

ASSESSMENT AND REMEDIATION OF CONTAMINATED SEDIMENTS (ARCS)

Assessment of Sediments in the Buffalo River Area of Concern

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1. INTRODUCTION

1.1 Overview of the ARCS Program

The 1987 amendments to the Clean Water Act, in Section 188(c)(3), authorized the U.S. Environmental Protection Agency's (EPA) Great Lakes National Program Office (GLNPO) to coordinate and conduct a 5-year study and demonstration project relating to the control and removal of toxic pollutants in the Great Lakes, with emphasis on removal of toxic pollutants from bottom sediments. Five areas were specified in the Clean Water Act as requiring priority consideration in locating and conducting demonstration projects: Saginaw Bay, Michigan; Sheboygan Harbor, Wisconsin; Grand Calumet River, Indiana; Ashtabula River, Ohio; and Buffalo River, New York (see Figure 1.1). In response, GLNPO undertook the Assessment and Remediation of Contaminated Sediments (ARCS) Program. ARCS was an integrated program for the development and testing of assessment and remedial action alternatives for contaminated sediments. Information from the ARCS Program activities is used to guide the development of Remedial Action Plans (RAPs) for the 42 Great Lakes Areas of Concern (AOCs, as identified by the International Joint Commission), as well as Lakewide Management Plans.

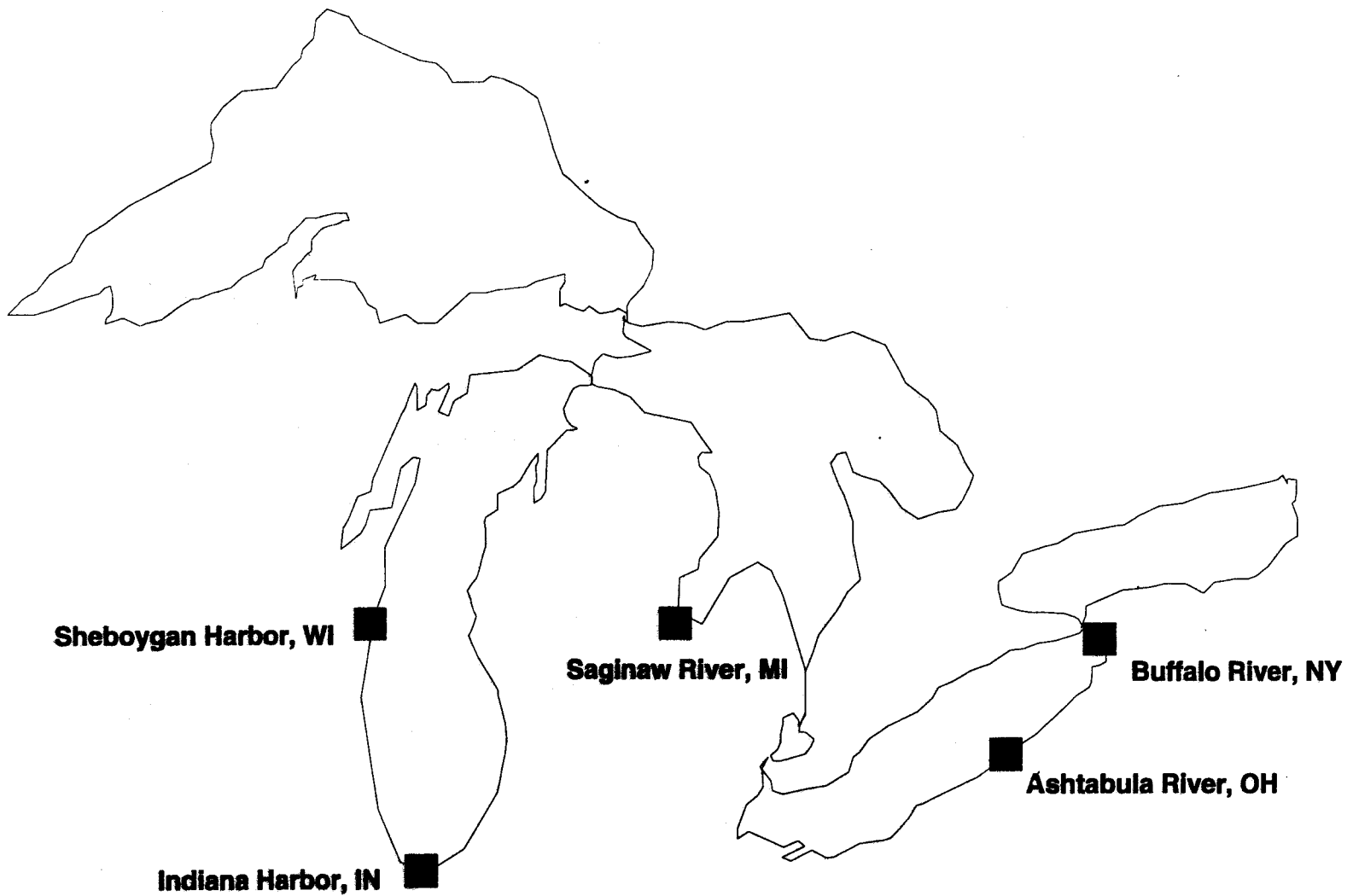
Although GLNPO is responsible for administering the ARCS Program, it is a multi-organization endeavor. Other participants in the ARCS program include the U.S. Army Corps of Engineers (ACE), the U.S. Fish and Wildlife Service (FWS), the National Oceanic and Atmospheric Administration (NOAA), EPA headquarters offices, EPA Regions 2, 3, and 5, Great Lakes State Agencies, numerous universities, and public interest groups.

The Management Advisory Committee provides overall advice on ARCS Program activities. The Management Advisory Committee is made up of representatives from the organizations noted above. Three technical Work Groups identify and prioritize tasks to be accomplished in their areas of expertise. These are the Toxicity/Chemistry, Risk Assessment/Modeling, and the Engineering/Technology Work Groups. The Communication/Liaison Work Group oversees technology transfer, public information, and public participation activities. The Activities Integration Committee coordinates the technical aspects of the work groups' activities.

The overall objectives of the ARCS Program are:

- To assess the nature and extent of bottom sediment contamination at selected Great Lakes Areas of Concern;
- To evaluate and demonstrate remedial options, including removal, immobilization and advanced treatment technologies, as well as the "no action" alternatives; and
- To provide guidance on the assessment of contaminated sediment problems and the selection and implementation of necessary remedial actions in the Areas of Concern and other locations in the Great Lakes.

Figure 1.1 ARCS Program Demonstration Areas



The primary aim of the ARCS Program is to develop guidelines that can be used at sites throughout the Great Lakes. Another goal of the ARCS Program is to develop and demonstrate sediment remediation procedures that are scientifically sound, and technologically and economically practical. The intent is to provide the environmental manager with methods for making cost-effective, environmentally sound decisions. As a result, application of existing techniques is stressed over basic research into new ones.

It is important to stress that the ARCS Program is not a cleanup program, and will not solve the contaminated sediment problems at the five priority consideration areas. The Program will, however, provide valuable experience, methods, and guidance that could be used by other programs to actually solve the identified problems.

There are several important aspects of the management of contaminated sediments that will not be fully addressed by the ARCS Program. Regulatory requirements and socioeconomic factors in decision-making are two such aspects that will be critical in the choice of a remedial alternative (or whether to remediate at all). While not addressing such issues in depth, the ARCS Program will identify issues that need to be resolved before sediment cleanups can go forward.

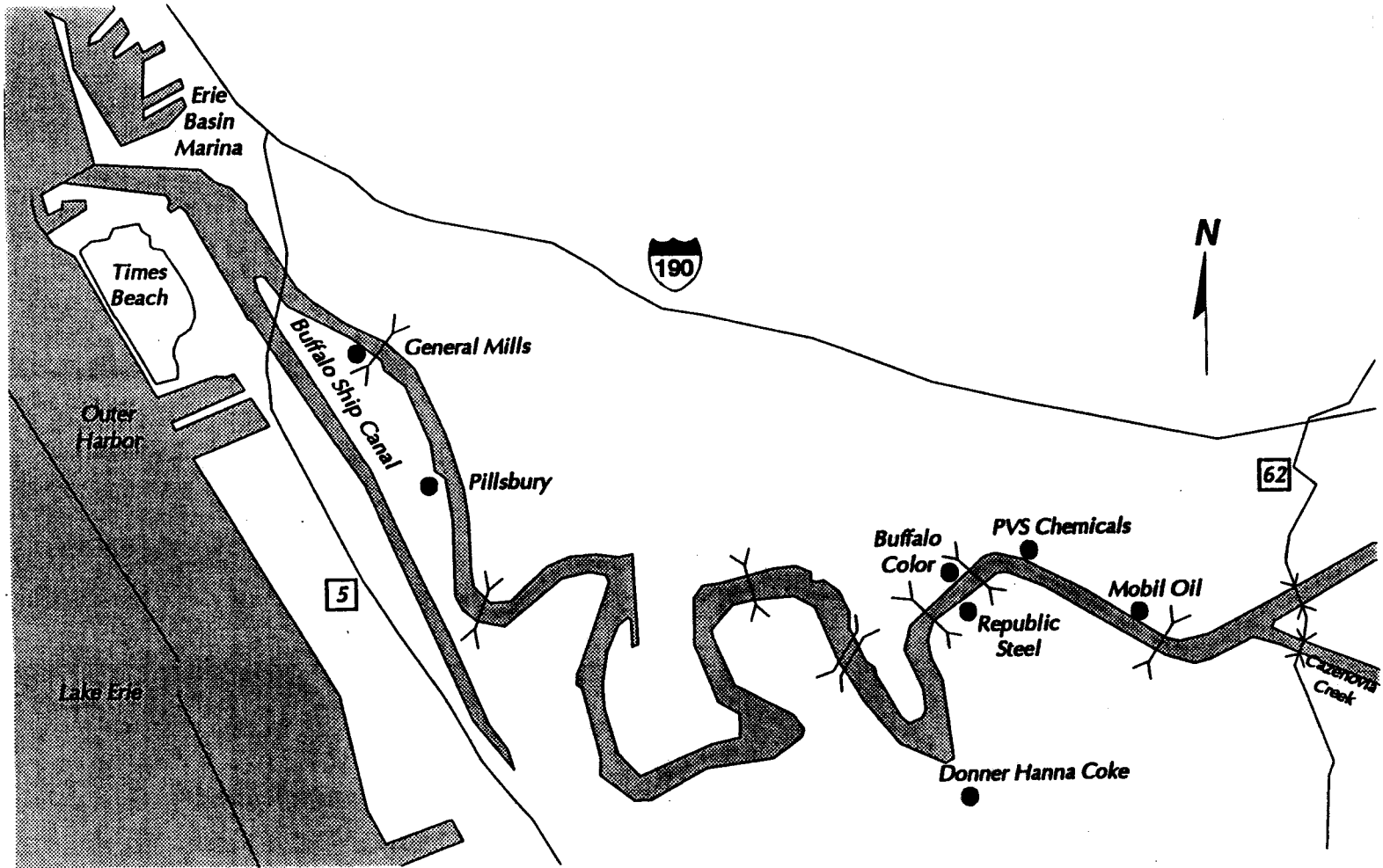
1.2 Overview of the Buffalo River Area of Concern

This report will focus on the Buffalo River Area of Concern (see Figure 1.2). Since the 1940s, the Buffalo River has experienced pollution problems such as excess nutrients, bacteria, and toxic chemicals. Municipal wastewater treatment plants and controls on industrial discharges have reduced many waterborne pollutants. Currently, the most pressing problems are discharges of persistent toxic pollutants, careless disposal of hazardous wastes near waterbodies, combined sewer overflows (CSOs), and sediments contaminated with toxic metals, industrial organic chemicals, polychlorinated biphenyls (PCBs), and polynuclear aromatic hydrocarbons (PAHs). Both surficial as well as deeper sediments throughout the Buffalo River are contaminated from years of industrial activity. Fisheries and benthic populations are severely impaired; fish consumption advisories exist for many fish species. An increased frequency of fish tumors and other deformities have also been reported. River sediments at some locations are also contaminated with cyanide and metals to levels that prohibit open lake disposal of dredge materials.

1.3 Purpose and Organization of the Report

The purpose of this report is to summarize and analyze the existing ARCS sediment data from the Buffalo River Area of Concern (AOC), in order to aid conclusions regarding the nature and extent of sediment contamination within the AOC. The report brings together data from two sampling surveys that have not been provided in a single source or in comparable formats. The two primary sampling surveys are the survey of the 10 Master Stations performed in October, 1989 (Survey 1) and the intensive survey of 37 sampling points performed in August, 1990 (Survey 3). Survey 2 was aborted due to sampling difficulties and the data supplanted by Survey 3.

Figure 1.2 Buffalo River Area of Concern



This report uses sediment quality guidelines and criteria to analyze the relative impact of sediment contamination and does not attempt to analyze or present actual biological impact data. The sediment guidelines may not be robust measures of the absolute impact of sediment contamination but they provide a good relative measure for the probability for impacts. The guidelines and criteria that are used in this report are discussed in detail in Chapter 3.

Chapter 2 of this report provides a complete description of the sampling and analytical methods used in the collection and analysis of sediment samples from the Buffalo River. The text of Chapter 2 draws heavily from documents produced by the the ARCS Toxicity/Chemistry Workgroup.

Chapter 3 contains the summary and analysis of the data from the two sampling surveys. The data are analyzed both by chemical and by location. A complete description of the guidelines and criteria used for the analysis is presented in this chapter as well.

Chapter 4 presents the general conclusions which can be drawn from the results of the analysis.

2. SAMPLING AND ANALYTICAL METHODOLOGY

This chapter summarizes the methodologies used to sample and analyze the sediments in the Buffalo River area of concern (AOC). The methodology is discussed only to allow for an understanding of the nature of the samples used to generate the data presented in this report. The majority of the material in this chapter was taken from the report entitled *ARCS Toxicity/Chemistry Work Group Sediment Assessment Guidance Document* (Filkins, et.al. 1993). The methodologies have been edited from this reference for the purposes of presenting only the highlights of the sampling methodology. More detailed information can be found in the original report.

Assessment of sediment quality must begin by locating deposits of polluted sediments and by collecting representative samples of them. The overall quality of the assessment depends on this, since investigations based on non-representative samples should not be used to support any decision-making processes.

In general, contaminants tend to be associated more with silty sediments of high organic content than with clay or sand. Silts originate in part from suspended organic particles that absorb various contaminants from the water column. Once they settle and are buried over time by newer sediments, the original link with pollutant sources and water quality in general may be broken.

Waters and sediments of each harbor in the Great Lakes possess a unique mosaic of chemical and physical characteristics that reflects the sum of all its historic, anthropogenic alterations. These mosaics of chemical and physical characteristics are sufficiently complex that conducting even a general inventory is very difficult. Complete accounts of historic waste compositions, treatment and disposal practices are seldom available. Changing industrial locations can sometimes be mapped, but provide little information on waste disposal practices. Almost no prior surveys of contaminated sediments include the third dimension of depth, since collecting long cores has been difficult until recently. Consequently, studies of contaminated sediments usually involve a limited number of chemical and toxicological assays performed on surficial samples. These conventional assays are usually expensive, time-consuming and require relatively large volumes of material.

In most urban-industrial harbors, like those studied in the ARCS Program, contaminant distribution in sediments may be highly variable and "patchy". In shipping channels or wherever navigational dredging occurs regularly, deposits of polluted sediments are likely to be thin. However, where dredging was once practiced and then ceased years ago, thick layers of contaminated material may accumulate. Sediment quality in these depositional areas can reflect a complex history of pollution events occurring over a span of decades. Consequently, it is unrealistic to think that a few grab samples of surficial sediment will accurately represent sediment quality. Too often, however, this approach to sampling has formed the only basis for sediment quality assessment. Significant laboratory resources have been spent analyzing sediment samples that may not adequately characterize the system.

The ARCS Program addressed this dilemma by conducting two suites of assays: a set of quick, less expensive assays ("indicator assays") at a large number of reconnaissance stations, and conventional chemical and toxicological assays, performed at a limited number of "Master" stations throughout the study area. Multivariate equations relating the indicator values to the conventional assays were then generated and used to predict endpoints for the conventional assays at the many stations at which only

the indicator assays were conducted. The following sections provide details of the field, laboratory, and statistical procedures employed.

2.1 Collecting and Processing Sediment Samples

2.1.1 *Sampling Vessel*

The sampling vessel, the Research Vessel *Mudpuppy*, capable of operating in shallow waters of less than three feet (1 m), was needed for the ARCS work. It had a climate controlled cabin for electronic equipment and was capable of lifting a ton (900 kg) of weight and 20 foot (6 m) sediment cores onto the deck. Electronic instruments used in the vessel operations included: a marine radio, a fathometer, a Global Positioning System (GPS), computers for data logging and ship's navigation, and a Loran-C receiver serving as a backup for the ship's positioning system.

2.1.2 *Grab Samples*

Grab samples of surficial sediments were collected by steel Ponar or Van Veen grab samplers at each master station and at a few reconnaissance stations where coring was not possible. Benthos samples were collected prior to grab sampling for contaminants and bioassay analysis, to minimize disturbance of the organisms. Five replicate samples were collected at each of the master stations. For more details see USEPA GLNPO (1993).

2.1.3 *Core Samples*

Sediment cores were collected at each of the reconnaissance stations and at most of the master stations. The coring unit used in the Buffalo River was a model P-4 Vibrocorer, manufactured by Rossfelder Corporation (La Jolla, California). This unit proved powerful enough to collect cores over 16 feet (5 meters) in length, even when they included several feet of clay. However, it should be noted that few cores longer than 16 feet were collected even when the 20 foot core tube fully penetrated the bottom. One obvious reason was that the cross-sectional area inside the core nose was about 10 percent less than that of the core tube inner diameter, reducing the collected sediment volume by that much. Another reason may be that friction inside the core tube can exceed the bearing strength of soft sediments, resulting in a plugged core tube that continues to penetrate without collecting more sediment. In addition, gaseous sediments may compress slightly when cored.

During the ARCS Program, each core was described and subsampled on board the sampling vessel. In subsequent, post-ARCS sediment surveys, cores were cut into 3 foot (1 meter) sections and transported to a shore-based facility where they were examined, described, and subsampled. This required a slightly larger field crew, but increased the number of cores that could be collected in a day and also facilitated in-field analyses of selected subsamples.

2.1.4 *Core Documentation*

Proper identification of individual cores and their subsamples was especially important in this project because of both the number of samples collected and the number of laboratories receiving splits of those samples. The visual characteristics of each sediment core total length, position of layers within the core,

and color, texture, and composition of the material were recorded. Ancillary information collected in the field included percent fullness of the Ponar sampler and water chemistry information (dissolved oxygen, conductivity, temperature, and reduction potential) measured with a Hydrolab sonde positioned 3 feet (1 m) above the bottom.

2.2 Characterizing Sediment by Remote Sensing

In larger areas, remote sensing or profiling as a supplement to coring provides a means to interpolate sediment quality between infrequent sampling points. Remote sensing ensured that the locations of all principal sediment types were directly sampled for chemical analysis. Remote sensing also measured whether sediment chemical contamination was associated primarily or entirely with selected sediment deposits which have been geophysically mapped, or distributed in a fashion apparently independent of the mapped deposits. Seismic subbottom profiling and electrical resistivity are two geophysical profiling techniques used for remote sensing sediment characterization. Seismic subbottom profiling of sediments utilizes the reflection of sound waves from different subsurface sediment layers. These layers, exhibiting interfaces of different elasticity of density, are distinguished as distinct layers within the profile trace. Fine-grained sediments, such as clay, demonstrate high porosity, and are, if uncompacted, poor acoustical reflectors. Coarse-grained sediments, such as sand, exhibit lower porosity and tend to be good reflectors (Guigne' et al. 1991).

Electrical resistivity or conductivity profiling is the most common geophysical approach to pollution-related land studies. Despite a wide range of instrumentation and procedures, all of these techniques attempt to measure lateral and vertical variations in electrical resistivity or its reciprocal, electrical conductivity. With the exception of clay-rich material, the electrical resistivity of sediments is determined primarily by porosity, and pore fluid chemistry. For clay-rich sediments, the clay mineralogy is also a significant factor. While it is generally not possible to separate the effects of porosity, pore fluid chemistry, or mineralogy on resistivity measurements, the method is regularly used in land studies for the detection and mapping of clay units or inorganically contaminated groundwater. Thus, electrical resistivity surveys provide a reasonable supplement to the acoustic measurements. Comparison of the electrical properties with actual cores would then provide a basis for associating the electrical properties with sediment types.

In theory, the interpretation of the seismic trace is accomplished by "ground truthing" using sediment cores collected at selected points along the ship's track followed during the seismic survey. The visual description of core stratigraphy is compared to the seismic profile record for that position. A comparison of the core profile to the seismic record allows interpretation of seismic reflectors (layers) as sediment types, such as gravel, sand, silt and clay. The characterization of sediment stratigraphy between cores is mapped using the interpreted seismic profiles, providing a complete picture of sediment distribution in the study area.

2.2.1 Geophysical Survey Design

In portions of the study areas which were less than 100 meters wide, three equally spaced lines parallel to the shoreline were surveyed. In wider portions of the study areas, three parallel lines were utilized with an additional series of diagonal lines forming a diamond pattern overlying the parallel lines. In all cases, the intervals between survey lines were approximately one third of the channel width or finer

resolution. This survey geometry was efficient while it provided adequate coverage and an acceptable number of tie-points (line intersections). The tie-points serve to evaluate the how reproducible of seismic measurements taken at the "same point". The reproducibility of these measurements is a function of the reproducibility of the acoustical profiler and the ship's positioning system. In a quality assurance sense, the number of tie-points used depends on the requirements established in the Quality Assurance Project Plan. It ensured the geophysical profiling of all sediment areas with linear dimensions equal to one quarter of the channel width.

The accuracy of sediment strata thickness and depth measured from the seismic record was limited by the extent to which subsurface velocities were known. Marker beds seen within the "ground truthing" cores were compared to the seismic record for depth correction. When using cores for "ground truthing" seismic records consideration must be given to core compaction which may occur during sample collection. Compaction can be variable throughout the core with greater compaction occurring in the upper core containing less consolidated sediment. The sediment character, corrected depth and thickness of the strata were then mapped between core sites using seismic records.

2.3 Collecting, Storing and Handling Sediment Samples for Chemical Analyses and Bioassays

About 10 liters (L) of bulk sediment grab samples or 4 L of bulk core samples were collected from 10 stations in Buffalo River, New York in October 1989. All chemical analyses of sediment samples were provided by Battelle Laboratory in Sequim, Washington. The chemical samples were collected by personnel of the Large Lakes Research Station (LLRS) in Grosse Isle, Michigan. For analyses, the samples were divided as follows:

1. 50 grams (g) for metals, percentage solids, and total organic carbon (TOC);
2. 250 g for PAHs;
3. 50 g for tributyltin;
4. 20 g for acid volatile sulfides (AVS) and 20 g for methylmercury; and
5. 100 g for Ames and Mutatox assays.

The percentage solids in each sediment sample was estimated by freeze drying the sample and then comparing wet and dry weights. Freeze drying provided a fine, powdery sample that could be more uniformly homogenized. The TOC in samples was determined with a Leco Model WR-12 carbon determinator. Samples were pre-treated with concentrated hydrochloric acid to remove inorganic carbon. Then the samples were burned at 800 °C in an oxygen atmosphere connected to a boat inlet that transferred the evolved carbon dioxide (CO₂) directly into an organic carbon analyzer. Particle size was determined with a Gilson Model WV-2 wet sieve, using U.S. Standard #18 (1 mm), 60 (250 um), 230 (63 um) and 400 (38 um) sieves. Acid volatile sulfides (AVS) were determined according to the method of Cutter and Oattes (1987).

The sediment samples were analyzed for total metals concentrations using USEPA Method 200.4 (USEPA 1990). These techniques are not intended to measure the biologically significant portion of metals. The samples were completely dissolved by digestion with nitric, perchloric and hydrofluoric acids in Teflon[®] pressure vessels and then analyzed by use of cold vapor atomic absorption, or graphite furnace atomic absorption. For crustal elements that are difficult to dissolve with strong acids, a portion

of the freeze-dried samples was ball-milled to about 120 mesh, pelletized, and analyzed with x-ray fluorescence (Nielson and Sanders 1983).

In methylmercury analyses, the homogenized samples were digested in 10 milliliter (mL) of a 25 percent solution of potassium hydroxide in methanol at 60 °C for 2 to 4 hours. Samples were allowed to cool for 24 hours and an additional 10 mL of methanol was added and mixed well by shaking. Before analysis undissolved solids were allowed to completely settle. The samples were analyzed with a cold vapor atomic fluorescence technique (Bloom 1989). The technique is based on the emission of 254 nm radiation by exiting mercury atoms in an inert gas stream. An ethylating agent, sodium tetraethylborate, was added to the sample digestate to form a volatile methylethylmercury derivative. The derivative was then purged onto graphite carbon traps for pre-concentration and removal of interferences. Then the samples were subjected to cryogenic chromatography and pyrolytic degradation to elemental mercury, which was quantified with a cold vapor atomic fluorescence detector.

During analyses for organotins, samples were extracted with 0.2 percent tropolone in methylene chloride, then filtered through glass wool. The filtrates were derivitized with 1 mL hexyl magnesium bromide, a Grignard's reagent, and cleaned-up with a Florisil column. Organotin concentrations were measured with a Hewlett Packard Model 5890 gas chromatograph equipped with a flame photometric detector.

Three groups of organic chemicals were measured for each sediment sample: PAHs, PCBs and chlorinated pesticides, and PCDDs and PCDFs. The analytical procedure for each chemical group included solvent extraction, extract purification with column chromatography, and chemical quantification with capillary column gas chromatography. In the analyses for pesticides and PCBs, aldrin, beta-BHC, gamma-chlordane, 4,4'-DDD, endrin, endrin aldehyde, endrin ketone, heptachlor epoxide, Aroclor 1242 and 1254 were detected in some samples, but either a less than 25 percent difference between the two gas chromatography columns for detected concentrations was observed, or the analyses were conducted at secondary sample dilution factors.

PAHs in sediment samples were extracted according to the USEPA Method 3550 (USEPA 1986). Before extraction, three isotopically labelled surrogate PAH compounds (D10-fluorene, D10-anthracene, D10-pyrene) were added to the samples. Then the samples were extracted with methylene chloride in a Soxhlet extractor. Potential interferences by pigments, lipids and other macromolecules were removed by the use of the USEPA gel permeation chromatography (GPC) Method 3540 (USEPA 1986). Then the extracts were exchanged into hexane and analyzed with the USEPA Gas Chromatography/Mass Spectrometry (GC/MS) Method 8270 (USEPA 1986).

Aroclors quantified were 1016, 1221, 1232, 1242, 1248, 1254 and 1260. Aroclors were extracted from the sediment samples according to the USEPA Method 3550 (USEPA 1986). The GC surrogate compound dibutyl chlorendate (DBC) was added to the samples, and the samples were subsequently extracted with methylene chloride using sonication. Potential interferences by oily-type materials from highly contaminated sediments, lipids, and other macromolecules were eliminated by use of GPC or alumina column chromatography (USEPA 1986, Methods 3540 and 3610). Aroclors were quantified by USEPA Method 8080 (USEPA 1986) using a DB-5 fused silica capillary column (0.25 mm diameter x 30 m) and a Hewlett-Packard 5890 gas chromatography equipped with an electron capture detector (GC/ECD) and a computer for data acquisition. A dual column analysis was always performed

simultaneously and the results from both columns were accepted if they showed no more than a 50 percent variation.

The USEPA isotope dilution Method 8290 (USEPA 1986) was used to extract and clean-up the sediment samples for analysis of PCDDs and PCDFs. Isotopically labelled PCDDs and PCDFs were added to the samples before extraction. The samples were extracted with benzene in a Soxhlet extractor for 18 hours. Then a three step column chromatography procedure with acidified silica gel, alumina, and AX-21 activated carbon on silica gel was used to enrich the samples and remove interferences. Isotopically labelled 2,3,7,8-TCDD was added to the samples before the enrichment to determine the efficiency of the method. Two internal standards were added to the samples after sample enrichment to determine percent recoveries. The PCDDs and PCDFs were quantified with capillary columns gas chromatography of groups of ion masses described in the USEPA Method 8290 (USEPA 1986).

Pore water samples were prepared by Battelle's Marine Sciences Laboratory in Sequim, Washington from about 40 L of sediment samples. Aliquots of the 40 L samples were extracted in acid-cleaned 500 mL Teflon jars by centrifugation in a modified clothing extractor at 2,000 RPM for 15 minutes. The pore water was decanted into clean 150 mL glass centrifuge tubes and then centrifuged again at 2000 RPM for one hour. The pore water was then pipetted without filtration into 500 mL acid-cleaned Teflon bottles, acidified to pH 2 with nitric acid (HNO₃), and stored at room temperature for metal analyses.

Immediately after preparation, water quality characteristics of the dilution water and 100 percent elutriate samples were determined (APHA et al., 1975). Dissolved oxygen (mg/L) was measured with a YSI Model 54-A oxygen meter. Conductivity (umhos/cm, corrected to 25 °C) was measured with a YSI Model 33 S-C-T conductivity meter. The pH and alkalinity (mg/L as CaCO₃) was determined by burette titration. Ammonia (mg/L) was measured with an Orion 940E ionalyzer and a 95-12 ammonia electrode. Turbidity (NTU) was measured with a Cole-Palmer Model 8391-35 turbidity meter. Unionized ammonia was determined by converting the total ammonia measured in the samples to unionized ammonia, and then correcting for pH and temperature (Thurston et al. 1974). After preparation of the dilution water and 100 percent elutriates, samples for chloride (mg/L) were placed in 250 mL I-CHEM bottles, labeled, and stored at 4 ± 3°C until analysis with an Orion 940E ionalyzer and a 94-17B electrode. The pH, dissolved oxygen, and conductivity were measured at the beginning and end of each daphnid test in the 100 and 25 percent treatments, and in the dilution water control. About 500 mL of each 100 percent elutriate sample were placed in Teflon bottles, acidified to pH 2 with redistilled hydrochloric acid, and shipped via overnight courier to Battelle Marine Sciences Laboratory in Sequim, Washington for metals analyses.

Elutriate and pore water samples were analyzed for silver (Ag), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), selenium (Se), and zinc (Zn). With the exception of Hg and Zn in elutriates, all pore water and elutriate samples were analyzed without sample preparation. The Zn in elutriates was quantified by flame atomic absorption. The Hg in elutriates were analyzed for metals by cold vapor atomic fluorescence with sub-nanogram per liter (ng/L) detection limits. Organics prevalent in many of the samples were broken down before Hg analysis by use of a bromine monochloride/UV oxidation procedure (Bloom and Crecelius 1983).

2.4 Quality Control and Quality Assurance

Accuracy and precision of the chemical analyses were determined by analysis of one blank, one matrix spike, one certified reference material, and one sample in duplicate or triplicate for each set of 20 samples. Acceptable recovery values ranged from 85 to 115 percent of the spike concentration for organics and organometals. Analytical values for reference materials were acceptable if they were within 20 percent of the certified ranges. The acceptable coefficient of variation for duplicate or triplicate sample analyses was ≤ 20 percent.

During chemical analyses, three to five standards containing concentrations that bracketed the expected range of concentrations in the samples were used for daily instrument calibrations. In analyses of samples for metals by atomic absorption spectrophotometry, these standards were analyzed as matrix spikes, and the slopes from linear regression analyses were used to estimate sample concentrations. The minimum acceptable r^2 in the regression analyses was 0.97. The standards for each sample set were analyzed at the beginning and end of each analytical run. The analytical results were accepted if the values for standards were within 90 to 110 percent of their certified values. For some samples analyzed by atomic absorption, average response factors, rather than linear regression, were used for instrument calibration. The accuracy of this calibration method was checked by dividing each response factor by the average response value. The calibration values were accepted if they were within 5 percent of the average response value.

During chemical analyses, the method's detection limits (MDL) was estimated according to procedures in the USEPA Federal Register (1984).

Three sample matrices were analyzed; whole sediment (grain size, total and volatile solids, metals, solvent extractable residue, organohalogens, and TOC), sediment elutriates (ammonia and Microtox), and sediment pore water (conductivity). The elutriate creation procedure was originally designed to mimic the rapid desorption of contaminants from sediments resulting from the open-water disposal of dredged materials (Plumb 1981). Elutriates are cheaply and easily prepared, but the mixing of the sediment and water may influence the availability of some contaminants by changing their oxidative states. Pore water sampling better reflects the interstitial concentration of contaminants resulting from the partitioning of chemicals from sediments, and appropriate sampling techniques probably have a lesser impact on the chemistry of the contaminants than the elutriate procedure. Pore water squeezers and extractors are more expensive than the equipment required for elutriate preparation, however, and require a greater volume of sediment to produce a comparable volume of liquid test media.

