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*Geochemistry of Sediment Samples at TA-54,
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*Katherine Campbell
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GEOCHEMISTRY OF SEDIMENT SAMPLES AT TA-54, LOS ALAMOS NATIONAL LABORATORY

by

Katherine Campbell and Steven L. Reneau

ABSTRACT

A statistical evaluation of sediment data from Technical Area 54, Los Alamos National Laboratory, was used to examine the relation of concentrations of a series of inorganic and radionuclide analytes to general geographic setting and sediment texture. Significant differences exist between results from the north and south sides of Mesita del Buey, with analyte concentrations being generally higher to the north. These differences probably result primarily from variations in background levels in the source materials for the sediments, perhaps reflecting finer particle sizes and/or better developed soils on the north side of the mesa.

1. INTRODUCTION

This report presents a statistical evaluation of results from Los Alamos National Laboratory (LANL) Environmental Restoration (ER) Project sediment sampling activities that were conducted in 1994 along a series of drainages below material disposal areas (MDAs) at Technical Area (TA) 54 (LANL, 1996). The 1994 investigation was intended to evaluate potential contaminant transport by surface water from the TA-54 MDAs. It was designed to complement ongoing surveillance sampling of active channel sediments and storm water by focusing on historical sediment deposits, including deposits that might predate the surveillance sampling. Sampling was also designed to encompass the range of sediment texture (grain size) that occurs along each drainage.

Here we focus on the variations in analyte concentrations in 71 sediment samples and on the relationship between these variations and the topographic setting and sediment texture. The observed variation reflects both the nature and source of contamination within each basin and also possible differences in background concentrations between basins.

2. GEOMORPHIC SETTING

Sediment samples analyzed in this study were collected from a series of small drainage basins on the north and south sides of Mesita del Buey that receive runoff from the MDAs at TA-54 and drain into Cañada del Buey and Pajarito Canyon, respectively (Figs. 1 and 2). Basin length ranges from about 0.2 to 0.6 km. Basins draining south and northeast are the largest, including some that contain second-order channels, but many of the basins draining north are small and consist of relatively unincised canyon walls.

The source for the sampled sediment includes units 1v and 2 of the Tshirege Member of the Bandelier Tuff, soils and sedimentary deposits within each basin, and fill material associated with operations at TA-54. Sampled geomorphic settings include local areas of sediment deposition along channels that are confined within banks, particularly areas behind channel obstructions (such as trees, logs, and rocks), and small fan lobes associated with braided channels (Fig. 3a). Sampled areas also include larger fans that have been deposited on the canyon floors, where relatively coarse sediments (coarse to medium sand and gravel) are

Fig. 1. Drainage basins and sediment sample locations at MDAs H, J, and L, TA-54. Drainage basins calculated from topographic contours, and actual drainage areas differ because of low berms and shallow ditches on mesa top and diffuse, braided channels in canyons.

Fig. 2. Drainage basins and sediment sample locations at MDA G, TA-54. Drainage basins calculated from topographic contours, and actual drainage areas differ because of low berms and shallow ditches on mesa top and diffuse, braided channels in canyons.

found on the upper part of fans, while finer sediments (fine sand, silt, and clay) are carried to the lower part of the fans (Fig. 3b).

3. SAMPLING AND ANALYSIS

The 71 sediment samples analyzed for metals and radioisotopes are listed in Table 1 by drainage basin, and sample locations are shown in Figs. 1

and 2. The field strategy for the 1994 ER study was to identify the most likely historic sediment deposition areas within each drainage basin, based on the geomorphic characteristics of the basin. Within these areas of historical deposition, samples were screened for radioactivity in order to identify areas, if any, of radioactive contamination from the associated MDA. However, this attempt to bias the selection of samples for laboratory analysis was largely unsuccessful because of high detection limits and other method problems with the screening; among the selected samples there is no correlation between the screening and laboratory results. As a result, the four to five samples selected from each drainage basin can be considered to be unbiased representatives of the geomorphic settings and historic sediment deposits found to the north and south of Mesita del Buey.

Contaminant concentrations may also vary with the grain size distribution of the deposit, and the selected measurement sites include a range in sediment size to capture the variety of deposits present along each drainage. Most of the individual basins also include both fine- and coarse-grained samples, and the numbers of fine- and coarse-grained samples on the north (Cañada del Buey) and south (Pajarito Canyon) sides of TA-54 are approximately equal.

