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Characterization of Mercury Contamination at the East Fork Poplar Creek Site, Oak Ridge, Tennessee:

A Case Study

by

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TABLE OF CONTENTS

NOTICE ii

LIST OF FIGURES iv

LIST OF TABLES v

LIST OF ABBREVIATIONS vi

ACKNOWLEDGMENTS vii

ABSTRACT 1

INTRODUCTION 2

BACKGROUND 4

PHASE 1b: SAMPLING DESIGN OPTIMIZATION BY CONDITIONAL SIMULATION . . 7

PHASE 1b: GEOSTATISTICAL EVALUATION 11

MERCURY SPECIATION TECHNOLOGY 20

CONCLUSIONS AND RECOMMENDATIONS 28

REFERENCES 30

LIST OF FIGURES

Figure 1. An overview of the East Fork Poplar Creek site in the context of the Oak Ridge Reservation, Tennessee. 3

Figure 2. Sampling design optimization system overview 9

Figure 3. Linear loss curve for various levels of mercury. 10

Figure 4. Subregion 1 sampling surface at East Fork Poplar Creek (as shaded in index map). . 13

Figure 5. Subregion 2 sampling surface at East Fork Poplar Creek (as shaded in index map). . 14

Figure 6. Subregion 3 sampling surface at East Fork Poplar Creek (as shaded in index map). . 15

Figure 7. Subregion 4 sampling surface at East Fork Poplar Creek (as shaded in index map). . 16

Figure 8. Subregion 5 sampling surface at East Fork Poplar Creek (as shaded in index map). . 17

Figure 9. Subregion 6 sampling surface at East Fork Poplar Creek (as shaded in index map). . 18

Figure 10. Subregion 7 sampling surface at East Fork Poplar Creek (as shaded in index map). 19

Figure 11. Distribution of total mercury concentrations (as determined by ICP-MS) with depth. 27

LIST OF TABLES

Table 1. Summary statistics for observed total mercury concentrations in the eleven subregions at EFPC. 12

Table 2. Moisture content, depth, and description of soil samples from East Fork Poplar Creek. 22

Table 3. Comparision of total mercury in dried, pulverized East Fork Poplar Creek soil samples. 23

Table 4. Distribution of mercury species in East Fork Poplar Creek soil samples. 24

Table 5. Mercury concentration for each species in as-received East Fork Poplar Creek soil samples. 25

Table 6. Mercury concentration for each species in prepared East Fork Poplar Creek soil samples. 26

LIST OF ABBREVIATIONS

ASV	anodic stripping voltametry
BLUE	best linear unbiased estimator
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CLP	EPA Contract Laboratory Program
CRD-LV	Characterization Research Division - Las Vegas
CVAAS	cold vapor atomic absorption spectrometry
DOE	U.S. Department of Energy
DQO	data quality objective
EFPC	East Fork Poplar Creek
EMSL-LV	Environmental Monitoring Systems Laboratory-Las Vegas
EPA	U.S. Environmental Protection Agency
FP-XRF	field portable X-ray fluorescence
FS	feasibility study
ICP-MS	inductively coupled plasma-mass spectrometry
LCS	laboratory control samples
LESAT	Lockheed Environmental Systems and Technologies
NAA	neutron activation analysis
NEPA	National Environmental Policy Act
NERL	National Exposure Research Laboratory
NPL	National Priorities List
OK	ordinary kriging
ORAU	Oak Ridge Associated Universities
ORD	Office of Research and Development (EPA)
ORNL	Oak Ridge National Laboratory
ORR	Oak Ridge Reservation
PARCC	precision, accuracy, representativeness, completeness, comparability
PCB	polychlorinated biphenyl
PRG	preliminary remediation goal
QA	quality assurance
QAPjP	quality assurance project plan
QC	quality control
RCRA	Resource Conservation and Recovery Act
RI	remedial investigation
RSD	relative standard deviation
SAIC	Science Applications International Corporation
SARA	Superfund Amendments and Reauthorization Act
SEM	scanning electron microscopy
SLB	Sewerline Beltway
TSC-LV	Technology Support Center - Las Vegas
XRF	X-ray fluorescence

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ABSTRACT

Concern about the adverse health effects of mercury on human and ecological life has led to a need for more sensitive and reliable analytical and sampling procedures. Mercury contamination, in various matrices, is present at many Superfund sites throughout the United States.

The East Fork Poplar Creek (EFPC) Site in Oak Ridge, Tennessee, begins at, but is not confined to, the Y-12 Plant, a U.S. Department of Energy (DOE) facility. Historic accidental release of mercury-contaminated material associated with nuclear weapons production at the site resulted in a complex system of stream and floodplain contamination. The EFPC is designated as an Oak Ridge Reservation (ORR) operable unit under the Comprehensive Environmental Response, Compensation, and Liability Act of 1983 (CERCLA) and was included on the National Priorities List in 1989. As such, its remediation must follow specific procedures mandated by CERCLA. The EFPC involves off-site release of contaminants from the DOE Y-12 Plant, and therefore its remediation must also conform to the Resource Conservation and Recovery Act (RCRA) of 1980, Section 3004(v).

Beginning in 1991, the U.S. Environmental Protection Agency (EPA) Environmental Monitoring Systems Laboratory in Las Vegas (EMSL-LV) currently the National Exposure Research Laboratory's Characterization Research Division (CRD-LV) assisted in the Remedial Investigation/Feasibility Study (RI/FS) for East Fork Poplar Creek. Specifically, CRD-LV helped to: (1) test the use of field-portable X-ray fluorescence (XRF) as a rapid field analytical method for mercury; (2) design an optimum soil sampling strategy; (3) select and implement a method of estimating mercury concentrations using geostatistical methods; and (4) determine the species of mercury in the floodplain soils using an EPA developmental selective chemical extraction procedure.

XRF proved not to be a viable field technique for this site, possibly due to the high moisture content of EFPC soils. Sample design optimization was accomplished using an innovative application of a Monte Carlo technique known as conditional simulation. Initial geostatistical evaluation of the soil sample data using kriging had mixed results. Kriging was used for interpolating contaminant concentration between data points. Improvements were made and subsequent results using Rank-Order kriging were closer to actual data. The development of a new selective chemical extraction method based on sequential extraction contributed to the knowledge about the difficulties associated with mercury speciation.

INTRODUCTION

The U.S. EPA's Characterization Research Division in Las Vegas (CRD-LV) assists the EPA Regions in the characterization of Superfund and Resource Conservation and Recovery Act (RCRA) sites through its Technology Support Center (TSC). The CRD-LV TSC is part of the technical support project that was formed in 1987 by the Office of Research and Development, Office of Solid Waste and Emergency Response and all of the Regional offices. The function of the CRD-LV TSC is to provide assistance and ORD technical expertise to Regional personnel in characterizing site contaminants for remediation.

In 1991, the EPA Region 4, Remedial Project Manager requested the assistance of the TSC-LV in the Remedial Investigation/Feasibility Study (RI/FS) for East Fork Poplar Creek (EFPC) (Brown, 1991). Specifically, TSC-LV was asked to help: (1) test the use of field-portable X-ray fluorescence (XRF) as a rapid field analytical method for mercury; (2) design an optimum soil sampling strategy; (3) select and implement a method of estimating mercury concentrations using geostatistical methods; and (4) determine the species of mercury in the floodplain soils using an EPA developmental selective chemical extraction procedure. From 1991 through early 1994, TSC-LV assisted the Region and DOE with these technical challenges, beginning with sample design optimization and ending with mercury speciation. The results of the four related efforts were intended to be used at various stages in the development of the RI for EFPC.

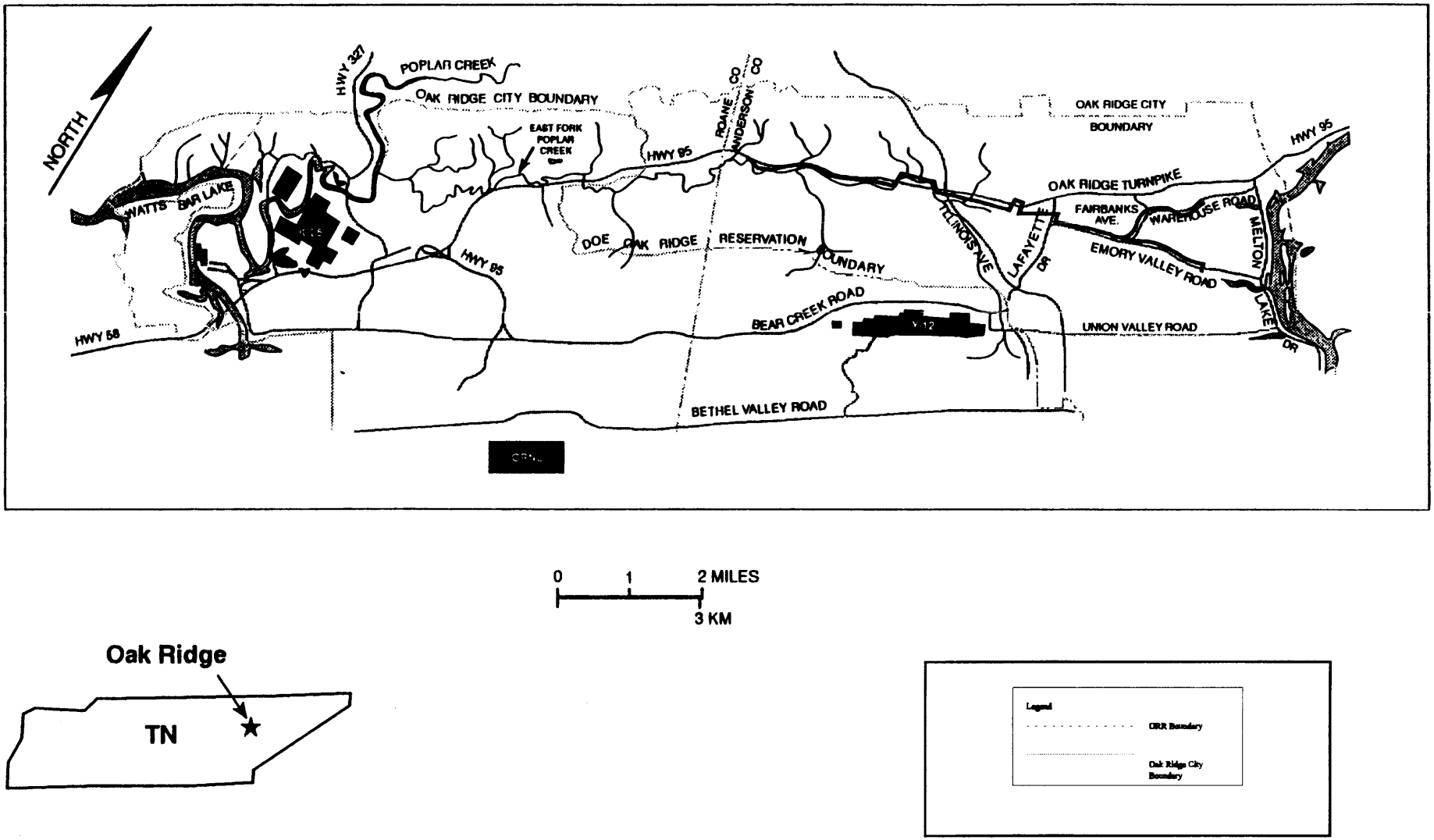

Figure 1. An overview of the East Fork Poplar Creek site in the context of the Oak Ridge Reservation, Tennessee.