Data storage, retrieval and manipulation were performed using Paradox, a PC-based relational database program. To facilitate use of the data, a user "shell" was created using the Paradox Applications Language (PAL). The user shell was designed to allow easy access to the data, calculate RPDs for QC checks, search for missing samples, format data for creation of icons and provide significant figure-formatted output. Analytical data were checked for entry accuracy by the analyst, and the quality of the data was verified by both the analyst and the project QC coordinators by examination of the QC data associated with each assay (blanks, replicate RPDs, reference materials, etc.). Data were not used for statistical calculations (nor released to GLNPO) until all applicable QC criteria were met. Raw data from this study are archived by GLNPO in their Ocean Data Evaluation System (ODES) database.

3. RESULTS

3.1 Introduction

This chapter presents a summary and analysis of the sediment chemical data collected from the Buffalo River based on the two major sampling surveys performed by the ARCS program. The purpose of the analysis is to provide a preliminary examination of the potential for chemical contaminants to cause adverse impacts to aquatic life or uses of the Buffalo River system. Since the data presented are chemical only and not biological, the analysis is limited in its ability to predict absolute biological effects.

The data in this chapter are analyzed in two ways:

- On a chemical-by-chemical basis, providing an analysis of where unusually high and/or potentially harmful concentrations of individual chemicals are found within the Buffalo River AOC, and
- On a sample-by-sample basis, providing an analysis of which locations contain elevated levels for the greatest number of contaminants.

The first type of analysis aids in the determination of which *chemicals* are of greatest concern. The second analysis assists in determining which *areas* of the AOC suffer the greatest levels of sediment contamination. The analysis relies on the comparison of measured sediment concentrations to chemical-specific guidelines or criteria.

In order to estimate potential effects, benchmark criteria or guidelines were necessary against which the potential for a given concentration of sediment contamination to cause environmental harm could be assessed. USEPA has currently endorsed an equilibrium partitioning (EqP) based approach for assessing sediment contamination (USEPA, 1993a-e). Unfortunately, this method has only been fully developed for a limited number of heavy organic contaminants. A more comprehensive set of sediment quality guidelines has been developed by Long and Morgan (1990) for the NOAA Status and Trends program. The NOAA guidelines lack the toxicological precision of the EqP-based criteria, but their applicability to a wider set of parameters makes them useful for the current analysis. Both EqP and NOAA COSED guidelines are discussed more completely in Section 3.2.

The data presented in this section are based on the results of two primary sampling surveys. Survey 1, or the Master Station survey, consists of grab samples taken from the ten ARCS Buffalo River Master Stations. The locations and sample numbers of the Buffalo River Master Stations are shown in Figure 3.1. The second survey referred to in this section, Survey 3, consists of a series of 4 to 8 foot depth core samples collected at the Master Stations plus a number of additional sampling locations chosen to provide greater resolution on the areal extent and depth of sediment contamination in the AOC. The locations of the Survey 3 sample points are shown in Figure 3.2. Methods for sample collection and analysis are more fully described in Chapter 2.

FIGURE 3.1 BUFFALO RIVER SURVEY 1 SAMPLE LOCATIONS (MASTER STATIONS)

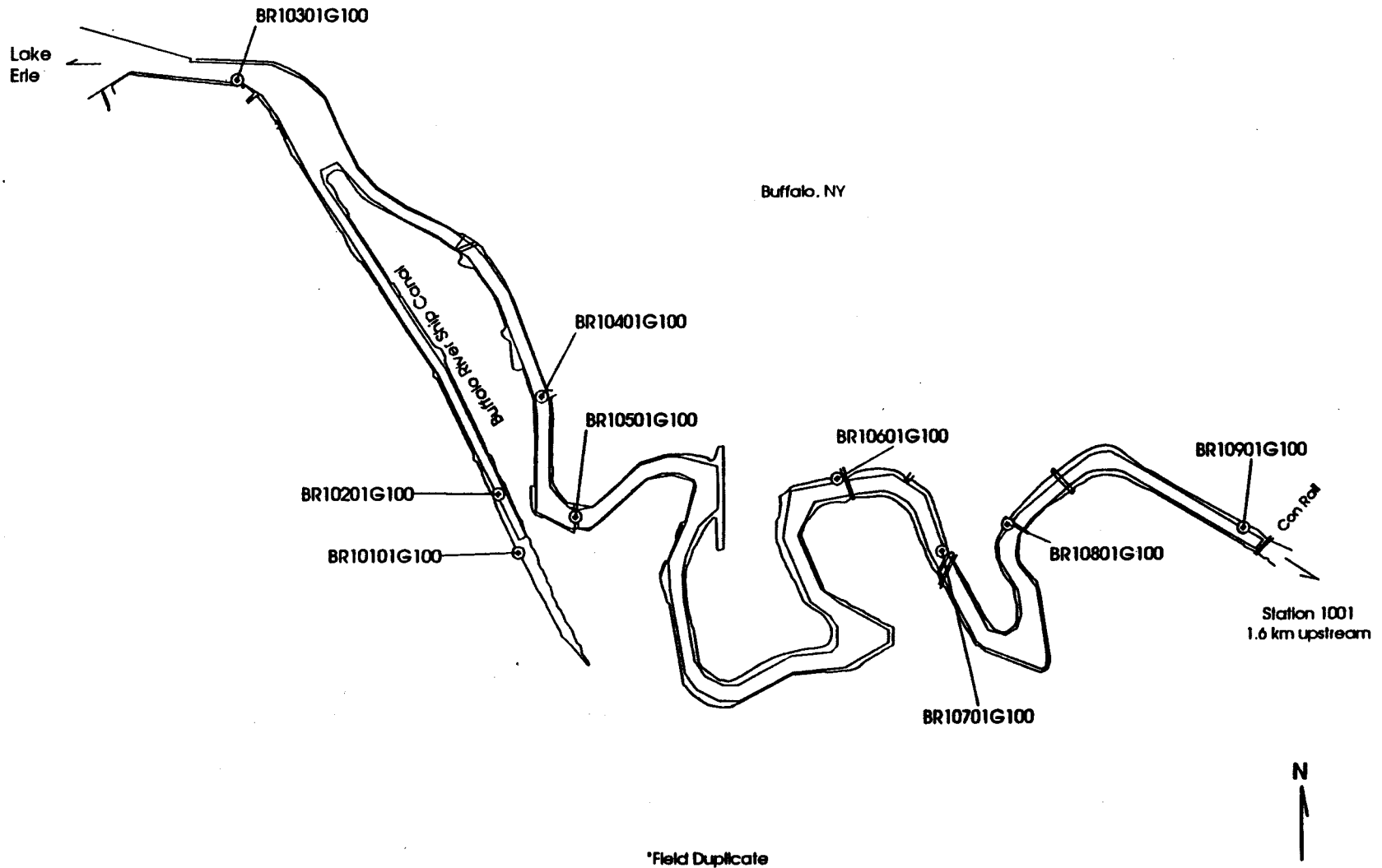
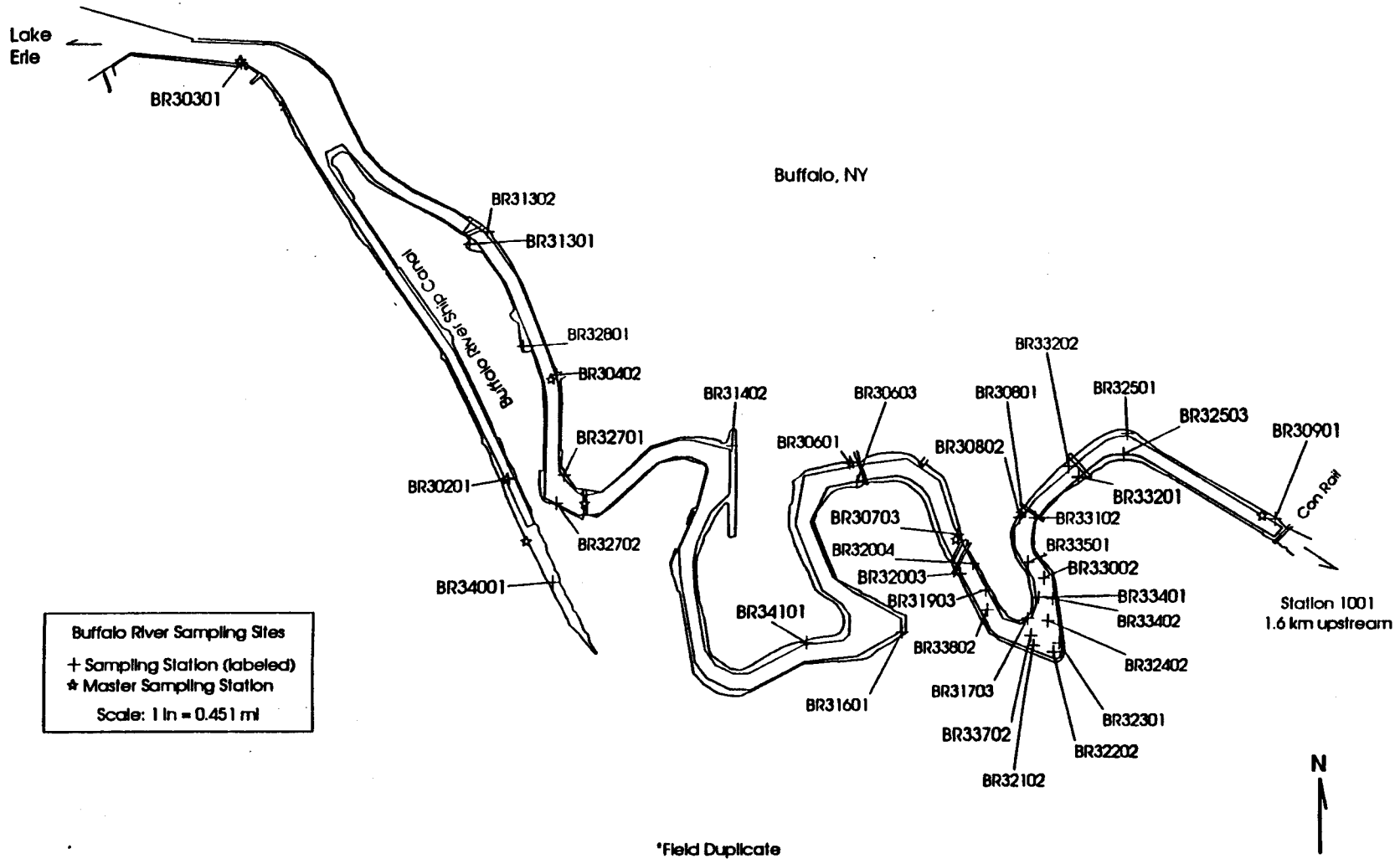


FIGURE 3.2 BUFFALO RIVER SURVEY 3 SAMPLE LOCATIONS



3.2 Availability of Sediment Quality Guidelines

The need for easily applicable yardsticks to make decisions regarding the impact of contaminated sediments is obvious. The primary EPA effort at preliminary sediment criteria development has focused upon Equilibrium Partitioning based approaches (EPA, 1993a-e) that utilize the concentration of organic carbon in sediments along with a measure of the relative tendency of a contaminant to bind with organic carbon (the partitioning coefficient) to predict the interstitial water concentration of the contaminant within a particular sediment.

Other efforts have focused on the use of standardized bioassays, comparisons of concentration and effects data (e.g., AETs and PELs), and leachate and elutriate testing, among others. A complete overview of the available sediment assessment methods can be found in the *Sediment Classification Methods Compendium* (USEPA, 1992).

3.2.1 Background on EPA EqP-Based Criteria

EPA has selected the equilibrium partitioning (EqP) method as its primary approach to developing numeric sediment quality criteria for contaminated sediments. The EqP approach is based on three primary observations about the toxicity of organic contaminants in sediment (EPA, 1993). These are:

- The toxicity of non-ionic organic contaminants in sediments is most closely related to the interstitial water concentrations of the contaminant rather than the bulk sediment concentration of the contaminant;
- Non-ionic organic contaminants bind primarily to the organic carbon within the sediment and partitioning models can relate the relative concentrations of contaminants bound to organic carbon and in pore water; and
- Benthic and water column organisms show similar sensitivities to chemicals so that currently established water quality criteria can be used to determine acceptable pore water chemical concentrations.

The EqP model uses the bulk concentration of contaminant and organic carbon in the sediment and a chemical-specific partitioning coefficient to predict the pore water concentration of the contaminant at equilibrium conditions. The term "equilibrium conditions" indicates that sediment conditions are not in a state of flux and that sufficient time has passed for sediment and pore water concentrations to stabilize. Examples of non-equilibrium conditions include situations where there is significant erosion or deposition of sediments or changes in contaminant concentrations.

There are several limitations to the EqP-based approach. The most obvious is that the method is currently only applicable to non-ionic organic contaminants. This eliminates the approach as a tool for determining the potential toxicity of lighter organic contaminants and toxic metals. Another drawback is that complete criteria are currently developed for only five contaminants. These contaminants are the polynuclear aromatic hydrocarbons (PAHs) phenanthrene (USEPA, 1993e), acenaphthene (USEPA, 1993a), and fluoranthene (USEPA, 1993d), and the pesticides dieldrin (USEPA, 1993b) and endrin (USEPA, 1993c).

For the five EqP-based criteria that are currently available, only phenanthrene and fluoranthene were analyzed for at the Buffalo River Master Station locations. A complete list of analytes for Master Station samples and the applicable sediment quality criteria are presented in Table 3.1.

3.2.2 Background on NOAA Status and Trends Guidelines

Several sets of sediment quality guidelines have been developed through comparison of sets of sediment contaminant concentration data and associated biological impact data. The best known of these was published in Long and Morgan (1990). In the Long and Morgan approach, sediment concentrations of contaminants were compared to associated biological impacts data and evaluated to determine concentration ranges in which biological impacts were likely to occur, based on a preponderance of evidence approach.

The evaluation was performed by arranging all concentration data for a single contaminant in ascending order. Only data that had associated effects data were utilized and only where that associated data showed some measurable level of impact greater than zero. Therefore all data utilized in the analysis are from sediments that have been associated with some adverse biological effect.

Long and Morgan used the tabulated data to determine two guideline numbers for each contaminant. These are:

- An Effects Range-Low (ER-L) which corresponds to the lower 10th percentile of the tabulated data; and
- An Effects Range-Median (ER-M) which corresponds to the 50th percentile of the tabulated data.

The ER-M and ER-L values are not official NOAA standards but are intended to be useful as guidance in the evaluation of bulk sediment chemistry data. They are utilized in this document with this intent. Exceedances of chemical concentrations of ER-L and ER-M levels should not be construed as an absolute indicator of biological impacts but only as a relative indicator for the potential for such.

Of the total number sediment guidelines determined in the NOAA guidance, 25 are applicable to the analytical data collected for the Buffalo AOC. A complete listing of all analytes and the applicable NOAA guidelines is presented in Table 3.1.

TABLE 3.1 ANALYTES AND SEDIMENT QUALITY GUIDELINES

CHEMICAL	Parameters Sampled		Sediment Quality Guidelines		
	Survey 1 (Master Stations)	Survey 3	NOAA ER-M	NOAA ER-L	EPA EqP Criteria
PAHs					
Benzo(a)anthracene	X	X	1,600 ng/g	230 ng/g	
Benzo(a)fluoranthene		X			
Benzo(b)fluoranthene	X				
Benzo(a)pyrene	X	X	2,500 ng/g	400 ng/g	
Benzo(k)fluoranthene	X	X			
1,4-Dichlorobenzene	X				
Naphthalene	X		2,100 ng/g	340 ng/g	
2-Methylnaphthalene	X		670 ng/g	65 ng/g	
Dimethylphenol	X				
Dibenzofuran	X				
Fluorene	X		640 ng/g	35 ng/g	
Phenanthrene	X		1,380 ng/g	225 ng/g	180 ug/gOC
Anthracene	X		960 ng/g	85 ng/g	
Fluoranthene	X		3,600 ng/g	600 ng/g	620 ug/gOC
Pyrene	X		2,200 ng/g	350 ng/g	
Butyl benzyl phthalate	X				
Bis(2-ethylhexyl)phthalate	X				

TABLE 3.1 ANALYTES AND SEDIMENT QUALITY GUIDELINES

CHEMICAL	Parameters Sampled		Sediment Quality Guidelines		
	Survey 1 (Master Stations)	Survey 3	NOAA ER-M	NOAA ER-L	EPA EqP Criteria
Chrysene	X		2,800 ng/g	400 ng/g	
Di-n-octyl phthalate	X				
Indeno(1,2,3)pyrene	X				
Benzo(g,h,i)perylene	X				
Total PAH	X		35,000 ng/g	4,000 ng/g	
PESTICIDES					
Cis-chlordane		X			
DDD		X	20 ng/g	2 ng/g	
DDE		X	15 ng/g	2 ng/g	
DDT		X	7 ng/g	1 ng/g	
Dieldrin		X	8 ng/g	0.02 ng/g	11 ug/gOC
1,2-D		X			
Heptachlor		X			
Heptachlor Epoxide		X			
TCMX		X			
Trans-chlordane		X			
PCBs		X	400 ng/g	50 ng/g	

TABLE 3.1 ANALYTES AND SEDIMENT QUALITY GUIDELINES

CHEMICAL	Parameters Sampled		Sediment Quality Guidelines		
	Survey 1 (Master Stations)	Survey 3	NOAA ER-M	NOAA ER-L	EPA EqP Criteria
METALS					
Cadmium	X	X	9 ug/g	5 ug/g	
Chromium	X	X	145 ug/g	80 ug/g	
Copper	X	X	390 ug/g	70 ug/g	
Iron	X	X			
Nickel	X	X	50 ug/g	30 ug/g	
Lead	X	X	110 ug/g	35 ug/g	
Zinc	X	X	270 ug/g	120 ug/g	
Silver	X		2.2 ug/g	1 ug/g	
Arsenic	X		85 ug/g	33 ug/g	
Mercury	X		1.3 ug/g	0.15 ug/g	
Manganese	X				
Methylmercury	X				
Tributyltin	X				
MBT	X				
Dibutyltin	X				

TABLE 3.1 ANALYTES AND SEDIMENT QUALITY GUIDELINES

CHEMICAL	Parameters Sampled		Sediment Quality Guidelines		
	Survey 1 (Master Stations)	Survey 3	NOAA ER-M	NOAA ER-L	EPA EqP Criteria
NON-METALS					
Total Organic Carbon	X	X			
Acid Volatile Sulfides	X				
Extractable Residue		X			
pH	X	X			
Conductivity	X	X			
Percent Solids	X				
Solids, Total	X				
Volatile Solids	X				
Mircrotox	X	X			
Ammonia	X	X			
Bromine	X	X			
Chlorine	X	X			
Iodine	X				
Grain Size	X	X			

3.3 Analysis of Chemical-Specific Data

This section reviews the analytical data on a chemical by chemical basis in order to determine sampling locations associated with exceedances of criteria or guidelines. For the application of EqP-based criteria, data were normalized using the sediment concentration of organic carbon. NOAA Guidelines have been applied on a bulk chemistry basis. The fact that a location contains chemical concentrations that exceed guideline levels is not an indicator of definite biological impacts but only of a heightened

probability for such. On the other hand, levels below guidelines for a single chemical are obviously not an indication that a sediment is "safe". The additive or synergistic effects of multiple contaminants are not addressed by single chemical criteria or guidelines.

3.3.1 *Explanation of Data Presentation*

The data in this section of the report are presented both in narrative and graphical forms. The narrative section provides:

- Summary statistics in the form of minimum, maximum, and median concentrations;
- The applicable sediment quality criteria or guidelines; and
- A narrative explanation of graphic data with conclusions on the areal distribution of high concentration data.

The summary statistics are chosen to indicate the range of concentrations present (through the minimum and maximum) and the central concentration (through the median) of a chemical. The use of the median rather than average concentrations eliminates the effect of outliers and the averaging of non-detect data. It should also be noted that the summary statistics presented for Survey 3 results are independent of core depth (i.e., the minimum value may be from a surface sample and the maximum value from a subsurface core depth). However, any significant distinctions between core depths is noted in the text for each chemical.

Appendix A presents the raw data collected from Surveys 1 and 3. In determining summary statistics, Survey 1 and Survey 3 data are not combined. The combining of the two data sets was considered inappropriate given the differences in both sampling (grab samples versus core samples) and analytical methods between the surveys (refer to Chapter 2 for a complete description of sampling and analytical methods).

The graphical portion of the analysis consists primarily of a series of bar graphs indicating the relative level of contaminant concentration between various sampling location within a given survey. The use of bar graphs was chosen over maps since the number of sampling points and the number of sampling depths in Survey 3 make it difficult to present the data on maps in a way in which data from the multiple sampling depths could be directly compared. However, for reference, maps containing the data plotted by Survey 1 and 3 sample locations are provided in Appendix B.

The data in the bar graphs is separated by survey. Data in each of the graphs is arranged downstream to upstream starting from the ship canal up to the Con Rail bridge. Because of the greater number of sampling locations and subsampling at multiple depths, Survey 3 data are presented in a somewhat different format. Also, in order to simplify the cross references between the maps, graphs and text, the sampling locations have been renumbered with single digit location identifiers. Table 3.2 presents a cross-reference between the original sample numbers presented in Figures 3.1 and 3.2 and those used in the remaining figures in this chapter. Figures 3.3 and 3.4 depict the location of the renumbered sample locations for Survey 1 and Survey 3, respectively. The bar charts (Figures 3.5 through 3.24) are located at the end of the chapter (starting on page 49 of this report).

TABLE 3.2 SURVEY 3 - CROSS REFERENCE TABLES

Organized by Chart Number	
Report	Original Sample
1	BR34001
2	BR30201
3	BR30301
4	BR31301
5	BR31302
6	BR32801
7	BR30402
8	BR32701
9	BR32702
10	BR31402
11	BR34101
12	BR31601
13	BR30601
14	BR30603
15	BR30703
35	BR32503
36	BR32501
37	BR30901
Intensive Zone	
16	BR32003
17	BR32004
18	BR31903
19	BR33801
20	BR33702
21	BR31703
22	BR32102
23	BR32202

Organized by Sample Number	
Original Sample	Report
BR30201	2
BR30301	3
BR30402	7
BR30601	13
BR30603	14
BR30703	15
BR30801	31
BR30802	30
BR30901	37
BR31301	4
BR31302	5
BR31402	10
BR31601	12
BR31703	21
BR31903	18
BR32003	16
BR32004	17
BR32102	22
BR32202	23
BR32301	21
BR32402	25
BR32501	36
BR32503	35
BR32701	8
BR32702	9
BR32801	6
BR33002	28

TABLE 3.2 SURVEY 3 - CROSS REFERENCE TABLES

Organized by Chart Number	
Report	Original Sample
24	BR32301
25	BR32402
26	BR33402
27	BR33401
28	BR33002
29	BR33501
30	BR30802
31	BR30801
32	BR33102
33	BR33201
34	BR33202

Organized by Sample Number	
Original Sample	Report
BR33102	32
BR33201	33
BR33202	34
BR33401	27
BR33402	26
BR33501	29
BR33702	20
BR33802	19
BR34001	1
BR34101	11

The following features of the bar graphs should be noted:

- The numbers under each of the graphs correspond to the revised sample numbers for Survey 1 and Survey 3, presented in Figures 3.3 and 3.4, respectively.
- The parallel dashed lines through the graphs indicate the level of the applicable criteria or guideline value for the contaminant, either NOAA or EPA EqP-based.
- The Survey 3 graphs are grouped by sets of four in order to present various sampling areas and multiple sampling depths.

Figure 3.6b shows the typical graphical presentation for Survey 3 data. The top two graphs (Graphs A and B) present sampling points 1-15 and 35-37 shown in the map in Figure 3.4a. The bars are spaced proportionately to downstream river distance starting from inside the shipping channel. Graphs A and B are different in that they present samples from different core depths. Graph A presents data from 0-2 foot (solid bars) and 2-4 foot (hollow bars) samples. Graph B presents data from the 4-6 foot (solid bars) and 6-8 foot (hollow bars) samples. The samples from the intensive sampling zone (samples 16 - 34 shown in Figure 3.4b) are omitted from these graphs and displayed in Graphs C and D. Graph C presents data from 0-2 foot and 2-4 foot core samples; Graph D presents data from 4-6 foot and 6-8 foot samples.

FIGURE 3.3 BUFFALO RIVER SURVEY 1 CHART NUMBER CROSS REFERENCE

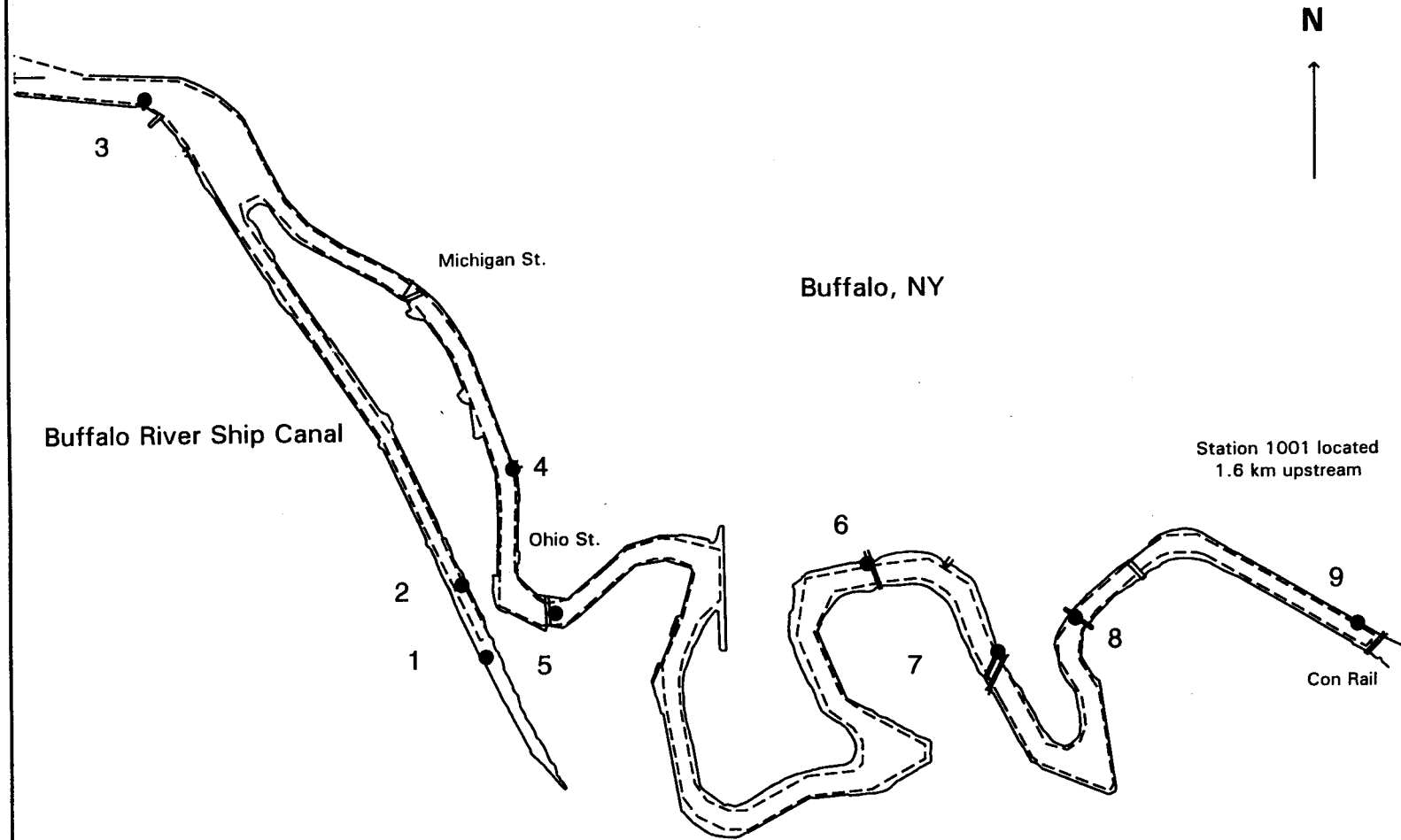


FIGURE 3.4a BUFFALO RIVER SURVEY 3 CHART NUMBER CROSS REFERENCE

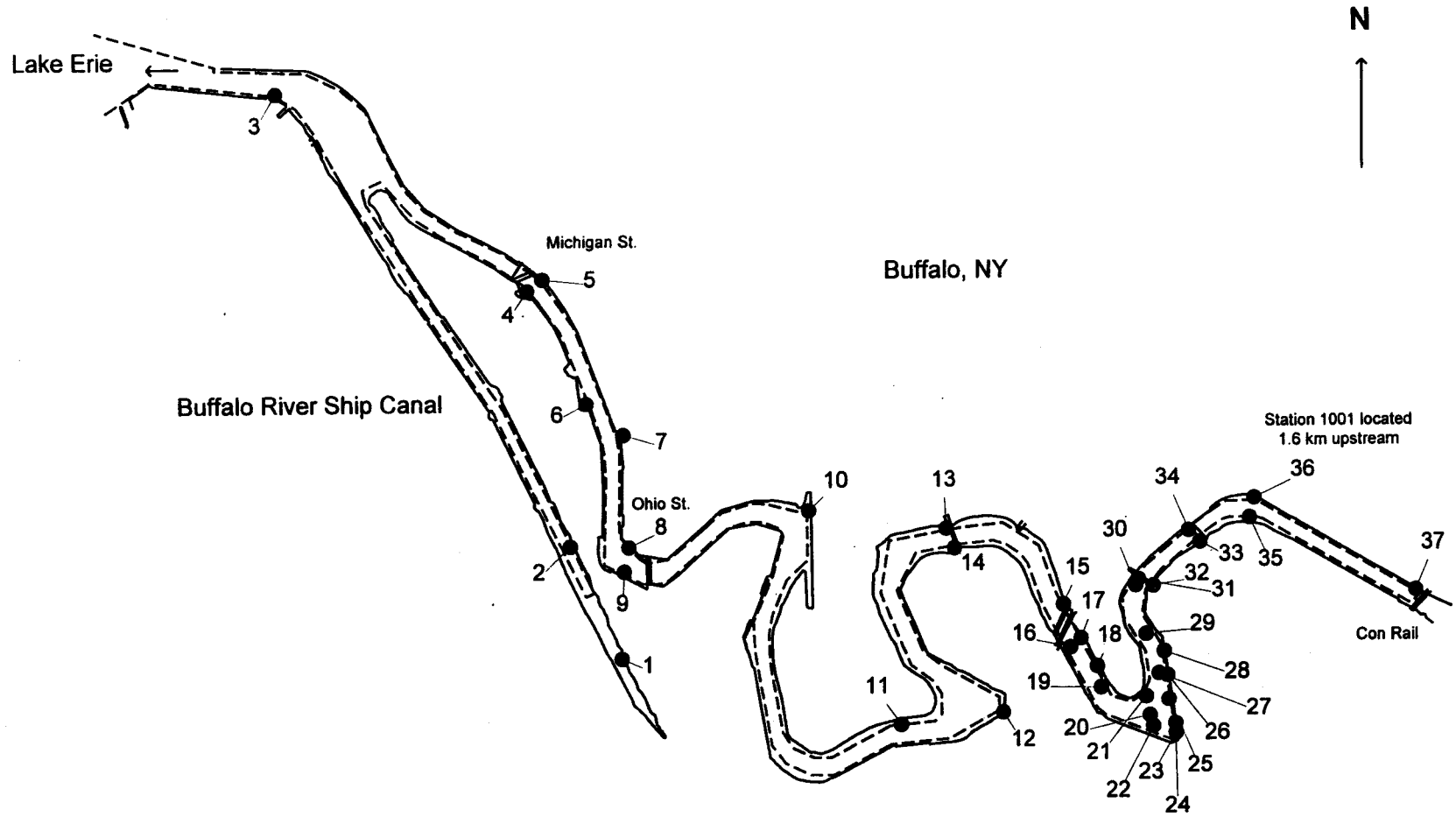
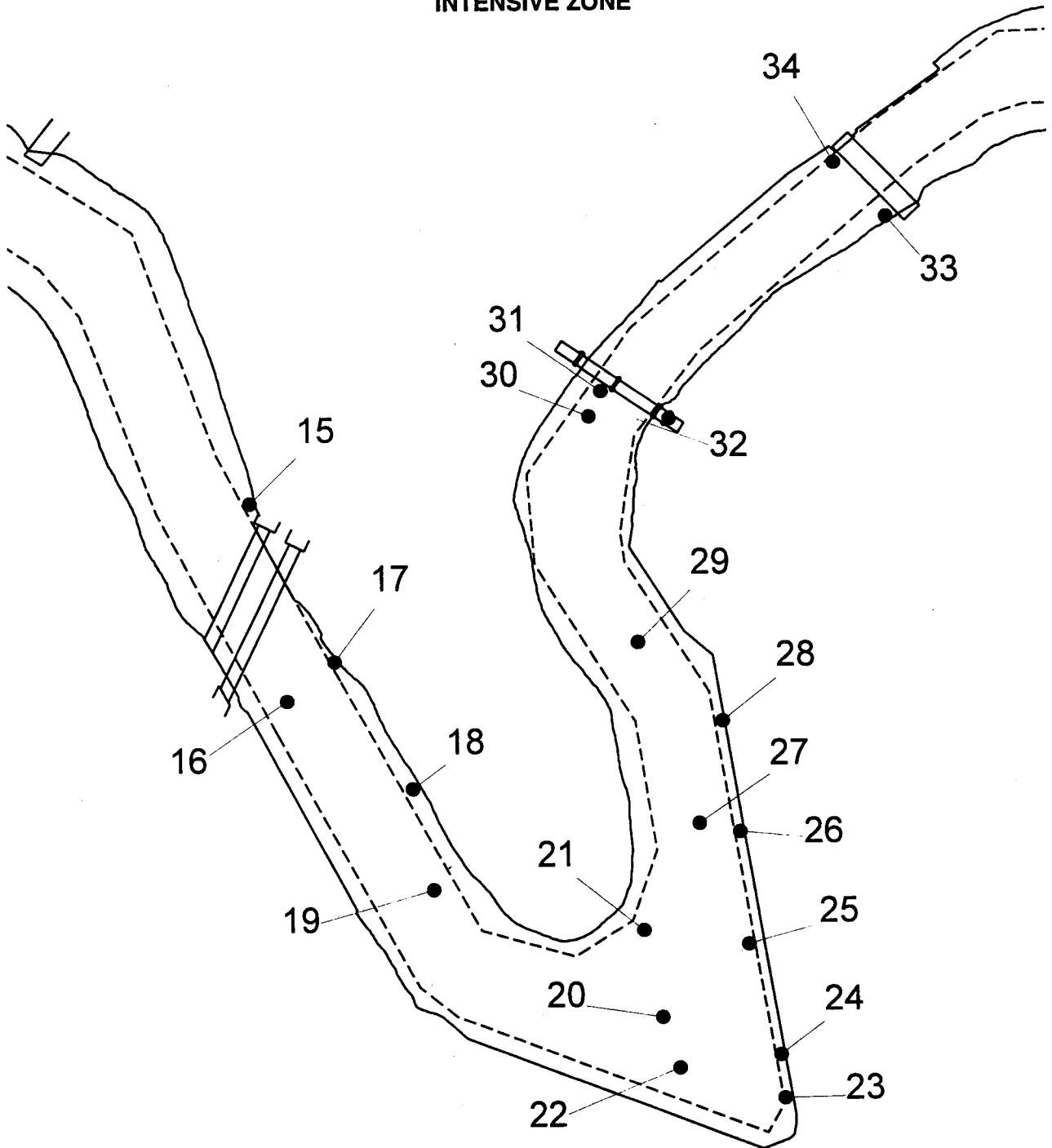


FIGURE 3.4b BUFFALO RIVER SURVEY 3
CHART NUMBER CROSS REFERENCE -
INTENSIVE ZONE



3.3.2 Analysis by Chemical Parameter

This section focuses on the chemicals for which either NOAA (ER-M and ER-L) or EPA (EqP-based criteria) are available. All other data are provided in Appendix A.