Metals were analyzed using the Environmental Protection Agency (EPA) SW-846 methods that are customary for investigations intended to produce data for risk assessment (EPA, 1992). In particular, the usual SW-846 sample preparation method involves only a weak acid leach, and this partial digestion method does not extract all of the element that is present in the sample. Thus, inorganic chemical data reported here are generally not comparable to data obtained by the total methods that are often preferred for geochemical studies. However, conclusions about the relative

Fig. 3. Geomorphic characteristics of drainage basins at TA-54, illustrating the setting of sediment sample sites. a) Some common depositional areas along channels. b) Typical drainage basin on the south side of MDA G, with a young fan.

Table 1. Summary of Channel Sediment Samples

Drainage Basin		Location	Sample ID	General Sediment Texture
South	G-1	5018	AAB3139	coarse (sand, gravel)
		5015	AAB3143	fine (sand, silt)
		5017	AAB3150	coarse (sand, gravel)
		5016	AAB3160	fine (silt, sand)
South	G-2	5022	AAB3187	fine (silt)
		5019	AAB3190	fine (silt)
		5026	AAB3195	fine (silt)
		5020	AAB3207	fine (silt, sand)
South	G-3	5029	AAB3120	coarse (sand, gravel)
		5027	AAB3122	coarse (sand, gravel)
		5031	AAB3123	coarse (sand)
		5034	AAB3126	fine (silt)
South	G-4	5035	AAB3194	coarse (sand, gravel)
		5042	AAB3204	fine (sand, silt)
		5037	AAB3208	fine (silt)
		5038	AAB3213	fine (fine sand)
South	G-5	5050	AAB3132	fine (sand, silt)
		5043	AAB3191	coarse (medium sand)
		5048	AAB3192	fine (silt)
		5045	AAB3196	coarse (medium/coarse sand)
South	G-6	5055	AAB3133	coarse (sand)
		5058	AAB3147	coarse (sand)
		5053	AAB3173	coarse (sand)
		5060	AAB3180	coarse (sand)
		5055	AAB3202	coarse (sand)
South	G-8	5068	AAB3118	fine (fine/medium sand)
		5066	AAB3121	coarse (sand, gravel)
		5063	AAB3124	fine (silt)
		5061	AAB3128	coarse (sand)
South	G-9	5076	AAB3106	fine (silt)
		5069	AAB3107	coarse (sand, gravel)
		5074	AAB3108	fine (sand, silt)
		5072	AAB3114	coarse (sand, gravel)
North	G-10	5077	AAB3170	coarse (sand)
		5082	AAB3171	fine (silt, fine sand)
		5078	AAB3172	coarse (sand, gravel)
		5080	AAB3177	fine (silt, sand, gravel)
North	G-11	5090	AAB3154	fine (fine/medium sand)
		5086	AAB3155	coarse (sand)
		5088	AAB3156	coarse (sand, gravel)
		5085	AAB3158	coarse (sand, gravel)
		5085	AAB3166	coarse (sand, gravel)

Table 1. (continued)

North	G-12	5095	AAB3157	fine (sand, silt)
		5093	AAB3159	coarse (sand)
		5094	AAB3161	coarse (sand, gravel)
		5096	AAB3164	coarse (sand, gravel)
North	G-13	5103	AAB3163	fine (silt, sand, gravel)
		5102	AAB3168	coarse (sand, gravel)
		5104	AAB3169	fine (silt, sand, gravel)
		5101	AAB3178	coarse (medium/coarse sand)
North	G-14	5111	AAB3116	coarse (sand)
		5108	AAB3117	fine (sand, gravel, silt)
		5110	AAB3127	fine (sand, gravel, silt)
		5113	AAB3167	fine (fine sand)
North	G-15	5117	AAB3109	fine (fine sand, silt)
		5122	AAB3110	fine (silt, fine sand)
		5118	AAB3111	fine (silt, fine sand)
		5122	AAB3112	fine (silt, fine sand)
		5125	AAB3113	fine (silt)
South	S-H	5130	AAB3219	coarse (sand, gravel)
		5132	AAB3131	coarse (sand)
		5126	AAB3142	fine (silt)
		5131	AAB3175	coarse (sand, gravel)
North	S-J	5141	AAB3130	coarse (sand, gravel)
		5136	AAB3151	coarse (sand, gravel)
		5142	AAB3162	coarse (sand)
		5138	AAB3174	coarse (sand, gravel)
North	S-L	5143	AAB3134	coarse (sand, gravel)
		5148	AAB3138	coarse (sand, gravel)
		5147	AAB3149	fine (sand, silt)
		5145	AAB3179	coarse (sand, gravel)

concentrations associated with different sediment grain sizes or basins may be drawn from these results.