BACKGROUND

The East Fork Poplar Creek (EFPC) operable unit includes approximately 14.5 miles of the EFPC, its floodplain, and the Oak Ridge Sewerline Beltway (SLB). The area of concern (Figure 1) begins at the Y-12 Plant, and continues through the city of Oak Ridge until its convergence with Poplar Creek back on the Oak Ridge Reservation. Both EFPC and its floodplain were contaminated by releases of mercury from the Y-12 Plant, primarily during the 1950s and 1960s.

The EFPC is a perennial stream located in Anderson and Roane Counties in Oak Ridge, Tennessee, approximately 25 miles west of Knoxville. Its headwaters are contained in 54 to 72 inch underground collection pipes that extend from the west end to the central area of the Y-12 Plant, where the above-ground portion of the creek begins. From the Y-12 Plant site, EFPC flows northward through a gap in Pine Ridge and enters Gamble Valley and the city of Oak Ridge. From there, the stream flows in a northwesterly manner along Illinois Avenue through commercial and light industrial areas in Oak Ridge, then trends generally westward, parallel to Oak Ridge Turnpike in East Fork Valley through primarily residential, agricultural, and undeveloped forest areas, until it joins Poplar Creek. EFPC waters, after entering Poplar Creek, flow into a river, which is impounded behind Watts Bar Dam.

The EFPC site is included on the National Priorities List (NPL) as part of the Oak Ridge Reservation and its environs and, as such, its remediation must follow specific procedures mandated by the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). EFPC involves off-site release of contaminants from the Y-12 Plant and, therefore, its remediation must also conform to the procedures of Section 3004(v) of the RCRA. Actions taken to remediate EFPC may affect the environment, and the potential environmental impact of those actions must be publicly addressed in accordance with the values stated in the National Environmental Policy Act (NEPA). The remedial investigation (RI) of EFPC has integrated the requirements of these three primary federal regulations as well as those of other federal and Tennessee state regulations.

The primary steps included in a CERCLA RI are:

- to collect data to characterize site conditions,
- to determine the nature and extent of contamination, and
- to assess current and future risks to human health and the environment, if no remediation occurs.

The first two steps are generally referred to as the site characterization, and the third step is termed the baseline human health and ecological risk assessment. These assessments are described in detail in the Risk Assessment Guidance for Superfund U.S. EPA Vol. 1, Parts A and B, 1989 and 1991. RCRA and NEPA investigations call for similar activities. After the RI is completed, work begins on the feasibility study (FS).

The EFPC RI was conducted in two segments, Phase 1a and Phase 1b (DOE 1994). Phase 1a was designed to determine the nature of contamination and to identify the contaminants of potential concern - primarily mercury and other metals, radionuclides, and various organic compounds including polychlorinated biphenyls (PCBs) and pesticides. Completion of this phase of the RI required the installation of 12 new groundwater monitoring wells and the quarterly sampling of 22 wells to characterize the groundwater quality and the hydrogeology of the floodplain. More than 500 surface water, creek sediment, and surface and subsurface soil samples were taken along the watershed and at an uncontaminated reference site during Phase 1a. The samples were analyzed for 182 inorganic, organic, and radionuclide analytes, with mercury being the primary contaminant of concern. In addition, geotechnical parameters and soil chemistry tests were performed that relate to treatability studies. Phase 1b was designed to establish the level and extent of contamination. More than 3,000 field samples were collected and analyzed, and soil-gas surveys were conducted to monitor mercury volatilization during Phase 1b.

Of all the media at the EFPC, the floodplain soils have the largest volume and highest concentration of contaminants. The Phase 1a data demonstrated that mercury accounts for approximately 85% of the total risk attributable to metals in the soil. A number of analyses were performed to detect inorganic, organic, and radionuclide compounds. An elevated level of mercury was observed when high concentrations of other contaminants were present. Mercury was found to be a surrogate for the presence of other metals and radionuclides, and was used as such to determine the distribution of other inorganic and even organic contaminants.

Risk potential played a critical role in the decisions made about remediation and, therefore, it was important to establish pertinent and appropriate data quality objectives (DQOs). Both qualitative and quantitative DQOs were established for the EFPC RI to meet the objectives of precision, accuracy, representativeness, completeness, and comparability (PARCC). Analytical precision and accuracy were controlled by adopting EPA Contract Laboratory Program (CLP) criteria and quality control (QC) frequency and types. Data verification and validation of the resulting analytical data packages indicated the quality of the data produced by the laboratories. Sampling precision was evaluated by the use of colocated samples (field replicates) and split samples (field duplicates). Representativeness of data from the EFPC RI was accomplished by selecting sampling methods and performing repetitive sampling events to accurately represent the characteristic population. Intervals for soil sampling were chosen based on historical site knowledge and geostatistical premises to obtain the strata with the highest concentration of contaminants in order to achieve the most conservative representation and to optimize the number of samples required, avoiding the wasted expense of non-detects. DQOs for completeness were set at 90% for laboratory completeness for both Phase 1a and Phase 1b. Percent completeness for field sampling was established at 90% for Phase 1a and at 70% for Phase 1b. To achieve comparability, the EFPC RI used one laboratory to perform its CLP analyses and applied the same sampling method.

Data uses were identified during the DQO process to include primary input into the site characterization study, the human health and ecological risk assessments, the initial screening of alternatives, and the FS. The DOE wanted to obtain the highest quality data possible. The data collection program was delineated in a sampling and analysis plan for each phase of the RI.

After completion of Phase 1a, it was obvious that the variability associated with the distribution of mercury combined with very high analytical costs associated with Level 4 data would become limiting factors. At this point, TSC-LV assistance was requested in optimizing an appropriate sampling strategy that would be sufficient to cover nearly 670 acres of floodplain soil. Concurrent with a sampling design, faster and less expensive techniques for rapid analysis of mercury were needed.

Phase 1b began with a search for the best analytical method for accurately determining mercury concentration. In 1991, CRD-LV technical staff, EPA Region 10 personnel, and Science Applications International Corporation (SAIC; a DOE contractor), tested field-portable XRF (FPXRF) equipment on-site at EFPC. Similar equipment had proven successful in detecting metals, including mercury at low concentrations, at some western U.S. sites. Seventeen soil samples from EFPC were analyzed by CRD-LV using laboratory-based XRF and cold vapor atomic absorption spectroscopy (CVAAS) to establish calibration standards for the FPXRF (Hillman, 1991). The field equipment was then tested under actual field conditions at EFPC. The results of these field tests indicated that there was great disagreement between FPXRF and CVAAS. It is speculated that the mesic (moist) conditions and other matrix effects associated with EFPC soil under field conditions caused interferences and resulted in rejection of XRF as a rapid analytical method for this site. Therefore, in Phase 1b, the DOE relied upon neutron activation analysis (NAA), a non-CLP method, for the large-scale soil analysis of the floodplain soil samples to determine the extent and distribution of contamination. DQOs for NAA were established to meet the precision and accuracy of CLP methods but with an exception for analytical sensitivity. The desired lower limit of detection for mercury in soils was 11 mg/Kg. This limit was specified based on previous remediation goals established by the State of Tennessee for mercury in EFPC soils. DOE demonstrated the equivalency of NAA to CLP methods and this approach was accepted by the regulators.

PHASE 1b: SAMPLING DESIGN OPTIMIZATION BY CONDITIONAL SIMULATION

The EFPC presented a complex sampling challenge to statisticians. The most desirable sampling plan would maximize the information obtained and minimize the number of samples taken. Sampling plan optimization was achieved using a geostatistical approach (kriging) and a novel application of Monte Carlo simulation call conditional simulation (Englund and Heravi, 1992).

Monte Carlo simulation is a statistical technique that imitates a real-world situation and uses repetitive iterations to solve complex problems that cannot be solved analytically. In the case of contaminant concentration data collected from different geographical locations at a site, a modified version, called conditional simulation, is used. Conditional sumulation is a method that generates realizations for a study from the available data and a "correlation structure model" that defines spatial dependency. A computerized site model is created by generating a dense grid of simulated sample points with contaminant values ("true points") that are consistent with the existing data. The study area is then divided into discrete blocks whose contaminant concentrations are estimated by the geostatistical method referred to as kriging. Kriging is a weighted moving average method used to interpolate values from a data set onto a contouring grid. The kriging weights are computed from a variogram, which measures the correlation among sample values as a function of the distance and direction between samples. "True" block means from the simulation are used for comparison to evaluate the effectiveness of a particular sampling scheme.

The site model described above is repeatedly sampled in a Monte Carlo fashion for each potential sampling scheme. In this case, the only difference between schemes was the number of samples. Each sampling iteration is used to compute block means by kriging. The block means computed from sampling are then compared against block estimates of the "true" points. The number of "detects" of blocks correctly identified as being above the action limit, the number of false negatives and positives, and the number of samples taken are recorded for each scenario. From these data, the cost of additional samples can be weighed against the resulting improvement in performance.

After considering the heterogeneity of contaminant concentrations within the soil medium as indicated by the results of the Phase 1a soil investigation, a sampling plan was developed that defined the extent and distribution of the primary contaminants throughout 670 acres of the EFPC floodplain. Historical data DOE (1994) was used as input to the conditional simulation software. These data include mercury analysis of 321 samples.

