SPATIAL STATISTICS, COMPOSITE SAMPLING, AND RELATED ISSUES
IN SITE CHARACTERIZATION WITH TWO EXAMPLES

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ABSTRACT

Data from two Superfund sites, the Dallas Lead Site and the Palmerton Site, were examined in order to assess what sources of variability were present in the data and how sampling at other sites of similar character should be designed. The results of the analysis indicate that the spatial variability in the accumulated heavy metal deposition at each site appears to be dominated by variability on the scale of the sampled region, by local industrial contamination at the Dallas Lead Site, and by variability of nearby soil volumes. Sampling of sites with these variability sources should probably be designed to capture the large-scale trend, to identify the sources and extent of local contamination, and to reduce the large variability of nearby soil samples by composite sampling.

1. INTRODUCTION AND BACKGROUND

Superfund site-characterization requires that estimation of contaminants be statistically and substantively accurate and precise while maintaining cost-effectiveness of sampling and remediation. Costs are incurred to the society by exposure to hazardous wastes and by expensive assessment and cleanup at hazardous waste sites. The purpose of this study was to retrospectively examine data from two Superfund sites, the Dallas Lead Site and the Palmerton Site, in order to examine what components of variability were present in the data and to explore sampling schemes efficient in producing data for accurate prediction of contaminants if sites with similar variability are sampled in the future.

We approximate large-scale trend in the chemical concentration data by fitting a bicubic spline function (Hayes and Halliday, 1974) and we judge the presence or absence of a small-scale stochastic process contributing to data variation by the presence or absence of autocorrelation in the spline fit residuals. By choosing the number of knot points to be less than the number of data points, the bicubic spline fit smooths, rather than interpolates, the data. Decomposing spatial variability into a large-scale trend and a small-scale stochastic process can be problematical if the trend model and the covariance structure of the stochastic process are indeterminate (Armstrong, 1984). A common approach to approximating the trend is to fit polynomials in
local data neighborhoods. It would seem that as the data neighborhood size decreases, the polynomial fit to these data might increasingly tend to fit variation contributed by a small-scale stochastic process. Therefore, an appeal of approximating the trend by noninterpolative bicubic splines is that the fit is made in one operation to all the data, and small-scale variation might not be fit if there is a high degree of smoothing. Subsequent to the data decomposition, a crossvalidation study was performed in order to examine how a response surface predicted by kriging might differ if the actual sampling had been less intense.

1.1 The Two Sites

Data from the Dallas Lead Site and the Palmerton Site were chosen for this exploratory analysis because of common features of these sites and prior investigations: the similarity in the contamination processes, to the sampling schemes, and to the extensiveness of prior statistical analyses. The processes sampled at both sites were of heavy metal accumulation from the fallout of air-borne particles emitted from point sources. The sampling schemes were designed to provide information about the data autocorrelation structure so as to enable response surface prediction via kriging, composite sampling was utilized at both sites, and special samples were taken to estimate variability due to certain sources.

1.1.1 The Dallas Lead Site. The Dallas Lead Site, located in Dallas, Texas, consisted of three areas sampled during 1982, with subsequent assays of the soil lead content. These areas were in the vicinities of the Dixie Metal Company smelter (DMC area) and of the RSR Corporation smelter (RSR area), and in a region thought to be relatively uncontaminated from smelter lead fallout (reference area). The areas were sampled in a grid design, with grid squares measuring 228.6 m (750 ft) on a side. This intersample distance was selected to be approximately 2/3 of the range of autocorrelation estimated from prior monitoring. Four individual soil cores, each 2 cm in diameter and 7.5 cm in depth, were collected from the major compass points of the perimeter of a 10 m diameter circle and composited. After the soil samples were bulked, dried, sieved, and mixed, the soil lead content was measured on a 5 g aliquot of the approximately 180 g sample. At some locations, duplicate samples were taken to assess the variation of nearby composite samples. In addition, aliquots from three equal portions of some samples were assayed in order to assess subsampling and measurement error (Brown and Black, 1983; Brown et al., 1985).

1.1.2 The Palmerton Site. The Palmerton Site is centered around two zinc smelters located near the town of Palmerton, Pennsylvania, in the eastern part of the state. The first zinc smelter, which later became known as the West Plant, began operation in 1898. The town of Palmerton developed to the east of this smelter. Beginning in 1913, a second smelter, which became known as the East Plant, began operation at a
location just east of Palmerton. Heavy metal-containing dust was emitted from stacks, with the peak emissions probably occurring between 1949, when a process called sintering began, and 1954 when emission controls were installed. In 1980, the West Plant was shut down and primary zinc smelting at the East Plant was modified to secondary refining. Additional pollution control devices installed during 1967-1980 have reduced heavy metal emissions to levels within National Ambient Air Quality Standards. The contaminants of concern have been the heavy metals cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn). Heavy metals in the soil, groundwater, and surface water caused the site to be placed on EPA's National Priorities List.

A Remedial Investigation was begun on off-plant property by Gulf and Western, the former plant owner. This off-plant area consisted of approximately 50 square miles of land which was thought to have been contaminated over the years. As part of this remedial investigation, soil sampling was undertaken to assess the extent and severity of heavy metal contamination in the Palmerton area soils (R. E. Wright Associates, 1988).

The Palmerton Site was sampled in two phases during 1985-1986. Soil samples were assayed for Cd, Cu, Pb, and Zn concentrations, though measurements of Cu concentrations were not made on second phase samples since first phase Cu levels were thought to be acceptably low. The initial phase sampling design incorporated features of both grid and transect designs. The grid, covering a large portion of the Palmerton residential area between the two smelters, was designed to capture the data autocorrelation structure, using a 366 m (1200 ft) range of autocorrelation extrapolated from an analysis of Dallas Lead Site. A grid spacing of 122 m (400 ft), or 1/3 of the anticipated autocorrelation range, was selected. The transect pattern was design to delineate the overall trend in heavy metal concentrations, while the second phase sample locations were located to fill in gaps noted from first phase data (Figure 1). The lengths of transects were calculated from process model predictions of heavy metal accumulation. Gaussian dispersion models, based upon historical wind data and topography predicted that the majority of the deposition was expected on the valley floor, oriented in the southwest to northeast direction. Large deposition was also expected from air passing over Blue Mountain and through the Lehigh River gap in the mountain, to the south of the smelters. Differences in the spatial pattern of the different heavy metals was anticipated, as most of the Pb were thought to have been emitted from the West Plant, while most of the Cd and Zn emissions and all of the Cu emissions were thought to have been emitted from the East Plant. Except near the grid, the spacing of sample locations on the transects was either 345 m or 366 m (Starks et al., 1986, 1987; R. E. Wright Associates, 1988).

