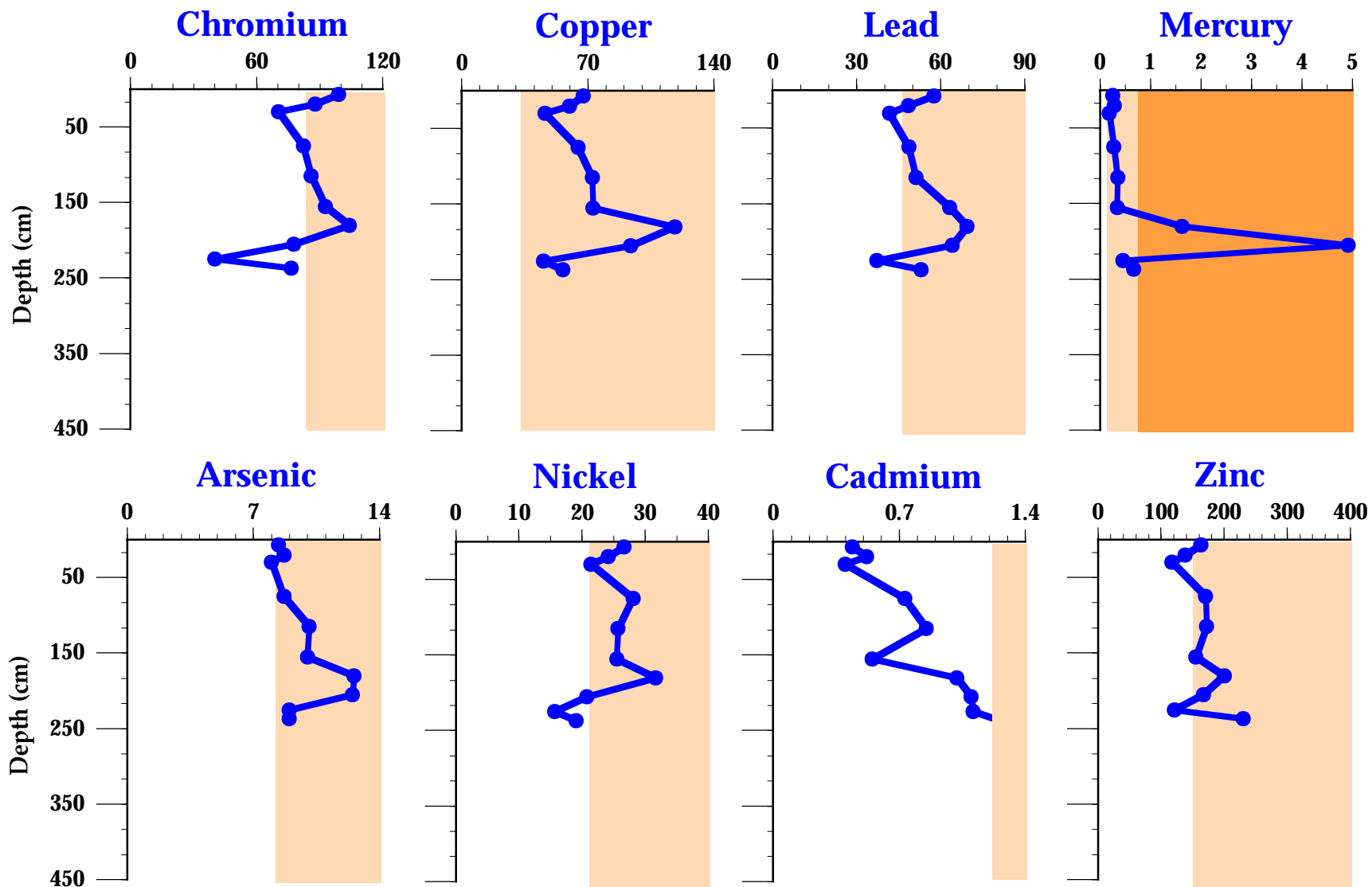


Figure 8D: Concentrations ( $\mu\text{g/g}$ ) of trace metals at site QP-1/3, in the Davisville area. Light orange bars indicate the ER-L range; dark orange bars designate the ER-M range.