An overview of the sampling design employed by the CRD-LV is displayed in Figure 2. A semivariogram (model for spatial dependence) was computed from the historical data, and a conditional simulation was performed in which a representative map was constructed with tens of thousands of data points representing mercury values. This simulated data set represented the reality against which multiple sampling scenarios were tested. Sampling scenarios ranged from 100 to 4,096 samples randomly distributed throughout the reality study area. The sampling results were block-kriged and compared to block-kriging results for the simulated map.

A linear loss function provides a means of estimating the "point of diminishing returns", where the value of the improved decision performance obtained from additional sampling is no longer worth the additional sampling cost. The linear loss function had three cost components: (1) sampling cost, which is simply the cost per sample and is linear with the number of samples taken; (2) remediation cost, which is an estimated cost to clean up each contaminated block; and (3) linear cost, which is an estimate of the societal/environmental cost associated with neglecting to identify and remediate a contaminated block. From this curve, the number of samples yielding the minimum total cost is obtained. Figure 3 shows linear loss curves for various levels of mercury. Within the range of the action levels considered in the simulation program, the optimal number of samples appears to be independent of the action level. The optimal number of samples is 484 for the study area, which translates to about a 20-m grid size. Thus, the geostatistical methods employed assisted in determining sampling and data analysis optimization for the EFPC study.

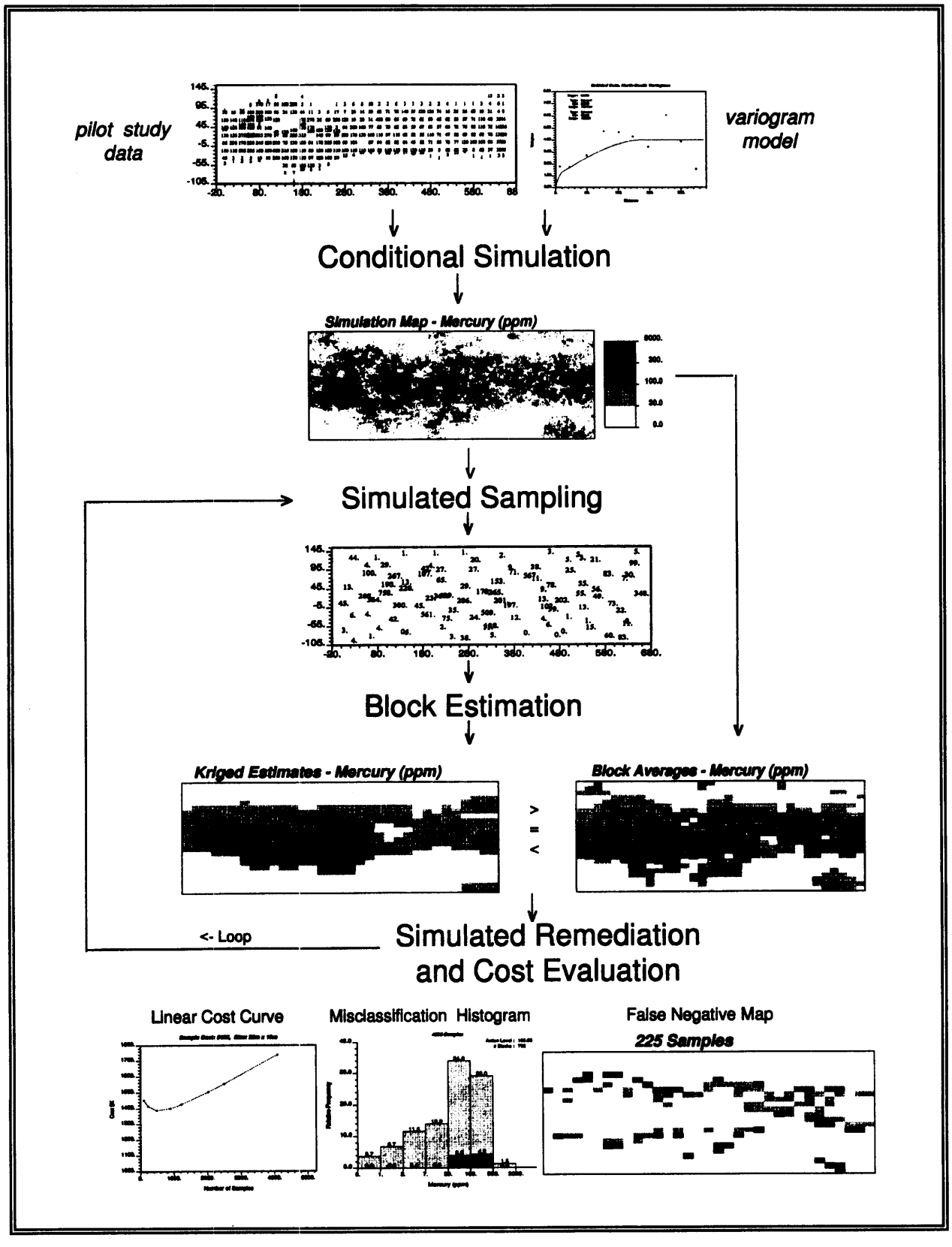

Figure 2. Sampling design optimization system overview.

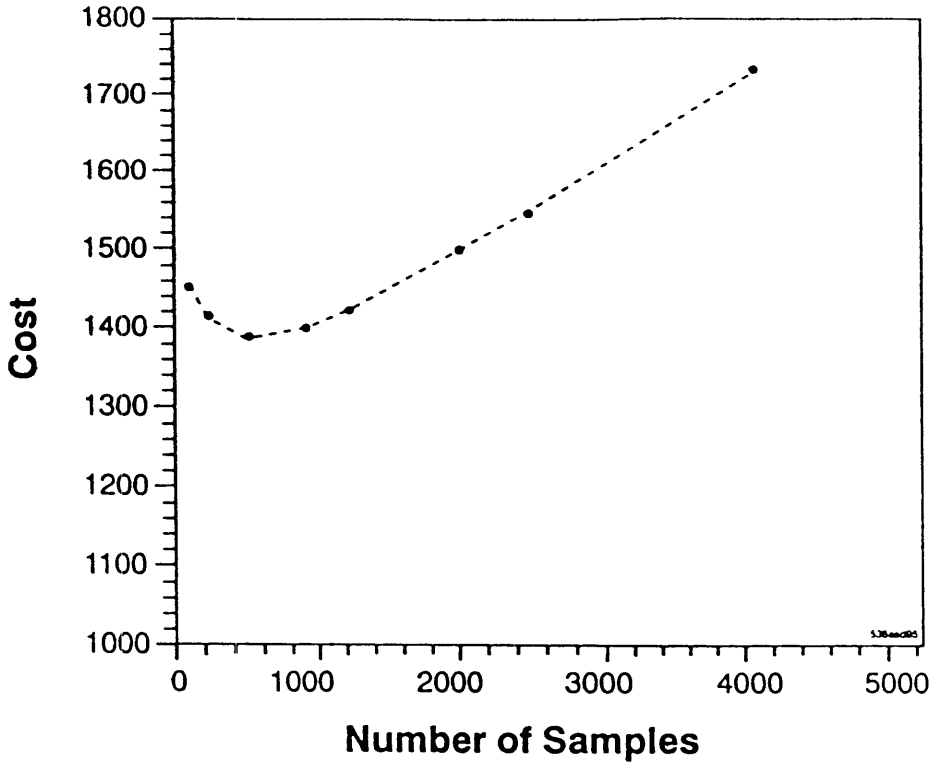

Figure 3. Linear loss curve for various levels of mercury.

One disadvantage of conditional simulation modeling is that it optimizes for a single round of sampling based on a given set of data. An underlying assumption is that the distribution and contaminant levels are consistent throughout the site and can be defined with a single sampling scenario derived from the model output. As it was not feasible to sample the entire area within the 100-year floodplain on a 20-m grid (65-ft), a compromise was agreed upon to devise a sampling plan based upon the results of the conditional simulation. The next step was to use a systematic sampling design where soil sampling transects were situated across the floodplain. The sample distance between points across the floodplain was 20 m (65 ft), and the transects were placed every 100 m (328 ft) along the length of the creek. A total of 159 transects were sampled over the length of the creek. Soil samples were obtained at the edge of the creek and every 20 m (65 ft) away from the creek until the elevation of the 100-year flood event was reached. Surface soil cores from 0 to 40.6 cm (0 to 16 in.) were collected at each station on the transects and each core was composited in a stainless steel bowl prior to the sample being placed in a 250-mL glass jar. At the even-numbered transects (i.e., every other transect), second- and third-layer samples were attempted (see figures 4-10 for the locations of transects and sampling locations). Due to the physical difficulties encountered in collecting samples from 40.6 to 81 cm (16 to 32 in.) and 81 to 122 cm (32 to 48 in.), the number of samples taken declined with depth. However, sufficient data were obtained to determine the vertical distribution of contaminants.

PHASE 1b: GEOSTATISTICAL EVALUATION

The EFPC RI employed the geostatistical method of kriging for spatial evaluation of contaminant concentrations. Geostatistics is a methodology used for the analysis of spatially correlated data. Its characteristic feature is the use of a semivariogram or related technique to quantify and model the spatial correlation structure. Kriging is then implemented using the selected mathematical function for the semivariogram as a weighted-moving average interpolator. Kriging produces estimates of contaminant concentration at a point or average concentration over a block. These estimates are linear functions of observed concentrations and have minimum estimation variance. This is often referred to as best linear unbiased estimator (BLUE).

The semivariogram modeling and kriging of the data was performed by the TSC-LV. A validated data set was supplied to TSC-LV from the NAA results of the Phase 1b soil transect samples. EFPC was subdivided into 11 sections to compensate for the sinuous nature of the creek and to permit processing subsets of about 3,000 samples. The summary statistics for total mercury concentration in the 11 sections (subregions) of the site are shown in Table 1.