Arsenic

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	<1.4	12.1	34	N/A	33	85
3	N/A	N/A	N/A			

N/A - Not available
(All units are in ug/g)

Arsenic levels do not exceed the ER-M at any Survey 1 sample location. The ER-L is slightly exceeded only in the southern end of the ship canal (34 ug/g). The lowest concentration of arsenic is found within the ship canal, just downstream of the northern end where it was undetected at 1.4 ug/g. Arsenic concentrations are shown relative to the ER-L and ER-M in Figure 3.5.

Cadmium

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	0.03	0.95	4.0	N/A	5	9
3	0	2.4	33			

N/A - Not available
(All units are in ug/g)

Neither ER-L nor ER-M values were exceeded by Survey 1 Master Station samples (see Figure 3.6a). Except for the southern end of the ship canal, all values are well below (less than 50 percent) the ER-L value for cadmium.

The Survey 3 data, however, demonstrates numerous exceedances of both the ER-L and the ER-M (see Figure 3.6b). The greatest exceedances were found in samples from the intensive sampling zone (Figure 3.6b; Graphs C and D), especially at the 2-4 foot depth where seven samples exhibited concentrations in excess of the ER-M. Four additional ER-M exceedances were found at 4-6 foot and 6-8 foot depths in the intensive zone. Several surface samples outside of the intensive zone also contained ER-M exceedances (Samples 7 and 8 in Figure 3.6b; Graph A)

Chromium

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	< 13	84.5	312	N/A	80	145
3	6.4	73.5	2,500			

N/A - Not available
(All units are in ug/g)

Survey 1 sediment concentrations of chromium exceeded the ER-M at one location at the southern end of the ship canal (Sample 1 in Figure 3.7a), with a value of 312 ug/g. The ER-L was exceeded at four additional locations (Samples 3, 5, 6, and 7) with values ranging from 92 to 113 ug/g.

Survey 3 sediment concentrations exceeded the ER-M in 41 samples (Figure 3.7b). The majority of the exceedances occurred within the intensive sampling area and below the surface (Figure 3.7b; Graphs C and D). The highest concentration (2,500 ug/g) was found at the 6-8 foot depth in Sample 32. Most of the exceedances of the ER-M were found within the 2-4 foot and 4-6 foot sections.

Copper

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	8.2	49.2	148	N/A	70	390
3	9.1	87.5	1,100			

N/A - Not available
(All units are in ug/g)

Copper levels do not exceed the ER-M at any Survey 1 sample location (see Figure 3.8a). The ER-L is exceeded at two locations; the southern end of the ship canal (148 ug/g) and just downstream of the intensive survey area (89.7 ug/g). The lowest concentration of copper was found within the ship canal, just downstream from the southern end of the canal.

Copper concentrations in Survey 3 samples were significantly higher, particularly in the intensive sampling area (Figure 3.8b). Whereas there was a single ER-M exceedance outside of the intensive area (just upstream of the intensive sampling zone), there were nine exceedances within the zone. The majority of the exceedances were at core depths 2-4 feet and greater. A group of exceedances were found at the 2-4 foot depth in samples 20, 22, 23, and 24, that correspond geographically to the outside of the sharp river bend in the intensive zone.

Lead

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	28.4	68.6	314	N/A	35	110
3	6.1	170	3,400			

N/A - Not available
(All units are in ug/g)

Lead levels exceed the ER-M or ER-L at all sampling locations except for Sample 2 within the ship canal, just downstream from the southern end (see Figure 3.9a). The ER-M is exceeded in the southern end of the ship canal (286 ug/g), at the Ohio Street bridge (314 ug/g), and downstream of the intensive survey zone (143 ug/g). The ER-L is exceeded at all locations except within the ship canal (Sample 2).

Survey 3 lead concentrations also exceed the ER-M at the majority of the sampling locations (see Figure 3.9b). While several surficial samples exceed the ER-M, samples from 2 foot and greater depths most frequently exceed the guideline. The highest concentrations are found in the 2-4 foot sections of samples 20 through 24 that correspond to outside of the sharp bend in the intensive survey area. Concentrations in these samples range from 1,500 ug/g to 3,400 ug/g (about 14 and 30 times the ER-M, respectively).

Mercury

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	0.01	0.12	1.93	N/A	0.15	1.3
3	N/A	N/A	N/A			

N/A - Not available
(All units are in ug/g)

As shown in Figure 3.10, mercury levels exceed the ER-L and ER-M at most Survey 1 stations sampled (mercury was not an analyte in Survey 3). The ER-L is exceeded in 6 of the 10 stations located within and downstream of the intensive survey area. The ER-M is exceeded at the southern end of the ship canal (1.93 ug/g) and downstream of the intensive zone (1.62 ug/g).

Nickel

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	5.2	44.7	57	N/A	30	50
3	4.3	36	180			

N/A - Not available
(All units are in ug/g)

As depicted in Figure 3.11a, the ER-M for nickel is exceeded at three of the sample locations; downstream of the intensive survey area, downstream of the Ohio Street bridge, and in the southern end of the ship canal. The ER-L for nickel is exceeded at all sample locations except within the ship canal (Sample 2). All remaining samples exhibit nickel levels between 3.4 and 47 ug/g.

The highest Survey 3 nickel concentrations were found in the 2-4 foot core depth at sample locations 20-24 within the intensive zone (Figure 3.11b; Graph C). Concentrations within this area range from 100-175 ug/g (2 to 3.5 times the ER-M). A second zone of high concentrations is found in samples from the 4-6 and 6-8 foot sediment core depths at sample locations 27-32 (Figure 3.11b; Graph D). These concentrations range from 55 to 110 ug/g.

Silver

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	<0.03	0.14	0.46	N/A	1	2.2
3	N/A	N/A	N/A			

N/A - Not Available
(All units are in ug/g)

Silver concentrations in all Survey 1 samples were less than half of the ER-L for silver (Figure 3.12). The highest concentration was found in the southern end of the Buffalo ship canal (0.46 ug/g). Silver was not an analyte in Survey 3.

Zinc

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	32	210	900	N/A	120	270
3	38	325	6,400			

N/A - Not available
(All units are in ug/g)

The ER-L or ER-M are exceeded at all locations except within the ship canal (Sample 2) where zinc was found at 32 ug/g level (see Figure 3.13a). The ER-M is exceeded at four locations with the greatest exceedance at the southern end of the ship canal (900 ug/g or over three times the ER-M). The ER-M is also exceeded downstream of the intensive sampling zone (389 ug/g), at Ohio Street (371 ug/g), and at the mouth of the river (286 ug/g). The ER-L is exceeded at all other locations at levels from 142 ug/g (at the Con Rail tracks) to 224 ug/g (between Ohio Street and Michigan Street).

Survey 3 zinc concentrations exceed both the ER-L and ER-M for zinc at the majority of sampling locations and at most depths (see Figure 3.13b). As with other sampled metals, peak concentrations occur within the intensive sampling zone at the 2-4 foot and 6-8 foot sampling depths. The maximum zinc concentration of 6,400 ug/g occurs at the 2-4 foot depth in sample 21. Adjacent cores 20, 23, and 24 contain concentrations of 2,300 to 3,700 ug/g at the same depth.

Anthracene

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	< 34	205	4,300	N/A	85	960
3	N/A	N/A	N/A			

N/A - Not available
(All units are in ng/g)

The ER-L or ER-M are exceeded at all sampling locations except within the ship canal (Sample 2) where anthracene is undetected at the 34 ng/g level (see Figure 3.14). The ER-M is exceeded at three locations; at the river mouth (1,100 ng/g), at the southern end of the ship canal (1,700 ng/g), and downstream of the intensive survey area (4,300 ng/g or more than four times the ER-M). All other samples exceed the ER-L at levels ranging from 99 ng/g (at the ConRail tracks) to 640 ng/g at Ohio Street. Anthracene was not sampled for in Survey 3.

Benz(a)anthracene

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	<21	470	3,500	N/A	230	1,600
3	74	714	34,680			

N/A - Not available
(All units are in ng/g)

Figure 3.15a presents the Survey 1 sample results for benz(a)anthracene. ER-M values were exceeded at sample location 1 at the southern end of the ship canal (3,500 ng/g) and sample location 6, just downstream from the intensive survey area (1,800 ng/g). All other samples exceeded the ER-L except for the sample within the ship canal (Sample 2) that had a concentration below the detection limit.

Under Survey 3, benz(a)anthracene was only sampled at a limited number of discrete sampling locations and depths (see Figure 3.15b). The highest levels of benz(a)anthracene were found within the intensive sampling zone at the 4-6 foot and 6-8 foot sample depths. The maximum concentration was found at location 22 in the sharp bend in the intensive zone (34,680 ng/g). Additional high concentrations were detected at the upstream end of the intensive zone at 4-6 feet depth (ranging from 4,600 ng/g to 6,200 ng/g). Additional high concentrations were found in surficial samples 5, 7, and 9 in the stretch between the Michigan Street and Ohio Street bridges (ranging from 2,000 ng/g to 5,000 ng/g).

Benzo(a)pyrene

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	<27	540	5,800	N/A	400	2,500
3	62	702	24,577			

N/A - Not available
(All units are in ng/g)

One Survey 1 sample exceeded the ER-M for benzo(a)pyrene; Sample 1 at the southern end of the ship canal contained benzo(a)pyrene at 5,800 ng/g (see Figure 3.16a). All other samples exceeded the ER-L at concentrations between 440 ng/g and 1,300 ng/g, except for samples 2 (within the ship canal) and 8 (within the intensive survey area).

As with the other organic parameters sampled in Survey 3, benzo(a)pyrene was analyzed in a limited number of locations at discrete depths. The distribution of high concentrations generally mirrors that of benz(a)anthracene. Maximum concentrations were measured in the intensive zone at the 4-6 foot and 6-8 foot depths (Figure 3.16b; Graph D). The maximum concentration was found at location 22 in the sharp bend in the intensive zone (24,577 ng/g). Additional high concentrations were detected at the upstream end of the intensive zone at 4-6 feet depth (ranging from 3,700 ng/g to 4,200 ng/g). An additional high concentration was found in the surface sediments at sample location 9, just downstream from the Ohio Street bridge (4,400 ng/g).

Chrysene

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	<27	650	4,000	N/A	400	2,800
3	108	866	28,509			

N/A - Not available
(All units are in ng/g)

The ER-M for chrysene was exceeded at only one Survey 1 sample location, which was in Sample 1 from the southern end of the ship canal (see Figure 3.17a). All other chrysene samples exceeded the ER-L except for the sample within the ship canal (Sample 2), that was reported below the detection limit for chrysene.

Under Survey 3, chrysene was also analyzed in only a limited number of locations at discrete depths. All surficial and sub-surface samples, except for Sample 2, exceeded the ER-L guidelines (see Figure 3.17b). Maximum concentrations were measured in the intensive zone at the 4-6 foot and 6-8 foot depths (Figure 3.17b; Graph D). The maximum concentration was found at location 22 in the sharp bend in the intensive zone (28,509 ng/g). Six additional intensive zone sub-surface samples were in exceedance of the ER-M, with concentrations ranging between 4,002 ng/g and 17,900 ng/g. Additional ER-M exceedances were found in the surface sample at sample location 9, downstream of the Ohio Street bridge (4,632 ng/g), and within the intensive zone (at the upper- and lower-most ends of the area).

Fluoranthene

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	<55	1,200	7,500	620 ug/g OC	600	3,600
3	N/A	N/A	N/A			

N/A - Not available
(All units are in ng/g except as noted for the EPA EqP criteria)

The ER-L and ER-M are exceeded at all Survey 1 sampling locations except within the ship canal (Sample 2) where fluoranthene is undetected at the 55 ng/g level (see Figure 3.18a). The ER-M is exceeded at two locations; at the southern end of the ship canal (7,500 ng/g which is over twice the ER-M) and downstream of the intensive sampling zone (5,100 ng/g). All other samples exceed the ER-L with concentrations ranging from 760 ng/g (upstream of the intensive zone) and 2,700 ng/g (at Ohio Street). Fluoranthene was not an analyte in Survey 3.

The EPA EqP-based criteria for fluoranthene is 620 ug/gOC. When fluoranthene data for the Buffalo River are normalized with respect to organic carbon, the distribution criteria exceedances change somewhat from bulk sediment concentrations (see Figure 3.18b). At no location is the EqP-based criteria for fluoranthene exceeded. The maximum level is now found downstream of the intensive zone (239 ug/gOC, less than 1/2 of the criteria). All other locations exhibit carbon normalized levels less than one-quarter of the criteria.

Fluorene

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	< 30	106	3,400	N/A	35	640
3	N/A	N/A	N/A			

N/A - Not available
(All units are in ng/g)

As shown in Figure 3.19, two locations contained sediments with fluorene concentrations above the ER-M. These are sample 1 at the southern end of the ship canal (1,800 ng/g) and sample 6 just downstream from the intensive survey area (3,400 ng/g). Four other samples exceeded the ER-L at levels from 46 ng/g to 400 ng/g. Four samples did not contain fluorene at levels above the detection limit. Fluorene was not an analyte in Survey 3.

2-Methylnaphthalene

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	< 29	103.5	20,000	N/A	65	670
3	N/A	N/A	N/A			

N/A - Not available
(All units are in ng/g)

As shown in Figure 3.20, the ER-M for 2-methylnaphthalene was exceeded at two Survey 1 sample sites; at the southern end of the ship canal and just downstream of the intensive survey area. The highest concentration was found at the southern end of the ship canal (20,000 ng/g). The ER-L was exceeded at three sample locations, at the mouth of the Buffalo River (Sample 3), at the Ohio Street bridge (Sample 5), and in the intensive survey area (Sample 7). 2-methylnaphthalene was not detected at four sample locations, two of which were located upstream of the intensive survey area (Samples 9 and 10). 2-methylnaphthalene was not an analyte in Survey 3.

Naphthalene

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	<29	75	2,400	N/A	340	2,100
3	N/A	N/A	N/A			

N/A - Not available
(All units are in ng/g)

The ER-M for naphthalene was exceeded at two Survey 1 sample sites; at the southern end of the ship canal and just downstream of the intensive survey area (see Figure 3.21). The highest concentration was found at the southern end of the ship canal (2,400 ng/g). The ER-M and the ER-L values for naphthalene were not exceeded at any other sample location; naphthalene was not detected at four sample sites. Naphthalene was not an analyte in Survey 3.

Phenanthrene

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	<36	630	10,000	180 ug/gOC	225	1,380
3	N/A	N/A	N/A			

N/A - Not available
(All units are in ng/g except as noted for the EPA EqP criteria)

The ER-L and ER-M are exceeded at all Survey 1 sampling locations except within the ship canal (Sample 2) where it is undetected at the 36 ng/g level (see Figure 3.22a). The ER-M is exceeded at three locations; the river mouth (1,400 ng/g), the southern end of the ship canal (6,100 ng/g), and downstream of the intensive survey area (10,000 ng/g). All other samples exceed the ER-L. Phenanthrene was not an analyte in Survey 3.

The EPA EqP-based criteria for phenanthrene is 180 ug/gOC. When phenanthrene data for the Buffalo river are normalized with respect to organic carbon, the distribution of criteria exceedances change somewhat from bulk sediment concentrations. Only one location exceeds the criteria for phenanthrene (see Figure 3.22b). The maximum level is now found downstream of the intensive zone (469 ug/gOC). Most other locations exhibit carbon normalized levels less than one-half of the criteria.

Pyrene

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	< 68	1,005	6,700	N/A	350	2,200
3	N/A	N/A	N/A			

N/A - Not available
(All units are in ng/g)

Figure 3.23 presents the results from Survey 1 for pyrene. As shown in Figure 3.23, all samples exceed either the ER-M or ER-L for pyrene, except one sample located in the ship canal (Sample 2), which did not contain any detectable amounts of pyrene at 68 ng/g. Three sample locations had pyrene concentrations greater than the ER-M, including at the southern end of the ship canal (6,100 ng/g), at the Ohio Street bridge (2,500 ng/g), and just downstream from the intensive survey area (6,700 ng/g). The remaining samples range in concentrations from 690 ng/g (within the intensive survey area) to 2,100 ng/g (at the river mouth). Pyrene was not an analyte in Survey 3.

Total PCBs

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	N/A	N/A	N/A	N/A	50	400
3	43.9	1,124.29	49,935.16			

N/A - Not available
(All units are in ng/g)

Total PCBs were not analyzed as part of Survey 1. As shown in Figure 3.24, most Survey 3 samples exceeded the ER-M or ER-L for total PCBs. Surface samples throughout the river exceeded the ER-M, with the highest value located at the downstream end of the intensive survey area (10,036 ng/g). The highest concentrations of total PCBs, however, were found in the sub-surface sediment cores (4-6 and 6-8 foot core depths) located upstream from the sharp bend in the intensive survey area. The highest values occur in the 6-8 foot cores in the furthest upstream sample sites within the intensive survey area (Sample 34).

Total PAHs

Survey	Minimum	Median	Maximum	EPA EqP Criteria	NOAA ER-L	NOAA ER-M
1	880	26,147	177,330	N/A	4,000	35,000
3	N/A	N/A	N/A			

N/A - Not available
(All units are in ng/g)

As shown in Figure 3.25, total PAH concentrations for all Survey 1 samples except for within the ship canal (Sample 2), exceed the ER-M or ER-L values. The two sample locations with the highest concentrations exceed the ER-M. These high concentrations are found in the southern end of the ship canal (177,330 ng/g) and just downstream of the intensive survey area (116,070 ng/g). All other samples exceed the ER-L, with the values ranging from 6,801 ng/g (within the intensive survey area) to almost 67,000 ng/g (upstream of the ConRail bridge). Total PAHs were not sampled for under Survey 3.

Dieldrin, DDT, DDD, and DDE

No pesticides were analyzed for under Survey 1. However, under Survey 3 several pesticides were monitored for, and the majority of sample values were found below detection limits. However, for two of the four pesticides for which ER-M and ER-L values are available (DDT and DDD), the few detectable values were found to exceed both the ER-M and ER-L. This was particularly true in the sub-surface samples located between the Ohio Street bridge and the Michigan Street bridge (Samples 4, 6, 7, and 9).

3.3.3 Ranking by Chemical Parameter

To provide a preliminary indication of which chemicals may be of concern in the Buffalo River AOC, a simple comparative analysis was performed based on the relative exceedance of the ER-M value. In particular, the mean measured value of each parameter (assuming zero for any nondetect value) was compared to the ER-M value for the parameter. The resulting ratio (herein referred to as the "Mean Exceedance") was calculated for each chemical within each survey. Data between the two surveys are not combined, therefore each parameter may have two mean exceedance values (if the parameter was analyzed in both surveys). The ER-M was chosen for comparative purposes since one was available for all chemicals discussed in Section 3.3.2, and was assumed to be a better indicator for concern (as particularly compared to the ER-L).

Once mean exceedance values were determined, the values were ranked. For the purposes of ranking, metals and organic parameters were ranked separately and separate ranks were determined for each survey. The results of the ranking are presented in Table 3.3.

TABLE 3.3 MEAN EXCEEDANCE VALUES AND RELATIVE RANKS FOR CHEMICAL PARAMETERS

Parameter	Survey 1		Survey 3	
	Mean Exceedance	Relative Rank	Mean Exceedance	Relative Rank
Metals				
Arsenic	0.13	8	N/A	N/A
Cadmium	0.13	7	0.51	5
Chromium	0.67	4	1.44	3
Copper	0.15	6	0.42	6
Lead	1.05	2	2.72	1
Mercury	0.40	5	N/A	N/A
Nickel	0.83	3	0.84	4
Silver	0.09	9	N/A	N/A
Zinc	1.06	1	2.41	2
Organics				
Anthracene	0.88	6	N/A	N/A
Fluoranthene	0.616	7	N/A	N/A
Phenanthrene	1.67	2	N/A	N/A
Benz(a)anthracene	0.54	8	N/A	N/A
Benzo(a)pyrene	0.45	9	1.01	3
Chrysene	0.41	10	1.19	2
Fluorene	0.96	5	N/A	N/A
Naphthalene	0.24	11	N/A	N/A
Pyrene	0.99	4	N/A	N/A
2-Methylnaphthalene	3.23	1	N/A	N/A

TABLE 3.3 MEAN EXCEEDANCE VALUES AND RELATIVE RANKS FOR CHEMICAL PARAMETERS

Parameter	Survey 1		Survey 3	
	Mean Exceedance	Relative Rank	Mean Exceedance	Relative Rank
Total PAHs	1.35	3	N/A	N/A
Total PCBs	N/A	N/A	15.88	1

N/A - Not Available

Of the nine toxic metals analyzed for in the Buffalo River AOC, zinc, lead, nickel and chromium rank the highest of the metals in both Survey 1 and Survey 3. The high concentrations for these parameters were particularly found in the subsurface samples in Survey 3.

As for the organic chemicals, the highest ratios were found for the PAHs 2-methylnaphthalene and phenanthrene in Survey 1. In Survey 3, total PCBs had the highest mean exceedance (on average a sample was found at almost 16 times the ER-M value). Also under Survey 3, chrysene and benzo(a)pyrene were found on average to exceed the ER-M value. It should be noted that many of the ER-M exceedances for the organics were found in the deeper sediment cores, as opposed to the surface sediment.

3.3.4 Analysis by Sample Location

The second portion of the analysis of Buffalo River sediment samples focuses on which sample locations are of concern. For purposes of this analysis, sample locations are examined in one of two ways; the number of chemicals that exceed the NOAA guidelines at a sample site, and the relative exceedance of the guidelines at the site.

One difficulty directly comparing sampling locations stems from differences in the total number of parameters sampled and the number of samples collected from different locations. While some locations are sampled at four sediment core depths, others are sampled at only two. Several parameters have been sampled at only a few sampling locations and usually only at one depth (typically surface samples). In light of these differences, an analysis by sample location was still performed to provide a preliminary indication of the areas of concern within the Buffalo River AOC.

As shown in Table 3.4, sample sites 1 (at the southern end of the ship canal) and 6 (downstream of the intensive survey area) had the greatest number of ER-M exceedances for both metals and organic chemicals under Survey 1. Under Survey 3, the greatest number of exceedances tend to occur in three areas of the Buffalo River AOC, two of which are located in the intensive survey area. The locations within the intensive survey area include sampling locations 30 - 34 (the most upstream sample stations within the intensive survey area) and sampling locations 21 - 27 (at the sharp turn within the intensive

survey area). The third location within the Buffalo River AOC is for sampling locations 4 - 9 (between the Ohio Street and Michigan Street bridges. It should also be noted that the greatest number of exceedances generally occurs in the 2-4 foot core samples.

TABLE 3.4 TOTAL NUMBER OF NOAA ER-M EXCEEDANCES BY SAMPLE LOCATION

Sample Site Reference Number	Toxic Metals				Organic Pollutants (PAHs and PCBs)			
Survey 1								
1	5				11			
2	0				0			
3	1				2			
4	0				0			
5	2				2			
6	4				9			
7	0				0			
8	0				0			
9	0				0			
10	0				1			
Survey 3								
	Core Depth (Feet)							
	0-2	2-4	4-6	6-8	0-2	2-4	4-6	6-8
1	2	3	--	--	--	--	--	--
2	0	0	--	--	0	--	--	--
3	3	3	0	--	0	--	--	--
4	0	3	2	--	0	--	--	--
5	2	0	--	--	2	--	--	--
6	2	3	3	--	0	--	--	--

TABLE 3.4 TOTAL NUMBER OF NOAA ER-M EXCEEDANCES BY SAMPLE LOCATION

Sample Site Reference Number	Toxic Metals				Organic Pollutants (PAHs and PCBs)			
7	5	3	3	--	2	--	--	--
8	4	2	--	--	--	--	--	--
9	0	3	3	--	3	--	--	--
10	1	0	3	--	0	--	--	--
11	0	0	1	--	0	--	--	--
12	0	4	2	--	0	--	--	--
13	1	2	1	1	0	--	--	--
14	1	0	0	2	0	--	--	--
15	1	2	3	2	--	--	--	--
16	0	3	0	--	--	--	--	--
17	0	6	0	--	0	--	--	--
18	0	0	0	0	0	--	--	--
19	5	5	2	5	3	--	--	--
20	0	0	0	--	--	--	--	--
21	0	3	4	0	0	--	2	--
22	0	5	3	2	0	--	--	3
23	0	6	0	--	0	--	0	--
24	1	--	--	--	--	--	--	--
25	0	6	2	2	0	--	3	--
26	0	5	4	0	--	--	--	--
27	1	6	--	--	0	--	--	--
28	0	3	3	--	--	--	--	--

TABLE 3.4 TOTAL NUMBER OF NOAA ER-M EXCEEDANCES BY SAMPLE LOCATION

Sample Site Reference Number	Toxic Metals				Organic Pollutants (PAHs and PCBs)			
29	0	0	3	--	0	--	3	--
30	0	1	6	--	--	--	--	--
31	0	0	4	--	--	--	3	--
32	0	6	6	0	0	--	3	--
33	0	4	0	0	--	--	--	--
34	5	6	0	6	2	--	--	2
35	3	--	--	--	0	--	--	--
36	0	1	1	--	0	--	0	--
37	1	--	--	--	2	--	--	--

-- No Data

The second analysis performed provides a preliminary indication of which locations may be of concern in the Buffalo River AOC, using a simple comparative analysis based on the relative exceedance of the ER-M value. In particular, the average of the mean exceedances of chemical concentrations (shown previously in Table 3.3) was compared to the ER-M value. For purposes of this analysis, two different mean exceedances were calculated for each sample location for each survey; one for all metals and one for all organic chemicals (PAHs and PCBs). Data between the two surveys are not combined, therefore each location may have two mean exceedance values (if a sample was analyzed at a location in both surveys). The ER-M was chosen for comparative purposes since one was available for all chemicals discussed in Section 3.3.2, and was assumed to be a better indicator for concern (as particularly compared to the ER-L).

Table 3.5 presents the mean exceedance values determined for each Survey 1 sample location, and ranks them in relation to all other locations. Figures 3.26 and 3.27 present bar graphs of the mean exceedances for the metals and organic chemicals for Survey 1 sample sites, respectively. As shown, sample location 1 (southern end of the ship canal) possesses mean exceedances greater than one for both metals and organics. Sample location 6 (just downstream from the intensive survey area) possesses the highest mean exceedance of all locations for organic chemicals. Survey 1 sample location 5 (at the Ohio Street bridge) also ranked high for both metals and organic chemicals. The results of the comparative analysis follow the results of the total number of exceedances analysis.

TABLE 3.5 SURVEY 1 MEAN EXCEEDANCE VALUES AND RANKS FOR METALS AND ORGANICS

Sample Location	Metals		Organics (PAHs and PCBs)	
	Mean Exceedance	Relative Rank	Mean Exceedance	Relative Rank
1	1.35	1	5.08	1
2	0.06	10	0.002	10
3	0.54	4	0.61	4
4	0.4	5	0.21	7
5	0.72	2	0.72	3
6	0.71	3	2.69	2
7	0.39	6	0.33	5
8	0.32	7	0.16	9
9	0.29	8	0.19	8
10	0.25	9	0.33	6

Table 3.6 presents the mean exceedance values determined for each Survey 3 sample location and sediment core depth, and ranks them in relation to all other locations and core depths. Figures 3.28 and 3.29 present bar graphs of the mean exceedances for the metals and organic chemicals for Survey 3 sample sites, respectively. As shown, a trend similar to Survey 1 exists in that the highest ranked Survey 3 sample locations are mostly within the intensive survey area for both metals (particularly sample locations 25 - 27) and organic chemicals (sample locations 21 - 25). The highest mean exceedances also tend to occur in the sub-surface samples at each location (particularly the 2-4 foot cores for metals and the 4-6 foot cores for organic chemicals). Several sample locations within the stretch of river between the Ohio Street and Michigan Street bridges also had relatively high mean exceedances for organic chemicals (sampling locations 5 and 9).

