

ornl

ORNL/TM-12897

**OAK RIDGE
NATIONAL
LABORATORY**

MARTIN MARIETTA

RECEIVED

OCT 16 1995

OSTI

**Inorganic Soil and Groundwater
Chemistry Near Paducah Gaseous
Diffusion Plant, Paducah, Kentucky**

G. K. Moore

Environmental Sciences Division
Publication No. 4365

**MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY**



This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Environmental Sciences Division

INORGANIC SOIL AND GROUNDWATER CHEMISTRY NEAR
PADUCAH GASEOUS DIFFUSION PLANT,
PADUCAH, KENTUCKY

G. K. Moore¹

¹The University of Tennessee, Knoxville

Environmental Sciences Division
Publication No. 4365

Date Published: March 1995

Prepared for
Martin Marietta Energy Systems
Groundwater Program
Paducah Gaseous Diffusion Plant

Prepared by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6035
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR214000

This page left intentionally blank.

9372AM

CONTENTS

	<u>Page</u>
LIST OF FIGURES	v
LIST OF TABLES	vi
ACRONYMS AND INITIALISMS	vii
EXECUTIVE SUMMARY	ix
1.0 INTRODUCTION	1
2.0 PREVIOUS REPORTS	2
3.0 METHODS.	4
4.0 GENERAL CHEMICAL CHARACTERISTICS OF SOILS	6
5.0 GENERAL CHEMICAL CHARACTERISTICS OF GROUNDWATER	10
6.0 GENERAL RELATIONSHIPS OF SOIL AND GROUNDWATER CHEMISTRY	18
7.0 DATA ACCURACY AND PRECISION	21
8.0 ELEMENT CONCENTRATIONS	24
8.1 Aluminum	24
8.2 Antimony	26
8.3 Arsenic.	26
8.4 Barium.	27
8.5 Beryllium	28
8.6 Bicarbonate	28
8.7 Cadmium	29
8.8 Calcium	30
8.9 Chloride	30
8.10 Chromium	31
8.11 Cobalt	31
8.12 Copper	32
8.13 Cyanide.	33
8.14 Iron.	33
8.15 Lead	34
8.16 Magnesium.	34

	<u>Page</u>
8.17 Manganese	35
8.18 Mercury	35
8.19 Nickel	36
8.20 Nitrate	37
8.21 Potassium.	38
8.22 Selenium	38
8.23 Silver	39
8.24 Sodium	39
8.25 Sulfate	40
8.26 Thallium	40
8.27 Vanadium	41
8.28 Zinc.	41
9.0 CONCLUSIONS.	42
10.0 REFERENCES	45
APPENDIX A CUMULATIVE PROBABILITY PLOTS AND STATISTICAL TABLES FOR SOILS AND GROUNDWATER ANALYSES	A-1
APPENDIX B EVALUATION OF PHASE I AND II DATA FOR ADEQUACY FOR DETERMINATION OF BACKGROUND CONCENTRATIONS OF PESTICIDES AND POLYNUCLEAR AROMATIC HYDROCARBONS	B-1
APPENDIX C RADIONUCLIDE DATA OF BACKGROUND AND CONTAMINATED SOILS AT PADUCAH GASEOUS DIFFUSION PLANT..	C-1

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1 Cumulative probability graphs for specific conductance of groundwater near PGDP	16
2 Cumulative probability graph showing two statistical populations for aluminum in water samples from the RGA	25

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Chemical characteristics of near-surface soils	7
2	Chemical characteristics of soil borings	8
3	Chemical characteristics of sediment samples	9
4	Comparison of metal concentrations in near-surface soils at PGDP with other U.S. soils	11
5	Chemical characteristics of water from the upper continental recharge system	12
6	Chemical characteristics of water from the regional gravel aquifer	13
7	Chemical characteristics of water from the McNairy Formation	14
8	Chemical relationships between near-surface soil and water in the regional gravel aquifer	19
9	Dilution and attenuation factors (DAF) and groundwater protection levels for soil concentrations	20
10	Accuracy checks on water analyses near PGDP	22

ACRONYMS AND INITIALISMS

DAF	dilution/attenuation factor
DOE	U.S. Department of Energy
DCE	dichloroethene
EPA	U.S. Environmental Protection Agency
MCL	maximum concentration limit
McN	McNairy Formation
MW	monitoring well
ORNL	Oak Ridge National Laboratory
PGDP	Paducah Gaseous Diffusion Plant
RGA	regional gravel aquifer
RW	residential well
TCE	trichloroethene
TVA	Tennessee Valley Authority
UCRS	upper continental recharge system
WMU	waste management unit
USGS	U.S. Geological Survey

This page left intentionally blank.

EXECUTIVE SUMMARY

The inorganic chemistry of soil (near-surface, borehole, and sediment samples) and groundwater near Paducah Gaseous Diffusion Plant (PGDP) is reinterpreted in this report because some constituents were reported to exceed background levels or maximum concentration limits (MCLs) in previous reports and because there might have been pollution at PGDP. Maximum background concentrations and anomalous data that may represent contamination of soil and water have been determined from cumulative probability graphs.