The software package Geo-EAS, developed by CRD-LV, was used for semivariogram modeling and kriging of the data. This software package performs Ordinary kriging (OK). In OK, it is assumed that the concentration data have no spatial trends (e.g., an increasing or decreasing contaminant concentration trend over the site in question). The symmetry of data distribution is an implicit assumption. The data distribution was not normally distributed but was heavily skewed and, therefore, log transformation was used to obtain a symmetric distribution. The estimates of block averages, obtained by using log-normal OK, were then back-transformed to mercury concentrations. The back-transformation formula involves not only the block-averages of log-data, but also their kriging standard deviation. For this reason, the initial attempt at log-normal OK resulted in back-transformed block averages that were much higher than the observed maximum concentrations of mercury in areas farthest from the actual sample locations. The method of Rank-Order kriging, developed by Singh, et al. (1993) was then used. This method is a nonparametric statistical method and is accomplished by sorting the concentration data by their ordered rank from 1 to n. A variogram model is then fitted to the rank data, and OK is performed on the concentration data using the rank variogram model. The kriging variance is multiplied by a correction factor (equal to the variance of concentration data/variance of rank data). The variance of the concentration distribution is estimated from the raw concentration data.

Figures 4 through 10 display the average surface mercury concentrations for 7 of the 11 subregions in 20-m blocks overlain on the hand-drawn estimates of the distribution of mercury for 50 and 200 ppm levels (only surface concentrations were kriged). The class boundaries (i.e., cutoffs) for mercury are taken from the preliminary remediation goals (PRGs) which are based on risk to human health.

Based on a comparison of the kriged results to actual field measurements, the DOE decided not to rely solely on the kriging results to define the extent of contamination. Some results showed poor predictions, possibly due to the large area of "edge" associated with the sides of the creek. Background levels of inorganics in soils and sediments by Breckenridge and Crockett, 1995 provides a useful insight into the complexity of sites with widely varying contaminant concentrations. Kriging, however, was a valuable tool for interpolating contaminant concentration between data points, and the final results better reflected the actual data.

TABLE 1. SUMMARY STATISTICS FOR OBSERVED TOTAL MERCURY CONCENTRATIONS IN THE ELEVEN SUBREGIONS AT EFPC

Subregion	Number of samples (n)	Minimum (ppm)	Maximum (ppm)	Mean (ppm)	Standard deviation (ppm)
Subregion 1	135	1.4	216.0	18.6	37.9
Subregion 2	148	0.4	186.0	9.9	24.7
Subregion 3	148	0.9	99.0	4.5	11.3
Subregion 4	140	0.5	103.0	7.6	16.4
Subregion 5	148	0.6	10902.2	93.7	898.9
Subregion 6	148	0.8	180.0	15.3	34.1
Subregion 7	143	0.4	198.0	11.7	26.5
Subregion 8	239	0.4	1070.0	49.5	139.5
Subregion 9	148	0.5	387.0	37.0	68.3
Subregion 10	150	0.5	1320.0	51.7	153.0
Subregion 11	47	0.7	1170.0	43.1	180.0

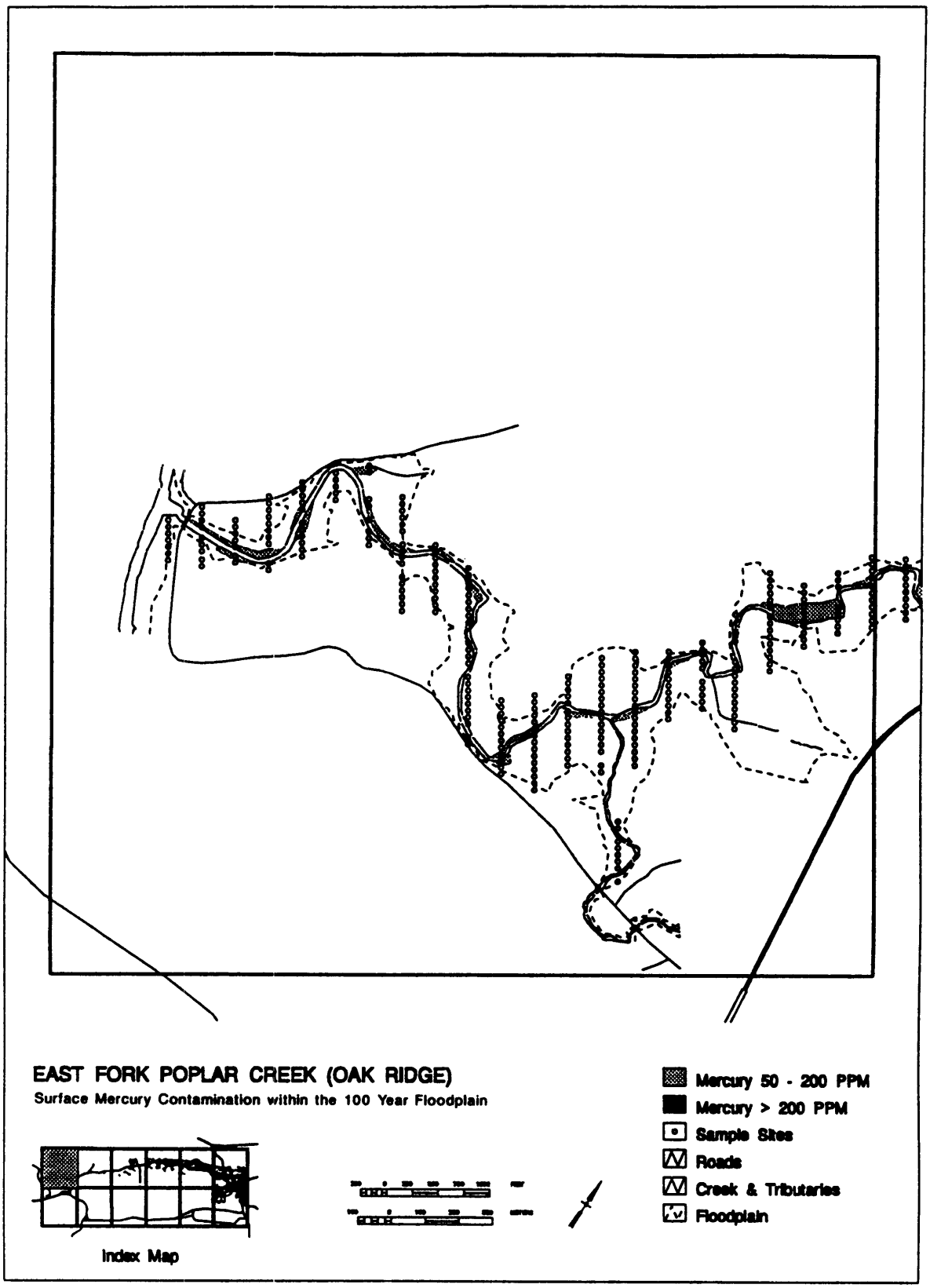

Figure 4. Subregion 1 sampling surface at East Fork Poplar Creek (as shaded in index map).

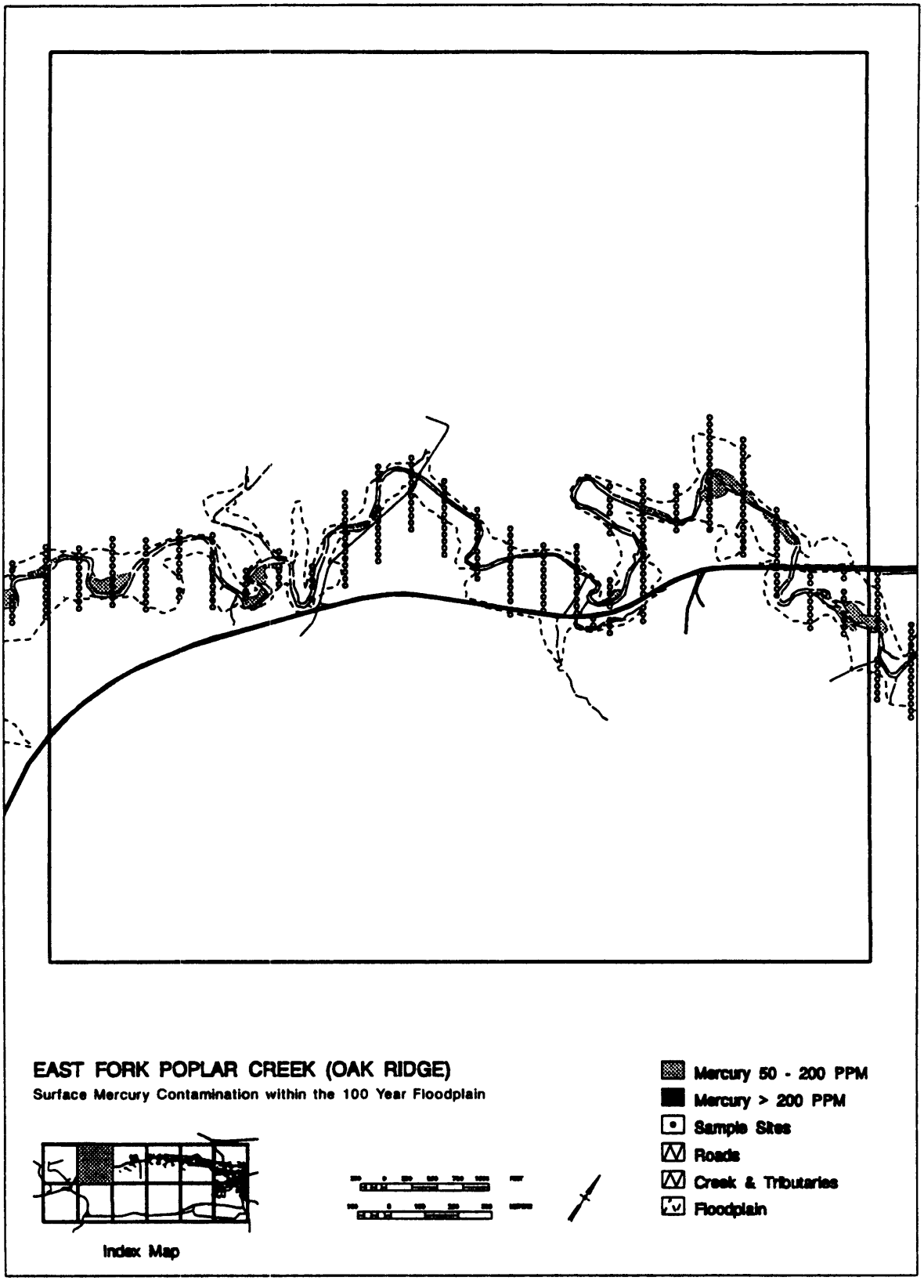

Figure 5. Subregion 2 sampling surface at East Fork Poplar Creek (as shaded in index map).