Soil sampling at the Palmerton Site was performed by compositing four individual soil cores in the first sampling phase and nine individual soil cores in the second sampling phase. In the first sampling phase, individual soil cores taken at each of the major compass points on a 6 m diameter circle were composited. In the second sampling
phase, individual cores from the four major compass points on a 6 m
diameter circle, from the four minor compass points on an inner 4.25 m
diameter circle and from the joint center point of both circles were
composed. Each soil core was 1.9 cm in diameter and 15 cm in depth.
After the soil samples were bulked, dried, sieved, and mixed, heavy metal
concentrations (ppm) were measured on 5 g aliquots (Starks et al., 1986;
Brown et al., 1989).

Soil samples were also taken in order to allow estimation of certain
variance components. Individual soil samples were not composited at ten
first phase locations so as to measure their variation and the variance
reduction from compositing. Duplicate composite samples were taken 0.5 m
apart for assessing the variation of nearby composite samples. Some
composite samples were split, for duplicate chemical analyses, so as to
estimate variation induced by subsampling and measurement (Starks et al.,
1986). The magnitude of the duplicate sample variability relative to
measurement error lead to the decision to increase the composite sample
size in the second sampling phase from that used in the first sampling
phase (Starks et al., 1987).

Geostatistical analyses of the Palmerton Site data were previously
reported. No autocorrelation was judged to exist in the data of each samplir
phase after removal of trend fit by second-order polynomials in moving
neighborhoods. Kriging predictions were made using pure nugget
autocorrelation models (Starks et al, 1987; Brown et al., 1989).

1.2 The Sampling Model

The following model (Cressie, 1988) appears to have been implicitly
assumed in designing the Dallas Lead Site and the Palmerton Site sampling
schemes.

\[ Z(x) = \mu(x) + \xi(x) + \delta(x) + \nu, \]  

where \( Z(x) \) is the process of measured contaminant concentration at
location \( x \), \( \mu(x) \) is a large-scale deterministic trend, \( \xi(x) \) is a
small-scale stochastic process with \( \text{Var}(\xi) = \sigma_\xi^2 \Xi \), \( \delta(x) \) is a micro-scale
stochastic process with \( \text{Var}(\delta) = \sigma_\delta^2 \Delta \), and \( \nu \) represents measurement
errors which are independent with \( \text{Var}(\nu) = \sigma_\nu^2 \). \( \Xi \) and \( \Delta \) are correlation
matrices.

The small-scale stochastic process is regarded as occurring on a spatial
scale larger than the minimum inter-sample distance (or at least the
smallest distance for which there is sufficient information), but much
smaller than the entire region. The micro-scale stochastic process is
regarded as occurring within the spatial scale of the minimum inter-sample
distance.
When the process, \( Z(x) \), is sampled, variability due to measurement is added. This can be due to errors in recording the exact sampling location or the soil volume extracted, inability to thoroughly mix the composite sample, or inexactness in laboratory procedures.

The model assumes stationarity at least within small data neighborhoods. Three levels of stationarity can be distinguished. Strong stationarity requires that the joint distribution of \( Z(x_1), Z(x_2), \ldots \)

\( Z(x_n) \) is equivalent to the distribution of \( Z(x_1+\vec{h}), Z(x_2+\vec{h}), \ldots, Z(x_n+\vec{h}) \)

for each vector \( \vec{h} \).

Second order stationarity requires that the means, \( E[Z(x)] \), and variances, \( \text{Var}(Z(x)) \), exist and do not depend upon \( x \), and also that the covariance between \( Z(x_1) \) and \( Z(x_2) \) exist and depend only upon the vector \( \vec{h} = x_2-x_1 \) joining \( x_1 \) and \( x_2 \). Under second order stationarity, the correlogram, \( \rho(\vec{h}) = \rho(\vec{h}) = \text{Corr}(Z(x_1), Z(x_1+\vec{h})) \) is related to the semivariogram, \( \gamma(\vec{h}) \) by

\[
2\gamma(\vec{h}) = E[|Z(x)-Z(x+\vec{h})|^2] = 2\sigma^2[1-\rho(\vec{h})].
\]

The process is (second order) isotropic when \( \rho(\vec{h}) \) is a unique function of the distance \( h = |x_2-x_1| \), in which case we write \( \rho(h) \) for the correlogram.

A third form of stationarity, weak stationarity, requires that the means exist and do not depend on the location \( x \), and that the semivariogram be a unique function of the vector \( \vec{h} \). Strong stationarity, together with the existence of the first two moments, implies second order stationarity, which in turn implies weak stationarity.

Usually, the correlogram becomes small for large \( h \) and the semivariogram levels off to the value \( \sigma^2 \), which is called the sill. A nugget effect detected by a positive intercept in the sample semivariogram, reflects the presence of micro-scale variation and/or measurement error.
1.3 Composite Sampling

Composite sampling becomes a useful technique for reducing the response surface prediction error when the support (i.e. area or volume) that is used for sampling differs from that used for prediction. For practical purposes, the sample support is usually much smaller than the prediction support. For example, the prediction support might be the size of a soil block removed in a single pass of a bulldozer (Englund, 1987). The soil sampled for contaminant assays is typically much smaller than such a soil block that might be remediated. Inference is desired on the spatial scale of the estimation support, while minimizing the effect of heterogeneity present on the scale of the sample support. Composite sampling can decrease the micro-scale variance and thus the overall response surface prediction variance (Starks, 1986). Composite sampling to minimize the effect of such micro-scale variability upon inferences targeted for a larger scale was applied to the Dallas Lead and Palmerton Sites (Brown and Black, 1983; Starks et al., 1987). The effectiveness of composite sampling in reducing micro-scale variation was also examined in this study.