Only a few of the data for soil and sediment samples are clearly anomalous. Analytical errors are possible, and if contamination has occurred, it is localized at the surface or at shallow (<2 m) depths. Anomalously high concentrations of arsenic occur in samples from test pit 3 in the C-747-A area, soil borings H351 and H352 in waste management unit (WMU) 97, site 1 on the N-S ditch, and site 7 on Little Bayou Creek. One or more of the samples from test pit 3 also exceeds the groundwater protection levels for cadmium, chromium, copper, lead, and nickel; the surface sample from boring H210 in the C-747-C area exceeds the groundwater protection levels for lead and mercury; the near-surface sample from boring H353 in WMU 97 has a thallium concentration above the national average; and the near surface sample from boring H382 in WMU 26 exceeds the groundwater protection level for mercury. Among the sediment samples, those from WMUs 17 and 19 have concentrations that exceed the groundwater protection levels for antimony, silver, and zinc. If there are questions as to whether the relatively high concentrations at these locations represent analytical errors or whether contamination has occurred, new soil samples will be required.

A possible correlation between contaminant levels in soil and groundwater was detected at only one location. Well MW 186 in the C-747-A area contains anomalously high concentrations of arsenic and sodium; both constituents are anomalous in the samples from test pit 3 but not in samples from test pits 1 and 2. Also, other contaminants in test pit 3 occur only at background levels in the water from MW 186. Thus, even this correlation might be coincidental.

There are no detectable contaminant plumes for inorganic constituents of the groundwater samples near PGDP. Also, the concentrations of these constituents within the trichloroethene (TCE) and technetium-99 (⁹⁹Tc) plumes are not higher than elsewhere in the area. Nevertheless, low levels of nitrate contamination have apparently occurred at a few isolated locations, and contamination at seven wells is possible for antimony, chloride, chromium, lead, nickel, sulfate, or zinc. Some water samples exceed MCLs for mercury and thallium, but both contents are probably natural, and mercury occurs in the metallic form, not the methyl form, in groundwater near PGDP. Some of the anomalously high concentrations are probably erroneous, and new samples will be needed if there is a question as to whether or not groundwater contamination has occurred.

The interpretations of inorganic water chemistry in previous reports were based mostly on data from unfiltered water samples. The smaller concentrations of nearly all constituents in the filtered samples show that the unfiltered samples are mixtures of water and soil particles. Except for colloids, these particles are immobile in the regional gravel aquifer (RGA) and in the McNairy Formation (McN). Comparisons of aluminum, barium, and chromium contents in the filtered samples show that colloid concentrations are highest in the upper continental recharge system (UCRS) and that little colloidal transport occurs in the RGA and in the McN. Future water samples should be collected without disturbing particles in the aquifer and in the wells, especially if the samples are unfiltered and are acidified for preservation. Well purging and sampling rates of <100 mL/min may be necessary for this purpose.

1.0 INTRODUCTION

Near-surface soils, boreholes, and sediments near the Paducah Gaseous Diffusion Plant (PGDP) were sampled in 1989-91 as were monitoring wells, TVA wells, and privately-owned wells. Most wells were sampled two or three times. The resulting chemical analyses have been published in previous reports and have been previously described (CH2M HILL 1991, 1992; Clausen et al. 1992). The two reports by CH2M HILL are controversial, however, because, the concentrations of some constituents were reported to exceed background levels or drinking water standards and because both on-site (within the perimeter fence at PGDP) and off-site pollution was reported to have occurred. The groundwater samples upon which these interpretations were based may not be representative, however. The CH2M HILL findings are discussed in the next section of the present report.

The purpose of this report is to characterize the inorganic chemistry of groundwater and soils near PGDP, using data from the CH2M HILL reports (1991, 1992), and to determine whether or not any contamination has occurred. The scope is limited to analysis and interpretation of data in the CH2M HILL reports because previous interpretations of these data may not be valid, because samples were collected in a relatively short period of time at several hundred locations, and because the chemical analyses are nearly complete. Recent water samples from the same wells were not considered because the characterization of inorganic chemistry for groundwater and soil requires only one representative sample and an accurate analysis from each location.

To facilitate use of this document in further determination of background soil concentrations, evaluation of organic soil chemistry and radionuclide data was conducted by others at ORNL as collateral efforts. Summary reports on those evaluations are included as Appendices B and C.

The objectives of the present study are (1) analyze and interpret the groundwater and soil chemistry data for inorganic constituents in the PGDP area; (2) test the precision and accuracy of these data; (3) determine means, ranges, maximum background concentrations, and any anomalous concentrations; (4) compare soil concentrations near PGDP with other U.S. soils; (5) determine solubility limits for groundwater, where possible, and whether or not the samples are representative of the flow system; (6) detect and document anomalies that may indicate contamination or the need for additional samples; (7) determine the relationship between soil and groundwater concentrations, including dilution and attenuation factors along groundwater flow paths; (8) calculate groundwater-protection concentration levels for soils; and (9) evaluate the relationships of the data to the conceptual model of groundwater occurrence and flow.