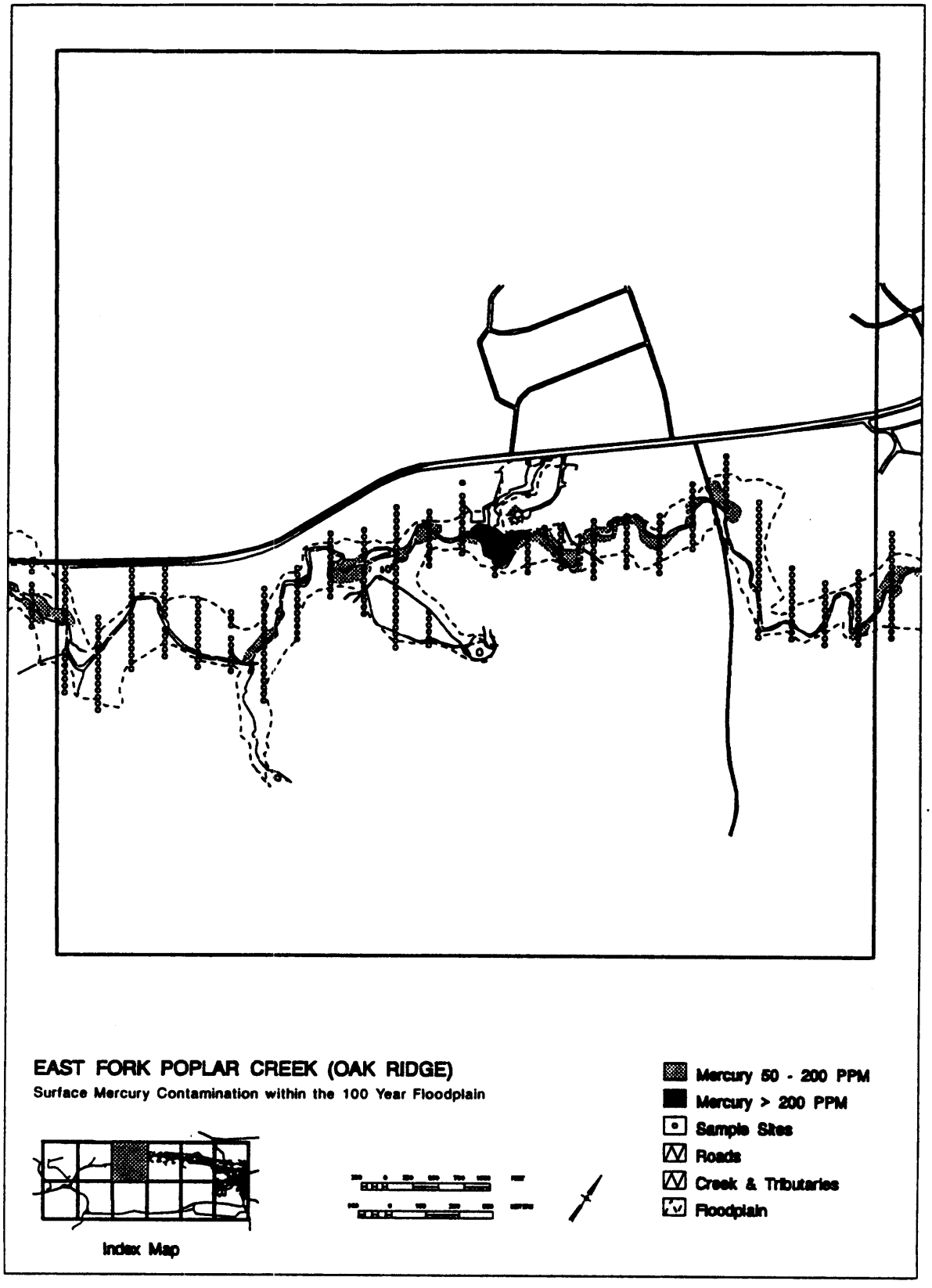

Figure 6. Subregion 3 sampling surface at East Fork Poplar Creek (as shaded in index map).

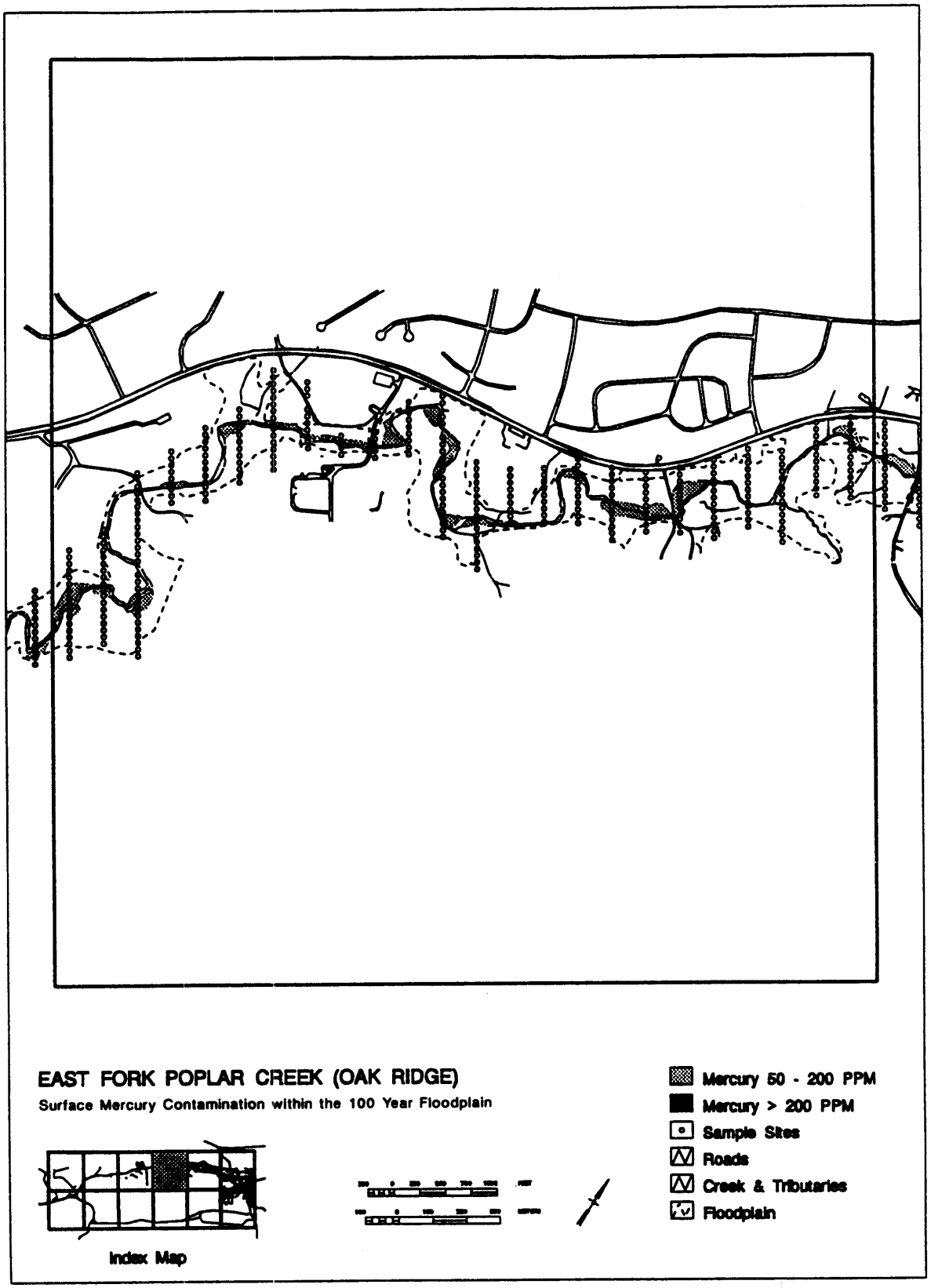

Figure 7. Subregion 4 sampling surface at East Fork Poplar Creek (as shaded in index map).