2. METHODS

2.1 The Data Analysis

The data were first examined for inconsistencies. Then, some features of the data were examined through frequency distributions, contour plots, identification of outliers, plots of variance versus mean, sample semivariograms, and variance component estimates from individual, duplicate, and split sample data. Decomposition of the data into large-scale trend versus small-scale stochastic process was explored through fitting trend models via a bicubic spline algorithm of Dierckx (1981) and examining residual semivariograms.

The sample semivariogram was calculated by

\[
\gamma = \frac{1}{2n(h)} \sum_{i=1}^{n(h)} (Z(x_i) - Z(x_i+h))^2,
\]

(1)

where \(Z(x_i)\) is an observation at point \(x_i\), \(Z(x_i+h)\) is an observation a distance \(h\) away, and \(n(h)\) is the number of observations \(h\) units apart. Intervals of \(h\) were determined so that \(n(h)\) was at least 30, a minimum suggested by Journel and Huijbregts (1978).

2.2 The Spline Model

The data locations are in a closed rectangular domain

\[D = [a,b] \times [c,d].\]

Here, we consider locations as pairwise coordinates
(x, y). The spline function

\[ s(x, y) = \sum_{q=-k}^{h} \sum_{r=-\ell}^{h} c_{q, r} M_{q, k+1}(x) N_{r, \ell+1}(y) \]

where

\[ c_{q, r} \text{ are coefficients and } M_{q, k+1}(x) \text{ and } N_{r, \ell+1}(y) \]

are normalized B-splines, defined on the knots

\[ \lambda_{q}, \lambda_{q+1}, \ldots, \lambda_{q+k+1} (\lambda_{-k} = \ldots = \lambda_{-1} = a; \lambda_{g+2} = \ldots = \lambda_{g+k+1} = b), \]

and \[ \nu_{r}, \nu_{r+1}, \ldots, \nu_{r+\ell+1} (\nu_{-\ell} = \ldots = \nu_{-1} = c; \nu_{h+2} = \ldots = \nu_{h+\ell+1} = d). \]

On any subrectangle

\[ D_{i,j} = [\lambda_{i}, \lambda_{i+1}] \times [\nu_{j}, \nu_{j+1}], \quad i = 0, 1, \ldots, g, \quad j = 0, 1, \ldots, h, \]

\( s(x, y) \) is given by a polynomial of degree \( k \) in \( x \) and \( \ell \) in \( y \).

All derivatives

\[ \frac{\partial^{i+j} s(x, y)}{\partial x^{i} \partial y^{j}} \text{ for } 0 \leq i \leq k-1 \text{ and } 0 \leq j \leq \ell-1 \]

are continuous in \( D \). The bicubic splines have the property that

\[ M_{q, k+1}(x) = 0 \text{ if } x \leq \lambda_{q} \text{ or } x \geq \lambda_{q+k+1} \]

\[ N_{r, \ell+1}(y) = 0 \text{ if } y \leq \nu_{r} \text{ or } y \geq \nu_{r+\ell+1} \]

For data values \( z_{r} \) at points \((x_{r}, y_{r})\), \( r = 1, 2, \ldots, m \) and with positive weights \( w_{r} \), the spline function is fit so that

a measure of the goodness of fit,

\[ \mathcal{E} = \sum_{r=1}^{m} w_{r} \left[ z_{r} - s(x_{r}, y_{r}) \right]^{2}, \]

and a measure of the lack of smoothness in \( s \),

\[ \mathcal{G}(c) = \sum_{i=1}^{g} \sum_{r=-\ell}^{h} \left( \sum_{q=-k}^{h} u_{q, i, q, r} \right)^{2} + \sum_{j=1}^{h} \sum_{q=-k}^{h} \left( \sum_{r=-\ell}^{h} v_{r, j, q, r} \right)^{2}, \]

satisfy the constraints.
Minimize \( G(\bar{c}) \)

subject to \( E(\bar{c}) \leq S \),

where \( S \) is a specified parameter.

In practice, it is suggested that the choice of \( S \) be in the range of \( n \pm \sqrt{2n} \) if the weights \( w_r = 1/\sigma \), where \( \sigma \) is the anticipated error standard deviation. The suggested maximum number of knot points is \( k + 1 \pm \sqrt{n/2} \), where \( k \) is the polynomial order. As \( S \) decreases, more knot points are added and a closer fit is realized. The number of knot points and their position is determined automatically by sequentially adding knots at those locations where the fit is poorest (Dierckx, 1981).

2.3 A Crossvalidation Study of Sampling Intensity

A crossvalidation analysis was performed in order to examine how the predictive power of data changed with different sampling intensities. This was performed by resampling the data at intensities lower than the realized intensity and assessing how well data omitted one at a time could be predicted by the resampled data. Observations were randomly assigned to one of two groups: a subset regarded as resampled points to be used in calculating kriging predictions and a subset omitted in the calculation of kriging predictions. The selection of data was performed by first stratifying the data to insure that there was some degree of systematic coverage of the sampled site, and then by permuting the observations within strata and choosing permuted points in order until the desired density was realized. All observations, from both the resampled subset and its complement, were predicted from the resampled subset, however. In each of 100 runs per selected sampling intensity, each datum in the nonresampled subset was predicted from the resampled data and each resampled datum was predicted from the remaining resampled points. The measure of prediction performance was the mean squared error (MSE) of crossvalidation.

\[
\text{MSE of crossvalidation} = \frac{\sum_{i=1}^{n} (Z_i - Z_i^*)^2}{n}.
\]  