The interpretation of groundwater chemistry in the present report uses data from filtered water samples because the well-purging and sampling procedures apparently caused turbulent flows and incorporated particulates from the zones around the well screens. As a result, the unfiltered groundwater samples typically contain much higher concentrations of most constituents than the filtered samples; the unfiltered samples represent mixtures of water and soil. Linear groundwater

velocity in the RGA is ~0.3-0.7 m/d, and, except for colloids, particles are immobile. Even the filtered groundwater samples may not be completely representative of the flow system because, as is discussed later, concentrations of some constituents apparently exceed solubility limits in some filtered samples. These samples probably contain colloids. Some colloids can pass a 0.45 μm filter pad, and sorbed ions can then be dissolved or stripped from clay, iron, and manganese particles by acidification of the sample. Colloids rarely constitute more than 1-2 mg/L in a sample but can produce anomalously large contents of metals that otherwise have a concentration of <1 mg/L.

2.0 PREVIOUS REPORTS

The chemical analyses for soil and sediment samples collected in 1989-90 are shown in CH2M HILL (1991). These data were not interpreted, but maximum values for a few off-site samples were apparently used for risk analysis because statements were made that for "ingestion of soil, fish, deer, and crops; arsenic was primarily responsible for the 1×10^{-5} to 1×10^{-4} excessive lifetime cancer risk" and that inorganic constituents, primarily manganese, mercury, cadmium, and chromium were responsible for the high hazard indexes for the ingestion of fish and crops (p. 6-46). However, the data used for the risk analysis were not shown to be higher than the natural background concentrations.

The chemical analyses for soil and sediment samples collected from late 1990 to the middle of 1991 are shown in CH2M HILL (1992). Soil and sediment samples from most WMUs were reported to contain metals in concentrations higher than the reference values (CH2M HILL 1992, pp. 4-33 to 4-209), and at a few locations, these results are interpreted as contamination by PGDP. Thus, for example, "arsenic, beryllium, lead, and nickel have been found off site in groundwater and at this source [WMU 91] in groundwater, but no plume of migration linking transport from this source to off-site wells is apparent" (p. 4-48); "mercury contamination was found in all three soil samples from MW 163 [WMU 99]" (p. 4-55); "the contaminants of concern . . . at WMUs 7 and 30 are . . . arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, lead, nickel, vanadium, and zinc" (p. 4-78); "the contaminants of concern [in WMU 15] are chromium, copper, and zinc" (p. 4-86); "metals appear to be migrating out of . . . and directly contaminating the shallow groundwater system at WMUs 2, 3, and 30, . . . [but] lateral migration of metals within the shallow groundwater system is not indicated by the data" (p. 5-37); and "contaminants detected in surface water and sediment include . . . chromium, copper, nickel, selenium, and zinc" (p. 5-41). Also, metals (chromium, copper, nickel, and zinc) are listed as contaminants in surface soils at the C-747-A burial ground and burn area and in sediments (chromium and beryllium) at the C-616-E, sludge lagoon and C-616-F, full flow lagoon (CH2M HILL 1992, Table 5-3). These results are reinterpreted, statistically, in the present report.

The chemical analyses for groundwater samples collected in 1989-90 were described by CH2M HILL (1991), wherein arsenic is listed as an inorganic contaminant (Table 4-15), and the detection of arsenic, barium, cadmium, chromium, lead, selenium, silver, and zinc in concentrations that

exceed the MCLs (maximum concentration limits) for drinking water in a few wells is discussed (pp. 4-33, 4-34, 5-19). Concentrations above the MCLs were found mostly in unfiltered samples.

These and later data were reevaluated in CH2M HILL (1992), wherein relatively high concentrations of some constituents were interpreted as contamination. "Arsenic, beryllium, lead, nickel and zinc were detected in groundwater above regulatory limits (if limits were defined) and appear to be migrating off-site", and "other metals, including antimony, barium, chromium, silver, and vanadium were not detected above regulatory limits, did not appear to be migrating off-site, or had an undetermined source other than the PGDP" (p. 4-92).

Similar statements were made in other sections of this report (CH2M HILL 1992): "arsenic, beryllium, lead, nickel, and zinc may have on-site sources and may be migrating into groundwater [in the UCRS]" (p. 4-97); "contamination detected in groundwater for the RGA consisted primarily of TCE, ⁹⁹Tc, and several metals" (p. 4-101); "the nine inorganics and metals that are of interest at the PGDP and that are indicative of contamination were detected in the unfiltered or total fraction samples in 43 wells at concentrations above one or more regulatory criteria" (p. 4-113); "typically the metals show a random distribution [in the RGA] except near WMUs that are burial grounds, landfills, or scrap yards" (p. 4-123); and "metals appear to be . . . contaminating the groundwater system at WMUs 2, 3, and 30" (p. 5-31).

The authors of the two CH2M HILL reports (1991, 1992) apparently assumed that concentrations above the MCLs in groundwater are proof of contamination. However, many natural constituents in groundwater have concentrations that exceed MCLs in some areas of the United States. The two CH2M HILL reports do not explain the term "contamination" in reference to metals contents, and reasons are not given for the conclusion that contamination has occurred. Also, contaminant plumes for metals were not detected, and metals contents within contaminant plumes for TCE and ⁹⁹Tc were not shown to be any higher than elsewhere in the PGDP area. Instead, one statement was made that "the wide distribution of the metals and their presence in the unfiltered samples suggest that they arise from an equilibrium with the aquifer matrix" (CH2M HILL 1992, p. 5-19). All references to metals contamination in these reports must be assumed to be unreliable.