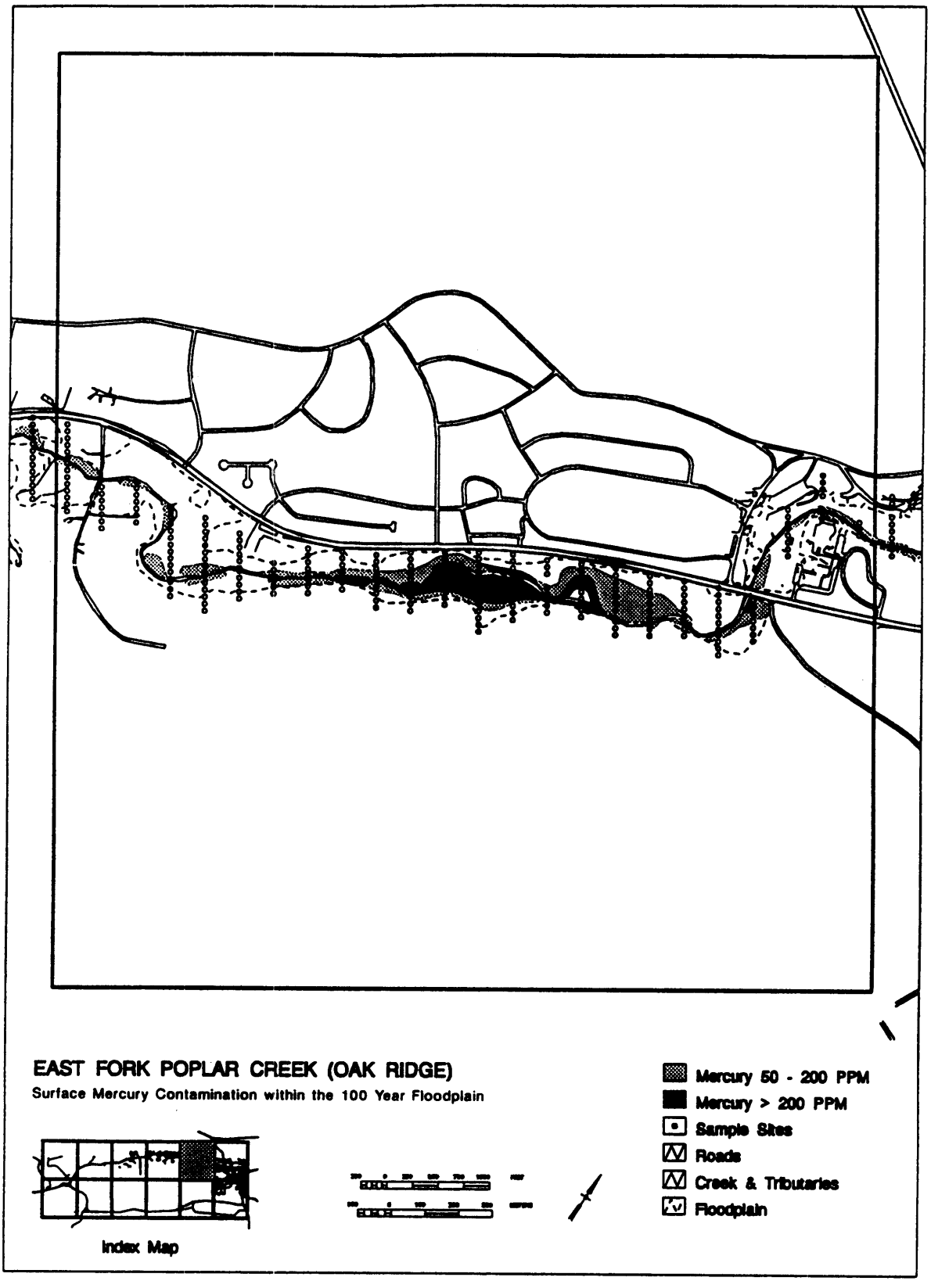

Figure 8. Subregion 5 sampling surface at East Fork Poplar Creek (as shaded in index map).

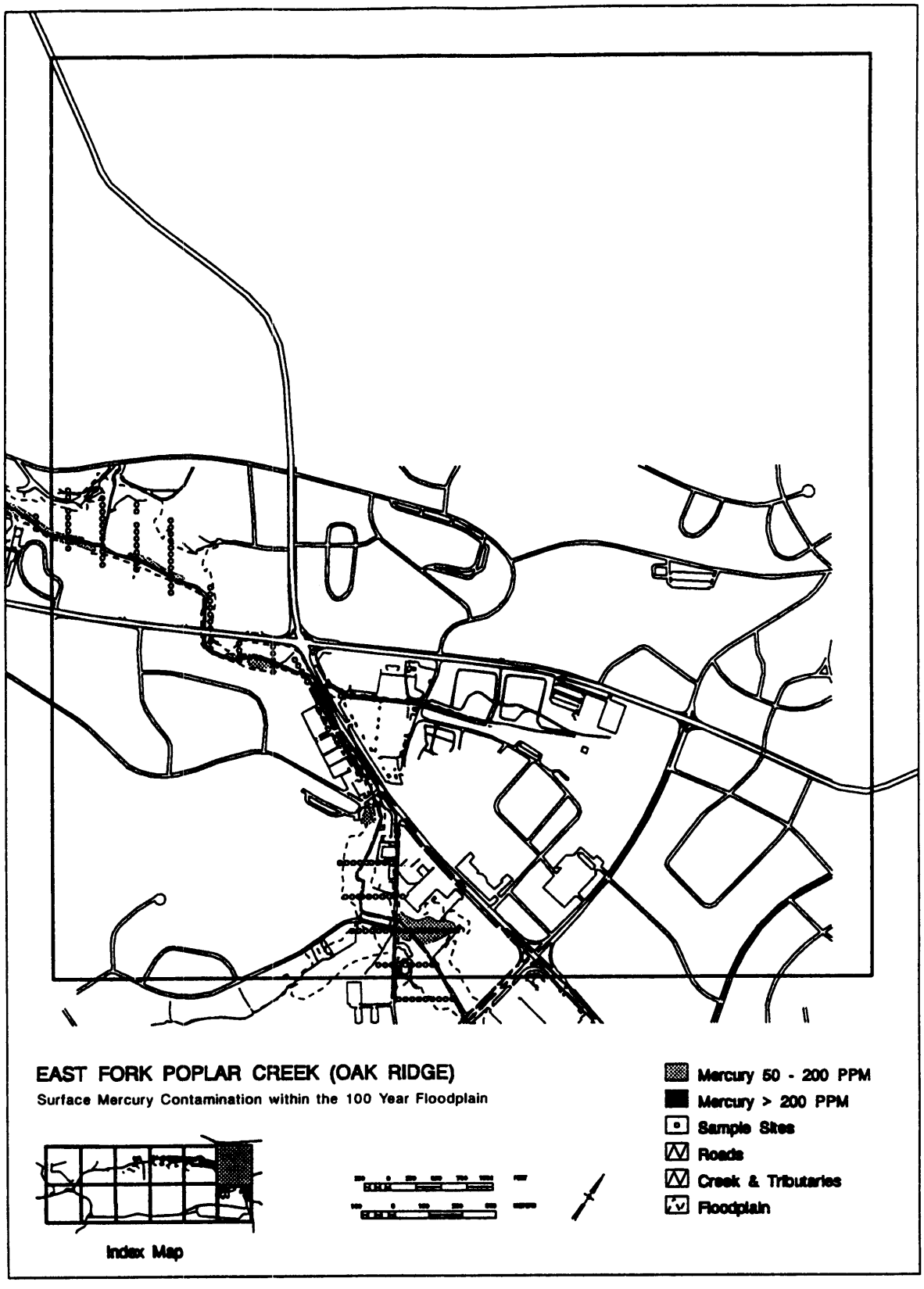

Figure 9. Subregion 6 sampling surface at East Fork Poplar Creek (as shaded in index map).

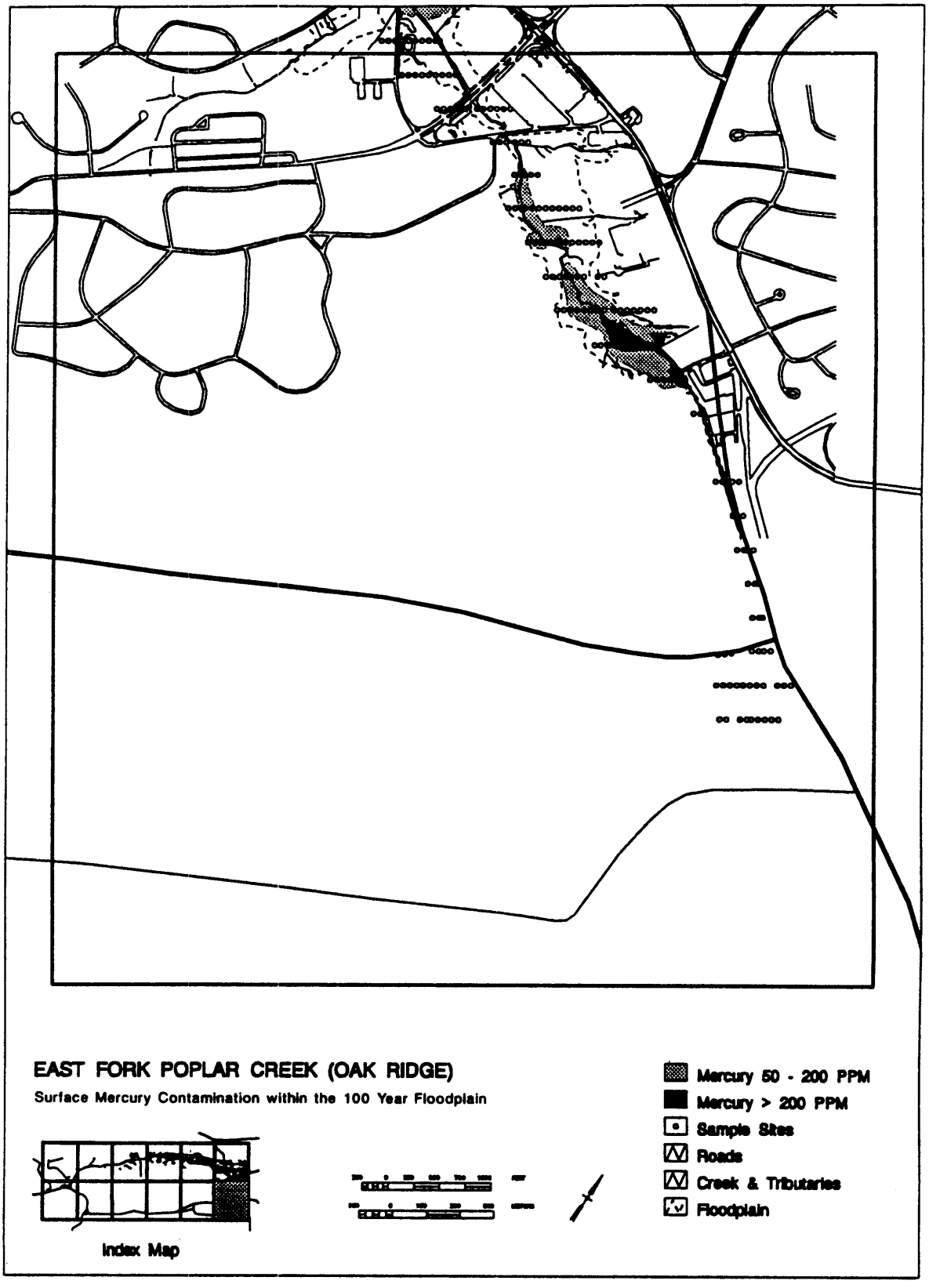

Figure 10. Subregion 7 sampling surface at East Fork Poplar Creek (as shaded in index map).

MERCURY SPECIATION TECHNOLOGY

The relative toxicity of the different species of mercury makes speciation methods necessary and, in the long run, cost effective. Thoughtful and safe remediation efforts can be based on the results of speciation methods. When mercury is present, it is important to know if it is present in the highly toxic, and bioavailable, organic form or in the most stable, and least bioavailable form, mercury sulfide. Mercury speciation technology, based on sequential selective extraction, is the process whereby the various forms, or species, of mercury are separated so that individual quantitative results may be obtained. There are currently at least three sequential extraction methods used for mercury speciation (Revis et al., 1989; Sakamoto et al., 1992; Miller et al., 1994). One extraction method, which is under development by CRD-LV scientists, was tested in response to the analytical requirements of the EFPC Site. The innovation of the CRD-LV method is twofold: it is able to separate more species individually, and it does not rely upon heating, which can drive off more than one species.