TABLE 3.6a SURVEY 3 MEAN EXCEEDANCE AND RANK BY SITE FOR METALS (RANK OUT OF TOTAL 112 SAMPLES)

Sample Location	Core Depth							
	0-2 Feet		2-4 Feet		4-6 Feet		6-8 Feet	
	Mean Exceed.	Relative Rank	Mean Exceed.	Relative Rank	Mean Exceed.	Relative Rank	Mean Exceed.	Relative Rank
1	1.04	46	1.89	23	--	--	--	--
2	0.07	112	0.11	111	--	--	--	--
3	1.27	38	1.29	37	0.23	104	--	--
4	0.5	68	1.51	32	1.04	45	--	--
5	1.36	33	0.13	109	--	--	--	--
6	0.72	55	1.68	28	2.38	19	--	--
7	1.81	25	1.9	22	1.83	24	--	--
8	1.32	36	0.89	50	--	--	--	--
9	0.46	73	1.71	27	1.74	26	--	--
10	0.54	66	0.5	69	1.35	34	--	--
11	0.38	83	0.38	84	0.53	67	--	--
12	0.42	77	2.46	18	0.81	52	--	--
13	0.64	58	1.17	41	0.59	62	0.47	71
14	0.43	76	0.22	105	0.18	108	0.72	54
15	0.61	60	0.86	51	1.32	35	0.8	53
16	3.07	12	3.19	10	1.26	40	3.02	13
17	0.31	99	0.35	89	0.3	100	--	--
18	0.33	95	1.59	31	2.63	15	--	--
19	0.34	93	2.92	14	0.97	48	0.93	49

TABLE 3.6a SURVEY 3 MEAN EXCEEDANCE AND RANK BY SITE FOR METALS (RANK OUT OF TOTAL 112 SAMPLES)

Sample Location	Core Depth							
	0-2 Feet		2-4 Feet		4-6 Feet		6-8 Feet	
	Mean Exceed.	Relative Rank	Mean Exceed.	Relative Rank	Mean Exceed.	Relative Rank	Mean Exceed.	Relative Rank
20	0.34	92	5.92	5	0.44	75	--	--
21	0.62	59	--	--	--	--	--	--
22	0.38	82	11.94	1	1.14	42	0.97	47
23	0.33	96	5.46	6	2.03	21	0.25	103
24	0.56	63	6.99	3	--	--	--	--
25	0.36	86	1.66	29	1.14	43	--	--
26	0.33	98	0.36	88	1.27	39	--	--
27	0.36	87	0.66	56	3.86	8	--	--
28	0.3	101	0.39	81	2.53	17	--	--
29	0.42	79	3.69	9	6.46	4	0.61	61
30	0.45	74	1.63	30	0.22	106	0.55	64
31	2.58	16	4.57	7	0.26	102	7.49	2
32	2.14	20	--	--	--	--	--	--
33	0.34	91	0.47	72	0.5	70	--	--
34	0.65	57	--	--	--	--	--	--
35	0.42	78	1.07	44	0.37	85	--	--
36	0.33	97	3.14	11	0.21	107	--	--
37	0.34	90	0.54	65	0.39	80	0.33	94

-- No Data

TABLE 3.6b SURVEY 3 MEAN EXCEEDANCE AND RANK BY SITE FOR ORGANICS (RANK OUT OF TOTAL 36 SAMPLES)

Sample Location	Core Depth							
	0-2 Feet		2-4 Feet		4-6 Feet		6-8 Feet	
	Mean Exceed.	Relative Rank	Mean Exceed.	Relative Rank	Mean Exceed.	Relative Rank	Mean Exceed.	Relative Rank
2	0.08	36	--	--	--	--	--	--
3	2.16	11	--	--	--	--	--	--
4	0.27	31	--	--	--	--	--	--
5	1.54	14	--	--	--	--	--	--
6	0.72	17	--	--	--	--	--	--
7	2.86	9	--	--	--	--	--	--
9	1.86	13	--	--	--	--	--	--
10	0.6	22	--	--	--	--	--	--
11	0.36	26	--	--	--	--	--	--
12	0.36	24	--	--	--	--	--	--
13	1.08	16	--	--	--	--	--	--
14	0.35	27	--	--	--	--	--	--
16	10.43	4	--	--	--	--	--	--
18	0.28	30	--	--	5.44	7	--	--
19	0.16	34	--	--	--	--	6.32	5
20	0.32	28	--	--	0.68	18	--	--
22	0.2	33	--	--	--	--	11.24	3
24	0.36	25	--	--	--	--	--	--
26	0.22	32	--	--	--	--	28.3	10
28	5.86	6	--	--	--	--	--	--

TABLE 3.6b SURVEY 3 MEAN EXCEEDANCE AND RANK BY SITE FOR ORGANICS (RANK OUT OF TOTAL 36 SAMPLES)

Sample Location	Core Depth							
	0-2 Feet		2-4 Feet		4-6 Feet		6-8 Feet	
	Mean Exceed.	Relative Rank	Mean Exceed.	Relative Rank	Mean Exceed.	Relative Rank	Mean Exceed.	Relative Rank
29	0.53	23	--	--	26	2	--	--
31	5.23	8	--	--	--	--	29.83	1
32	1.37	15	--	--	--	--	--	--
33	0.12	35	--	--	0.06	37		
34	1.89	12	--	--	--	--	--	--
36*	0.66-0.67	19-21	--	--	--	--	--	--
37	0.29	29	--	--	--	--	--	--

-- No Data

* Sample 36 was analyzed as three duplicate samples

Figure 3.5 Survey 1 Arsenic Concentration vs. NOAA Guidelines

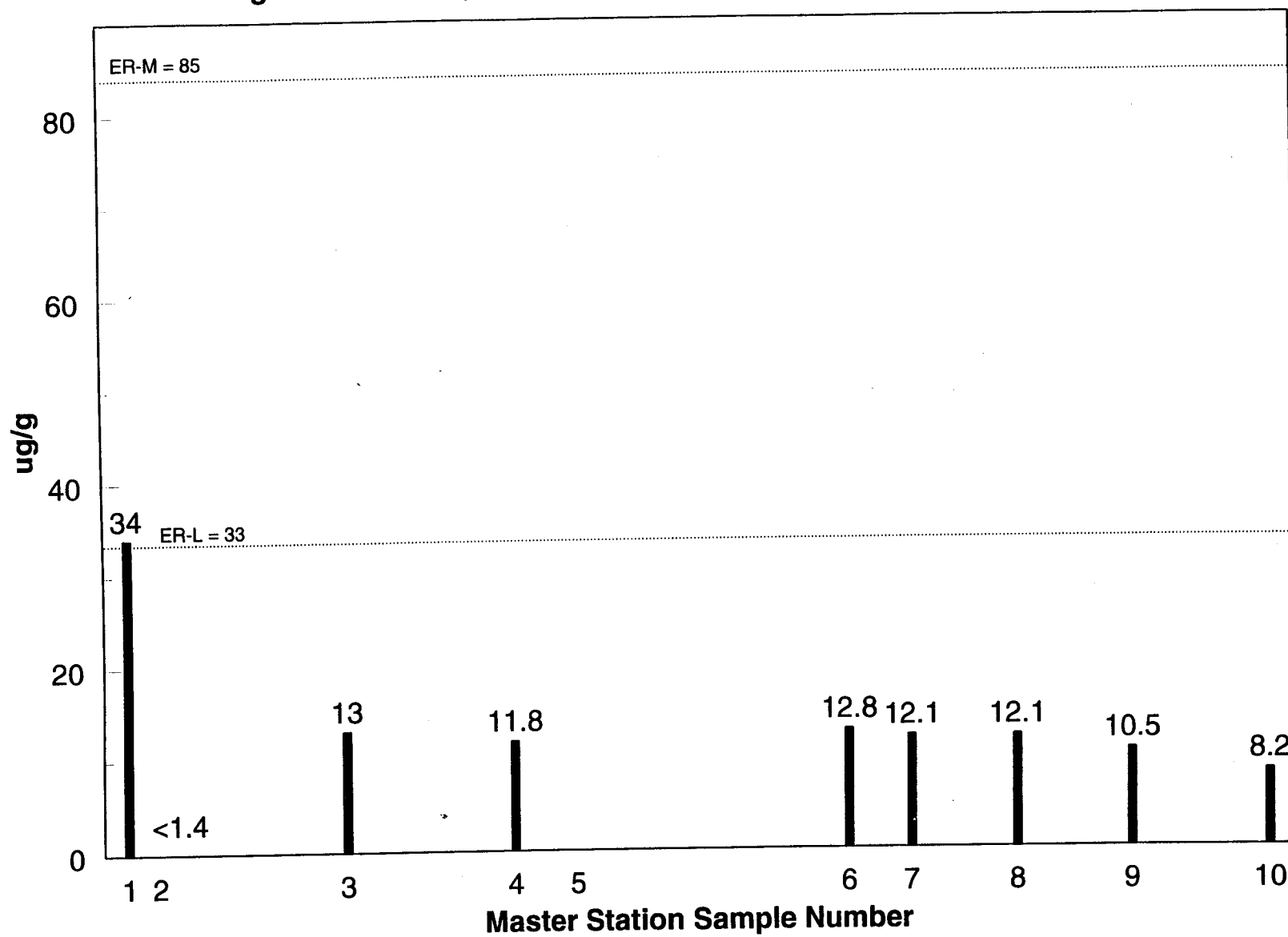


Figure 3.6a Survey 1 Cadmium Concentration vs. NOAA Guidelines

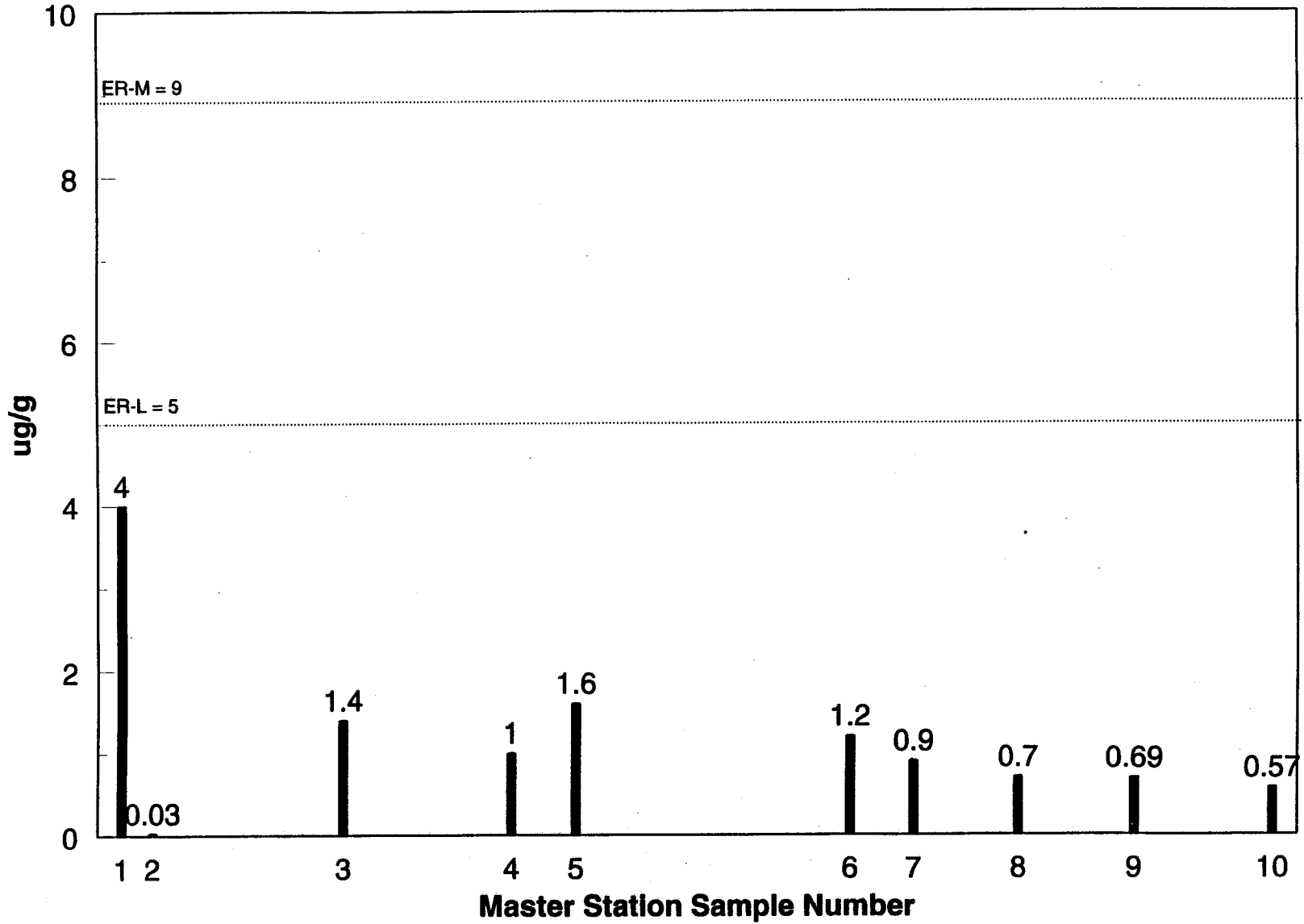


Figure 3.6b Survey 3 Cadmium Concentration vs. NOAA Guidelines

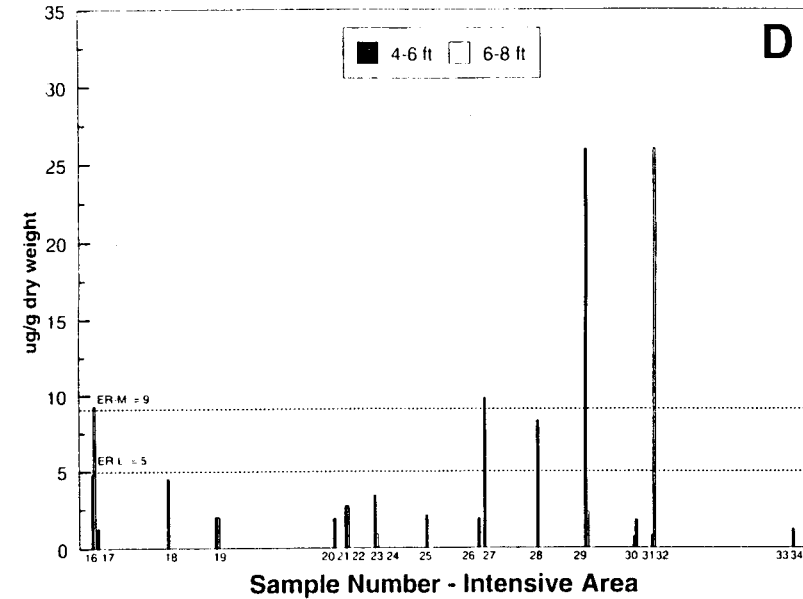
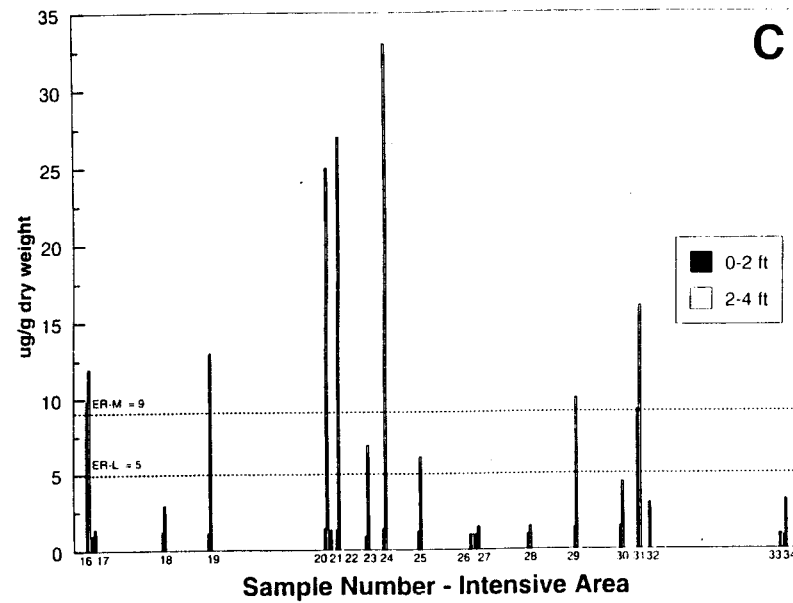
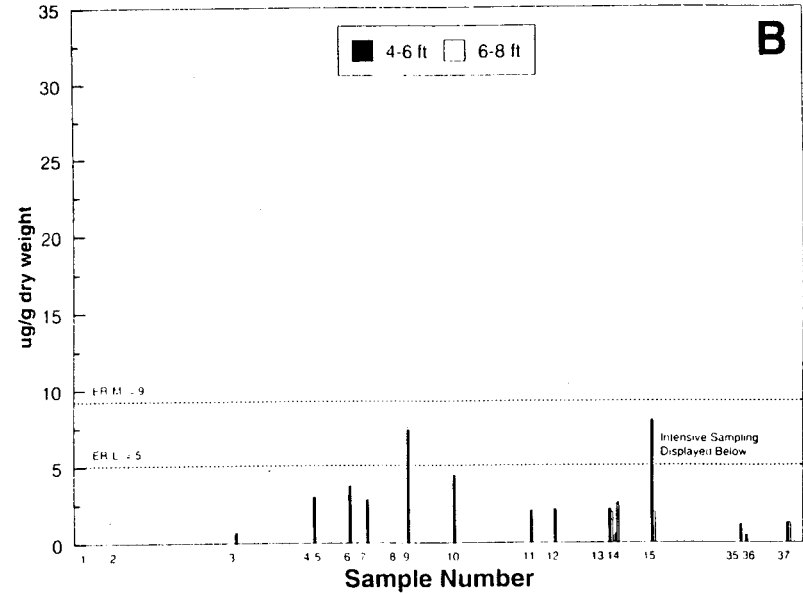
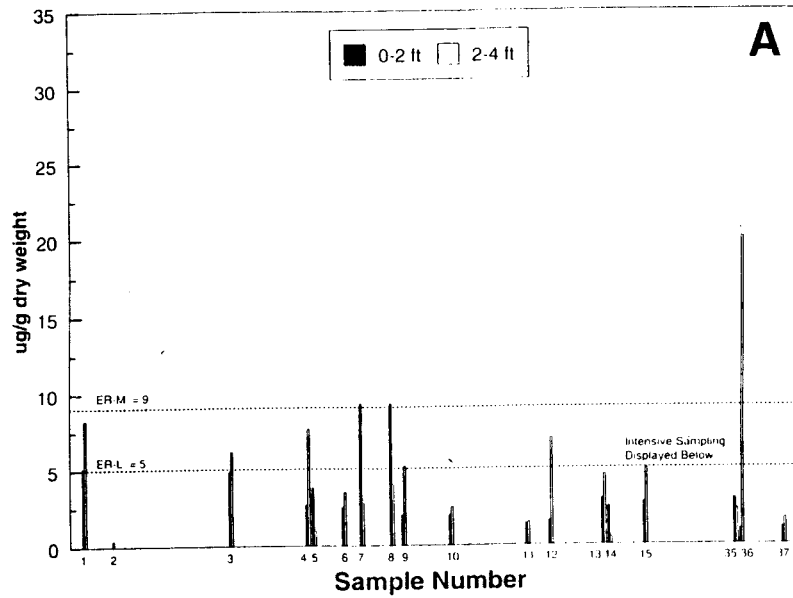


Figure 3.7a Survey 1 Chromium Concentration vs. NOAA Guidelines

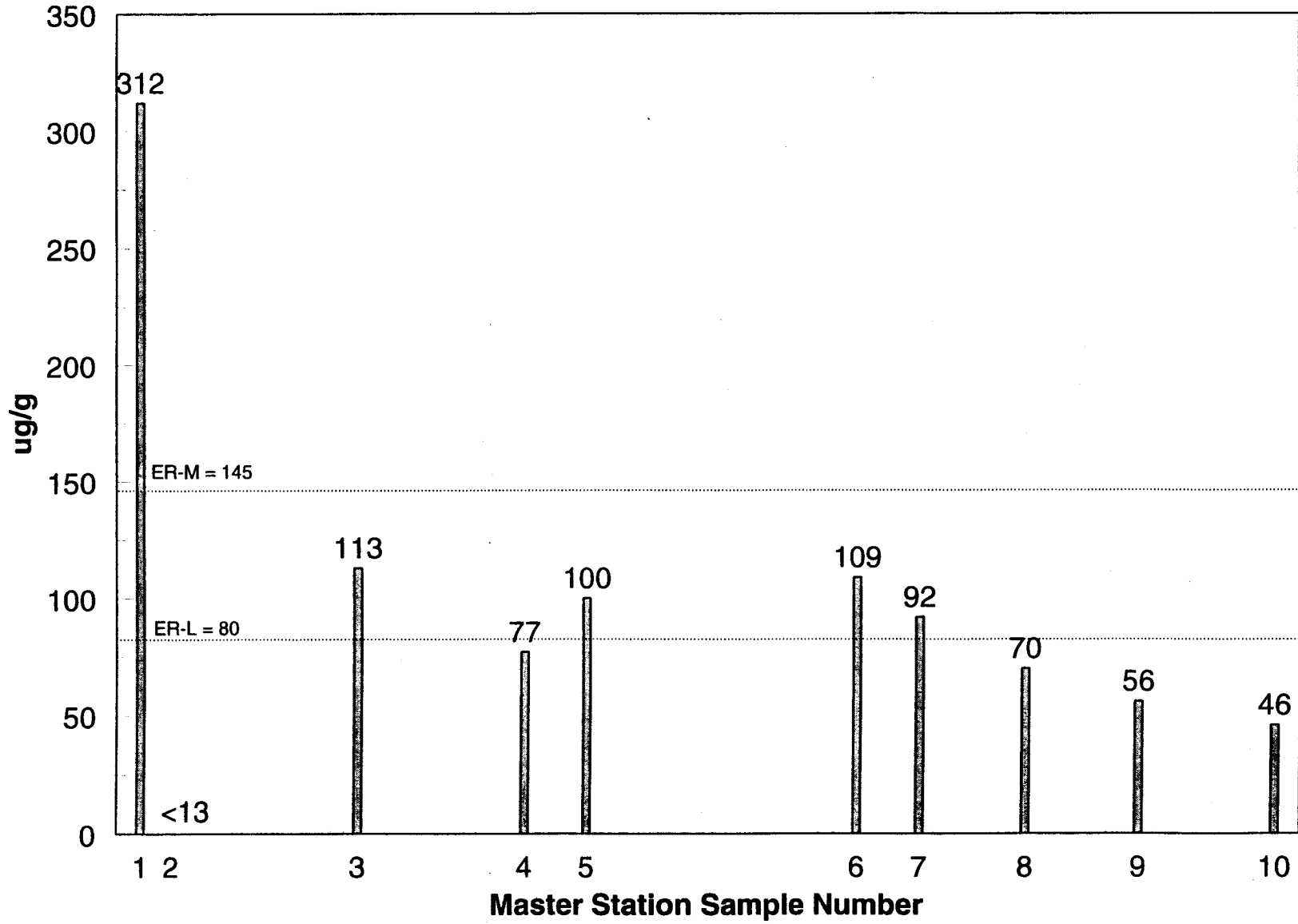


Figure 3.7b Survey 3 Chromium Concentration vs. NOAA Guidelines

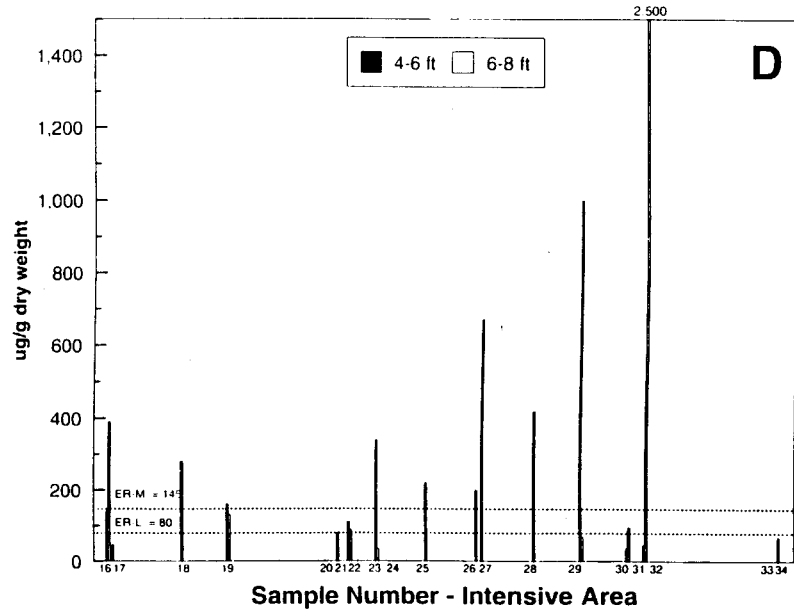
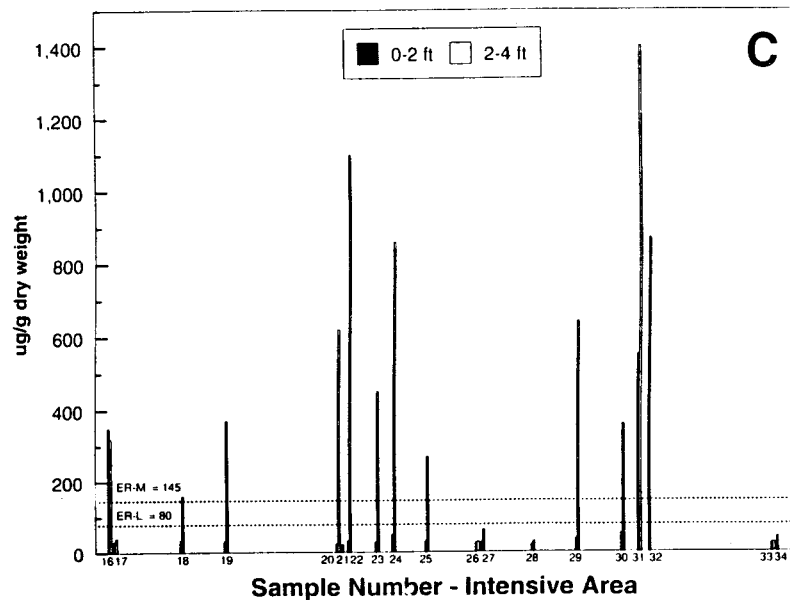
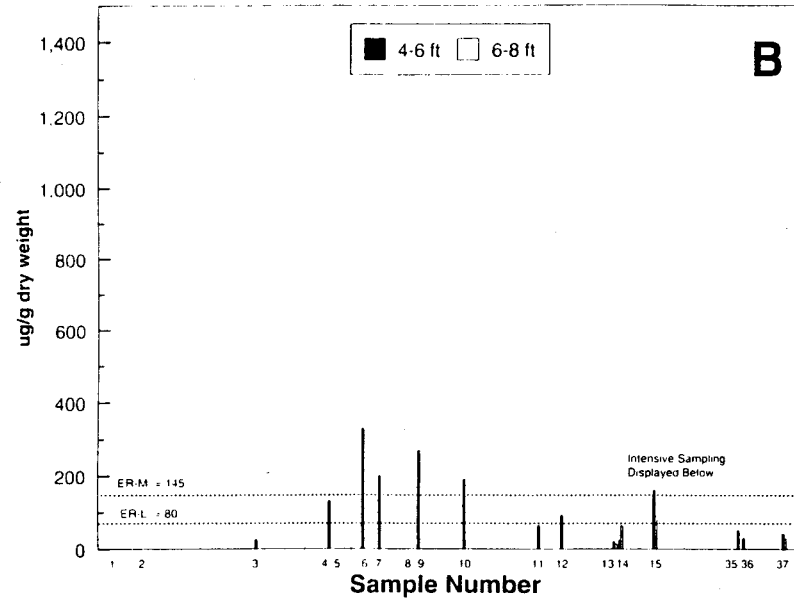
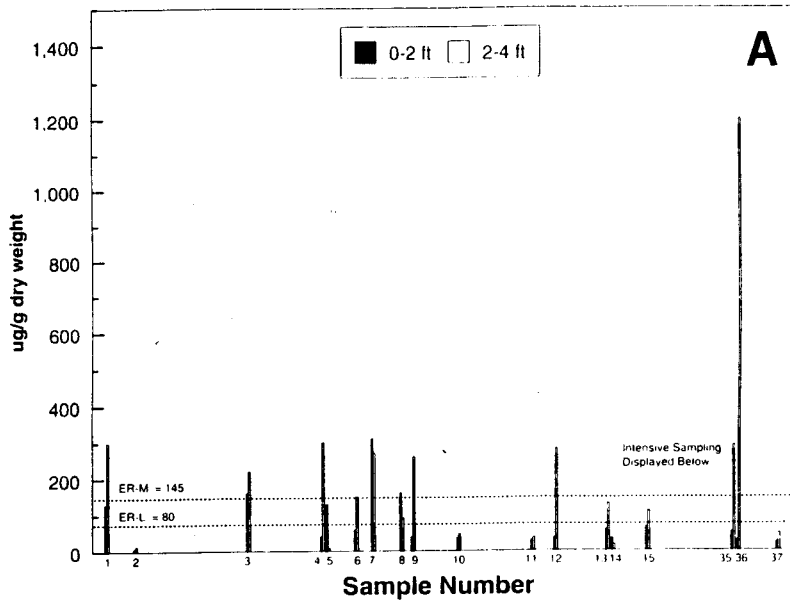


Figure 3.8a Survey 1 Copper Concentration vs. NOAA Guidelines

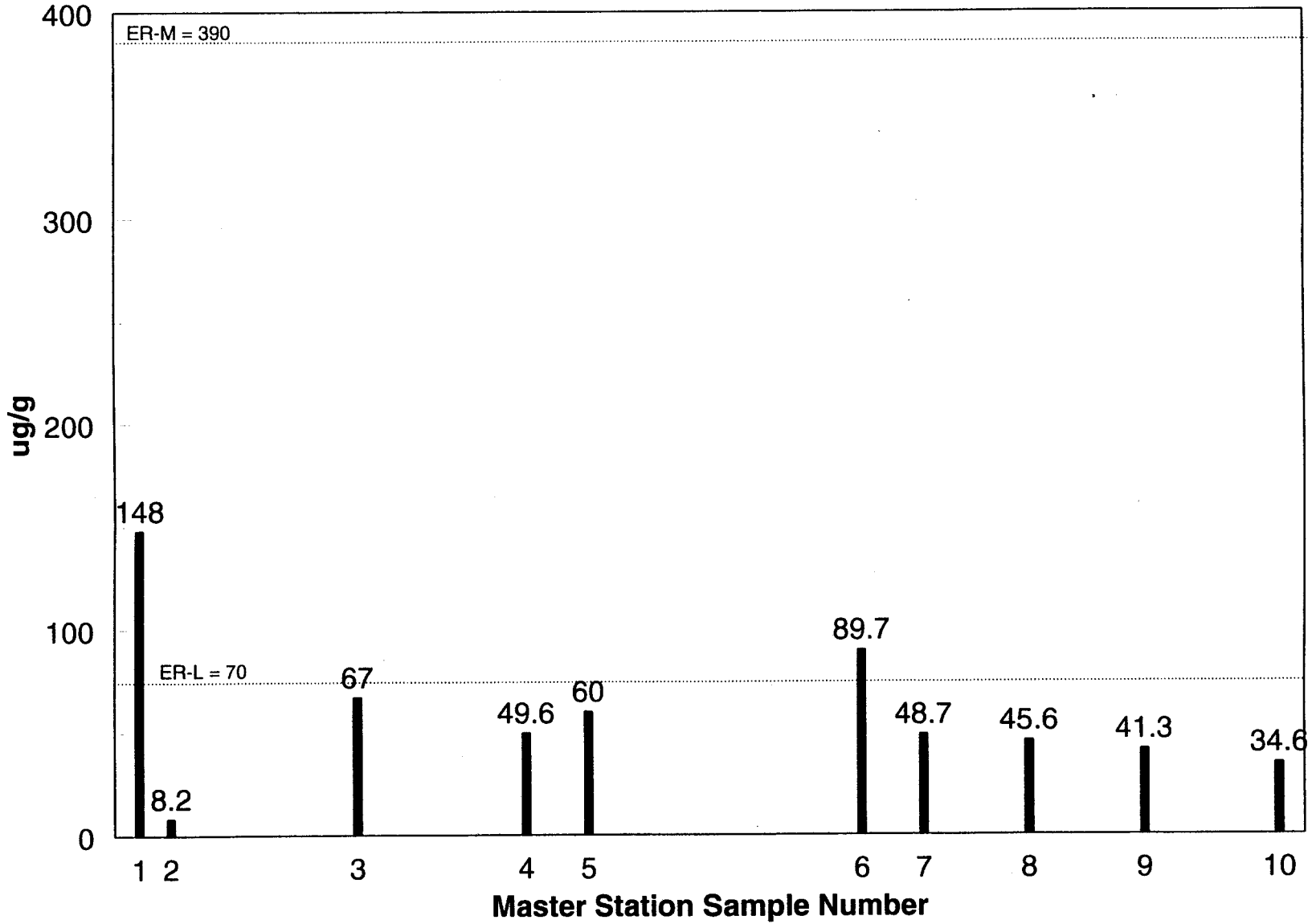


Figure 3.8b Survey 3 Copper Concentration vs. NOAA Guidelines

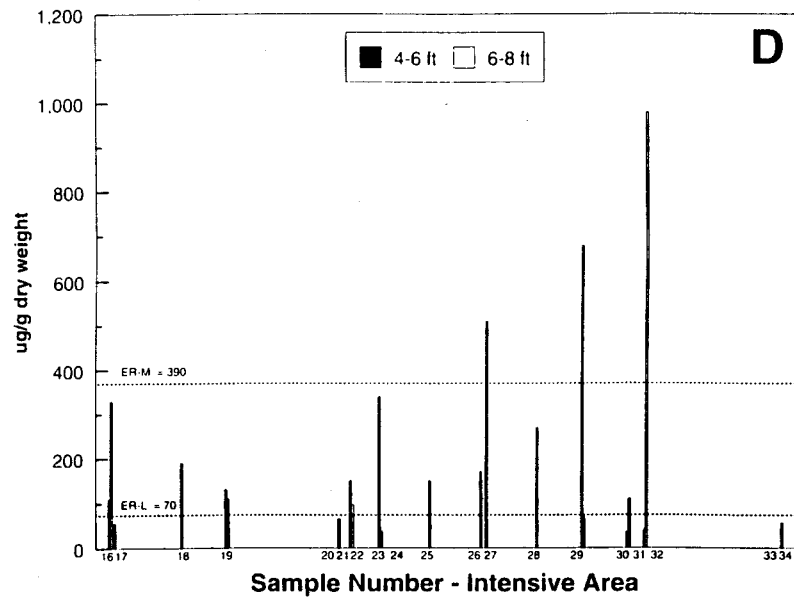
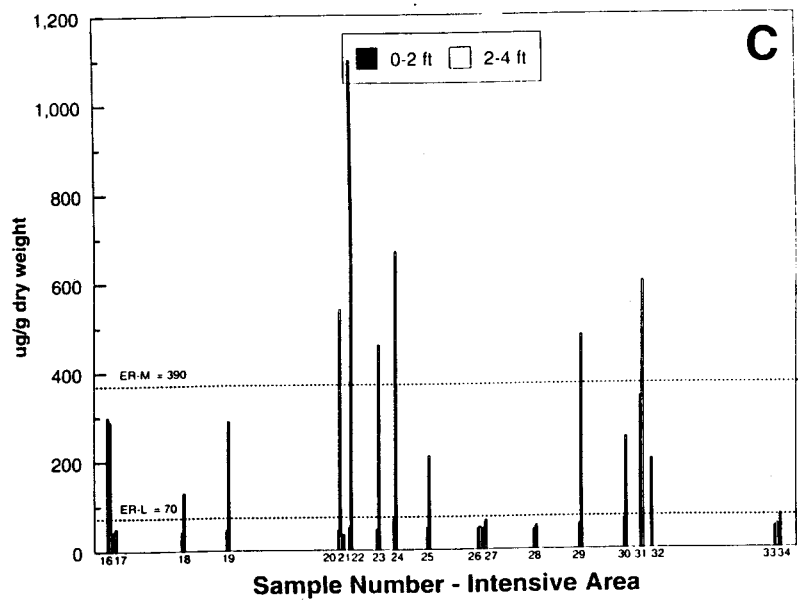
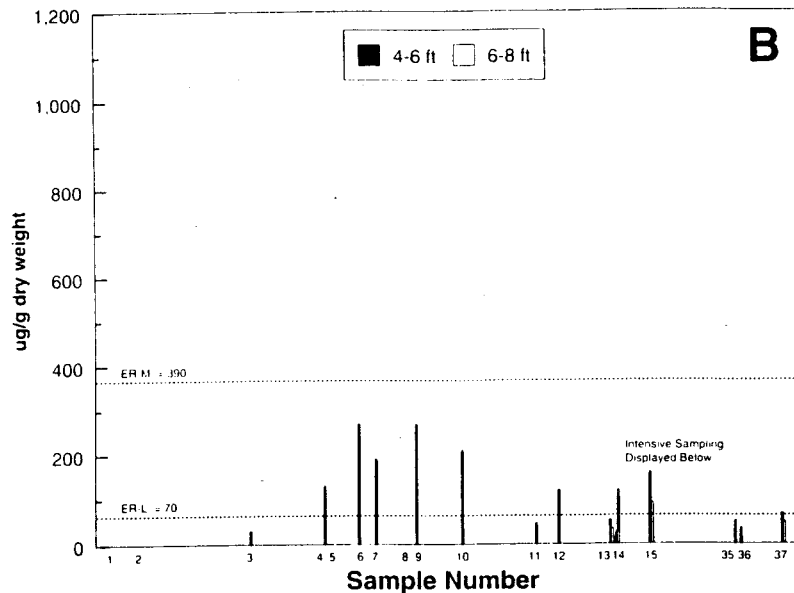
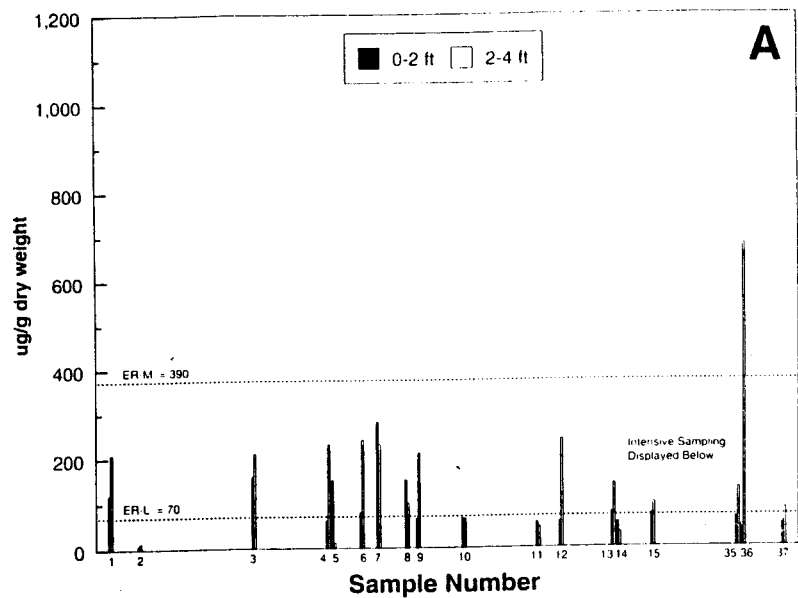