The distribution of major ions in groundwater near PGDP is shown on a trilinear diagram and is discussed in Clausen et al. (1992). This report and the two reports by CH2M HILL (1991, 1992) also describe groundwater contamination by TCE, ⁹⁹Tc, and other possible organic and radioactive constituents, which are beyond the scope of the present report. In earlier reports, the concentrations of major ions in groundwater from privately-owned wells near PGDP were shown in Davis et al. (1973), and analyses of water from the wells of Tennessee Valley Authority (TVA) near Shawnee Steam Plant were shown in Lindquist and Bohac (1989).

3.0 METHODS

Chemical constituents in water and soils near PGDP have a wide range in concentration; the ratio (maximum value):(minimum value) has a range of <8 to >1000, but is ~100 for most elements. Cumulative probability graphs were used for analysis of the chemical data because samples from background locations have these large ranges in concentration and because several types of information can be obtained from the graphs, as described below. Probability graphs have been long used and generally accepted for mineral exploration, where data may consist of many samples with relatively low background concentrations and a few samples with relatively high concentrations near ore deposits; the same mixture of background and anomalous data should occur where there is local contamination of water or soil. Early descriptions of the methods were those by Goodrich (1927), Otto (1939), Tennant and White (1959) and Lepeltier (1969). The construction and interpretation of these graphs are fully described by Sinclair (1976).

More recently, Gilbert (1987, pp. 135, 168-69) and Fleischhauer and Korte (1990) describe the application of cumulative probability graphs to data that may include contaminated soils or water; the graphs are now commonly used for this purpose. Currently, for example, cumulative probability graphs are being used to determine maximum background concentrations and to identify anomalously high concentrations in water and soils at the Lawrence Livermore National Laboratory (Carlson 1994), the Department of Energy (DOE) Hanford Site (Petersen 1994), the DOE Oak Ridge Reservation (Winters 1994), and the Sandia National Laboratory (Myers 1994). Also, cumulative probability graphs are a part of the GEO-EAS statistical software program (EPA 1991).

As described by Sinclair (1976), the construction of a cumulative probability graph consists of plotting sorted (usually lowest to highest) data values on cumulative probability paper; the data are those that would be used for a cumulative histogram. The percentiles or probabilities are generally calculated as

$$100(n)/(N+1) ,$$

where n is the rank and N is the total number of data values. The addition of one to the total permits plotting the highest concentration, has little effect on the other data or the results, and is a standard procedure in other statistical analyses. If a straight line can be fitted to the data points, this line defines the cumulative density distribution of the population.

A Gaussian distribution plots as a straight line on arithmetic probability paper. A lognormal population plots as a straight line on logarithmic probability paper or on arithmetic probability paper after a log transformation of the data. The 50th percentile value of the line represents the arithmetic mean of a normal population or the geometric mean of a lognormal population. Similarly, values for the mean minus or plus one and two standard deviations can be read from the 5th, 16th, 84th, and 95th percentile values of the line. If the data have been log transformed before plotting, however, the values along the line must be calculated as e^x , where x is the value from the line.

All of the log-transformed inorganic chemistry data for groundwater and soils near PGDP plot as a single straight line or as two or more intersecting lines on cumulative probability paper (Figs. 1 and 2 and Appendix); all data are thus shown to be approximately lognormally distributed. If the data were not lognormally distributed, the plots would be curvilinear. As stated by Sinclair (1976, p. 12), "many geoscience variables . . . have density distributions that are closely approximated by the lognormal law." The close approach of minor elements in geochemistry to a lognormal distribution may have been first discussed by Shaw (1961).

If each sample set were a perfect representation of a single population, all data would plot on one line, but graphs of the PGDP data have some data scatter; some graphs are irregular; and some graphs show anomalous values or two or more intersecting lines. Irregularities and scatter in the graphs are more common with a small sample size but are also produced by censored data (values below detection limits), analytical quantification limits (multiple samples with the same low concentration), and analytical errors. Anomalous points, which plot above the population line at the top of the range, can be caused by different concentrations of natural minerals in source areas, analytical errors, and contamination. Data near the center of the range generally produce a smoother plot and better define the line that represents the population than do data near the top and bottom of the range, where departures from the lognormal distribution would be likely to occur. There are several reasons for multiple populations, as discussed below.

Groundwater and soils chemistry data for PGDP were not separated into contaminated and background locations. Instead, an assumption was made that nearly all samples would contain background concentrations of most or all constituents, and this proved to be the case. As a result, some sample values plot above the population line, which represents background concentrations, at the top of the range. In a few cases, these points define a second intersecting line which has a steeper slope. In most cases, however, the anomalous points constitute <5% of the data and have irregular plotted positions above the line for background concentrations.

If the data are adequately described by lognormal models, changes in the slope of the data points on a cumulative probability graph represent different populations; this seems to be the case for data near PGDP. The lines may intersect at a point or at an "s" curve depending on various factors, including the relative proportions of each population, the differences in standard deviation, and the amount of overlap in the ranges. The separation of any two populations on a cumulative probability graph is generally assumed to occur at the intersection of the two lines on the graph or at the inflection point of the connecting "s" curve. Fleischhauer and Korte (1990, pp. 100-101) used skewness tests for data near the intersections to show that this assumption is approximately correct for several data sets from a contaminated site.