In 1994, 20 additional soil samples were taken from the EFPC site and sent to the CRD-LV for total mercury and mercury species analysis. Mercury species were sequentially removed, in order of increasing stability and decreasing toxicity, by exposing a soil sample to solvents of increasing acidity and oxidizing strength. The residue from each extraction step was separated by centrifugation and subjected to the next extraction step. Extracts were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) with confirmatory analyses by anodic stripping voltametry (ASV). Step 1 is extraction with toluene, which removes organo-mercury compounds such as methyl mercury. Step 2 is extraction of water-soluble compounds including mercuric chloride. Step 3 is extraction with dilute nitric acid, which removes compounds like mercuric oxide and mercuric sulfate. Step 4 is extraction with strong nitric acid, which removes mercury metal and amalgams. The final step is extraction in modified aqua regia, which removes the least soluble compound: mercuric sulfide. For a complete discussion of the method, see Miller, 1993. The method development and application followed the guidelines set forth in the quality assurance project plan (Ecker et al, 1994). Total mercury analyses were determined by summation of individual compounds and confirmed using CVAAS and ICP-MS. Complete extraction and separation of mercury compounds were confirmed through spike recoveries and the analysis of spent residues for residual mercury by XRF.

Samples were taken at two depth ranges: shallow (0-3 inches), and varying deeper depths (down to 32 inches) (Table 2). These samples (Table 3) were found to contain total mercury concentrations between 20 mg/Kg and 3000 mg/Kg. The deeper soil samples generally contained higher concentrations of mercury. In most of the shallow samples, the selective extraction indicated that 80 to 90 percent of the total mercury was present primarily as the metal or as an amalgam. In deeper samples, the CRD-LV method indicated that mercury was predominantly mercury metal and mercury sulfide in approximately equal proportions. Minor, but significant, amounts of acid-soluble mercury compounds (probably mercury oxide) were seen in most of the samples. In two of the samples, mercury oxide was the predominant form of mercury.

The analytical results indicate that three sample parameters are strongly correlated: sample depth, total mercury concentration, and the ratio of mercury sulfide to metallic mercury (tables 2 through 6). Specifically, these parameters tend to be correlated: deeper samples have greater mercury concentrations and higher ratios of mercury sulfide to mercury metal. The correlation

between greater depth and higher total mercury concentrations is particularly strong, with nine of the ten sample pairs containing ten times as much mercury at greater depth. At these depths there was no decrease in contamination. The extent of the contamination with increasing depth could not be definitely determined because mercury was detected in all samples. In the single apparently aberrant sample pair, ZE3770810 and ZE3770822, the shallower sample has a total mercury concentration approximately ten times that of the deeper sample. However, subsequent discussion with ORNL personnel indicated that this sample pair was taken at a point where the creek bank had eroded and the overhanging embankment had collapsed so that the original strata were reversed: the "deep" soil was at the surface and the original surface soil was buried. This could explain the reversal in the mercury measurement data. If this is the case, then all samples exhibited higher mercury levels with greater depth. Figure 11 shows the correlation between depth and total mercury concentrations as determined by ICP-MS. The depth ranges for Figure 11 are shown in Table 2, and the summed total ICP-MS data used in the figure are shown in Table 3.

Total mercury concentrations were determined by four methods and, for three samples, by five methods (Table 3). Methods included: strong-acid digestion followed by ICP-MS; acidic permanganate/persulfate digestion followed by CVAAS, EPA Method 7471 SW-846, summation of results from the ICP-MS analysis of the speciation extracts; summation of results of the ASV analysis of the speciation extracts; and summation for results for three samples by XRF analysis. The ASV technology only responds to dissolved species. The ICP-MS detects total mercury available in a sample, dissolved as well as suspended colloidal compounds. The agreement among method results is evidence that the extracts analyzed by ICP-MS only contained dissolved species. This is also evidence that centrifugation efficiently separated dissolved species from undissolved species. Concentrations of individual mercury species as determined by ICP-MS were in good agreement with the values obtained by ASV. Although a few discrepancies were noted, agreement was good among all the methods, indicating that the results for total mercury are accurate. It is believed that sampling error is a major contributor to most disparate results between duplicate samples. Details on the analytical results from the study can be found in Dobb et al., 1994.

With a few exceptions, the results of quality control (QC) sample analyses conformed to the requirements specified in the quality assurance project plan (QAPP) associated with the task. The only exceptions occurred in the replicate precision where two questionable values were generated by ICP-MS. The two extracts in question were reanalyzed by ASV and the results, which indicated that there was no precision problem, were confirmed. Overall, method precision was near 10 to 15 percent relative standard deviation (RSD). Speciated matrix spike and laboratory control sample (LCS) results indicated a satisfactory recovery of all mercury species from both spiked samples and the spiked blank. Recoveries of 102 to 112 percent were typical. Preparation blanks demonstrated a satisfactory freedom from positive interferences for all mercury species. All QC samples for total mercury determinations were satisfactory.

TABLE 2. MOISTURE CONTENT, DEPTH, AND DESCRIPTION OF SOIL SAMPLES FROM EAST FORK POPLAR CREEK.

Soil Sample Number	Moisture Content, Percent (%)	Depth (inches)	Description
ZE3181013 ZE3181025	25.9 22.0	0-3 16-32	Dark Brown, Medium Texture, Artifacts (roots) Reddish Brown, Fine Texture (clay)
ZE3740918 ZE3740920	23.4 26.8	0-3 8-12	Dark Brown, Medium Texture, Artifacts (roots) Dark Brown, Medium Texture
ZE3770810 ZE3770822	20.9 21.4	0-3 10-16	Dark Brown, Medium Texture, Artifacts (roots) Light Brown, Medium Texture
ZE5150717 ZE5150729	23.4 30.8	0-3 5-8	Dark Brown, Medium Texture, Artifacts (roots) Dark Clay, Medium Texture
ZE5340619 ZE5340621	26.0 28.9	0-3 10-16	Dark Brown, Medium Texture Dark Brownish-Gray, Medium Texture
ZE5380512 ZE5380524	22.3 42.4	0-3 10-14	Brown, Fine Texture (clay) Dark Gray, Medium Texture (clay)
ZE5470412 ZE5470424	27.1 35.1	0-3 10-20	Dark Brown, Medium Texture Dark Gray, Medium Texture, Artifacts (roots)
ZN3210115 ZN3210127	26.7 33.0	0-3 13-19	Grayish-Brown, Medium Texture, Artifacts (roots) Brownish-gray, Medium Texture
ZN3340211 ZN3340223	24.4 35.6	0-3 5-16	Grayish-Brown, Medium Texture Brownish-Gray, Medium Texture
ZN3340312 ZN3340324	30.0 45.8	0-3 3-9	Grayish-Brown, Medium Texture Dark Gray, Medium Texture, Artifacts (roots)

TABLE 3. COMPARISION OF TOTAL MERCURY IN DRIED, PULVERIZED EAST FORK POPLAR CREEK SOIL SAMPLES.

	Total Mercury (mg/Kg)				
Soil Sample	ASV Summed Total	ICP-MS Summed Total	ICP-MS Measured	CVAAS Measured	XRF Measured
ZE3181013	35.0	34.0	27.8	29.2	
ZE3181025	483.0	476.0	442.0	376.0	
ZE3740918	102.0	82.9	64.7	56.2	
ZE3740920	782.0	812.0	339.0	589.0	
ZE3770810	528.0	581.0	281.0	454.0	
ZE3770822	114.0	26.9	23.8	21.4	
ZE5150717	237.0	243.0	217.0	183.0	
ZE5150729	895.0	1,000.0	(a)	804.0	864(b)
ZE5340619	192.0	189.0	157.0	129.0	
ZE5340621	1,310.0	1,670.0	1,670.0	1,360.0	
ZE5380512	70.0	69.2	73.5	64.8	
ZE5380524	1,730.0	1,960.0	2,090.0	1,830.0	
ZE5470412	99.0	75.5	96.4	85.6	
ZE5470424	1,100.0	1,230.0	1,060.0	1,190.0	
ZN3210115	247.0	326.0	294.0	258.0	
ZN3210127	2,250.0	3,140.0	3,300.0	2,850.0	2,830
ZN3340211	224.0	350.0	301.0	281.0	
ZN3340223	1,860.0	2,050.0	2,130.0	2,020.0	
ZN3340312	201.0	305.0	247.0	226.0	
ZN3340324	1,810.0	2,420.0	2,630.0	2,060.0	2,360

(a) During microwave digestion, this sample generated gases causing the container pressure-relief valve to vent, resulting in loss of sample. Repeated digestion attempts were also unsuccessful.

(b) Values are extrapolated beyond the XRF calibration curve high standard.

TABLE 4. DISTRIBUTION OF MERCURY SPECIES IN EAST FORK POPLAR CREEK SOIL SAMPLES.

Species Distribution, as Percentages of the Total Summed Mercury					
Soil Sample	Organic	Water-Soluble	Acid-Soluble	Metallic	Sulfide
ZE3181013	<0.1	0.1	71	21	7.7
ZE3181025	<0.1	1.0	25	36	38
ZE3740918	<0.1	0.1	49	26	26
ZE3740920	<0.1	0.3	13	66	20
ZE3770810	<0.1	<0.1	11	81	7.6
ZE3770822	<0.1	0.4	19	76	5.4
ZE5150717	<0.1	0.1	11	83	5.8
ZE5150729	<0.1	0.1	11	56	33
ZE5340619	<0.1	0.2	3.9	90	6.2
ZE5340621	<0.1	<0.1	0.7	57	42
ZE5380512	<0.1	0.1	1.1	91	7.6
ZE5380524	<0.1	<0.1	3.2	32	65
ZE5470412	<0.1	<0.1	2.8	88	8.9
ZE5470424	<0.1	0.1	14	49	37
ZN3210115	<0.1	0.1	19	74	7.2
ZN3210127	<0.1	0.3	7.1	35	57
ZN3340211	<0.1	<0.1	<0.1	92	8.4
ZN3340223	<0.1	<0.1	5.8	25	69
ZN3340312	<0.1	<0.1	<0.1	94	6.5
ZN3340324	<0.1	<0.1	6.2	36	57

TABLE 5. MERCURY CONCENTRATION FOR EACH SPECIES IN AS-RECEIVED EAST FORK POPLAR CREEK SOIL SAMPLES.