The radioisotopes considered in this report were measured by alpha spectrometry, and the corresponding sample preparation method requires total digestion of the samples.

4. STATISTICAL EVALUATION OF THE RESULTS

Since the preparation of the original report on this study (LANL, 1996), more data on the natural background geochemistry of sediments on the

Pajarito Plateau have been collected (McDonald et al., 1997; Rytí et al., 1998). New and more representative background values for both metals and naturally occurring radionuclides are presented by McDonald et al. (1997) and Rytí et al. (1998). Only a handful of observations from the 71 sediment samples exceed these background values. These include two samples with lead concentrations slightly above background levels in the drainage from MDA H (basin S-H), chromium in one sample from basin G-12, cadmium in one sample from G-14, and barium, magnesium, and iron in samples from G-15. Apart from these scattered "hits" (none of which exceed the background values for sediments reported by

McDonald et al. (1997) and Ryti et al. (1998) by as much as a factor of three), the results from these samples appear to be representative of background levels for sediments of the Pajarito Plateau.

The measured isotopes of radium, thorium, and uranium are within background ranges and appear to be in approximate secular equilibrium. In particular, there is no evidence of contamination by enriched, natural, or depleted uranium. There are, however, several samples with elevated levels of ^{241}Am , ^{238}Pu , and $^{239,240}\text{Pu}$. Unlike the generally normal distributions of the data for inorganic chemicals and naturally occurring radionuclides, the distributions of the data for these three isotopes tend to be skewed with long upper tails.

Tables 2, 3, and 4 summarize the results of statistical tests that were applied to the data. The following hypotheses were evaluated:

Hypothesis #1. Analytical results from fine-grained samples are systematically higher than those for coarse-grained samples, as suggested by previous studies such as McDonald et al. (1997) and Reneau et al. (1998).

Hypothesis #1 was tested using 1) all 71 samples, 2) only samples from the north side of Mesita del Buey, and 3) only samples from the south side. Tables 2, 3, and 4 summarize the results for the tests using all 71 samples in the columns headed "Fine>Coarse?," and test results based on subsets

Table 2. Summary of Statistical Tests Using Inorganic Analytical Results

Element	Number of results above DL	Number of outliers (a)	Fine>Coarse? (P-value) (a,b)	North>South? (P-value) (a,b)
Aluminum	71	0	<0.001	<0.001
Arsenic	3	NA	NA	NA
Barium	53	0	0.001	<0.001
Beryllium	5	NA	NA	NA
Cadmium	2	1	NA	NA
Calcium	53	1	0.002	0.016
Chromium	57	1	0.013	<0.001
Cobalt	2	NA	NA	NA
Copper	17	0	0.046	0.553
Iron	71	1	0.020	<0.001
Lead	71	2	0.001	0.023
Magnesium	28	0	0.016	0.001
Manganese	70	0	0.002	0.014
Mercury	1	NA	NA	NA
Nickel	3	NA	NA	NA
Potassium	20	0	0.008	0.019
Silver	1	NA	NA	NA
Sodium	1	NA	NA	NA
Vanadium	18	0	0.137	<0.001
Zinc	71	0	0.002	0.001

(a) NA indicates insufficient data (too many below-detection results) to test for outliers or significant differences.

(b) P-values in this table indicate results for statistical tests performed using all data in the named groups except outliers identified in Table 5.

Table 3. Summary of Statistical Tests for Naturally Occurring Radioisotopes

Isotope	Number of results above DL	Number of outliers	Fine>Coarse? (P-value) (a)	North>South? (P-value) (a)
²²⁶ Ra	71	0	0.016	0.091
²²⁸ Th	71	0	0.001	0.035
²³⁰ Th	71	0	<0.001	0.036
²³² Th	71	0	0.001	0.063
²³⁴ U	71	0	<0.001	0.102
²³⁵ U	71	0	0.017	0.114
²³⁸ U	71	0	0.001	0.074

(a) P-values in this table indicate results for tests performed using all data in the named groups.