Concentration differences between groundwater samples that contain only solutes and those that also contain colloidal particles apparently produce two populations on some graphs. On other graphs for both groundwater and soil samples, there may be two populations because of differences in the concentration of natural minerals in source areas. Clay commonly has higher concentrations of most minerals than sand or gravel, although iron and manganese contents may be higher in sand. Also,

loess and other fine-grained sediments in some near-surface locations at PGDP may not have been leached before deposition. Neither of these two interpretations is certain, and other changes in the slope of a graph may occur near the bottom of the concentration range. Some of the irregularities on the cumulative probability graphs cannot be explained, and no interpretation is inherently unique. Nevertheless, all groundwater and soils data below ~90th percentile on the graphs include background locations, and there is thus good reason to believe that the statistical populations below this level represent background concentrations.

For purposes of the present report, the maximum background concentration for soils and for most constituents in groundwater is assumed to be the highest value that falls on or only slightly above the population line near the upper right corner of the graph. For some groundwater constituents, a lower background limit was selected because points near the top of the graph exceed the solubility limit or because the highest concentrations in multiple samples from the same wells are probably erroneous, as is discussed later. Data points above the line in the upper right corner of the graph are anomalous and are discussed in the text. These criteria should produce more accurate results than an assumption that the maximum background concentration is the 95% confidence interval of the mean and more realistic results than an assumption that the maximum background concentration is twice the mean. The 95th percentile concentrations for soil and water samples are presented in the tables of this report for reference.

The CH2M HILL data contain analytical errors, as are discussed in Section 7.0, and an anomalously high concentration of any constituent in a soil or groundwater sample does not necessarily indicate contamination. The anomaly is suspect if it was obtained from a location where contamination is possible. The evidence for contamination is stronger if a sample contains anomalously high concentrations of at least two constituents and if other samples from the same or nearby locations contain concentrations above the background range. A pattern of high values in the shape of a contaminant plume or relatively high concentrations for a constituent within the contaminant plume for another chemical are generally considered to be conclusive evidence for groundwater pollution. However, the inorganic constituents of groundwater in the PGDP area do not show patterns of high concentration. Multiple laboratory errors are possible, and all conclusions about soils and groundwater contamination in this report are preliminary: contamination can only be confirmed by resampling.

4.0 GENERAL CHEMICAL CHARACTERISTICS OF SOILS

The CH2M HILL (1991, 1992) data include samples from surface and near-surface (<2 m) soils, soil borings at deeper levels, and sediments from on-site impoundments. The concentrations of all inorganic chemicals in soils near PGDP are lognormally distributed, and the statistical characteristics of these data are shown in Tables 1, 2, and 3. The maximum values that are flagged as anomalous represent either analytical errors or contamination by metals at a few on-site locations; all remaining data show the distribution of natural, background concentrations.

Table 1. Chemical characteristics of near-surface soils

Constituent	Number of values	Statistical Characteristics ^a						
		Minimum	5 th per-centile	Mean minus one standard deviation	Geometric mean	Mean plus one standard deviation	95 th per-centile	Maximum
Aluminum (mg/kg)	146	1120	4270	5540	8020	11700	15100	43100 ^b
Antimony (mg/kg)	146	0.32	0.45	0.92	2.7	8.2	16	45
Arsenic (mg/kg)	146	0.24	2.2	3.1	5.5	9.2	13	46 ^b
Barium (mg/kg)	146	14	33	50	95	178	268	657 ^b
Beryllium (mg/kg)	146	0.17	0.34	0.44	0.65	11	19	25
Cadmium (mg/kg)	146	0.25	0.05	0.15	0.70	3.3	9.2	235 ^b
Calcium (mg/kg)	146	235	473	1010	3200	44000	109000	293000
Chromium (mg/kg)	146	2.6	5.6	8.3	15	28	40	505 ^b
Cobalt (mg/kg)	146	1.2	2.6	4.2	8.8	19	30	69
Copper (mg/kg)	146	2.5	3.9	6.2	13	27	153	18700 ^b
Iron (mg/kg)	146	3500	6900	9410	14800	23600	31900	97600 ^b
Lead (mg/kg)	146	1.6	5.8	8.8	17	33	150	1160 ^b
Magnesium (mg/kg)	146	257	446	721	1560	3230	5270	12600
Manganese (mg/kg)	146	25	125	196	416	863	1350	8090
Mercury (mg/kg)	146	0.04	0.06	0.10	0.11	0.12	0.33	12 ^b
Nickel (mg/kg)	146	2.8	5.0	7.6	15	29	95	12300 ^b
Potassium (mg/kg)	146	110	213	295	498	820	1150	25000 ^b
Selenium (mg/kg)	146	0.11	0.08	0.15	0.27	0.73	1.2	25 ^b
Silver (mg/kg)	146	0.36	0.55	0.82	1.6	2.9	4.3	42 ^b
Sodium (mg/kg)	146	24	31	48	101	213	344	8170 ^b
Thallium (mg/kg)	146							13
Vanadium (mg/kg)	146	2.3	11	15	22	32	40	70
Zinc (mg/kg)	146	12	16	24	44	79	270	1130

^a Statistical characteristics are calculated from the population and may be smaller than the minimum value or larger than the maximum value.

^b Anomalous value that may be erroneous.