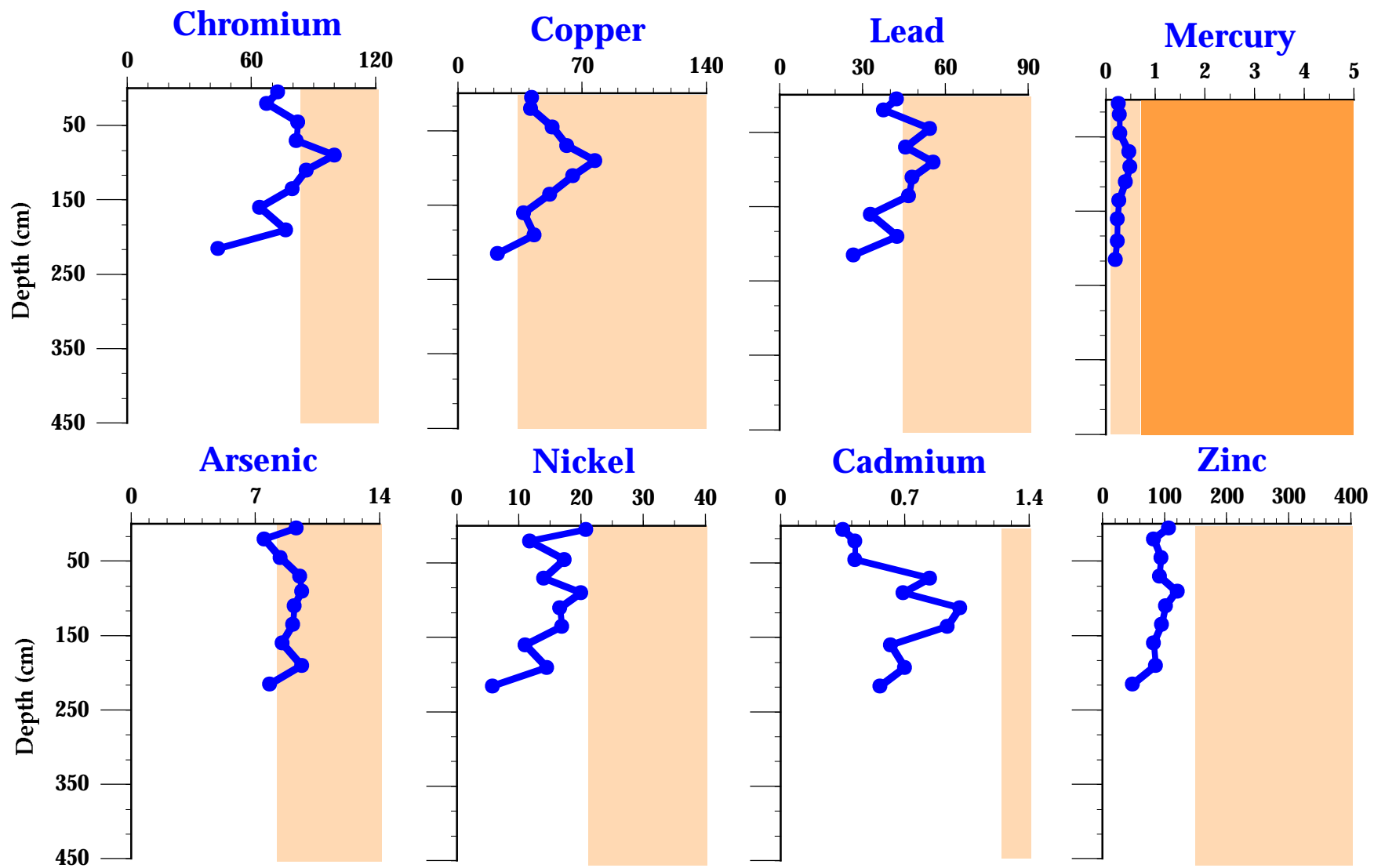


Figure 8E: Concentrations ( $\mu\text{g/g}$ ) of trace metals at site QP-5, in the Quonset Point area. Light orange bars indicate the ER-L range; dark orange bars designate the ER-M range.