Figure 3.9a Survey 1 Lead Concentration vs. NOAA Guidelines

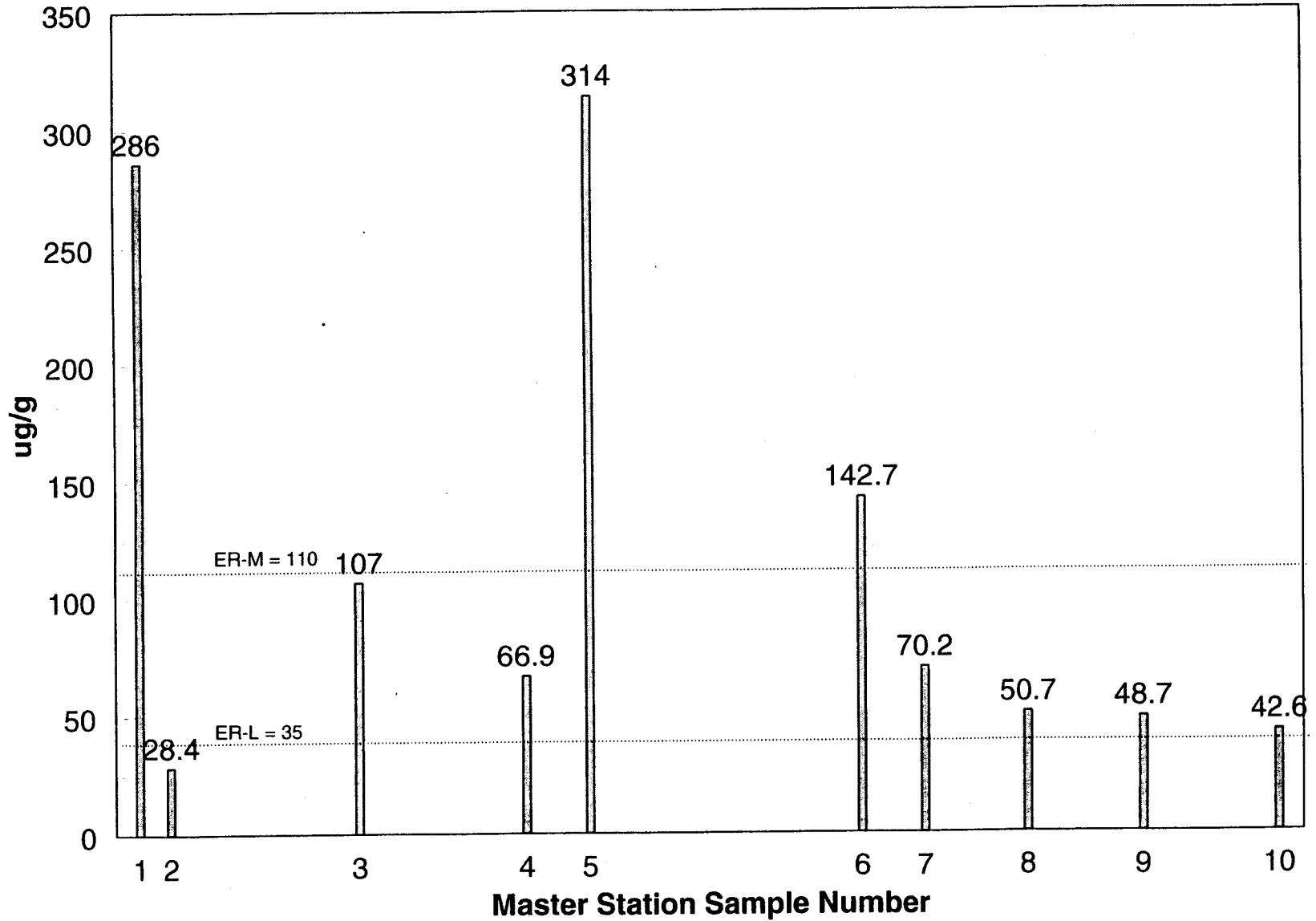


Figure 3.9b Survey 3 Lead Concentration vs. NOAA Guidelines

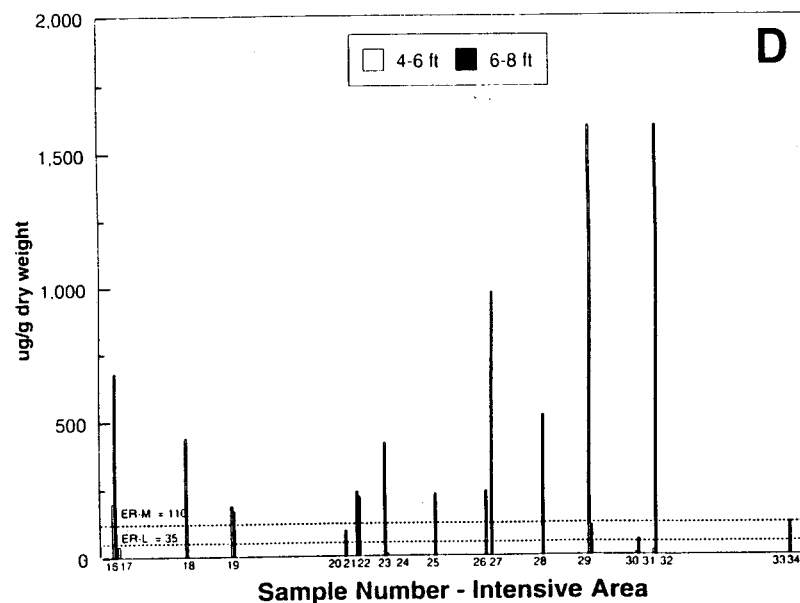
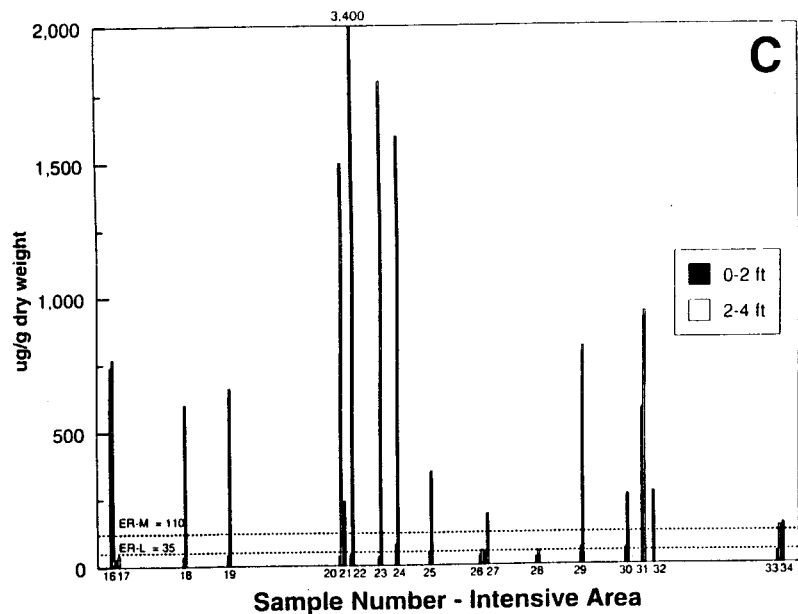
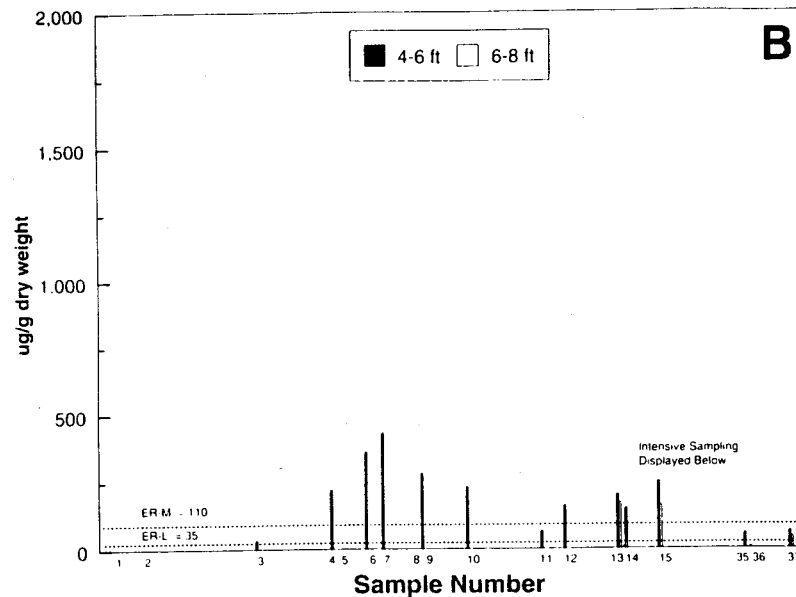
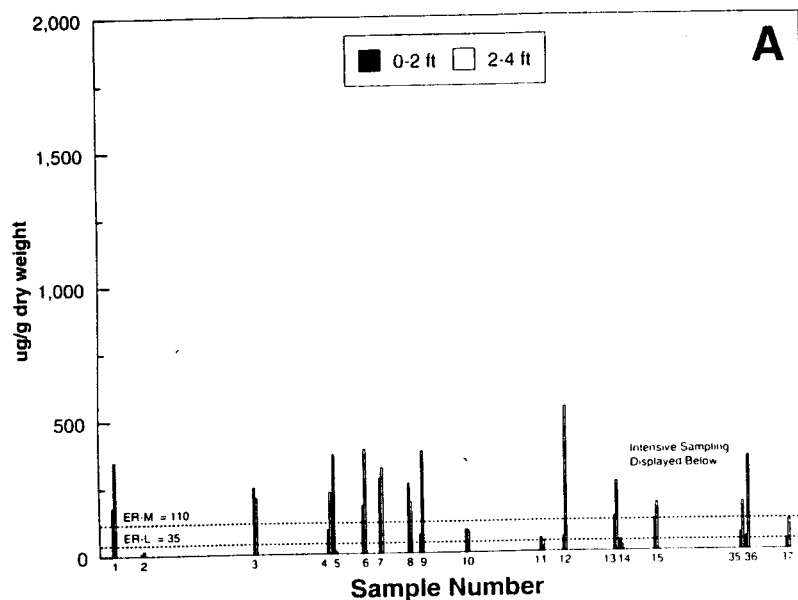


Figure 3.10 Survey 1 Mercury Concentration vs. NOAA Guidelines

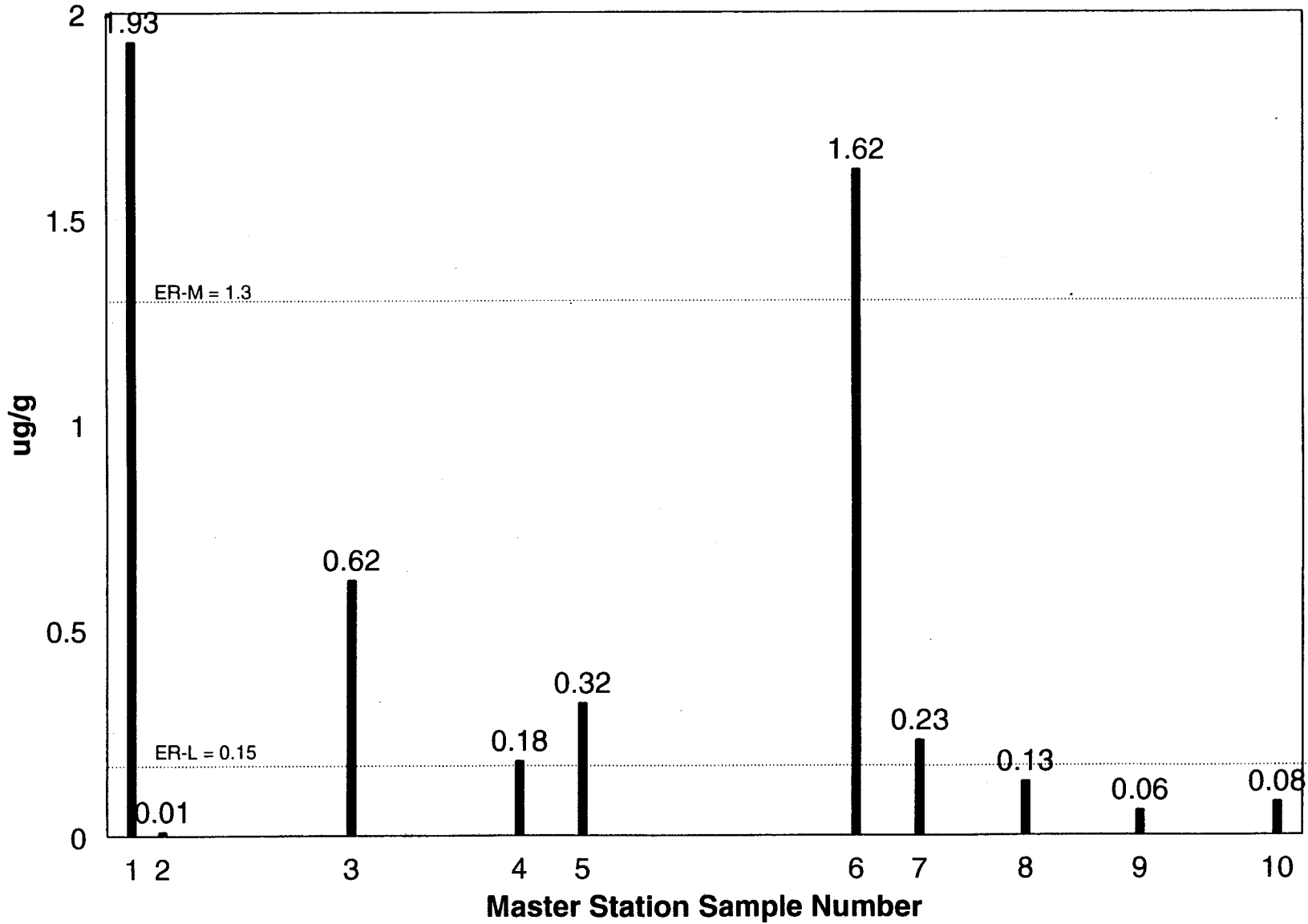


Figure 3.11a Survey 1 Nickel Concentration vs. NOAA Guidelines

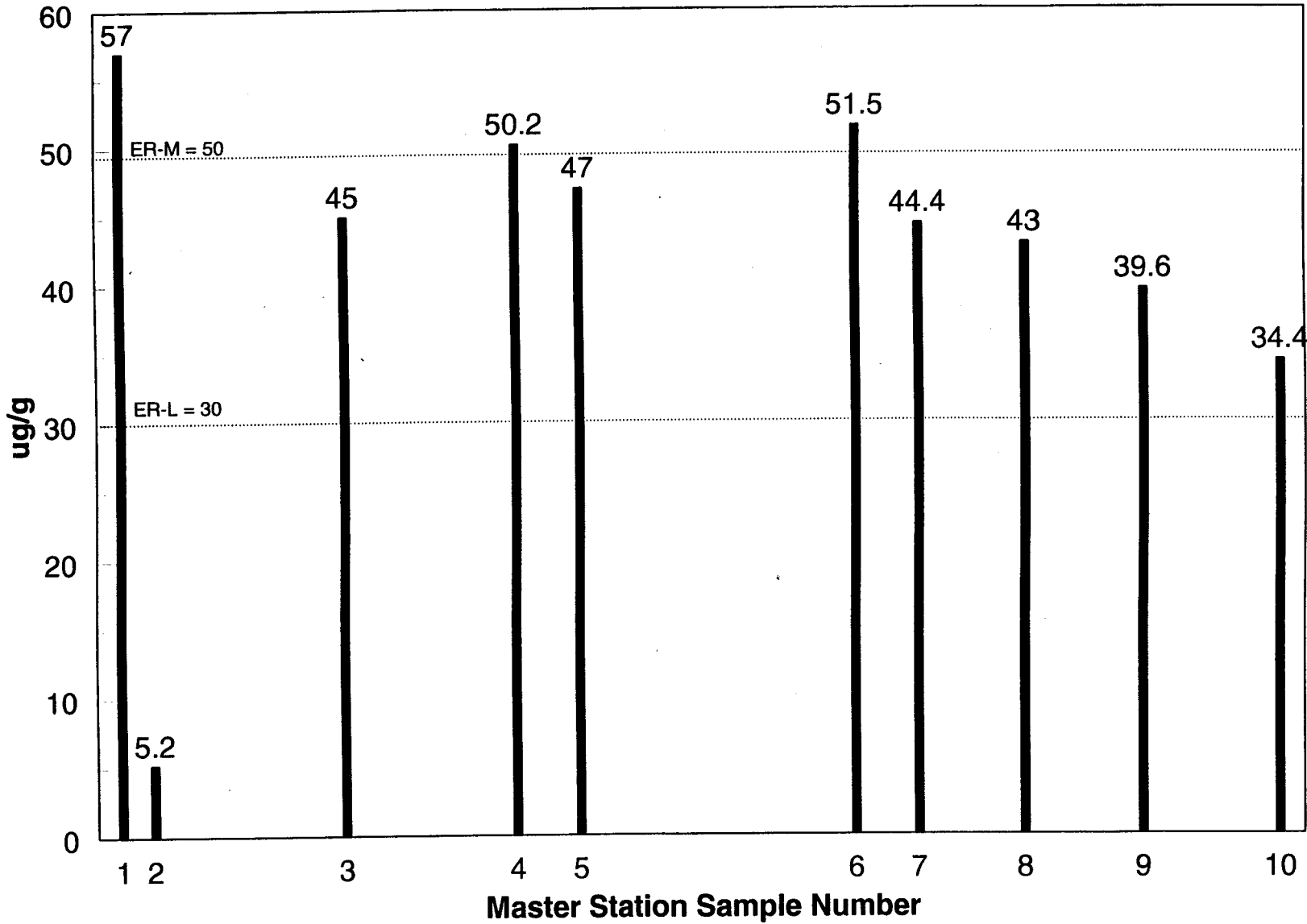


Figure 3.11b Survey 3 Nickel Concentration vs. NOAA Guidelines

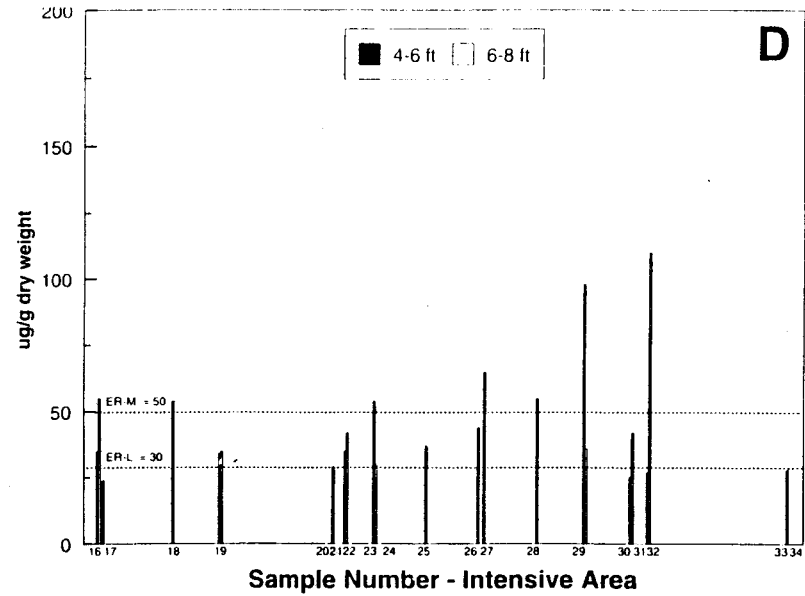
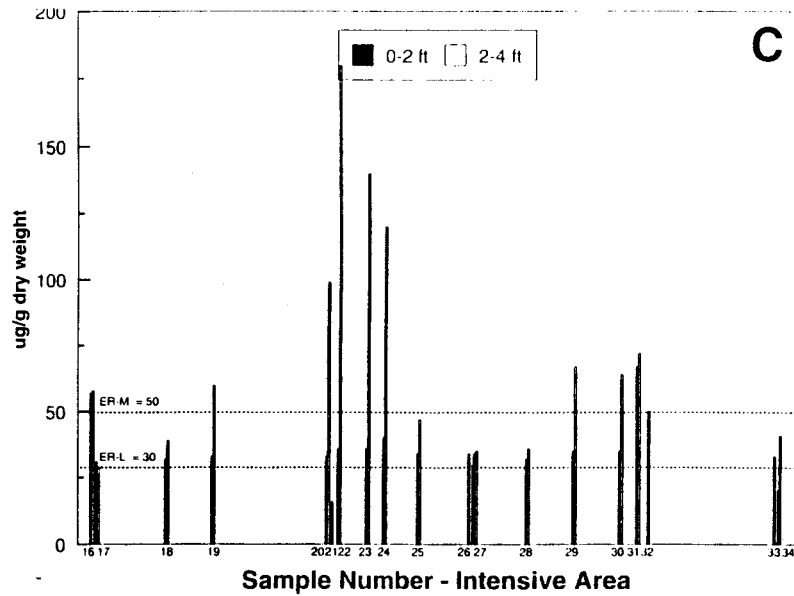
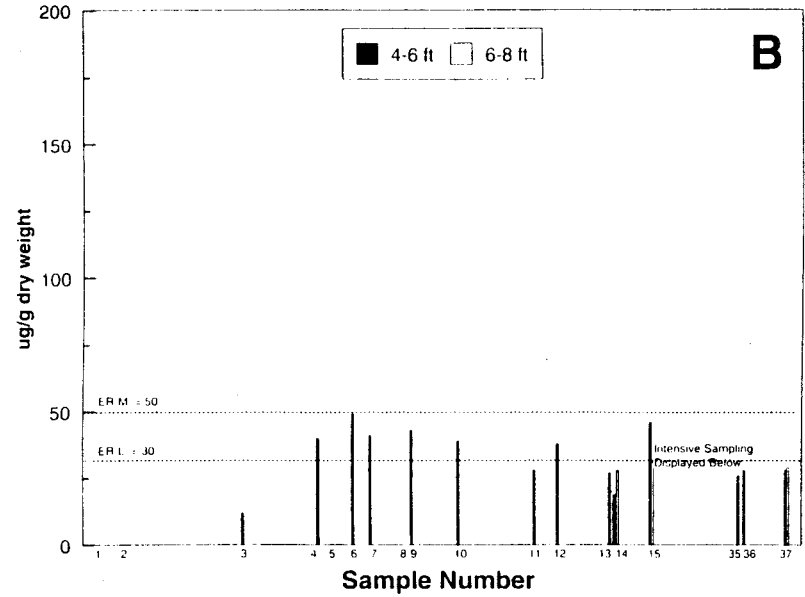
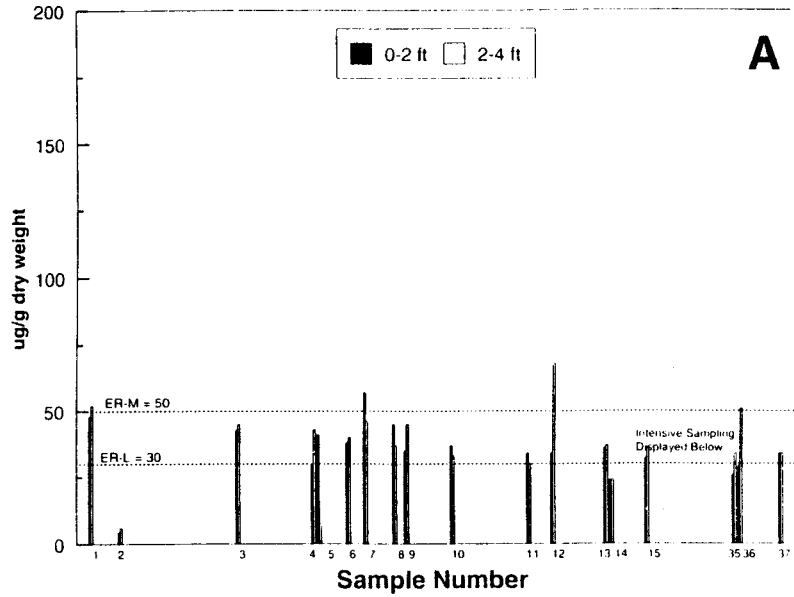