Table 4. Summary of Statistical Test Results for Antropogenic (Fallout) Radioisotopes

Isotope	Number of results above DL	Number of outliers	Fine>Coarse? (P-value) (a)	North>South? (P-value) (b)
²⁴¹ Am	71	0	0.005	0.065
¹³⁷ Cs	38	0	0.070	0.050
²³⁸ Pu	71	2	0.164	0.073
^{239,240} Pu	71	2	0.040	0.010

(a) P-values in this column indicate results for tests performed using all data except outliers identified in Table 5.

(b) P-values in this column indicate results for tests performed using data from the fine-grained samples only, excluding outliers identified in Table 5.

of samples from the north and south side of Mesita del Buey are discussed in the text.

Hypothesis #2. Analytical results for samples from the north side of Mesita del Buey are systematically higher than those for samples from the south side. McDonald et al. (1997) found at most small differences between canyons in their studies, but plots of the TA-54 sediment data suggest some systematic differences.

Hypothesis #2 was tested using 1) all 71 samples, 2) only fine-grained samples, and 3) only coarse-grained samples. Tables 2 and 3 summarize the results for the tests using all samples in the columns headed "North>South?," and Table 4 presents results for fine-grained samples in the corresponding column. Test results based on other

subsets of the data are discussed in the text.

All statistical comparisons were made using the nonparametric Wilcoxon test with the Gehan modification for nondetects, which is further described in the Appendix. A few outliers were eliminated before performing the statistical tests, although some values above background were retained. The numbers of outliers are indicated in Tables 2, 3, and 4, and the specific outliers are listed in Table 5. Statistical results are reported in Tables 2, 3, and 4 in terms of the significance level or "P-value" of the computed test statistic. Traditionally, a P-value of less than 0.01 is considered a highly significant result (one that would be obtained by chance less than one time in a hundred); P-values of up to 0.1 indicate results that might occur by chance up to one time in ten; and P-values greater

than 0.1 are generally considered too large to indicate a significant difference between the two populations being compared.

For 12 of the 20 elements reported from the inorganic chemical analyses, there are enough data above the method detection limit (DL) to perform statistical comparisons. The results of these statistical tests reaffirm the observations of earlier studies by confirming the preferential association of most elements with the fine fraction of the sediments. The results for the tests of Hypothesis #1 based on all of the samples were significant at the 5% level or better for eleven of the twelve elements. The exception (vanadium) is an element for which virtually all of the detected results are on the north side of Mesita del Buey; only two of the eighteen detected results were on the south side. When only samples from the north side are used, the test for vanadium gives a P-value of 0.086, despite the smaller sample size (which makes it more difficult to achieve a highly significant result).

The distributions illustrated by the box plot for iron in Figure 4 are typical. (Box plots such as Figure 4 are explained in the Appendix.) As suggested by Figure 4, the association with the fine fraction is generally true on both the north and south sides of Mesita del Buey. Exceptions were noted for zinc on the north side and for copper and potassium (and vanadium, here almost entirely undetected) on the south side. Potassium is another element with significantly larger numbers of nondetect results on the south side than the north.

As Figure 4 shows, there are also significant differences overall between the north and south sides of Mesita del Buey (Hypothesis #2). For eleven of the twelve metallic elements (all except copper), the difference between samples from the north-draining basins (in Cañada del Buey) and those from the south-draining basins (in Pajarito Canyon) was statistically significant at the 5% level or better. That is, sediments from the Cañada del Buey side appear to be significantly enriched, by comparison with those from the south side, with respect to both major and several minor elements.

In view of the fact that fine- and coarse-grained samples were collected in about equal numbers on each side of the mesa, this result appears to be independent of the fine- versus coarse-grained contrast discussed earlier. In general, the contrasts between north and south-side samples hold for coarse-textured as well as fine-textured samples, although the difference fails to be statistically significant (at the 10% level) for potassium in coarse-textured samples. The P-value is also slightly greater than 10% (0.106) for zinc in fine-textured samples.

Table 3 summarizes test results for the naturally occurring radioisotopes. There are no below-detection-limit results for the seven isotopes of radium, thorium, and uranium. Like the inorganic chemicals, all of these isotopes are significantly associated with the fine fraction, as are all of the anthropogenic radioisotopes with sufficient data above the detection level (Table 4) except ^{238}Pu .