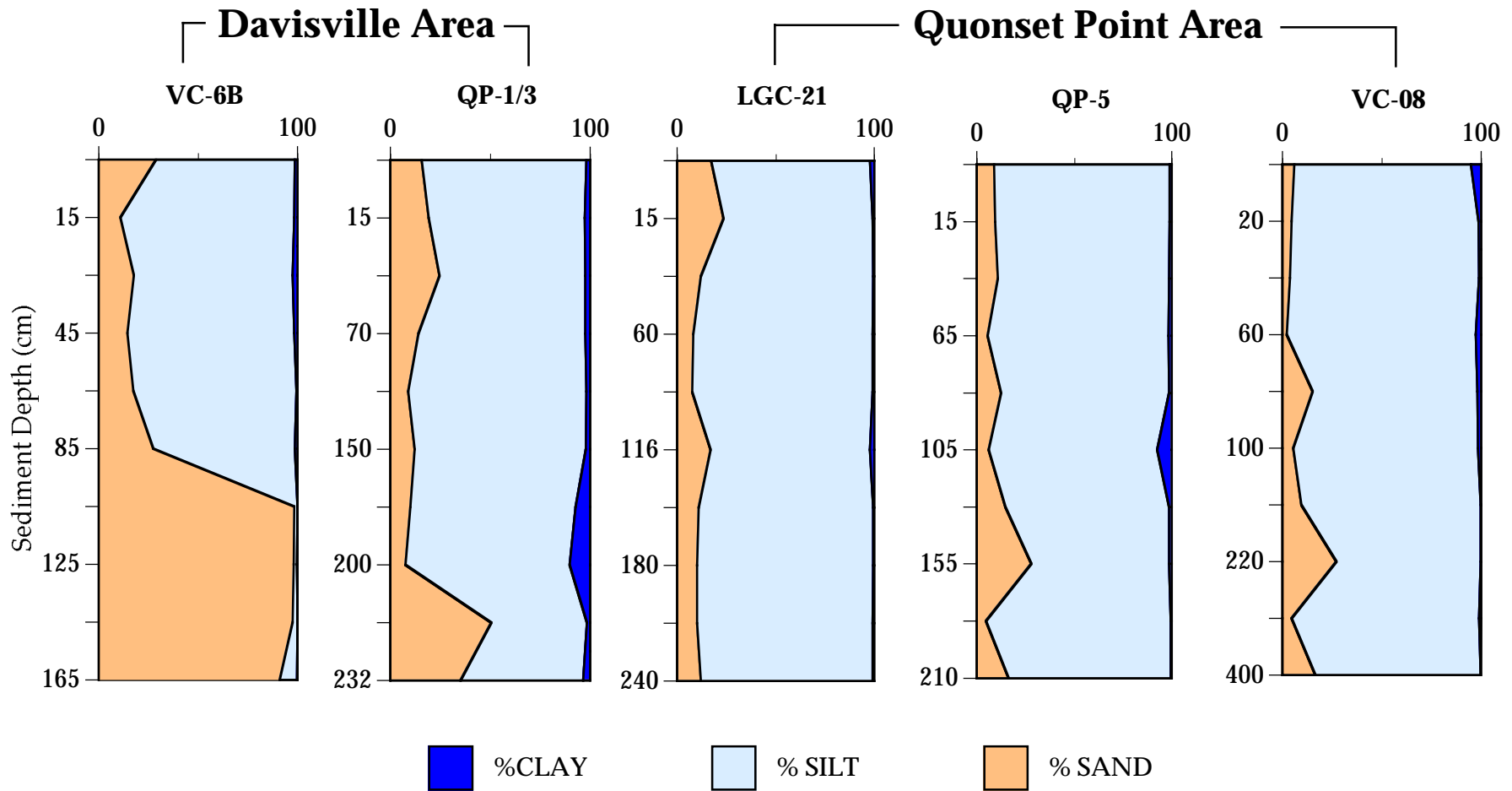


Figure 9: Grainsize (% sand, % silt, and % clay) of sediments from the Davisville and Quonset Point areas.



**Note:**

**The Appendices of the report exist only in hardcopy.**

**Please contact the University of Rhode Island**

**Transportation Center for the Appendices of the report**

**if you need them.**