Figure 3.12 Survey 1 Silver Concentration vs. NOAA Guidelines

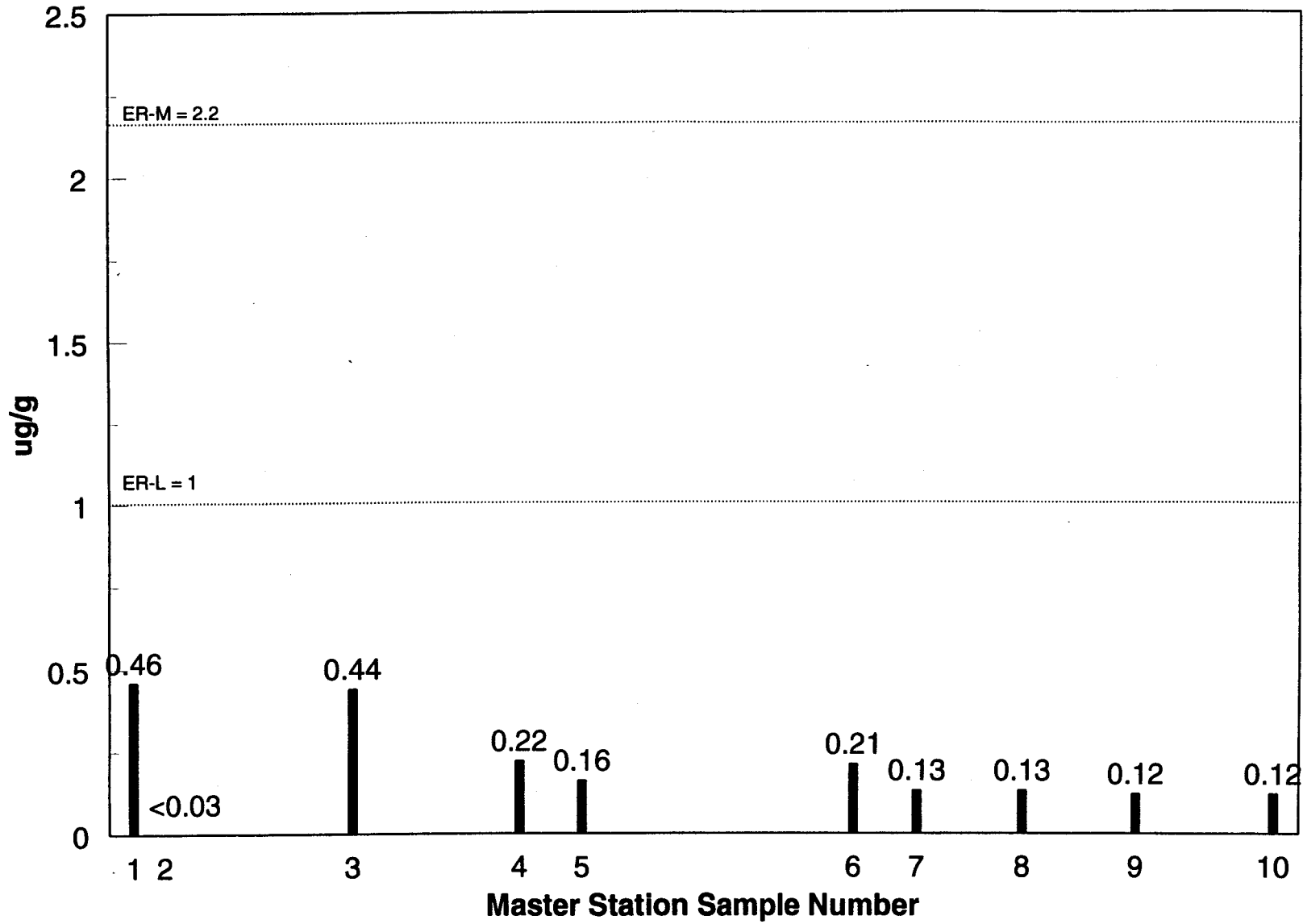


Figure 3.13a Survey 1 Zinc Concentration vs. NOAA Guidelines

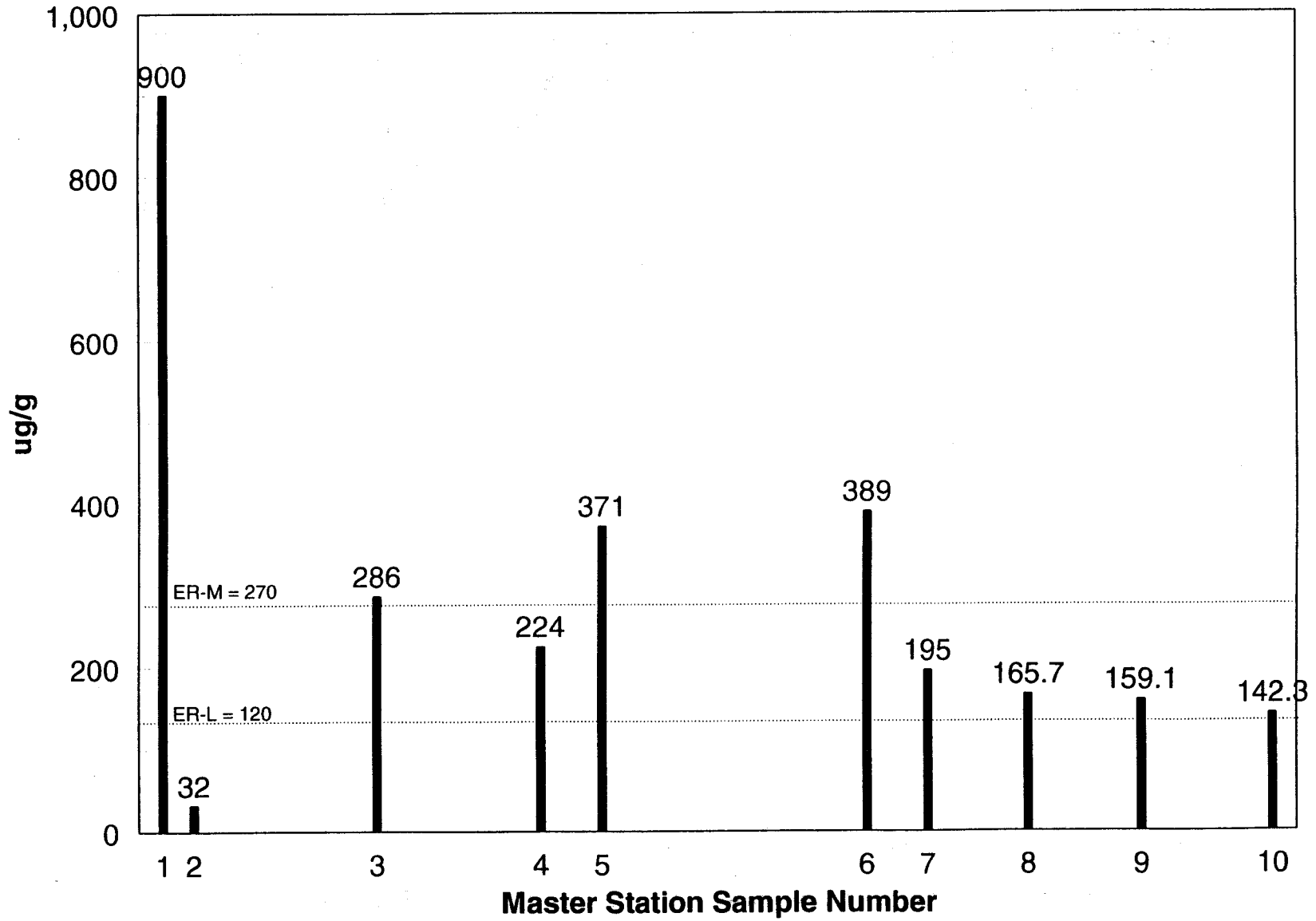


Figure 3.13b Survey 3 Zinc Concentration vs. NOAA Guidelines

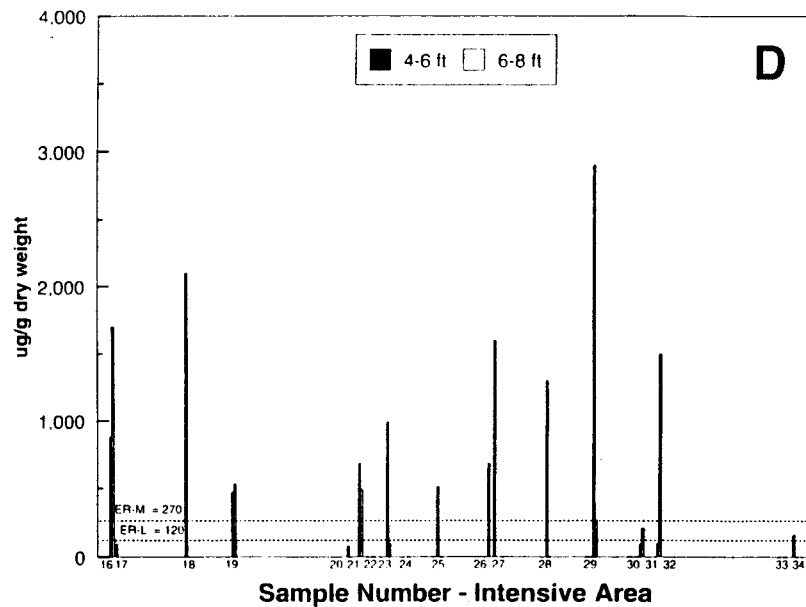
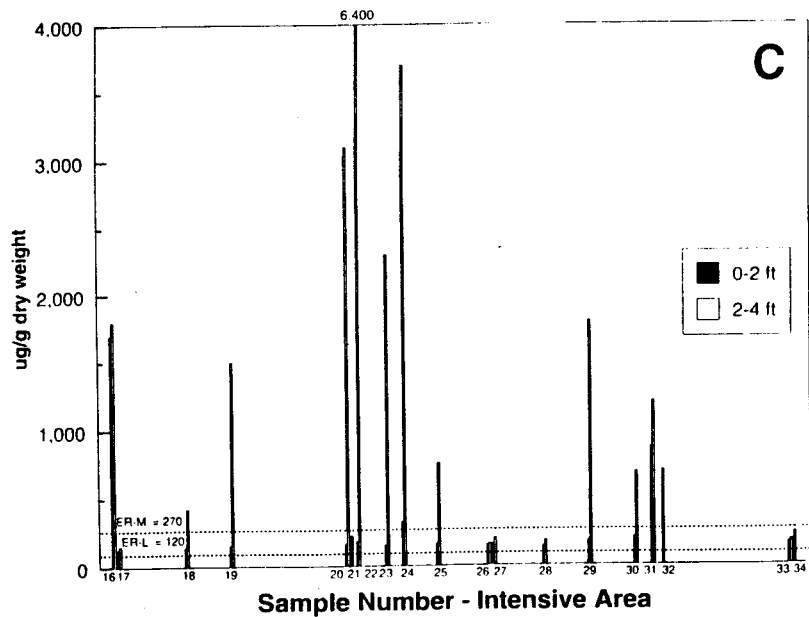
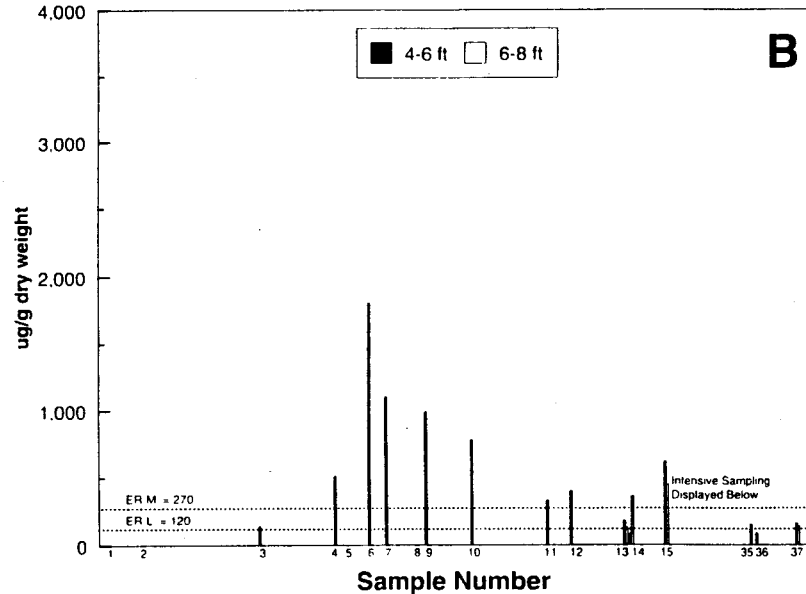
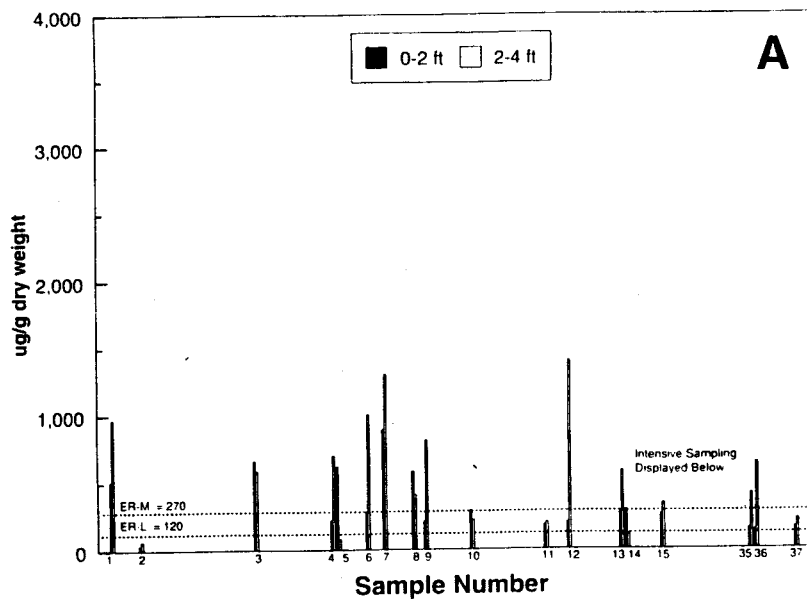


Figure 3.14 Survey 1 Anthracene Concentration vs. NOAA Guidelines

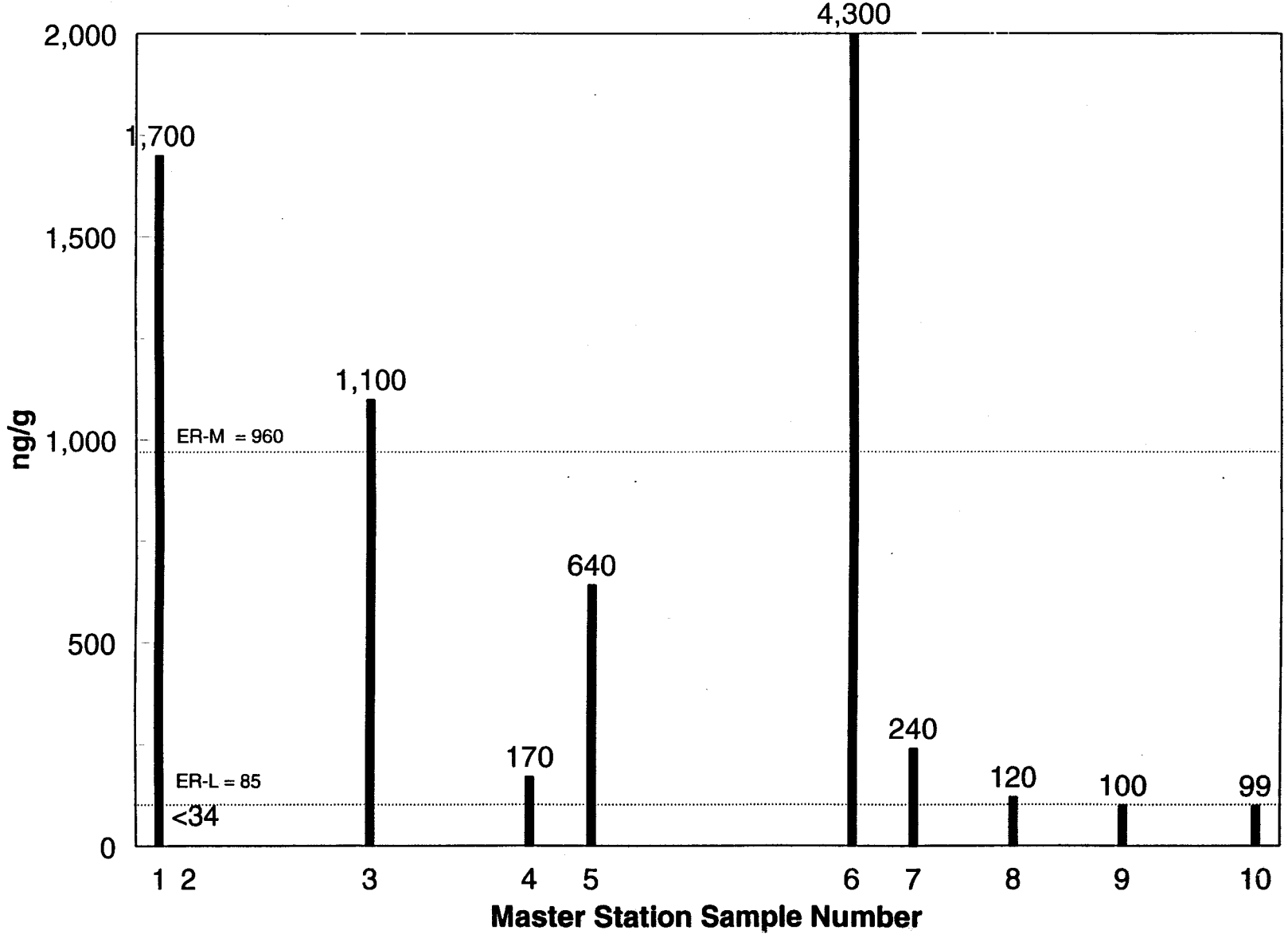


Figure 3.15a Survey 1 Benz(a)anthracene Concentration vs. NOAA Guidelines

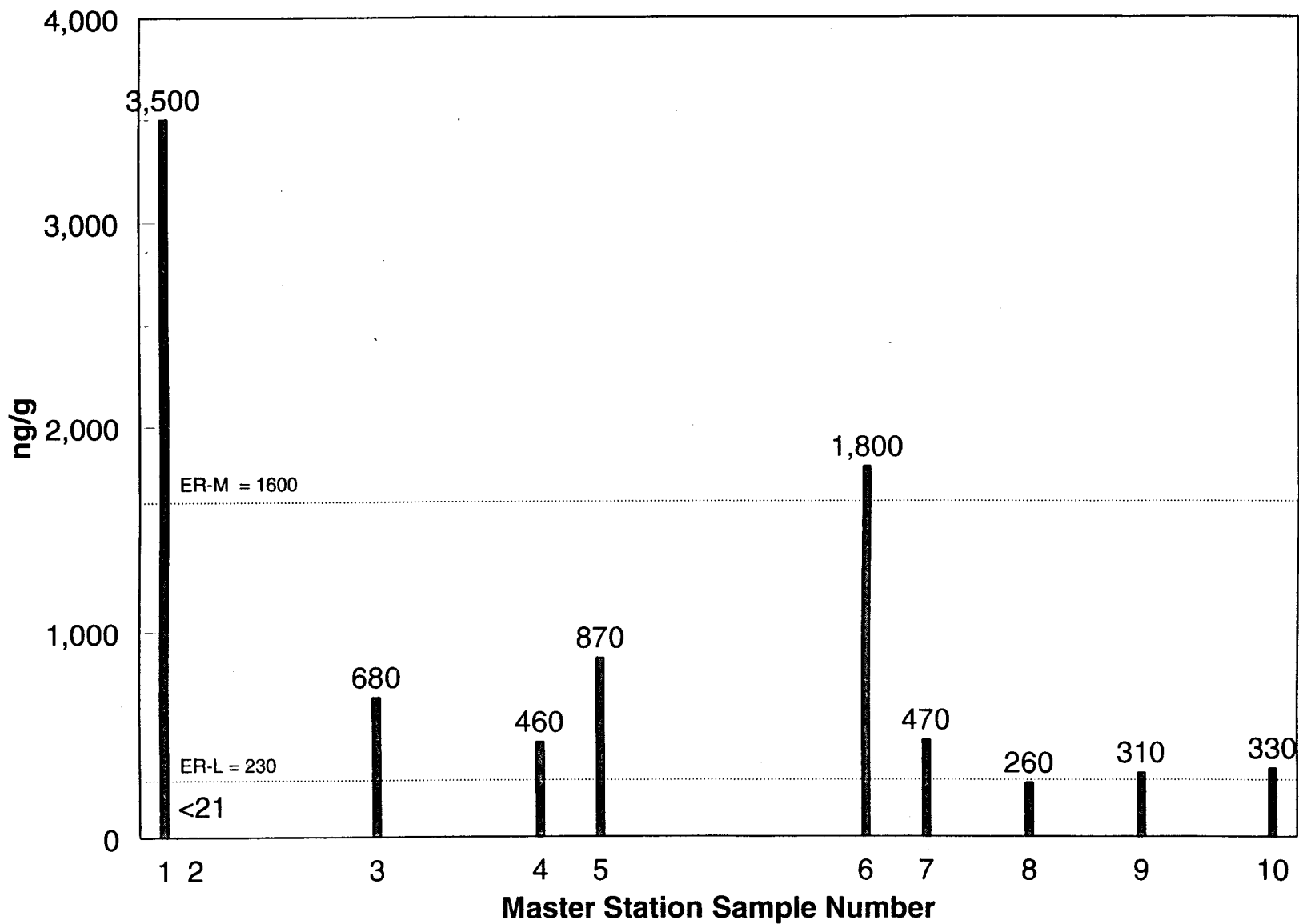
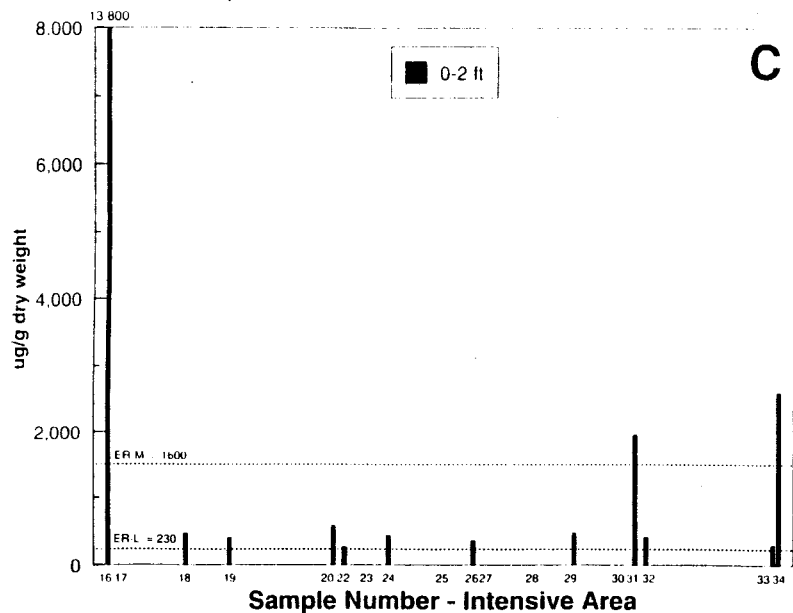
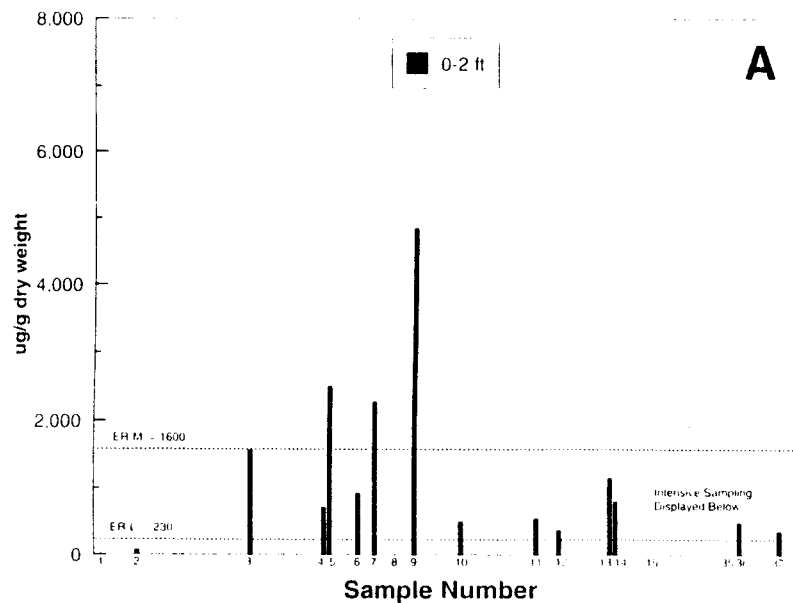
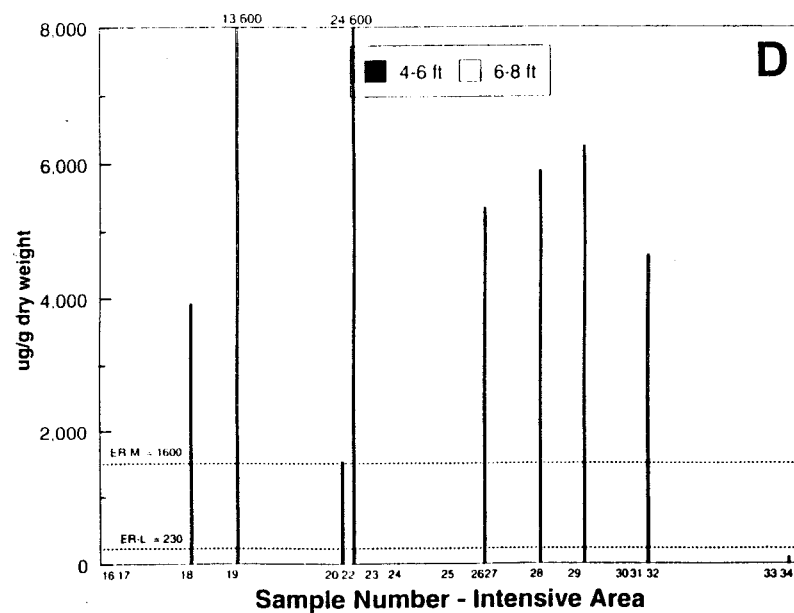


Figure 3.15b Survey 3 Benz(a)anthracene Concentration vs. NOAA Guidelines



Only first cross-section analyzed for BAA



B

D

Figure 3.16a Survey 1 Benzo(a)pyrene Concentration vs. NOAA Guidelines

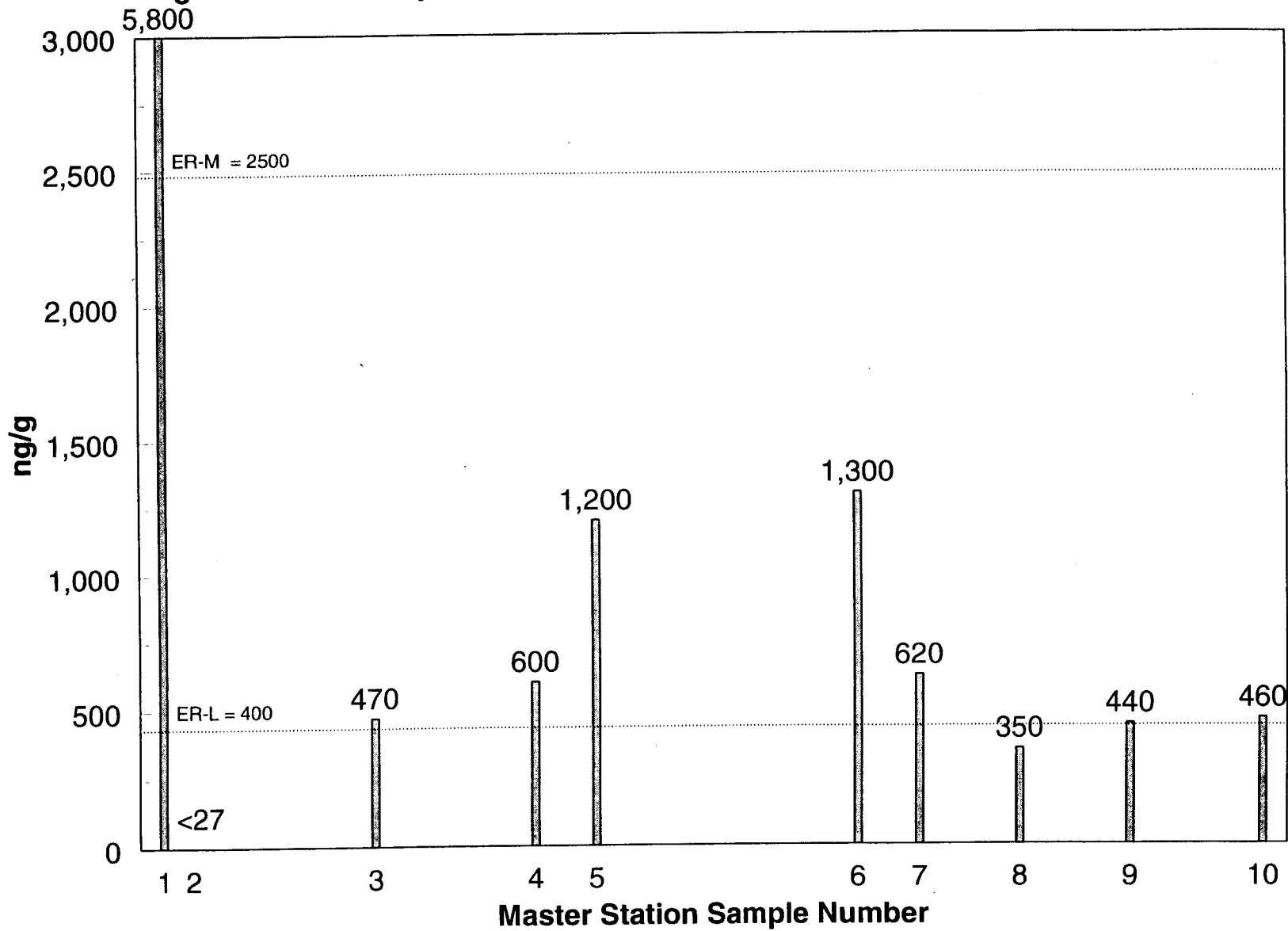
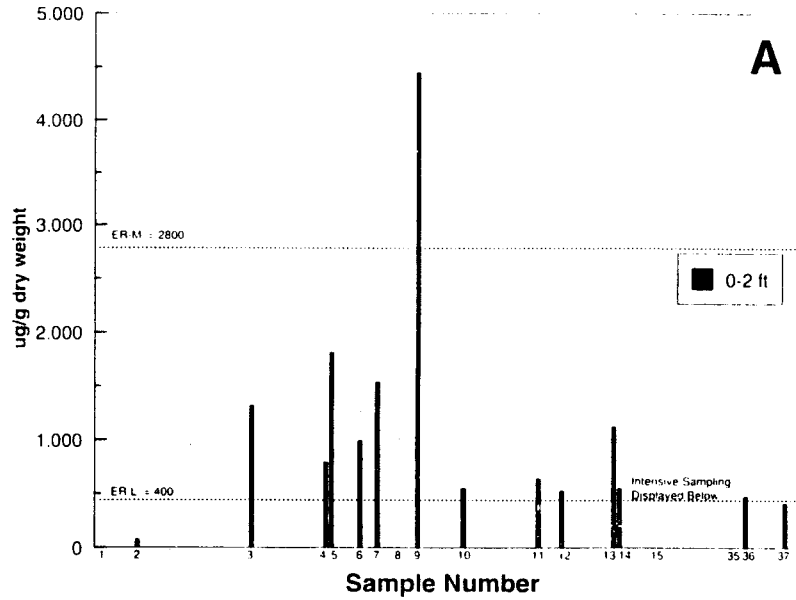


Figure 3.16b Survey 3 Benzo(a)pyrene Concentration vs. NOAA Guidelines



Only first cross-section analyzed for BAP

B

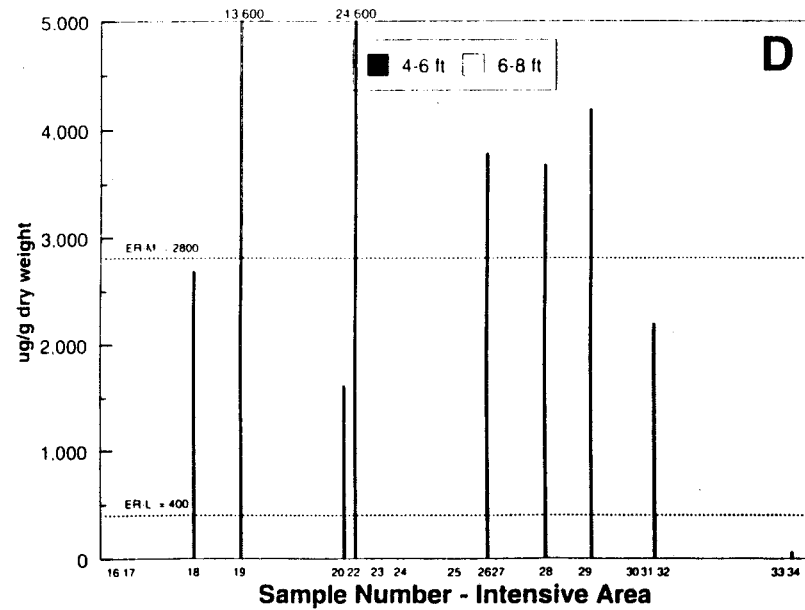
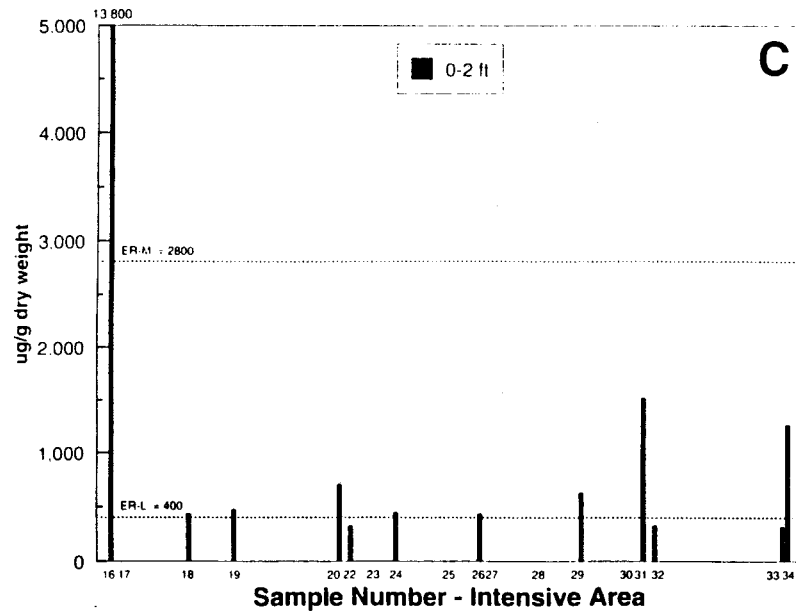


Figure 3.17a Survey 1 Chrysene Concentration vs. NOAA Guidelines

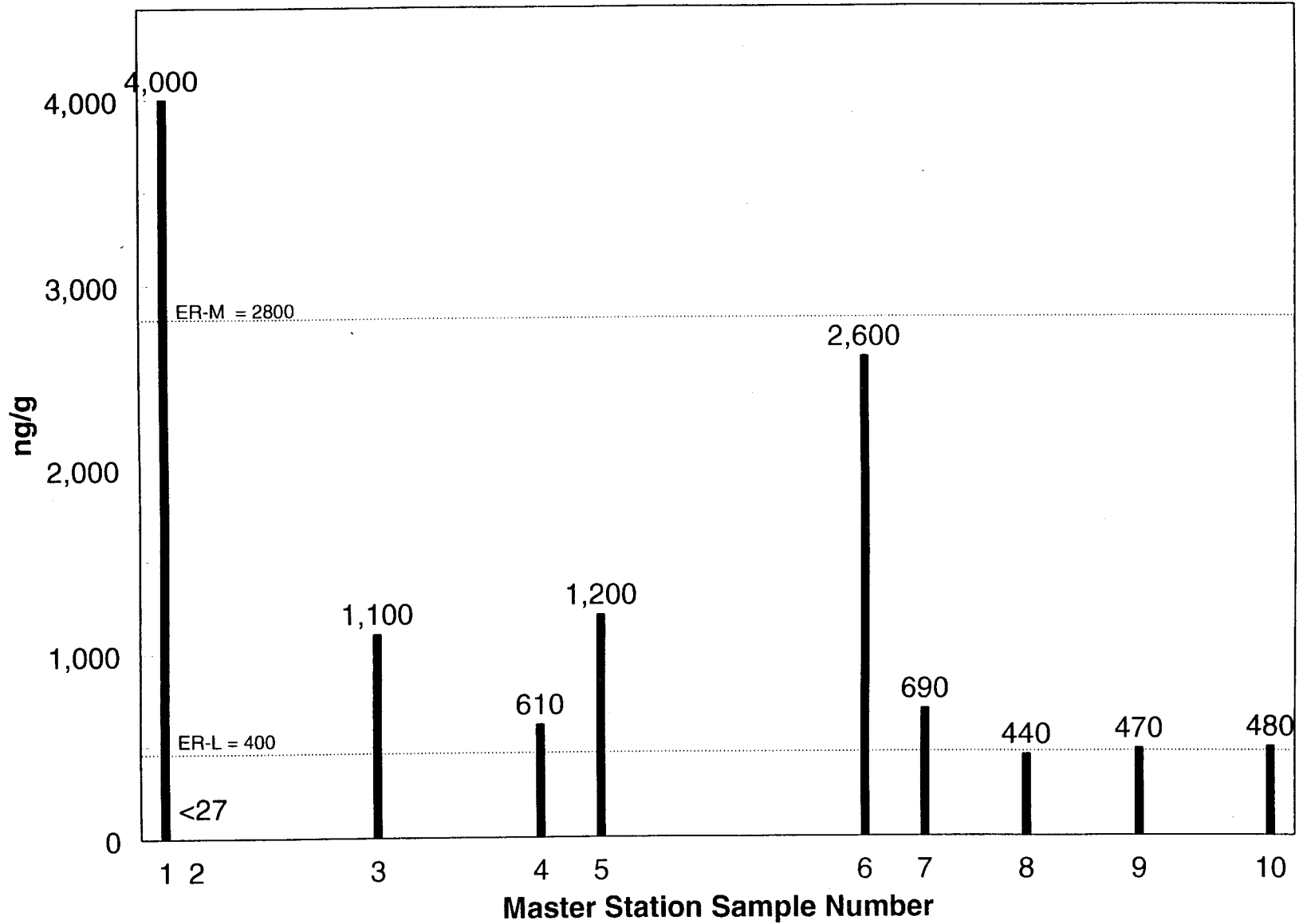
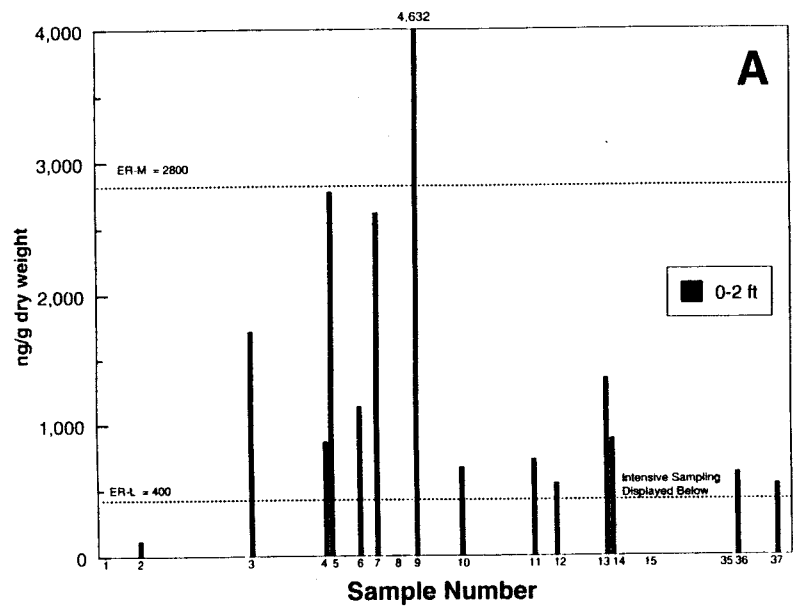