(7)

where \( Z_i \) is datum \( i, i=1,\ldots,n \), and \( Z_i^* \) is the predicted value of \( Z_i \). This statistic was also calculated for the case of all observations being resampled. A measure of intersample distance of the resampled points was calculated by the median minimum distance of points to neighbors.
3. RESULTS

3.1 Data Inconsistencies

Several apparent inconsistencies in both data sets were amended. A single observation of 0 parts per million (ppm) Pb from the Dallas Lead Site RSR area was omitted since it was considered suspect. In the Dallas Lead Site data, there were 43 sets of two observations and 11 sets of three observations having within-set intersample locations less than 0.91 m (3 ft) apart. Eight of the 11 sets of three observations corresponded to measurements on 8 of the 11 split samples previously reported (Brown et al., 1984, 1985). The other three split samples appeared to have been represented by their means or by single split sample measurements. The remaining 46 sets were considered to be duplicate sample measurements. The concentrations and coordinates of the observations within sets were averaged. In the Palmerton Site data, a discrepancy in the Zn data was traced to the first phase Zn concentrations units being of parts per $10^5$ and second phase observations units being of ppm.

3.2 Frequency Distributions and Summary Statistics

Frequency distributions of the measured concentrations indicated positive skewness. Coefficients of variation were high, especially for the Dallas Lead Site DMC and RSR Pb concentrations. The mean Pb concentration from the Dallas Lead Site reference area were lower than the mean Pb concentration from the DMC and RSR area. Of the Palmerton Site data, the mean Cd concentration was lower than the mean Pb concentration, which was lower than the mean Zn concentration (Figure 2, Table 1).

3.3 Contour Plots

Contour plots of the data indicated that the highest heavy metal concentrations generally occurred in the center of the sampled regions, except for the Dallas Lead Site reference area data for which no contamination focus was noted. The contours of the Dallas Lead Site DMC and RSR area data tended to be more circular than the contours of the Palmerton Site data, which tended to be more elliptical. There were also contours of high concentration in the Dallas Lead Site DMC and RSR area data located apart from the smelter location, which was near the center of the sampled site (Figure 3).

3.4 Identification of Outliers

Outliers, or observations inconsistent with neighbors, were identified in order to minimize noise in assessing semivariograms and to understand what processes might be occurring at a local level. Isaaks and Srivastava (1988)
found that noise in sample semivariograms of Dallas Lead Site data was reduced after omitting outliers.

Outliers from the Dallas Lead Site were previously identified (George Flatman, personal communication, Appendix A). These were mostly associated with industrial sites and coincide with the high local contours of the Dallas Lead Site data. The outliers constituted some of the largest measured Pb concentrations from Dallas Lead Site samples. Of the MDC area data, the largest and 4 of the top 9 Pb measurements were outliers. The largest and 6 of the top 7 RSR area Pb measurements were outliers, while the largest and 4 of the top 8 reference area measurements were outliers.

Outliers from the Palmerton Site were identified by noting inconsistencies of measured concentrations with neighboring points. During the first sampling phase, the occurrence of previous disturbance of the soil by human activity was recorded, and the 31 of 100 first phase grid points that were labeled as being from disturbed locations were omitted in the previous geostatistical analysis. Some of these observations appeared to be consistent with neighbors and were retained in this study. Some of the outliers identified here were much lower in concentration than their neighbors and were labeled as being from disturbed locations. Outliers were also identified as those observations with spline model absolute residuals $\geq 2.5$, when $S$ was 500 (Appendix A).

3.5 The Relationship Between the Variance and the Mean

Natural logarithm transformations were previously applied to the Dallas Lead Site and the Palmerton Site data, prior to kriging, for the purpose of inducing stationarity in the variance. The effect of this transformation upon stabilizing the variance of duplicate samples had been examined for the Palmerton Site data (Starks et al., 1987). Since there was much variation in the duplicate samples of size ten, we did not utilize the duplicate sample data for the purpose of examining the relationship between mean and variance. Instead, the sample data, excepting outliers, were subjectively grouped into subsets of similar data value (Figure 4) and sample statistics were calculated from data within subsets. This stratification was intended to limit the effect of trend upon the variance-mean relationship. There appeared to be a linear relationship between the sample standard deviation and the sample mean and a natural logarithm transformation removed much of this dependence (Figure 5).

3.6 Sample Semivariograms

Sample semivariograms were calculated after transforming the measured heavy metal concentrations by ln(ppm) to induce stationarity in the variance and after omitting outliers. Semivariograms in the directions of 0, 45, 90, and 135 degrees were calculated, except for the reference area data, for which it was difficult to attain enough distance groups of size $\geq 30$ to discern
patterns in the directional semivariograms.

Differences were observed in semivariogram patterns of the Dallas Lead Site data. The Dallas Lead Site reference area data semivariogram was roughly constant, while the semivariograms of the DMC area and RSR area data increased, then leveled off, with increasing distance. There did not appear to be a strong directional effect (Figure 6).

The Palmerton Site data semivariograms exhibited differences according to direction, with the slightest increase with increasing distance noted in the 0 degree directional semivariogram. At distances less than 3 km, the greatest increase with increasing distance was observed in the 90 degree directional semivariogram. The 45, 90, and 135 degree directional semivariograms of the first phase data were higher than the corresponding second phase data semivariograms. This may largely be due to the sample locations of data and not reflective of the differences in composite sample sizes. The similarities in the 0 degree directional semivariograms and in the nuggets of the different sampling phase data suggests that a substantial variance-reducing effect of increasing the composite sample size from four to nine cannot be noted from these sample semivariograms (Figure 6).

3.7 Pooled Sample Variances of Individual, Duplicate, and Split Samples

Sample variances of the individual, duplicate, and split sample sets were pooled, after transforming the data by ln(ppm), in order to: (1) assess the effectiveness of composite sampling, and (2) allow estimates of micro-scale variation and of subsampling and measurement error.