Table 5. Outliers in Channel Sediment Samples

Drainage Basin		Sample ID	Analyte	Value
South	G9	AAB3106	^{239}Pu	0.909 pCi/g
	G9	AAB3108	^{239}Pu	0.858 pCi/g
	G4	AAB3194	Ca	6370 mg/kg
	G5	AAB3191	^{238}Pu	0.576 pCi/g
	SH	AAB3129	Pb	21.3 mg/kg
	SH	AAB3175	Pb	19.9 mg/kg
North	G12	AAB3159	Cr	17.9 mg/kg
	G13	AAB3169	^{238}Pu	1.483 pCi/g
	G15	AAB3109	Fe	39,000 mg/kg

Fig. 4. Box plots of the distribution of iron in sediment samples.

By contrast with the inorganic chemical results shown in Table 2, however, the association of the naturally occurring radioisotopes with the fine sediments appears to hold strongly only on the south side of Mesita del Buey. Most of the statistical tests using only samples from the north side of the mesa fail to achieve the 10% significance level, although the P-values remain below 0.2. (Exceptions are ^{226}Ra at $P = 0.012$ and ^{230}Th at $P = 0.08$.) The plot of ^{238}U in Figure 5 is typical of these radioisotopes.

As shown in Figure 5 and Table 3, north/south contrasts similar to those for metals are also found for naturally occurring radioisotopes. In contrast to the results for inorganic chemicals, however, these differences appear to be due entirely to the concentrations in coarse-grained sediments; the significance levels of the tests using only coarse-grained sediments is lower than shown in the last column of Table 3 for all of the isotopes of thorium and uranium. Hypothesis #2 must be rejected for these isotopes in fine-grained sediments. Only the result for ^{226}Ra appears to be due to data from the fine-grained samples; the P-value for the north/south comparison for this isotope is 0.058 for fine-grained samples but slightly greater than 0.2 for coarse-grained samples.

The anthropogenic radioisotopes ^{241}Am , ^{137}Cs , and $^{239,240}\text{Pu}$ behave very differently from the naturally occurring isotopes. For these anthropogenic radioisotopes, reported at levels that at least in part represent releases from MDA G, the observed association with fine sediments is a consequence of a strong difference in fine- versus coarse-grained samples from the north side of the mesa, as seen for example in Figure 6 for $^{239,240}\text{Pu}$. Hypothesis #1 must be rejected for the south side of Mesita del Buey. Moreover, north/south differences are found only in the fine-grained samples, as reported in Table 5. Hypothesis #2 must be rejected for the coarse-grained samples and for all samples combined.

5. DISCUSSION

McDonald et al. (1997) found relatively few differences between canyons in their study, so the highly significant differences found in this study between sediments on the north and south sides of Mesita del Buey require some explanation. One possibility is that, despite the lack of observations above background among the metals and naturally occurring radionuclides, these differences are a subtle indication of more contaminant migration

Fig. 5. Box plots of the distribution of ^{238}U in sediment samples.

Fig. 6. Box plots of the distribution of $^{239,240}\text{Pu}$ in sediment samples (note logarithmic scale).

to the north than to the south or a higher percentage of the young sediments to the north being derived from contaminated areas. This hypothesis is consistent with the fact that the same pattern is found in the anthropogenic radionuclides. However, the north-south contrast is apparent in almost all of the naturally occurring analytes, and

it seems very unlikely that all of these analytes would be present as widespread contaminants across the MDAs without also being more frequently detected above background. We thus conclude that these north-south differences for inorganic chemicals and naturally occurring radionuclides indicate primarily variations in

background levels in the source materials providing sediment.

A second possibility is that the sediment samples on the north side typically have higher percentages of fine particles within a given grain size class (coarse versus fine) relative to the south side. Sampled drainages to the north typically have smaller basins than those to the south, which could result in smaller average runoff events and less effective winnowing of fines from the channels. It is also possible that the fine-grained component to the north typically contains more silt and clay relative to fine sand, perhaps reflecting differences in source material. This hypothesis cannot be tested without more detailed particle size data.

A third possibility is that the source for the sediments on the north side typically includes a higher portion of soils with stronger soil development than to the south. Background soil data from the Pajarito Plateau have demonstrated that better developed soils have significantly more iron, aluminum, and trace metals than weakly developed soils (Longmire et al., 1996; McDonald et al., 1996). The correlation between the trace and major elements (particularly iron) found in the TA-54 sediment samples mirrors the correlations found in other soil studies. This hypothesis is also supported by field observations that bare tuff is much more widely exposed on the south side of Mesita del Buey relative to the north, so that a larger portion of the source area for sediments to the south may consist of either freshly eroded tuff or weakly developed soils derived from tuff. Because of the larger runoff areas generally contained within disturbed areas at the MDAs in the south-draining basins, sediment from these basins may also contain a higher percentage of eroded fill material that is more similar to unweathered parent materials than to soils with pedogenic alteration. In connection with this observation, it is interesting that the data summarized by Rytí et al. (1998) suggest that while the concentrations of most inorganic elements are higher in soil than in the Tshirege Member of the Bandelier Tuff, the reverse is true for zinc, potassium, uranium, and thorium.