Table 2. Chemical characteristics of soil borings

Constituent	Number of values	Statistical Characteristics ^a						
		Minimum	5 th per-centile	Mean minus one standard deviation	Geometric mean	Mean plus one standard deviation	95 th per-centile	Maximum
Aluminum (mg/kg)	597	159	685	1590	4820	7630	14500	18200
Antimony (mg/kg)	597	1.5	2.1	2.9	5.1	8.8	12	21
Arsenic (mg/kg)	597	0.16	0.53	0.88	1.8	3.9	6.3	19
Barium (mg/kg)	597	2.0	8.2	15	35	84	148	341
Beryllium (mg/kg)	597	0.005 ^b	0.22	0.31	0.52	0.87	1.2	2.6
Cadmium (mg/kg)	597	0.13	0.30	0.45	0.84	1.6	2.4	13 ^b
Calcium (mg/kg)	597	1.7 ^b	158	395	871	1720	2640	27200 ^b
Chromium (mg/kg)	597	0.48	0.74	3.2	9.5	23	41	161
Cobalt (mg/kg)	597	0.58	1.1	1.8	4.1	9.0	15	48
Copper (mg/kg)	597	0.64	1.3	2.4	5.6	13	24	62
Iron (mg/kg)	597	545	2700	5270	11700	19500	26100	47400
Lead (mg/kg)	597	0.48	1.2	2.3	6.0	16	29	133
Magnesium (mg/kg)	597	17	67	172	503	1240	2160	3250
Manganese (mg/kg)	597	1.7	14	29	94	233	640	2920
Mercury (mg/kg)	597	0.01	0.03	0.055	0.091	0.17	0.27	1.1 ^b
Nickel (mg/kg)	597	0.84	1.9	3.1	6.2	13	20	122 ^b
Potassium (mg/kg)	597	36	88	137	270	528	837	3290 ^b
Selenium (mg/kg)	597	0.086	0.085	0.14	0.28	0.58	0.92	3.8
Silver (mg/kg)	597	0.28	0.42	0.61	1.1	1.8	2.7	14 ^b
Sodium (mg/kg)	597	3.1 ^b	44	68	134	270	416	882
Vanadium (mg/kg)	597	0.71 ^b	5.8	8.3	16	28	43	69
Zinc (mg/kg)	597	0.83	4.0	7.1	18	44	77	190

^a Statistical characteristics are calculated from the population and may be smaller than the minimum value or larger than the maximum value.

^b Anomalous value that may be erroneous.

Table 3. Chemical characteristics of sediment samples

Constituent	Number of values	Geometric mean	EMV ^a for near-surface soils	Maximum
Aluminum (mg/kg)	59	7350	15100	17500
Antimony (mg/kg)	59	0.42	16	425 ^b
Arsenic (mg/kg)	59	5.6	13	34 ^b
Barium (mg/kg)	59	84	268	922 ^b
Beryllium (mg/kg)	59	5.4	19	29
Cadmium (mg/kg)	59	1.2	9.2	7.2
Calcium (mg/kg)	59	1350	109000	47400
Chromium (mg/kg)	59	20	40	22100 ^b
Cobalt (mg/kg)	59	7.0	30	62
Copper (mg/kg)	59	12	153	335 ^b
Iron (mg/kg)	59	15200	31900	132000 ^b
Lead (mg/kg)	59	13	150	36
Magnesium (mg/kg)	59	1040	5270	4460
Manganese (mg/kg)	59	365	1350	4150 ^b
Mercury (mg/kg)	59	0.1	0.33	1.3
Nickel (mg/kg)	59	13	95	220 ^b
Potassium (mg/kg)	59	492	1150	1910
Selenium (mg/kg)	59	0.22	1.2	6.4 ^b
Silver (mg/kg)	59	1.4	4.3	79 ^b
Sodium (mg/kg)	59	60	344	1770 ^b
Vanadium (mg/kg)	59	24	40	81 ^b
Zinc (mg/kg)	59	47	270	4170 ^b

^a Expected maximum value; geometric mean plus two standard deviations.

^b Anomalous value that might be erroneous.

The principal constituent in the soils near PGDP is silica, but silica was not reported and must be estimated from the concentrations of other constituents. The borehole samples are ~54 to 64% silica, as are approximately 80% of the near-surface samples. Most of the near-surface soils with a silica content of only 14–53% have a calcium content of >100,000 mg/kg; these samples were apparently obtained from loess, which is partly cemented by calcite, or from unleached, fine-grained soils that contain gypsum. The other major constituents, which have average concentrations of ~100–15,000 mg/kg, are aluminum, calcium, iron, magnesium, manganese, potassium, and sodium (Table 1). The minor constituents, which generally occur in average concentrations of 10–100 mg/kg are barium, chromium, copper, lead, nickel, vanadium, and zinc. The elements that have average concentrations of ~1–10 mg/kg are antimony, arsenic, cobalt, and silver. The trace elements, which generally occur in amounts of <1.0 mg/kg, are beryllium, cadmium, mercury, and selenium.

The concentrations of metals in near-surface soils at PGDP are compared with other U.S. soils in Table 4. The 5–95% probability range was used for the PGDP soils to avoid anomalous values that might not be representative of background concentrations. The concentration ranges at PGDP are approximately the same as the national averages, and only the highest values for antimony and cadmium exceed the common range for other soils. In both cases, the geometric mean concentrations in PGDP soils are close to the national average; apparently the standard deviation for concentrations of antimony and cadmium in PGDP soils are somewhat larger than the national average.