The effectiveness of composite sampling in reducing micro-scale variation was noted by the decrease in the sizes of the individual and duplicate sample variances of the Palmerton Site data as the composite sample size increased. Though the relative differences in variance estimates were comparable between the changes in composite sample sizes, the absolute magnitude decreased as the composite sample size increased, indicating decreasing returns upon an increase in the composite sample size. The pooled individual sample variance was sensitive to a single individual soil sample exhibiting unusually low heavy metal concentrations. Omission of this observation lowered the estimated variance reduction by compositing (Table 2).

Further observations about the pooled sample variances were made. Duplicate sample variances were larger than split sample variances. The split sample variances of the second phase Palmerton Site data were lower than the split sample variances of the first phase data, a decrease that Brown et al. (1989) thought might be due to learning on the part of the analysts. Similar duplicate and split sample variance estimates were noted between the Dallas Lead Site Pb data and the Palmerton Site first phase Pb data (Table 2).
3.8 Decomposition of Spatial Variability into Regional Trend and Stochastic Process

Cubic spline models were fit to the Dallas Lead Site and the Palmerton Site data in order to decompose the spatial variability into regional trend and a stochastic process. Several levels of $S$ were selected to supply varying degrees of fit, after omission of the identified outliers. Apparent discontinuities associated with outliers caused rank deficiency in the design matrix as $S$ decreased. Weights of 2.0 were used, derived from an anticipated error standard deviation of 0.5.

Smooth fits to the trend in the Dallas Lead Site data and in the Palmerton Site data were provided by spline models with $S$ values of 300 and 500, respectively. However, as $S$ decreased, the spline models fit more of the spatial variability, as indicated by increased complexity in contour plots of fitted values and by lower sills of residual semivariograms. Sills were considerably lowered by spline models with relatively few knots as compared to semivariogram sills when no trend was removed (Figure 6). Omnidirectional semivariograms were calculated for the Dallas Lead Site data as there was no indication of anisotropy in these data. The Palmerton Site semivariogram was collapsed over sampling phase, since the difference in the nugget from increasing the composite sample size from four to nine appeared to be small relative to noise in the semivariogram. This judgement was made from viewing the semivariograms with no trend removed and from the pooled duplicate sample variances. As $S$ decreased, the semivariograms of spline fit residuals tended to exhibit a pure nugget pattern, with little difference according to direction (Figure 7).

The proportions of variability in the log (ppm) data attributable to different sources were calculated from the spline model results and the pooled sample variances. The proportions of variability due to combined subsampling and measurement error, to micro-scale variation, and to the combined effect of large-scale trend and local discontinuities associated with outliers were calculated as

$$\frac{\hat{\sigma}_{a}^2}{\hat{\sigma}_{n}^2 - \hat{\sigma}_{a}^2}, \quad \frac{\hat{\sigma}_{z}^2}{\hat{\sigma}_{n}^2 - \hat{\sigma}_{a}^2} \quad \text{and} \quad \frac{\hat{\sigma}_{a}^2 + \hat{\sigma}_{z}^2}{\hat{\sigma}_{n}^2}$$

respectively, where $\hat{\sigma}_{a}^2$, $\hat{\sigma}_{n}^2$, and $\hat{\sigma}_{z}^2$ are the estimated measurement error, nugget, and sample variances of the ln (ppm) data, respectively. The estimated proportion of variability due to subsampling and measurement error was small, being less than 1%. The proportion of variability due to micro-scale variation was larger, in the range of 15-25%, while the proportion of variability due to both the large-scale trend and to outliers was the largest, in the range of 75-84% (Table 3).
3.9 Crossvalidation Study Results

The purpose of this study was to assess the spatial scale necessary to capture the large-scale trend. Therefore, the identified outliers were omitted from the crossvalidation analysis, since they probably could not be predicted well from nearby data.

Omnidirectional spherical semivariograms were fit to the Dallas Lead Site data and to the Palmerton Site data and were used in calculating the kriging predictions. A linear anisotropic semivariogram provided a good fit to the Palmerton Site semivariogram data, but when the data were thinned below approximately half of the full data set, the kriging predictions with this model were unstable. When more than half of the data was resampled, the predictions based upon the spherical semivariogram and upon the linear anisotropic semivariogram were very similar. Neighborhoods of points with highest correlation were used in calculating kriging predictions, with chosen neighborhood sizes chosen to be 20 for the Dallas Lead Site data and 15 for the Palmerton Site data. A Lagrange multiplier for a constant mean was used in the calculation of kriging coefficients as it provided a lower MSE of crossvalidation than kriging predictions calculated without Lagrange multipliers.

The MSE of crossvalidation decreased in a nonlinear pattern with increasing percentages of data in the resampled subset. There was relatively little loss in prediction accuracy with up to about 60 percent omitted from the data subset. For example, when the resampled subset constituted 42-45 percent of the nonoutlier data set, the increase in the MSE of crossvalidation was just 10-17 percent over the MSE of crossvalidation when all nonoutliers were resampled. The median minimum intersample distance among resampled points exhibited a similar pattern with increasing resampling percentages (Figure 8). Standard errors of the mean for the 100 runs were 0.0005-0.007 and 0.0002-0.006 for the MSE of crossvalidation and for the median minimum intersample distance, respectively.

Standardizing intersample distances by estimated ranges of large-scale autocorrelation presented a different view of the scale of sampling from that anticipated in the sampling design. If the range of autocorrelation was estimated from omnidirectional spherical semivariogram models fitted to the data with only outliers omitted, then the median minimum intersample distances were 11-15% and 4-5% of the estimated ranges of autocorrelation, respectively (Figure 8). Calculating the intersample distance on the scale of the large-scale process thus gave a sampling scale much less than the 1/3-2/3 of the range of autocorrelation thought to have been required for sampling a small-scale stochastic process.