Figure 3.17b Survey 3 Chrysene Concentration vs. NOAA Guidelines



Only first cross-section analyzed for Chrysene

B

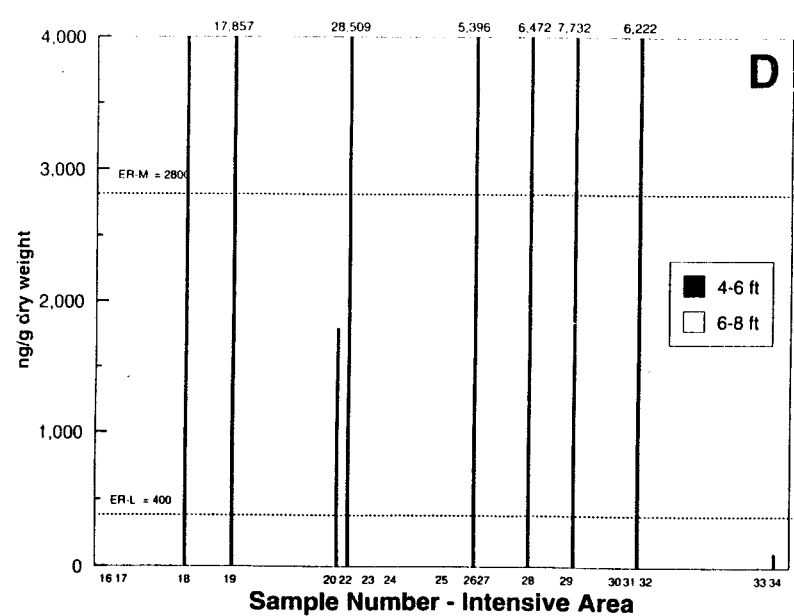
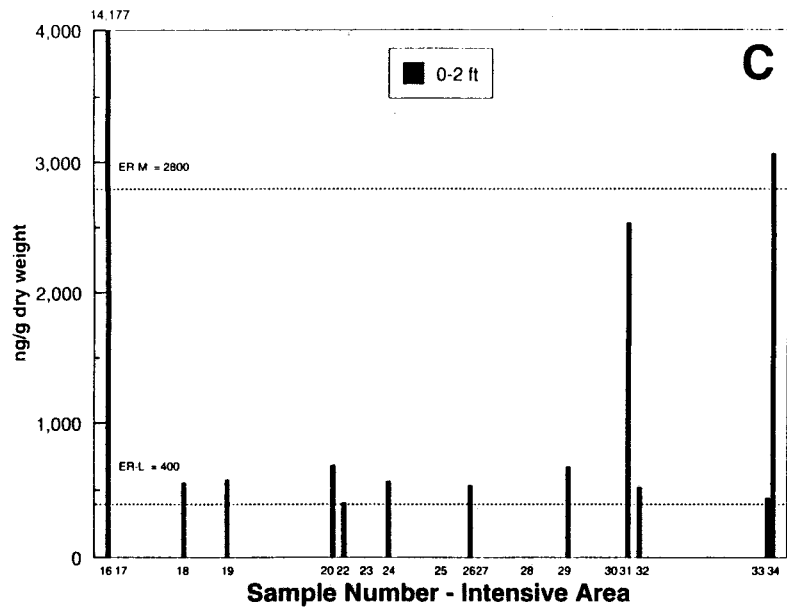


Figure 3.18a Survey 1 Fluoranthene Concentration vs. NOAA Guidelines

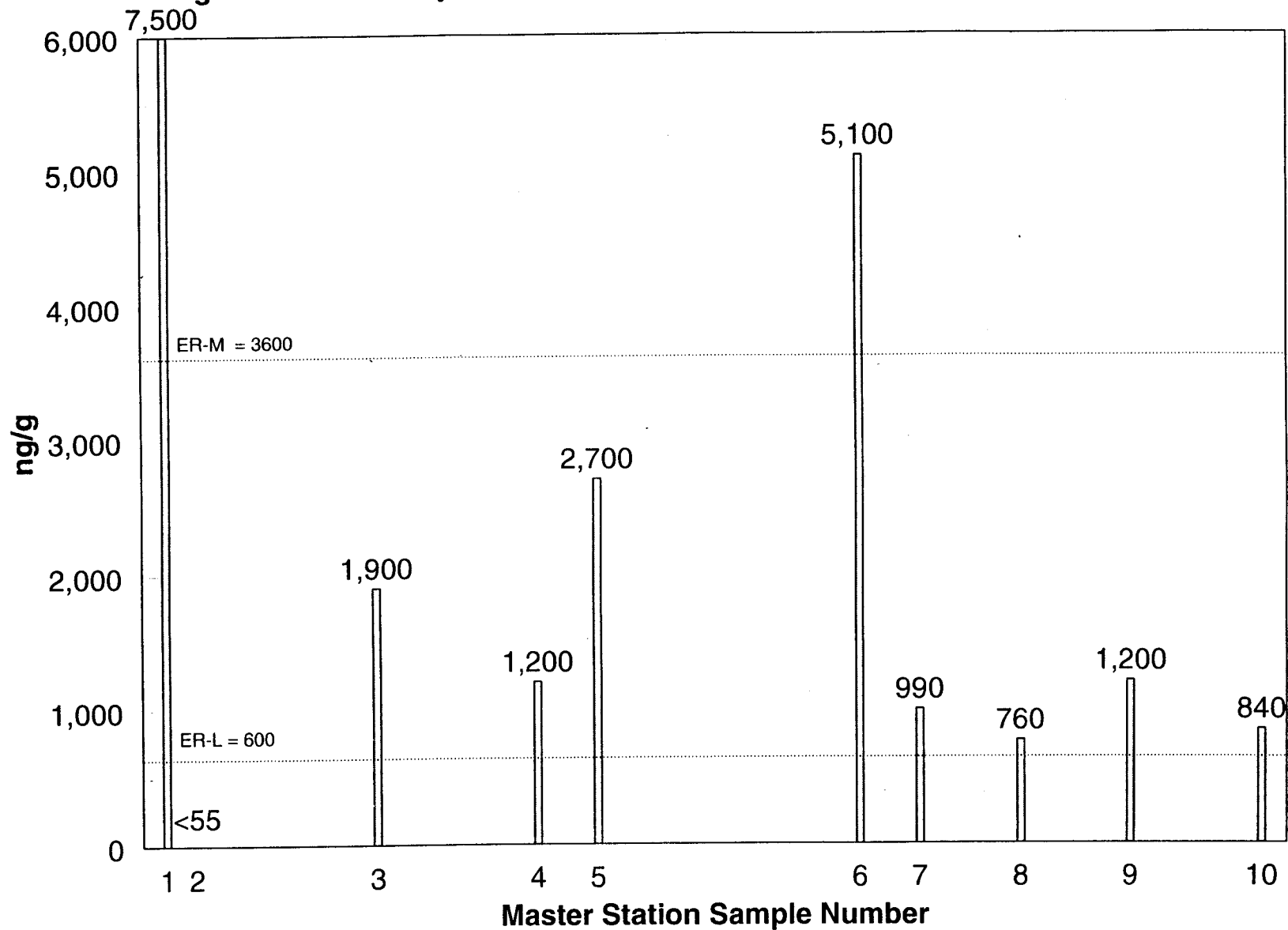


Figure 3.18b Survey 1 Organic Carbon Normalized Fluoranthrene vs. EPA Sediment Quality Criteria

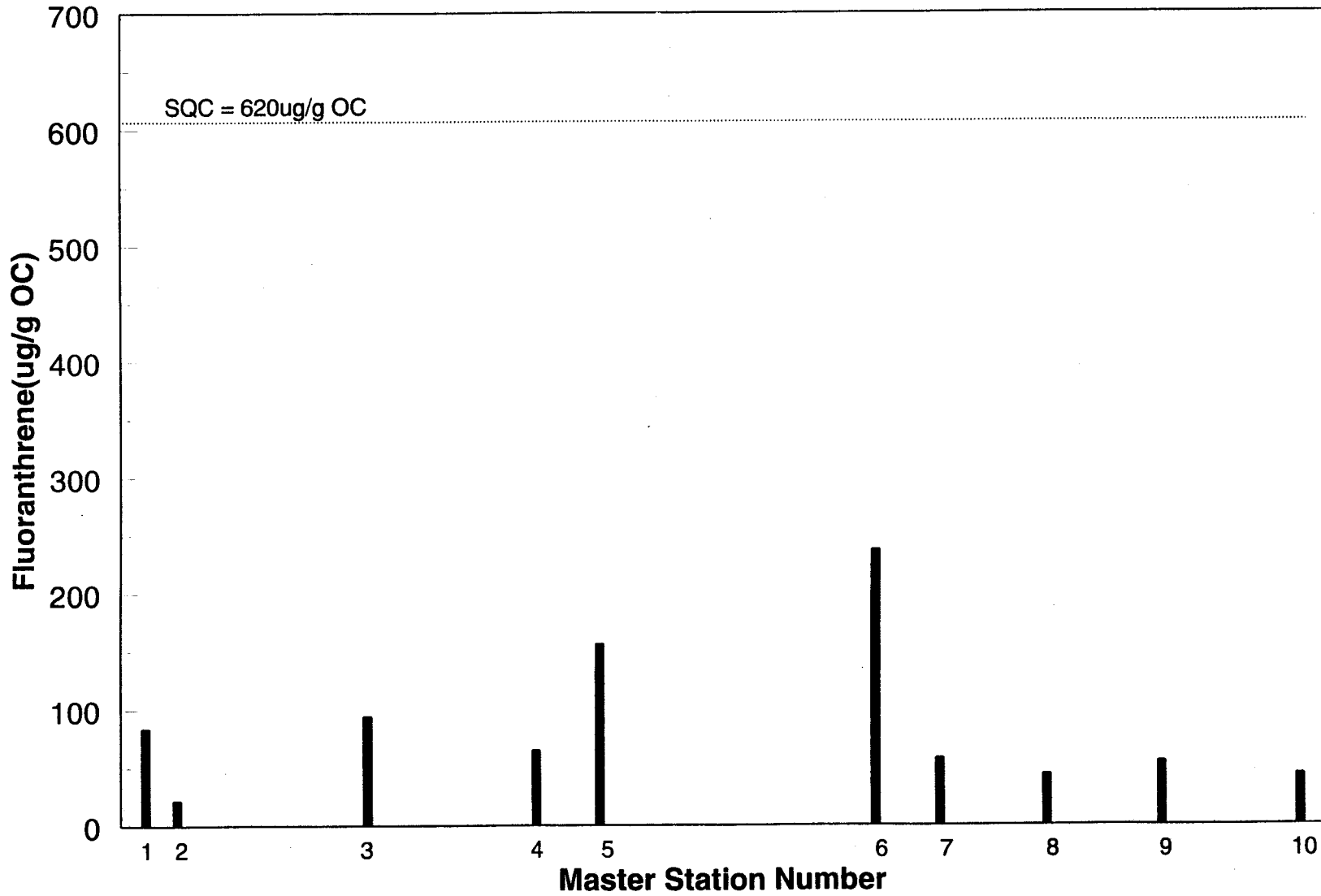


Figure 3.19 Survey 1 Fluorene Concentration vs. NOAA Guidelines

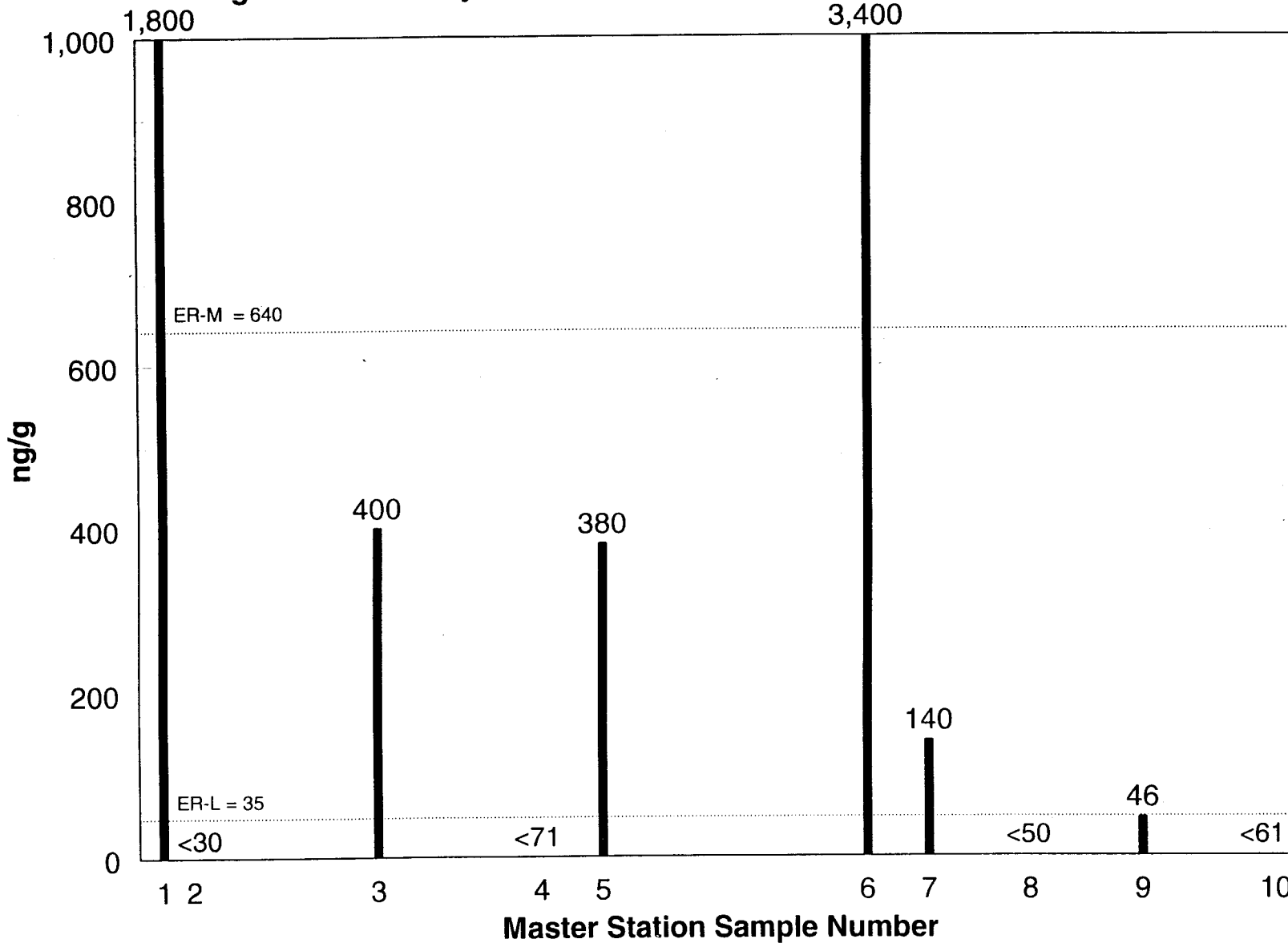


Figure 3.20 Survey 1 2-Methylnaphthalene Concentration vs. NOAA Guidelines

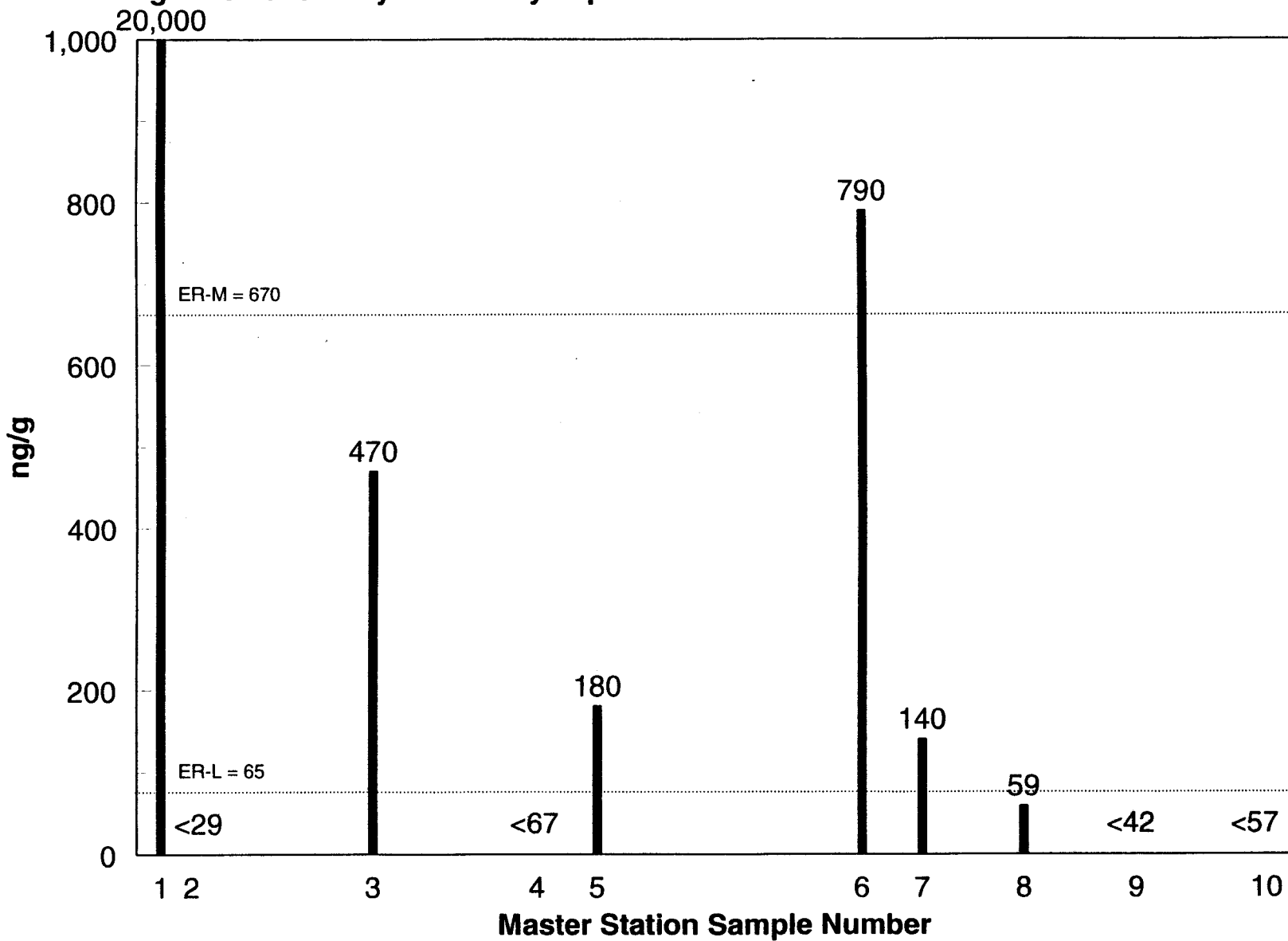


Figure 3.21 Survey 1 Naphthalene Concentration vs. NOAA Guidelines

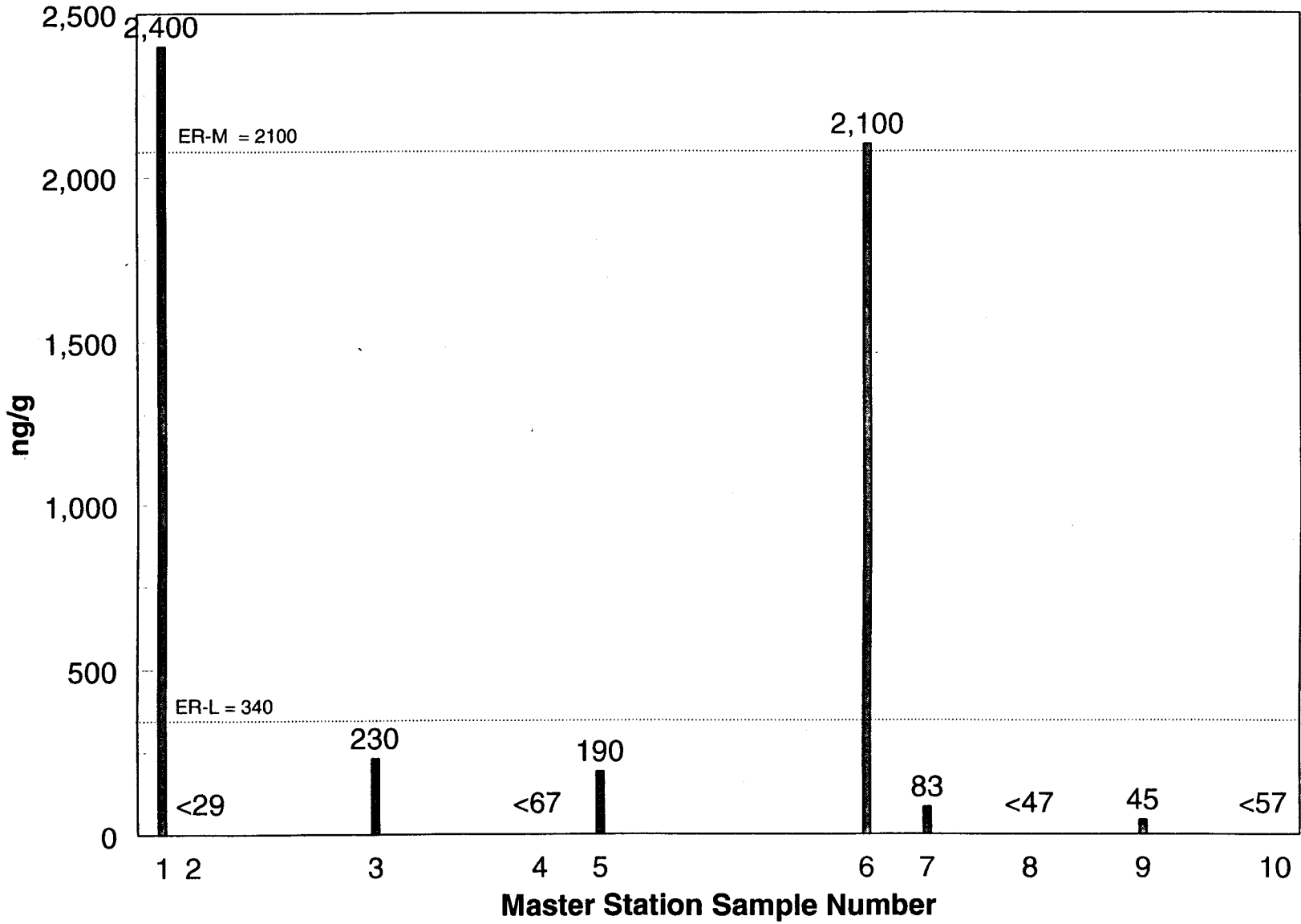


Figure 3.22a Survey 1 Phenanthrene Concentration vs. NOAA Guidelines

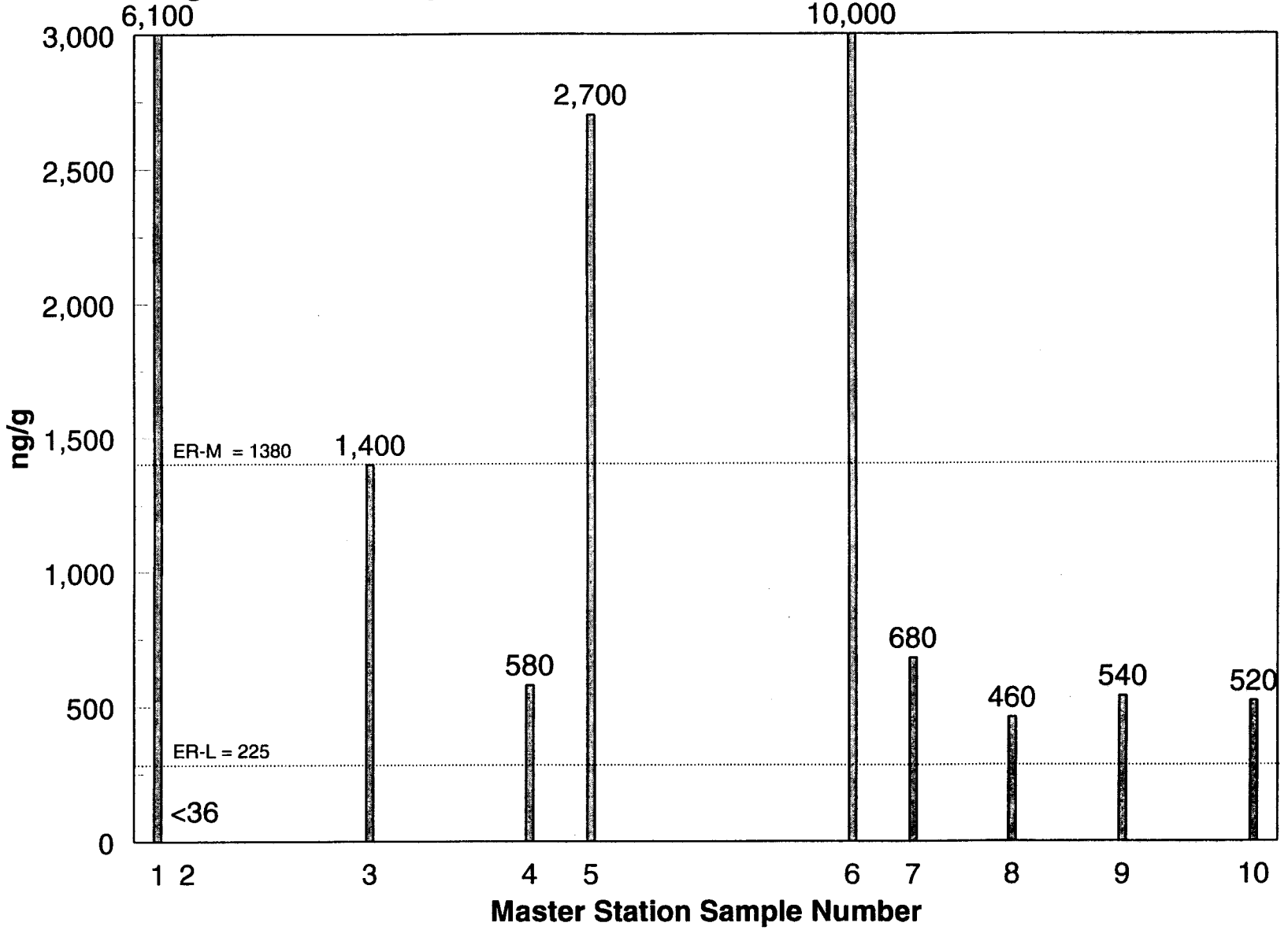


Figure 3.22b Survey 1 Organic Carbon Normalized Phenanthrene vs. EPA Sediment Quality Criteria