Thus, the greater exposure of tuff on the south side of Mesita del Buey may account for the relatively weak north/south contrasts for uranium, thorium, zinc, and potassium as compared with the remaining inorganic elements. These elements also do not show such strong correlations with iron and aluminum as many of the other inorganic elements.

Finally, as observed in the preceding section, the geographic and sedimentologic distribution of anthropogenic isotopes that are at least in part related to releases at the MDAs differs somewhat from that present in analytes that most likely represent background variations. These differences are probably related in part to the mixing of data from separate drainage basins with differing contributions from the MDAs for the purpose of statistical analysis. In particular, the two highest analyses for $^{239,240}\text{Pu}$, excluded from statistical analysis as outliers, actually came from fine-grained sediments in a south-side basin (G-9); this somewhat confounds the conclusions implied by Table 4 and Figure 6, which are based on the bulk of the $^{239,240}\text{Pu}$ data. The analytical results may also reflect spatial variations in erosion of contaminants originally deposited on the surface (whether from global fallout or airborne from more local sources within the MDAs), an effect that would not be seen in samples of native, relatively homogeneous material.

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APPENDIX. STATISTICAL METHODS

Box plots. A single box plot provides a quick visual summary of the distribution of a set of values, indicating its symmetry or skewness and whether it is tightly clustered around its central value or has long tails at one or both ends. The central rectangle (or "box") covers the middle 50% of the distribution (see Fig. A-1). Within this middle 50%, the location of the median or 50th percentile is indicated by a line drawn across the box. For a symmetric distribution, this line would fall midway between the ends of the box; when the line falls closer to one end than the other, this indicates that the distribution is skewed. "Whiskers" are drawn from each end of the box extending to the largest and smallest values in the data set that do not lie at a distance of more than 1.5 times the interquartile range from the 75th or 25th percentile, respectively. Values beyond these extremes appear as outliers relative to the bulk of the data and are plotted individually.

Because a box plot is essentially a one-dimensional plot, two or more of them can be presented on one page, as in Figure A-1 and in Section 4 of this report, permitting quick visual comparisons of two or more distributions.

Comparison of populations. To go beyond such visual comparisons, there are numerous statistical tests designed to compare two distributions. The best-known of these "two-sample tests" is the Student's t-test, but this test is based on the assumption that the data sets being compared are drawn from normal distributions (in particular, are symmetric and without exceptionally long tails or

Fig. A-1. Schematic components of box plots (arbitrary units).

outliers), although in fact the test is remarkably robust to departures from these assumptions. A nonparametric alternative (that is, an alternative that does not require parametric assumptions such as normality) is the Wilcoxon test, which uses the ranked data. (A ranked data set is one in which the n actual observations have been replaced by their ranks from 1 to n , with some suitable convention for handling ties. By reducing a data set to a set of ranks, the influence of outliers, skewness, and other departures from normality is greatly reduced.) Both the t -test and the Wilcoxon test are discussed by Gilbert (1987, Chapter 18).

When, as is frequently the case for environmental data, some of the data are "censored" or reported as below a detection level, and when moreover not all of these detection levels are identical, then the Gehan modification to the Wilcoxon test is useful. This procedure for ranking below-detection-level observations together with measured values so that the standard Wilcoxon test can be applied is discussed in detail by Gehan (1965) and Gilbert and Simpson (1990). It was used extensively in Section 4 of this report to accommodate the various types of distributions present in the data.

It is generally true that nonparametric tests are less "powerful" than parametric tests when applied to

data sets for which the parametric assumptions in fact hold. This means that they are less likely to detect a significant difference if one exists. However, as shown in Section 4, they identified many statistically significant differences among the data analyzed in this report, so clearly this is not a problem in the present application.

REFERENCES FOR APPENDIX

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- Gilbert, R. O., 1987, *Statistical Methods for Environmental Pollution Monitoring*: Van Nostrand Reinhold, New York, 320 pp.
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