The capability of estimating semivariograms was not lost when much of the data was omitted, though there may have been too few points to reliably estimate a semivariogram when only 17-19% of the Dallas Lead Site nonoutlier data were resampled. The sample semivariogram patterns when data were omitted in resampling were similar to the semivariogram patterns of all nonoutlier data (Figure 9).
4. DISCUSSION

This retrospective analysis of data collected at the Dallas Lead and the Palmerton Superfund Sites examined the nature of variability in the data and sampling considerations for sites possessing the variability scales hypothesized for these data. The size of variability sources and the spatial scale on which they occur are important factors in designing an efficient sampling scheme and accurately predicting a contaminant concentration response surface. Being able to allocate resources in light of anticipated sizes of variability sources can contribute to cost-effective sample design (Provost, 1984).

Traditionally, the sampling approach to geostatistics has implicitly assumed that there exists a stochastic process nested within the regional trend that can be captured by a systematic design (Yfantis et al., 1987; Flattman et al., 1988). However, the Dallas Lead Site data and the Palmerton Site data did not appear to exhibit small-scale variability. Instead, the variability appeared to consist of a large-scale trend with discontinuities caused by either local contamination processes or by local soil disturbance, by variability occurring on a micro-scale, and by a very small measurement error. The crossvalidation results implied that sampling of these large-scale processes might have been suitably achieved with a larger scale of sampling than the scale that was utilized.

One purpose of sampling a small-scale stochastic process is to achieve stationarity in the data, or at least to be able to assume approximate stationarity in local data neighborhoods. The importance of the stationarity assumption may depend upon the use for which the response surface prediction is intended and the importance of an accurate variance estimate. The kriging predictions may be less sensitive to stationarity violations than are kriging variance estimates, as the kriging weights are likely to be similar using different, but reasonable, semivariogram models, while the kriging variance estimate depends upon the assumed semivariogram. However, for these data, it appears that calculation of kriging coefficients by other than a pure nugget correlation model requires that the data correlation structure be modeled for the large-scale trend. Other authors have modeled the correlation structure of the large-scale trend and performed kriging using this estimated autocorrelation (see, for example, Cressie, 1989).

If the data correlation structure is to be estimated from data sampled in the large scale, then the guidelines for sampling on the small scale may not apply. The grid locations at the Dallas Lead Site and at the Palmerton Site were arranged to be 2/3 and 1/3, respectively, of the anticipated range of autocorrelation. Sampling this scale of a small-scale stochastic process is usually suggested for geostatistical studies (Flattman et al., 1988). If a systematic sampling scheme is designed to capture the regional trend, the intersample distance might be much smaller than 1/3–2/3 of the large-scale autocorrelation range.
If local contamination processes are important components of the entire contamination process, as was evident at the Dallas Lead Site, then sampling can be designed to detect hotspots (see Chapter 10 in Gilbert, 1987), as well as to capture the large-scale trend. However, at the Dallas Lead Site, the local hotspots were largely associated with industrial sites, and sampling of such locations might be planned rather than being randomly encountered. At the Palmerton Site, the outliers constituted a lower proportion of the data set and they were most frequently lower in concentration than their neighbors, presumably because the soil had been previously disturbed.

Prediction of the extent of hotspot contamination around the local industries would likely be overestimated if the autocorrelation structure of the large-scale process were employed for interpolation (Gensheimer et al., 1986). Perhaps the best data-based solution to predicting the extent of local hotspot contamination is realized by further sampling near those locations.

Spatial variability can be modeled by deterministic or stochastic components, or a combination of types, as in (1). Deterministic variability can be viewed as being a product of underlying mechanistic factors. For example, the large-scale variability at the examined sites might have resulted from a physical process that is a function of gravity, air flow, and contaminant particle size. Stochastic variability can be considered to have arisen from processes of unknown causes independent of spatial location. However, as a process is studied in greater detail, underlying causal mechanisms may become apparent, and so the designation of deterministic or stochastic is often applied relative to our scale of reference (Wilding and Drees, 1983; Cressie, 1988). The modeling of variability as deterministic or stochastic may depend, in part, upon the degree of model explanation versus model empiricism (Lehmann, 1990) that is sufficient for site characterization.

Modeling the spatial process as a stochastic process is the assumption of geostatistics and that approach has been valuable for mapping. However, future site characterization needs may require models of a more deterministic nature. At the Dallas Lead and the Palmerton Sites, it appears that most of the spatial variability might be regarded as deterministic by our scale of reference. Considering the spatial variability in a more deterministic nature could allow answers to questions that have been posed for both sites. Consideration of human health remediation at the Dallas Lead Site required knowledge of how both smelters and motor vehicles contributed to soil lead contamination (Carra, 1984). At the Palmerton Site, differences in lead variability from cadmium and zinc variability might be attributable to the additional contribution of lead from motor vehicles (Starks et al., 1987). Much of the pattern of heavy metal contamination at the examined sites seems to be related to spatial features, such as the alignment of the Palmerton Site contamination contours with the ridge and valley topography, and the lead level decrease in the Trinity River floodplain at the Dallas Lead Site DMC area. Spatial data analysis and response surface prediction that combine aspects of empiricism and determinism are likely to be topics of future research.

The Palmerton Site data provided an opportunity to examine the efficacy
of composite sampling upon reducing micro-scale variation. Compositing appeared to have been effective in reducing the micro-scale variation, as indicated by the sizes of variance component estimates from individual, duplicate, and split samples, though it appears that increasing the composite sample size from four to nine may have diminished the variance reduction returns compared to increasing the composite sample size from one to four. Compositing of individual soil samples may be desired when soil sampling by small cores and when the micro-scale variability is similar to that at the Palmerton Site.

Cost-effective sampling is likely to be achieved when the sampling design reflects knowledge about the sizes of variability components in the process of interest and the spatial scales on which they occur. If the regional trend and variation among nearby individual samples contribute significantly to spatial variability, then the choices of a sampling scale in measuring the important features of the regional trend and the use of composite sampling to minimize the micro-scale variation might be important to achieving cost-effectiveness in hazardous waste site characterization.