The geometric mean concentrations of all constituents are approximately the same in near-surface soils and in soil borings. However, the 95th percentile or maximum concentrations are more than twice as high in near-surface soils as in soil borings for all elements but vanadium. The source of the high concentrations apparently is loess or other fine-grained soils that have not been leached by percolating waters. If so, an unusually large concentration of any constituent in groundwater may indicate the occurrence of relatively unweathered soils at the surface.

The geometric mean concentrations of constituents in sediment samples (Table 3) near PGDP are approximately the same as those in near-surface soils. However, the maximum concentrations of antimony and chromium in sediment greatly exceed the maximum values for near-surface soils, and the maximum concentrations of barium, iron, manganese, silver, and zinc in sediment samples moderately exceed the near-surface values. As discussed in Section 8, these anomalies may represent contamination.

5.0 GENERAL CHEMICAL CHARACTERISTICS OF GROUNDWATER

The CH2M HILL (1991, 1992) data for groundwater include samples from the upper continental recharge system (UCRS), the regional gravel aquifer (RGA) and the McNairy Formation (McN). The concentrations of all inorganic constituents are lognormally distributed, and the statistical characteristics of these data are shown in Tables 5, 6, and 7. The maximum values that

Table 4. Comparison of metal concentrations in near-surface soils at PGDP with other U.S. soils. (Concentrations in mg/Kg).

		Other soils in United States	
		Near-surface soils at PGDP (5-95% range)	Kabata-Pendias and Pendias 1984 ^a
		Lindsay 1979	
Aluminum	4300-15000	10000-300000	0.05-4
Antimony	0.4-16		2-22
Arsenic	2-13	1-50	200-1500
Barium	33-270	100-3000	1-3
Beryllium	0.3-19	0.1-40	0.4-1.5
Cadmium	0.05-9	0.01-0.7	10-100
Chromium	6-40	1-100	3-30
Cobalt	3-30	1-40	5-100
Copper	4-15	2-100	10-30
Lead	5-150	2-200	50-1500
Manganese	120-1400	20-3000	0.01-0.4
Mercury	0.04-0.3	0.01-0.3	3-30
Nickel	5-95	5-500	0.02-2
Selenium	0.08-1	0.1-2	
Silver	0.6-4	0.01-5	
Vanadium	11-40	20-500	20-300
Zinc	16-170	10-300	20-110

^a Range, where given, for loess and alluvium.

Table 5. Chemical characteristics of water from the upper continental recharge system

Statistical Characteristics ^a								
Constituent or property	Number of values	Minimum	5 th percentile	Mean minus one standard deviation	Geometric mean	Mean plus one standard deviation	95 th percentile	Maximum
Aluminum (mg/L)	79	0.015	0.020	0.032	0.069	0.37	1.6	21 ^b
Antimony (µg/L)	83	7.5	8.4	12	22	38	55	54
Arsenic (µg/L)	83	0.34	0.61	1.2	3.5	10	20	330 ^b
Barium (µg/L)	83	14	27	49	120	300	520	1010
Beryllium (µg/L)	83	0.20	0.20	0.25	0.90	1.6	2.6	3.0
Bicarbonate (mg/L)	78	16	57	96	190	370	580	670
Cadmium (µg/L)	83	0.60	0.22	0.78	3.0	3.9	4.8	6.8
Calcium (mg/L)	79	7.3	7.2	13	32	81	140	210
Chloride (mg/L)	72	0 ^b	2.6	6.7	28	120	310	790
Chromium (µg/L)	83	1.3	0.90	1.6	4.1	10	18	33
Cobalt (µg/L)	83	0.69	1.5	2.5	6.0	15	25	44
Copper (µg/L)	83	0.90	0.82	1.6	4.8	13	27	99 ^b
Cyanide (µg/L)	77	0.02			5.0			20
Iron (mg/L)	78	0.0045	0.0041	0.017	0.27	3.3	16	74
Lead (µg/L)	83	0.40	0.27	0.55	1.6	4.8	9.3	18
Magnesium (mg/L)	79	0.80	2.6	4.5	11	25	42	72
Manganese (mg/L)	77	0.0003	0.0061	0.019	0.12	0.78	2.6	8.3
Mercury (µg/L)	83	0.1	0.10	0.12	0.16	0.23	0.30	0.38
Nickel (µg/L)	83	3.5	3.7	5.2	9.0	40	110	660 ^b
Nitrate (mg/L)	73	0.08	0.2	0.4	2.1	9.8	45	240 ^b
pH	72	5.3	5.7	6.0	6.5	7.0	7.7	14 ^b
Potassium (mg/L)	79	0.4	0.2	0.9	1.5	6.5	21	52
Selenium (µg/L)	83	0.5	0.39	0.67	1.5	3.7	6.2	12
Silver (µg/L)	83	1.6	1.4	2.0	3.7	6.7	9.5	64
Sodium (mg/L)	79	5.1	12	22	56	140	260	320
Specific conductance (µmhos/cm)	71	70	140	220	430	850	1340	2200
Sulfate (mg/L)	69	1.0	2.5	7.0	34	120	180	260
Thallium (µg/L)	83	0.4	0.50	0.90	2.1	5.0	8.2	7.0
Total dissolved solids (mg/L)	78	18	93	150	290	580	900	1580
Vanadium (µg/L)	83	1.0	0.58	1.2	3.9	12	25	68
Zinc (µg/L)	83	1.1	3.2	6.7	27	90	220	1100 ^b

^a Statistical characteristics are calculated from the population and may be smaller than the minimum value or larger than the maximum value.