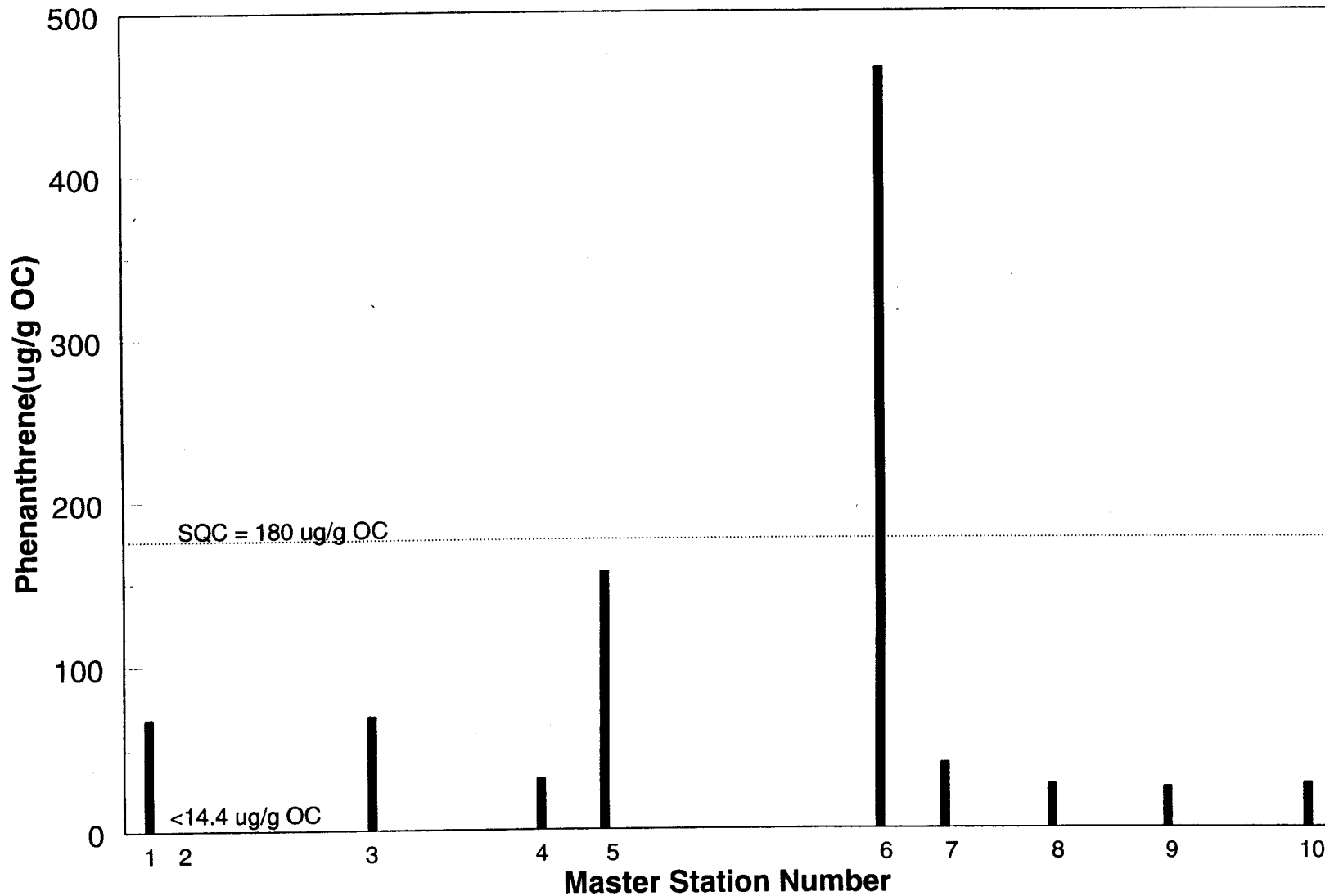


Figure 3.23 Survey 1 Pyrene Concentration vs. NOAA Guidelines

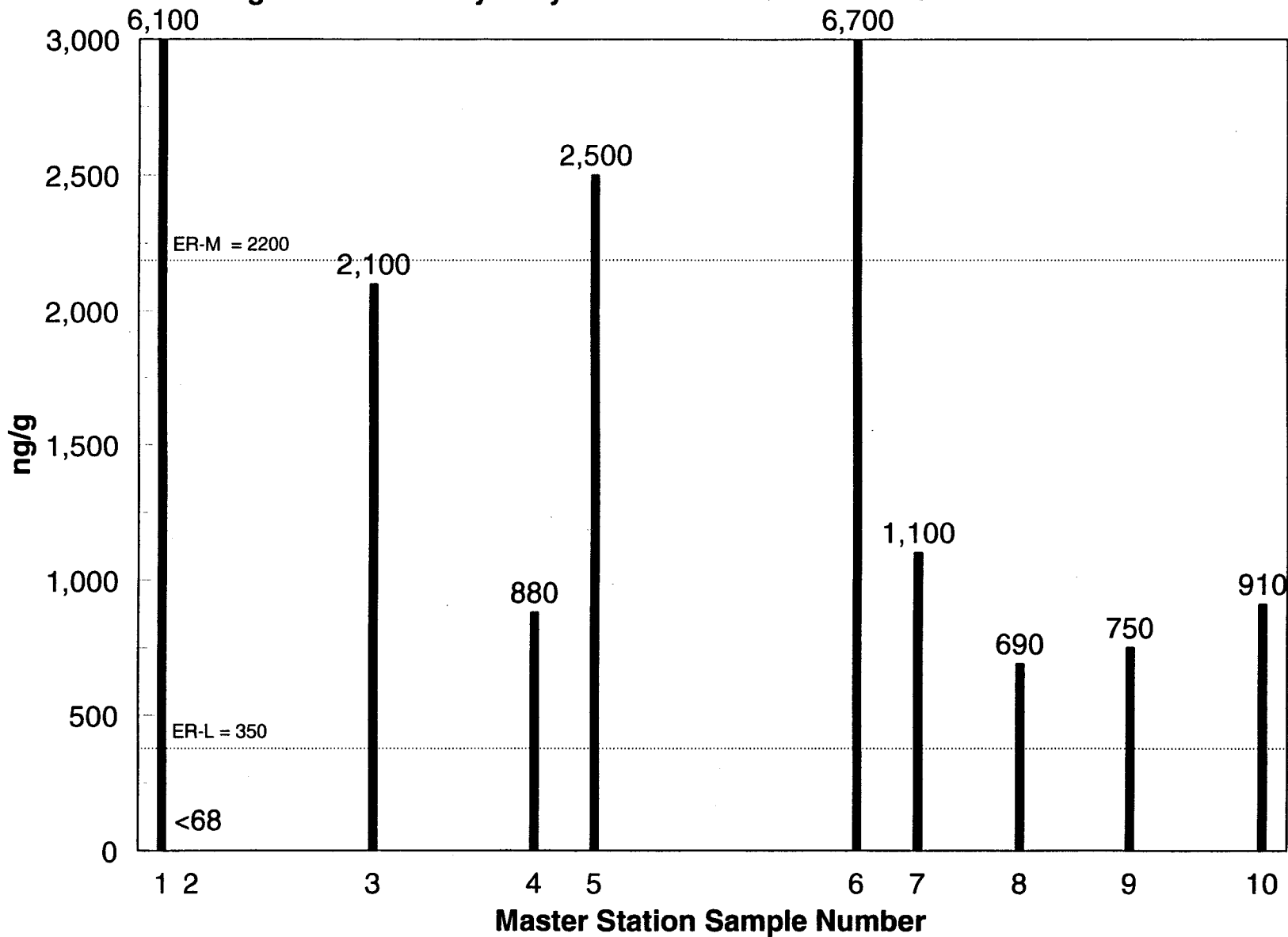
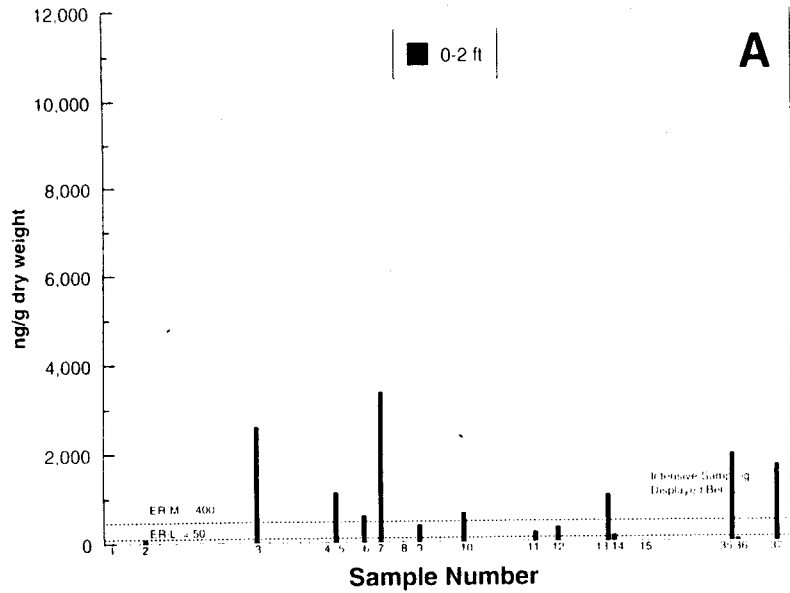


Figure 3.24 Survey 3 PCB Concentration vs. NOAA Guidelines



Only first cross-section analyzed for PCB

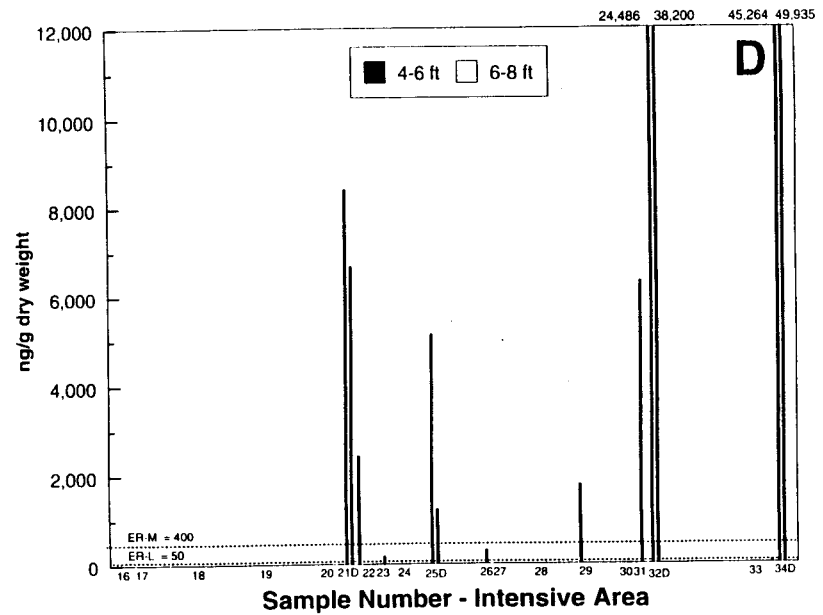
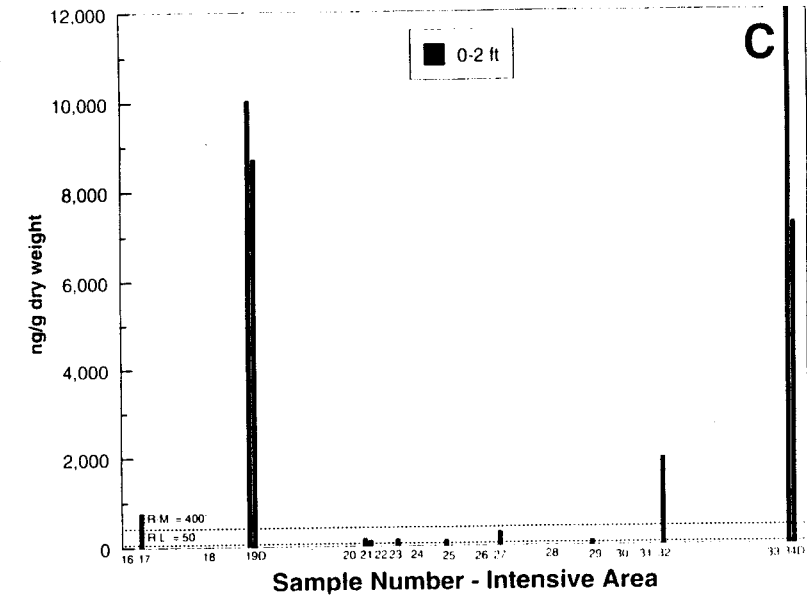


Figure 3.25 Survey 1 Total PAH Concentration vs. NOAA Guidelines

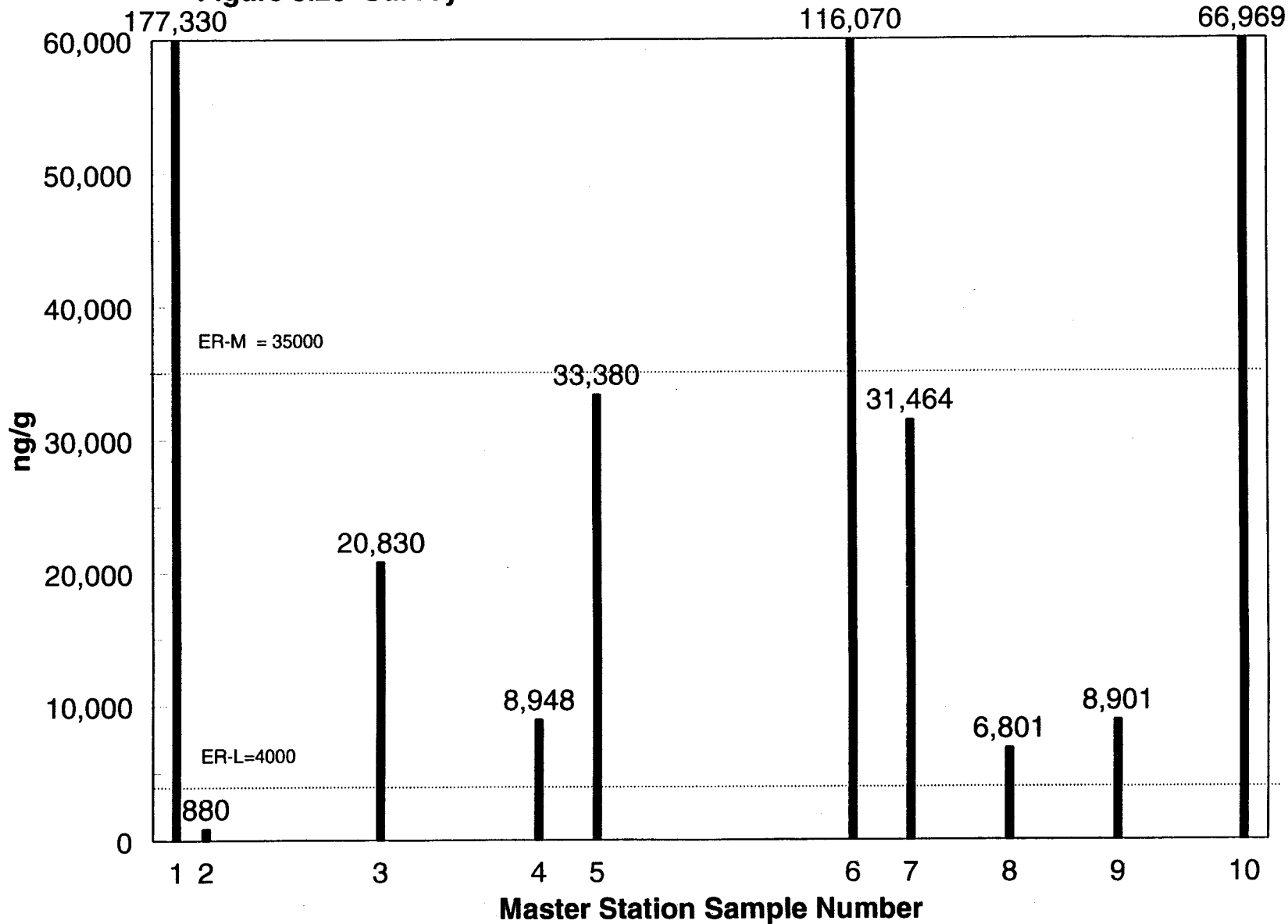


Figure 3.26 Survey 1 Mean Sample Location Exceedences for Metals

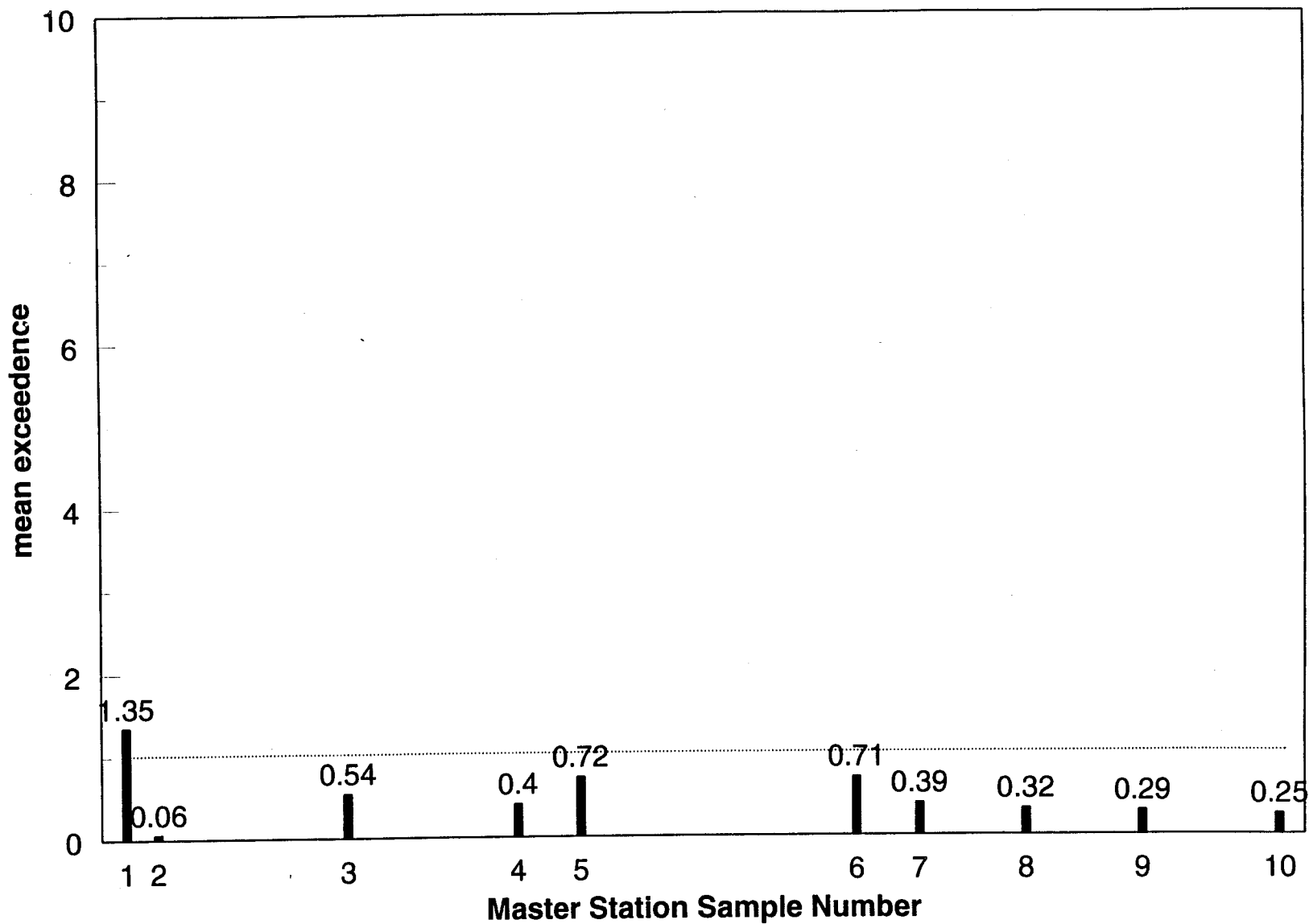


Figure 3.27 Survey 1 Mean Sample Location Exceedences for Organic Chemicals

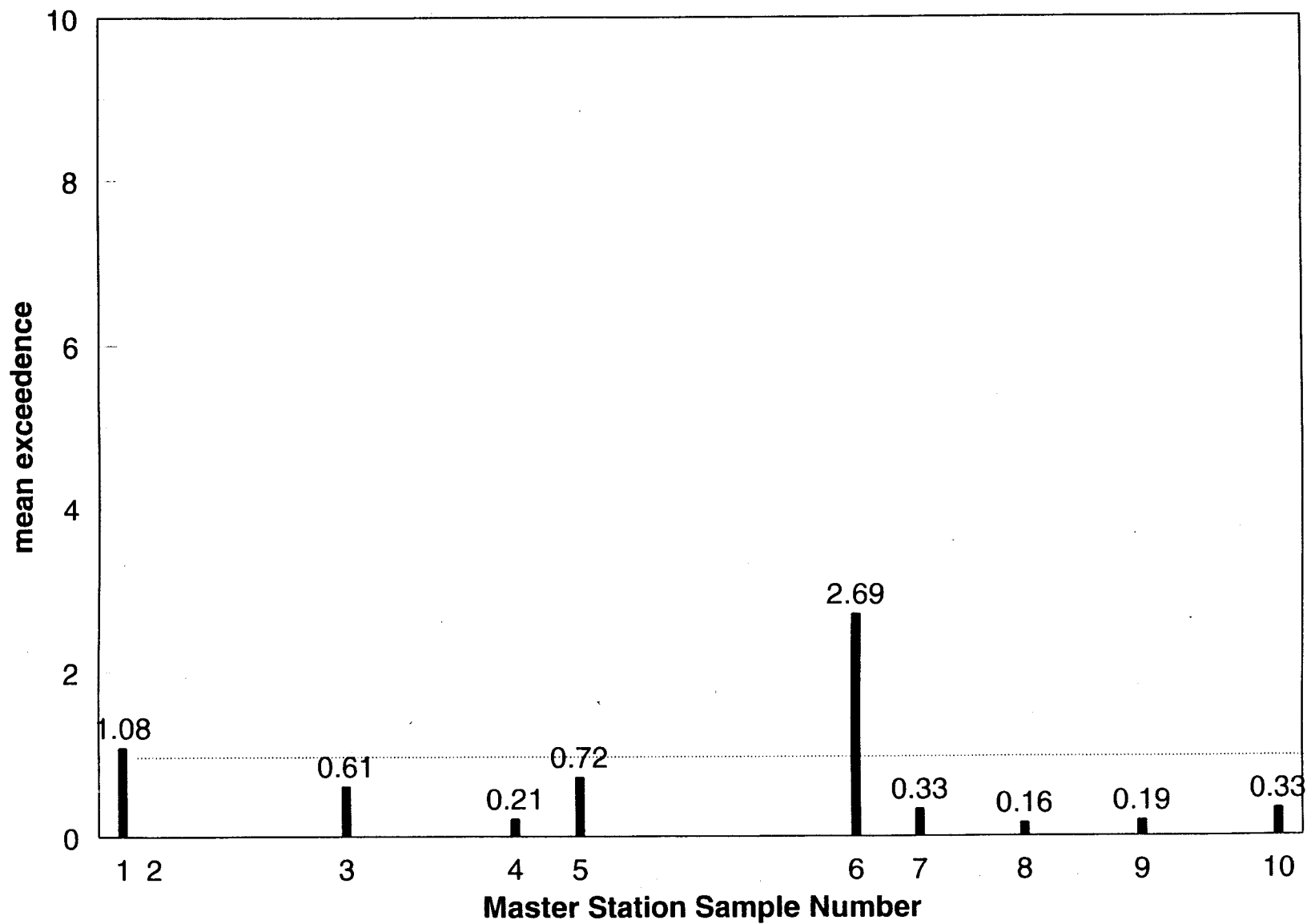


Figure 3.28 Survey 3 Mean Sample Location Exceedances for Metals

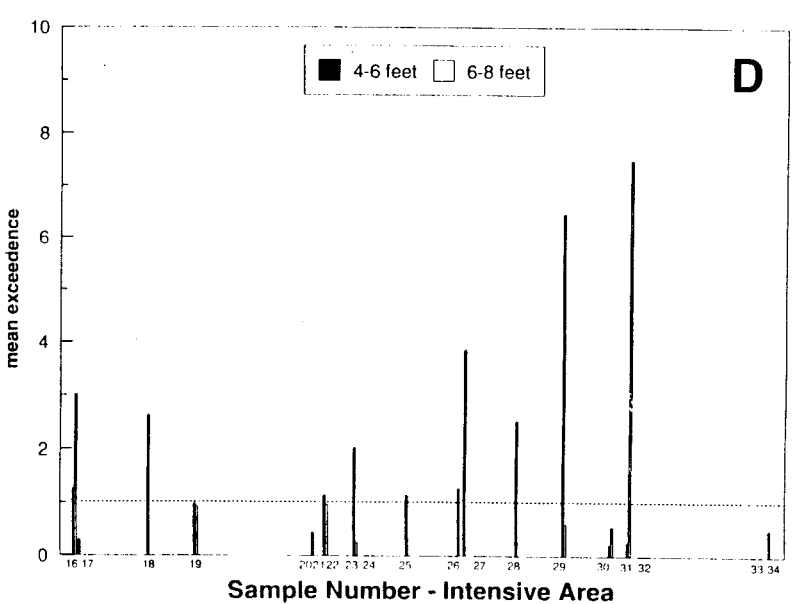
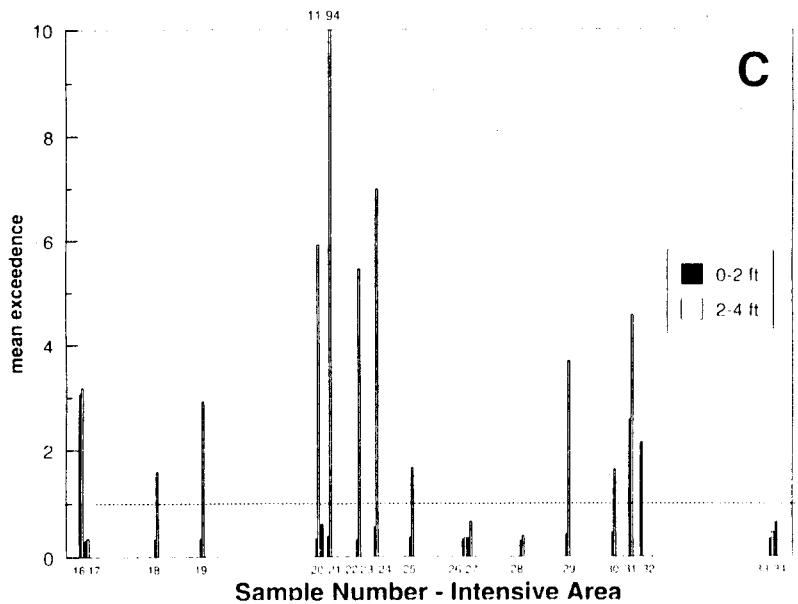
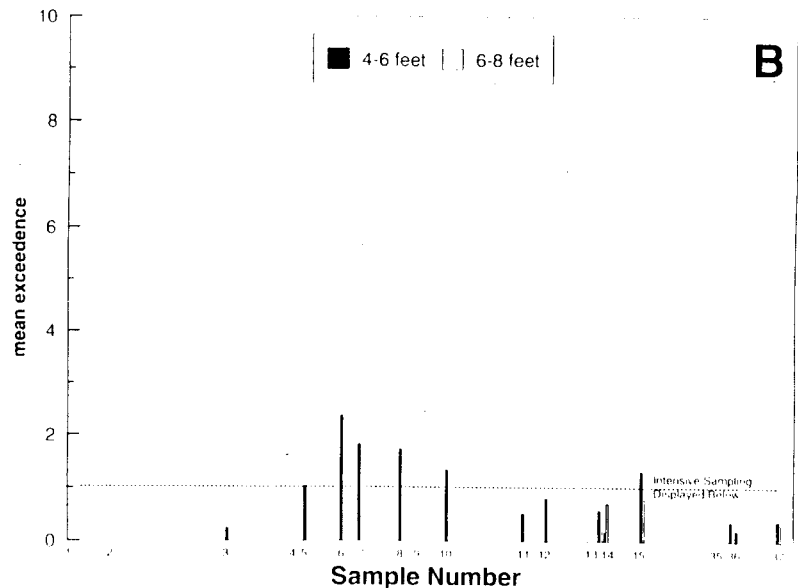
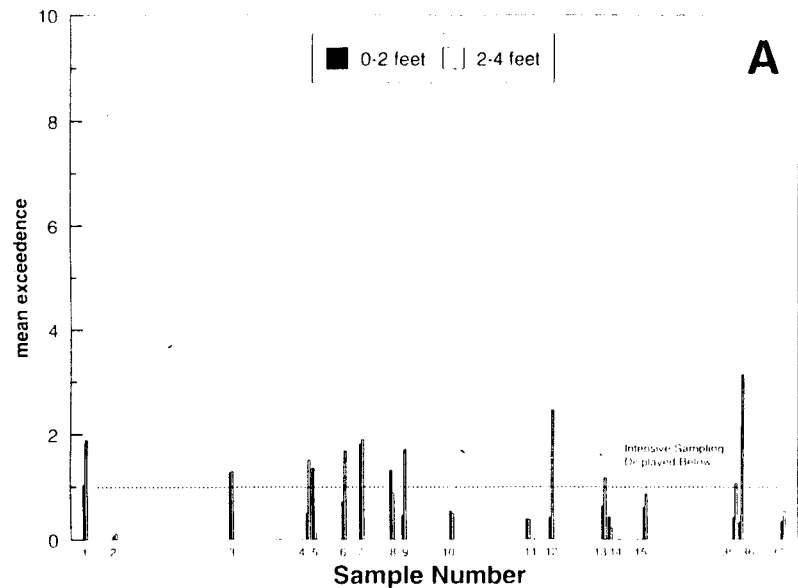
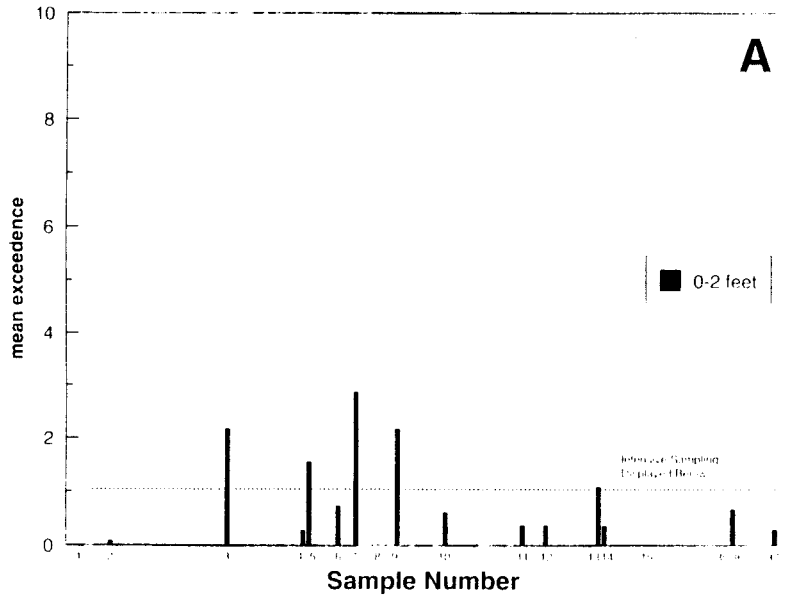
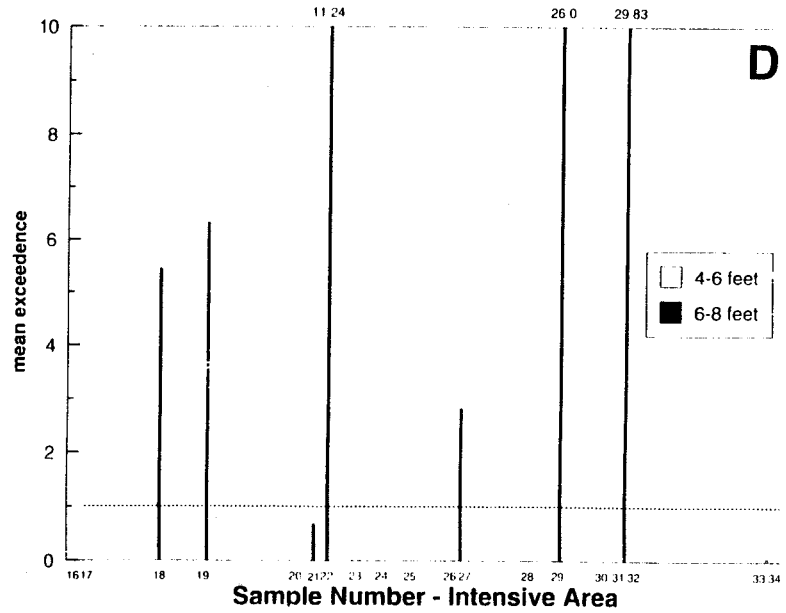
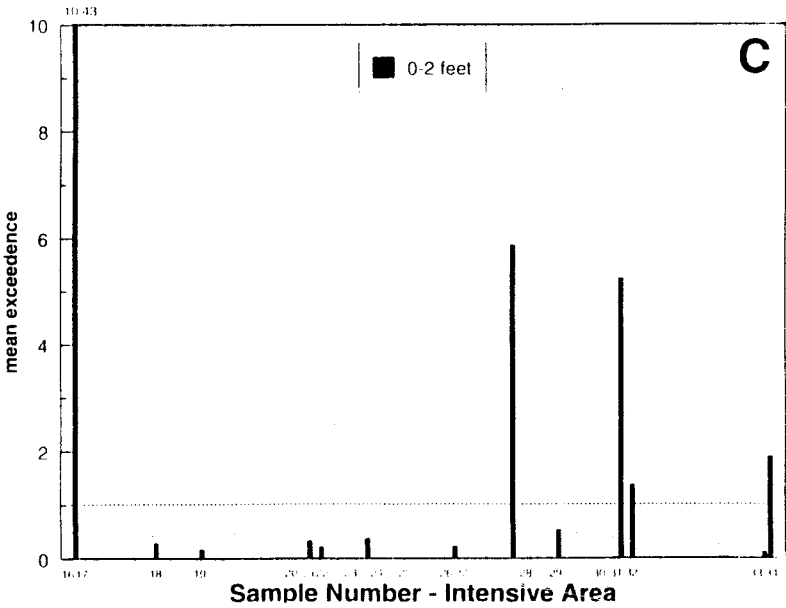


Figure 3.29 Survey 3 Mean Sample Location Exceedances for Organic Chemicals



Only first cross-section analyzed



4. CONCLUSIONS

This report summarizes the results from two sediment sampling surveys performed in the Buffalo River Area of Concern (AOC). This section presents several preliminary conclusions based on examination of the data resulting from the survey.

4.1 Metals

The only available guideline numbers for metals were taken from the NOAA Status and Trends guidelines document (Long and Morgan, 1990). Comparison of bulk sediment concentrations of arsenic, cadmium, copper, lead, mercury, nickel, silver and zinc indicate that zinc and lead pose the highest potential risk for impacts of biota in the Buffalo River. Nickel, chromium, and mercury may also be considered a potential risk, since the NOAA ER-M was exceeded at many stations, however, the magnitude of exceedance, on average, was lower than zinc and lead.

The areas where metal contamination of sediment occurred most significantly is in the southern end of the Buffalo River ship canal and downstream of the intensive survey area (based on surface samples from Survey 1), as well as throughout the intensive survey area (based on sub-surface samples from Survey 3).

4.2 Organic Chemicals

Based on the NOAA guideline numbers, total PCBs is the organic pollutant that poses the greatest risk in contaminated sediment in the Buffalo River AOC. On average, the total PCB concentration at a site was almost 16 times higher than the NOAA ER-M guideline. Other organics that on average exceeded, or came close to exceeding, the NOAA ER-M include the PAHs 2-methylnaphthalene, phenanthrene, and pyrene (based on Survey 1 data). The PAHs chrysene and benzo(a)pyrene on average exceeded the NOAA ER-M based on the limited Survey 3 results.

The Survey 1 locations with the most frequent and highest ER-M exceedances are in the southern end of the ship canal and the station downstream of the intensive zone. The Survey 3 results show that PAH exceedances occur primarily in the intensive survey area, along the sharp bend in the river. PCB exceedances however, most frequently and significantly occur in the upstream and downstream areas within the intensive survey area. Most significant exceedances of the NOAA ER-M for organic chemicals tend to occur in the deeper sediment cores, as opposed to the surface sediment.

Examination of the master station (Survey 1) sediment data under the EPA endorsed EqP-based criteria and the NOAA guidelines indicate two differing sets of conclusions. The examination of carbon normalized data for fluoranthene and phenanthrene (the two PAHs for which EqP-based criteria are available and that were sampled in the master survey) indicate that only phenanthrene should be considered as a potential source for adverse biological effects in the Buffalo River and only at a single location. The highest carbon normalized concentration for fluoranthene is less than one half of the criteria value considered to be protective of sensitive biota. For both of these contaminants the peak normalized concentration is found at the location downstream of the intensive zone as opposed to the southern end of the ship canal that contained the peak concentrations for the bulk sediment analyses.

5. REFERENCES

- APHA (American Public Health Association), American Water Works Association and Water Pollution Control Federation. 1975. **Standard method for the examination of water and wastewater, 14th ed.** American Public Health Association, Washington, D.C.
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