![Graph showing sample location patterns at the Palmerton Site.](image)

**FIGURE 1. Sample location patterns of the soil samples taken at the Palmerton Site.** The coordinate space has apparently been rotated from its geographical space, so that the easting coordinate is aligned with the ridge and valley orientation.
FIGURE 2: Sample frequency distributions of the Dallas Lead Site and the Palmerton Site ppm measurements. Categories with zero observations have been omitted.
TABLE 1. Descriptive statistics of the Dallas Lead and Palmerton Site heavy metal concentrations. The statistics $n$, $\bar{X}$, $S$, and $CV = 100 \times (S/\bar{X})$, represent the sample size, sample mean, sample standard deviation, and coefficient of variation, respectively.

<table>
<thead>
<tr>
<th>Site</th>
<th>Metal</th>
<th>$n$</th>
<th>$\bar{X}$</th>
<th>$S$</th>
<th>$CV$</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dallas Lead</td>
<td>Pb</td>
<td>88</td>
<td>125.2</td>
<td>123.1</td>
<td>98</td>
<td>16.0-703</td>
</tr>
<tr>
<td>reference area</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dallas Lead</td>
<td>Pb</td>
<td>180</td>
<td>429.9</td>
<td>999.7</td>
<td>233</td>
<td>24.4-10400</td>
</tr>
<tr>
<td>DMC area</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dallas Lead</td>
<td>Pb</td>
<td>180</td>
<td>364.2</td>
<td>854.5</td>
<td>235</td>
<td>11.2-6060</td>
</tr>
<tr>
<td>RSR area</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palmerton</td>
<td>Cd</td>
<td>413</td>
<td>42.5</td>
<td>47.7</td>
<td>112</td>
<td>1.29-364</td>
</tr>
<tr>
<td>Palmerton</td>
<td>Pb</td>
<td>413</td>
<td>207.1</td>
<td>205.6</td>
<td>99</td>
<td>7.30-1730</td>
</tr>
<tr>
<td>Palmerton</td>
<td>Zn</td>
<td>413</td>
<td>312.6</td>
<td>4267</td>
<td>137</td>
<td>146-40000</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 1. Contour plots of the Dallas Lead Site and the Palmerton Site ppm measurements. The contour line increment was 100, 500, and 500 ppm for the Dallas Lead Site reference area, DMC area, and RSR area data, respectively, and it was 50, 250, and 2500 for the Palmerton Site Cd, Pb, and Zn data, respectively. These plots were made by predicting concentrations at grid locations using a distance 4 weighting of the 8 closest data points using the SURFACE II algorithm (Sampson, 1984).
FIGURE 4. Stratification of the Dallas Lead Site and the Palmerton Site data for assessing the relationship between the variance and the mean. The numbers are the log(ppm) rounded to the nearest integer and plotted on sample locations, except that the Palmerton Site zinc data are rounded log(parts per 10^6) values. These transformations were used so as to represent observations by single digits. Outliers are denoted by *.
FIGURE 5. The sample standard deviation versus the sample mean of ppm and log/ppm) Dallas Lead Site and Palmerton Site data grouped as illustrated in Figure 4.
Figure 6: Sample semivariograms of the Dallas Lead Site and the Palmerton Site (in ppm) data. The angle tolerance of the directional semivariograms is ±22.5 degrees.
TABLE 2. Pooled sample variances of individual, duplicate, and split sample ln (ppm) data.

Dallas Lead Site

<table>
<thead>
<tr>
<th>Sample Component</th>
<th>Area</th>
<th>Number of Sets</th>
<th>Variance Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Duplicate</td>
<td>reference</td>
<td>9</td>
<td>0.0083</td>
</tr>
<tr>
<td></td>
<td>DMC</td>
<td>18</td>
<td>0.0157</td>
</tr>
<tr>
<td></td>
<td>RSR</td>
<td>19</td>
<td>0.0396</td>
</tr>
<tr>
<td>Split</td>
<td>combined</td>
<td>11</td>
<td>0.00528</td>
</tr>
</tbody>
</table>

Palmerton Site

<table>
<thead>
<tr>
<th>Sample Component</th>
<th>Sampling Phase</th>
<th>Number of Sets</th>
<th>Variance Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td>Individual</td>
<td>1</td>
<td>10</td>
<td>0.766</td>
</tr>
<tr>
<td></td>
<td>1*</td>
<td>10</td>
<td>0.275</td>
</tr>
<tr>
<td>Duplicate</td>
<td>1</td>
<td>10</td>
<td>0.0690</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>11</td>
<td>0.0116</td>
</tr>
<tr>
<td>Split</td>
<td>1</td>
<td>10</td>
<td>0.00275</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>7</td>
<td>0.000934</td>
</tr>
</tbody>
</table>

*After omitting a single individual sample of anomalously low concentrations
FIGURE 7. Contour plots of spline model fits and sample semivariograms of spline fit residuals for the Dallas Lead Site DMC and RSR area data and for the Palmerton Site data.
FIGURE 7 (continued).
FIGURE 7 (continued).
FIGURE 7 (continued).
FIGURE 7 (continued).
<table>
<thead>
<tr>
<th>Site</th>
<th>Metal</th>
<th>Total</th>
<th>Nugget</th>
<th>Measurement Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dallas Lead</td>
<td>Pb</td>
<td>1.315</td>
<td>0.313</td>
<td>0.00528</td>
</tr>
<tr>
<td>- DMC Area</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dallas Lead</td>
<td>Pb</td>
<td>1.277</td>
<td>0.314</td>
<td>0.00528</td>
</tr>
<tr>
<td>- RSR Area</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palmerton</td>
<td>Cd</td>
<td>1.238</td>
<td>0.199</td>
<td>0.00275</td>
</tr>
<tr>
<td>Palmerton</td>
<td>Pb</td>
<td>0.803</td>
<td>0.201</td>
<td>0.00453</td>
</tr>
<tr>
<td>Palmerton</td>
<td>Zn</td>
<td>1.266</td>
<td>0.206</td>
<td>0.00380</td>
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</table>