Species Concentration (mg/Kg Mercury)					
Soil Sample	Organic	Water-Soluble	Acid-Soluble	Metallic	Sulfide
ZE3181013	<0.003	0.019	18.0	5.26	1.95
ZE3181025	<0.003	3.88	93.6	135	140
ZE3740918	0.005	0.059	30.9	16.3	16.2
ZE3740920	0.004	1.85	79.8	395	118
ZE3770810	<0.003	0.028	51.9	373	35.0
ZE3770822	<0.003	0.094	3.92	16.0	1.13
ZE5150717	0.008	0.221	20.1	155	10.9
ZE5150729	0.004	0.347	77.5	386	23.0
ZE5340619	0.006	0.264	5.48	126	8.66
ZE5340621	<0.003	0.146	8.60	675	501
ZE5380512	0.002	0.041	0.611	49.0	4.07
ZE5380524	<0.001	0.123	36.5	357	737
ZE5470412	<0.002	0.016	1.52	48.6	4.91
ZE5470424	<0.001	0.520	111	390	295
ZN3210115	<0.002	0.166	45.7	176	17.2
ZN3210127	<0.001	6.90	145	717	1,170
ZN3340211	<0.002	0.058	0.039	242	22.2
ZN3340223	<0.001	0.077	76.0	327	914
ZN3340312	<0.001	0.038	0.045	200	13.8
ZN3340324	<0.001	0.163	81.3	477	753

TABLE 6. MERCURY CONCENTRATION FOR EACH SPECIES IN PREPARED EAST FORK POPLAR CREEK SOIL SAMPLES.

	Species Concentration (mg/Kg Mercury)				
Soil Sample	Organic	Water-Soluble	Acid-Soluble	Metallic	Sulfide
ZE31810	<0.004	0.025	24.3(a)	7.10(a)	2.63(a)
ZE31810	<0.004	4.98	120.0	173.0	179.0
ZE37409	0.007	0.077	40.3	21.3	21.2
ZE37409	0.005	2.52	109.0	540.0	161.0
ZE37708	<0.004	0.036	65.6	471.0	44.3
ZE37708	<0.004	0.119	4.99	20.3	1.44
ZE51507	0.011	0.289	26.3	202.0	14.2
ZE51507	0.006	0.502	112.0	558.0	332.0
ZE53406	0.008	0.357	7.40	170.0	11.7
ZE53406	<0.004	0.205	12.1	950.0	705.0
ZE53805	0.003	0.053	0.787	63.1	5.24
ZE53805	<0.002	0.214	63.4	619.0	1,280.0
ZE54704	<0.002	0.022	2.08	66.7	6.73
ZE54704	<0.002	0.802	171.0	601.0	454.0
ZN32101	<0.002	0.227	62.3	240.0	23.4
ZN32101	<0.002	10.3	216.0	1,070.0	1,740.0
ZN33402	<0.002	0.077	0.051	320.0	29.4
ZN33402	<0.002	0.120	118.0	507.0	1,420.0
ZN33403	<0.002	0.054	0.065	285.0	19.7
ZN33403	<0.002	0.300	150.0	880.0	1,390.0

(a) This number is the mean of three values.

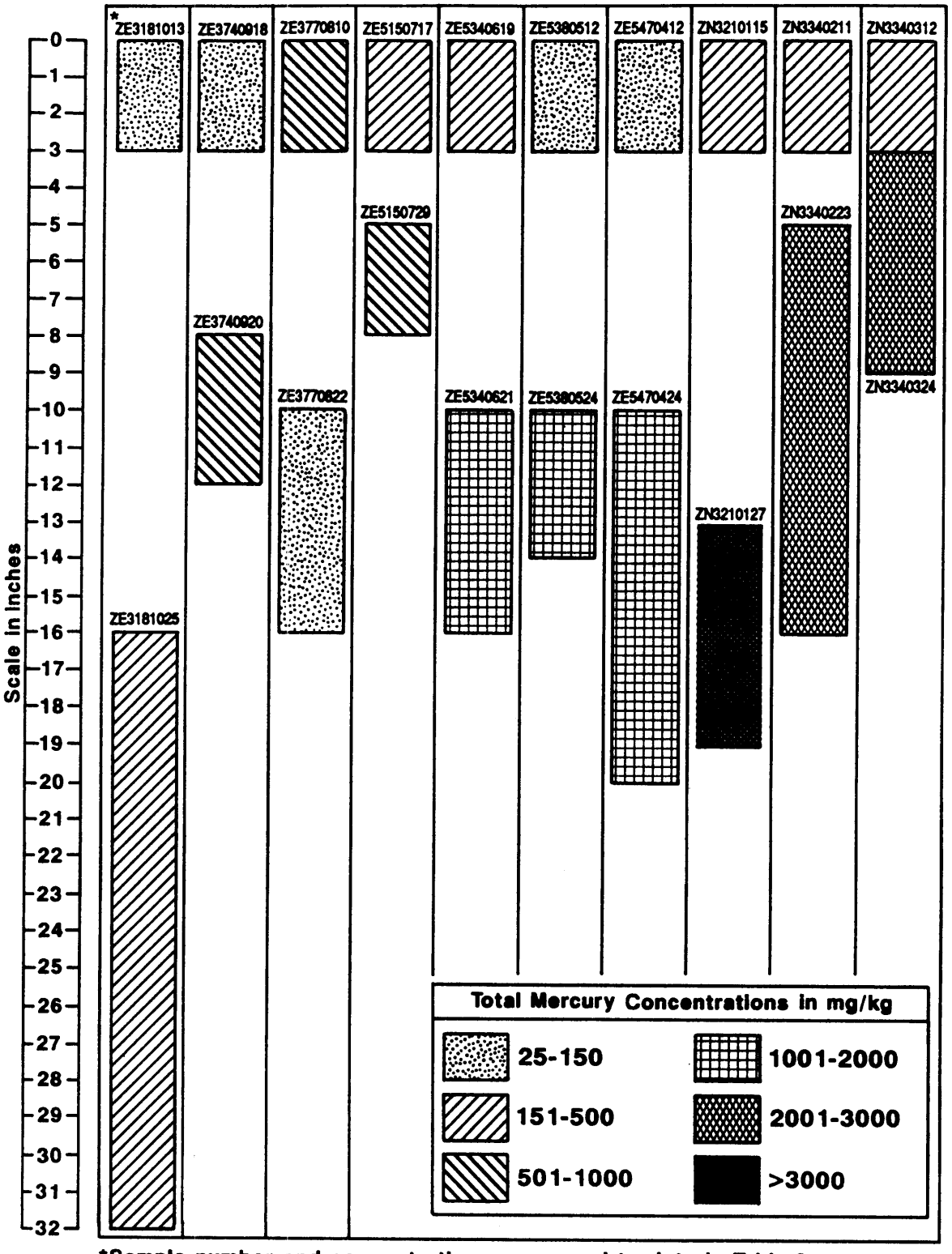

Figure 11. Distribution of total mercury concentrations (as determined by ICP-MS) with depth.

CONCLUSIONS AND RECOMMENDATIONS

The major aspects of these technology applications are noted below:

XRF can be used as a confirmatory device. However, in 1991, at the time of the ORNL field-samples analysis, FPXRF was not a viable method for analyzing EFPC soils in the field for mercury. Caution should be used when applying FPXRF to the analysis of metals in moist soils.

Conditional simulation was demonstrated to be a valuable method that optimized sampling efforts and saved time and costs while maintaining the integrity of the data. The successful use of conditional simulation at the EFPC site illustrates the pertinence of the Technology Support Center as liaison between research and practical field applications.

The use of kriging at the EFPC site is an example of a geostatistical process applied to characterizing contaminants at a hazardous waste site. The use of semivariograms, Ordinary and Rank-Order kriging, and other geostatistical methods is being applied by environmental scientists. The results of the work at the EFPC site are further proof of the validity and strength of these techniques. The use of geostatistics at the EFPC was integrated with the conceptual model of contaminant distribution, and all factors were considered in the final interpretation. A combination of geostatistics and professional judgment was employed to provide the final analysis.

The CRD-LV mercury speciation method gave good results and was successfully applied to the EFPC matrix. The deeper samples from the EFPC site had greater mercury concentrations. Almost universally, ratios of mercury sulfide to mercury metal were in approximately equal proportions. In most of the shallow samples, the selective extraction indicated that 80 to 90 percent of the total mercury present was predominately mercury metal or an amalgam.

The CRD-LV method gives reliable information about mercury concentrations, and the strength of the speciation technology was validated by the results from the EFPC study. This method provides a new way to determine and quantify mercury species which can be verified through total mercury concentrations tests.

Knowledge of mercury metal speciation not only provides a more realistic assessment of risk but also assists environmental decision-makers in determining the most appropriate remediation technologies. For example, when mercury oxide or mercury sulfate are present, remediation by volatilization can be a problem. After volatilization at temperatures sufficient to remove most other mercury species, significant amounts of the bioavailable and highly toxic mercury oxide or mercury sulfate can remain. The higher temperatures needed to remove mercury oxide and mercury sulfate will present practical problems.

This mercury speciation method is particularly valuable because the species are sequentially released in order of decreasing toxicity by solvents of increasing harshness. Therefore, levels of toxicity can be identified allowing scientists to better ascertain the degree of contamination. The method is relatively fast and simple allowing delivery of a preliminary site assessment in a shorter period of time.

The EPA and DOE worked in tandem on this project and, together, were successful in bringing the best in research, data analysis, sampling design, and risk assessment to meet the needs of the EFPC site. This would be an important site for future study where mercury speciation could be implemented to help decision-makers determine the type or extent of remediation needed at the site. This interdepartmental cooperation is the key to future work. The DOE facilities pose special challenges to technical personnel - challenges that often can be met by a combined task force.

The Technology Support Center is an integral part of the research laboratory network, providing a format for testing, demonstrating, evaluating, and establishing innovative technologies. The TSC can serve the Regions and the researchers by bringing together the problems of one with the solutions of the other. The application of research projects to site characterization serves two purposes: the in situ validation of an innovative technology and the opportunity to refine that technology to meet the rigorous conditions of field analytical procedures.

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