**Percent of Variability Estimate**

<table>
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<th>Micro-scale</th>
<th>Measurement Error</th>
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<tr>
<td>Dallas Lead</td>
<td>Pb</td>
<td>76.2</td>
<td>23.4</td>
<td>0.4</td>
</tr>
<tr>
<td>- DMC Area</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dallas Lead</td>
<td>Pb</td>
<td>75.4</td>
<td>24.2</td>
<td>0.4</td>
</tr>
<tr>
<td>- RSR Area</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Palmerton</td>
<td>Cd</td>
<td>83.9</td>
<td>15.9</td>
<td>0.2</td>
</tr>
<tr>
<td>Palmerton</td>
<td>Pb</td>
<td>75.0</td>
<td>24.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Palmerton</td>
<td>Zn</td>
<td>83.7</td>
<td>16.0</td>
<td>0.3</td>
</tr>
</tbody>
</table>

1. Sample variance of ln(ppm)
2. Estimated by semivariogram of spline model residuals collapsed over distance (S=200 for Dallas Lead DMC and RSR area data, S=300 for Palmerton Site data).
3. Includes error of subsampling
4. Includes local discontinuities of outliers
FIGURE 8. The crossvalidation results: (A) MSE versus the percent of data resampled, (B) median minimum intersample distance versus the percent of data resampled (Palmerton Site Cd, Pb, Zn data were nearly identical so only the Cd data is presented), and (C) MSE versus the median minimum intersample distance scaled by the range of autocorrelation estimated by omnidirectional spherical-semivariogram models. Values are the means of 100 runs except for the case of 100% of the data being resampled.
FIGURE 9. Sample semivariograms for different percentages of resampling for the Dallas Lea Site DMC and RSR area data and for the Palmetton Site data. The data are single resamples of the nonoutlier data and the smooth curve is the spherical semivariogram fit to the 100% resampled data.
ACKNOWLEDGEMENTS

The work on this paper has been carried out with partial support of
EPA Research Grant CR 815 273 010 and SRA/EPA Research Contract 40400-S-01;
the Penn State Center for Statistical Ecology and Environmental Statistics.
Our thanks are due to Karl Held of SRA Technologies, Inc. and to Herbert
Lacayo, Jr. and N. Phillip Ross of EPA Statistical Policy Branch for their
support and encouragement. We are also thankful to our colleague Marilyn T.
Boswell for his interest and several technical discussions.

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## APPENDIX A

### Dallas Lead Site and Palmerton Site Outliers

#### Dallas Lead Site Outliers

<table>
<thead>
<tr>
<th>Area</th>
<th>Sample Number</th>
<th>(x,y) coordinates (ft)</th>
<th>pm Pb</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>reference</td>
<td>05523</td>
<td>(5256, 3167)</td>
<td>324</td>
<td>Residential area</td>
</tr>
<tr>
<td></td>
<td>05522</td>
<td>(6291, 2803)</td>
<td>703</td>
<td>Residential area</td>
</tr>
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<td></td>
<td>05506</td>
<td>(2139, 6762)</td>
<td>16</td>
<td>Church lawn</td>
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<td></td>
<td>05858</td>
<td>(4928, 6720)</td>
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<td>Industrial area</td>
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<td></td>
<td>05504</td>
<td>(4935, 7476)</td>
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<tr>
<td>DMC</td>
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<td>(5754, 10869)</td>
<td>2950</td>
<td>Industrial area</td>
</tr>
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<td></td>
<td>01499</td>
<td>(9203, 9831)</td>
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<td>Industrial area</td>
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<td>(11434, 7587)</td>
<td>10400</td>
<td>Industrial area</td>
</tr>
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<td></td>
<td>05069</td>
<td>(1595, 6555)</td>
<td>2880</td>
<td>Hospital grounds</td>
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<tr>
<td></td>
<td>01210</td>
<td>(8977, 9292)</td>
<td>1060</td>
<td>Industrial area</td>
</tr>
<tr>
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<td>(3407, 1203)</td>
<td>6060</td>
<td>Industrial area</td>
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<td>05563</td>
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<td>Industrial area</td>
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<td>05139</td>
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<td>(2985, 4656)</td>
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</tr>
<tr>
<td></td>
<td>05770</td>
<td>(4456, 5438)</td>
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* - duplicate samples
### Palmerton Site Outliers ¹

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>(x,y) coordinates (thousands of ft)</th>
<th>Metal ppm</th>
<th>Phase</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>BU30</td>
<td>18.9576, 22.3850</td>
<td>2.14 32.5 410</td>
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</tr>
<tr>
<td>CD44</td>
<td>22.7808, 16.5992</td>
<td>14.2 47.8 750</td>
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<td>low, SE transect</td>
</tr>
<tr>
<td>BS34</td>
<td>18.3543, 20.8544</td>
<td>22.5 89. 1610</td>
<td>1</td>
<td>low, Palmerton Hosp</td>
</tr>
<tr>
<td>BN34</td>
<td>16.3961, 20.6209</td>
<td>21.6 84.0 2165</td>
<td>1</td>
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</tr>
<tr>
<td>CS72</td>
<td>29.1240, 5.4517</td>
<td>34.2 171. 1900</td>
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<td>high, S. of Blue Mt</td>
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<td>BM31</td>
<td>15.9516, 25.7348</td>
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<td>high, N. of Palmert</td>
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### Palmerton Site Outliers ²

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>(x,y) coordinates (thousands of ft)</th>
<th>Metal ppm</th>
<th>Phase</th>
<th>Comment</th>
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<td>26.20 151.0 2900 + 1</td>
<td>1</td>
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</tr>
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<td>4.7963 29.4709</td>
<td>29.50  770.0 2400 + 2</td>
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<td>AO23</td>
<td>6.0750 24.6304</td>
<td>6.75 12.4  - 780</td>
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<td>AR37</td>
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<td>6.41 131.0 660 - 2</td>
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<tr>
<td>AS24</td>
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¹ defined prior to spline fit.

² defined subsequent to spline fit (−, + denote outliers of low or high concentration, respectively).