^b Anomalous value that may be erroneous.

Table 6. Chemical characteristics of water from the regional gravel aquifer

Statistical Characteristics ^a								
Constituent or property	Number of values	Minimum	5 th percentile	Mean minus one standard deviation	Geometric mean	Mean plus one standard deviation	95 th percentile	Maximum
Aluminum (mg/L)	232	0.014	0.015	0.022	0.037	0.27	1.3	66 ^b
Antimony (µg/L)	238	4.0	7.7	10	18	30	43	66
Arsenic (µg/L)	238	0.30	0.55	1.0	2.5	6.0	11	15
Barium (µg/L)	237	6.3	37	56	120	240	380	630
Beryllium (µg/L)	237	0.04	0.12	0.20	0.82	2.2	3.0	4.4
Bicarbonate (mg/L)	189	1.0	31	80	120	180	240	350
Calcium (mg/L)	232	8.4	13	17	25	38	86	200
Cadmium (µg/L)	236	0.6	0.17	0.45	3.0	3.6	4.1	4.6
Chloride (mg/L)	183	0	5.9	11	26	65	110	250
Chromium (µg/L)	237	1.3	1.0	1.6	3.2	6.2	12	110 ^b
Cobalt (µg/L)	238	0.69	0.81	1.7	5.5	16	37	140
Copper (µg/L)	238	0.90	0.77	1.6	5.5	17	37	167 ^b
Cyanide (µg/L)	214	0.02			5.0			40 ^b
Iron (mg/L)	229	0.0006	0.0027	0.011	0.15	1.6	8.2	74
Lead (µg/L)	236	0.40	0.24	0.50	1.6	5.3	11	80 ^b
Magnesium (mg/L)	232	0.30	3.2	5.9	8.4	13	22	74
Manganese (mg/L)	230	0.0004	0.0007	0.047	0.082	1.3	8.2	9.2
Mercury (µg/L)	238	0.1	0.07	0.10	0.15	0.25	0.33	1.8 ^b
Nickel (µg/L)	237	3.5	3.3	4.5	7.0	22	49	120
Nitrate (mg/L)	183	0.05	0.2	0.5	2.4	11	31	140 ^b
pH	165	5.5	5.9	6.1	6.4	6.8	7.2	12 ^b
Potassium (mg/L)	232	0.2	0.8	1.2	2.0	5.0	14	120
Selenium (µg/L)	237	0.4	0.55	0.84	1.6	3.3	5.0	12
Silver (µg/L)	237	1.6	1.1	1.6	3.1	5.9	9.0	9.0
Sodium (mg/L)	232	1.2	11	15	31	59	88	150
Specific conductance (µmhos/cm)	167	70	140	190	280	420	550	1250
Sulfate (mg/L)	175	0.3	1.7	6.4	12	34	150	740
Thallium (µg/L)	238	0.4	0.50	0.79	1.6	3.5	5.5	50 ^b
Total dissolved solids (mg/L)	189	29	67	86	160	320	490	1300
Vanadium (µg/L)	237	1.0	0.67	1.2	3.1	7.8	15	38
Zinc (µg/L)	236	0.095	3.2	7.4	30	120	300	5090 ^b

^a Statistical characteristics are calculated from the population and may be smaller than the minimum value or larger than the maximum value.

^b Anomalous value that may be erroneous.

Table 7. Chemical characteristics of water from the McNairy Formation

Constituent or property	Number of values	Statistical Characteristics ^a						
		Minimum	5 th per-centile	Mean minus one standard deviation	Geometric mean	Mean plus one standard deviation	95 th per-centile	Maximum
Aluminum (mg/L)	14	0.015	0.017	0.019	0.024	0.18	0.70	1.9 ^b
Antimony (µg/L)	14	9.2	6.9	11	23	29	74	52
Arsenic (µg/L)	14	0.50			6.5			9.2
Barium (µg/L)	14	40	43	67	130	270	420	310
Beryllium (µg/L)	14	0.04	0.03	0.08	0.37	1.6	4.5	2.2
Bicarbonate (mg/L)	13	62	49	95	170	210	250	240
Cadmium (µg/L)	14	0.60	0.14	0.33	1.8	8.7	24	20
Calcium (mg/L)	14	6.7	7.2	11	21	40	62	49
Chloride (mg/L)	13	2.0	1.2	2.9	11	42	99	83
Chromium (µg/L)	14	1.3	1.0	1.6	3.3	7.1	11	33
Cobalt (µg/L)	14	0.69	1.6	2.7	6.7	15	25	20
Copper (µg/L)	14	0.90	1.2	2.6	8.2	25	52	42
Cyanide (µg/L)	13	3.0			3.3			9.0
Iron (mg/L)	14	0.020	0.21	0.48	2.2	9.3	24	17
Lead (µg/L)	14	0.60	0.14	0.30	1.0	3.2	7.0	5.7
Magnesium (mg/L)	14	1.3	3.5	4.9	7.8	13	17	15
Manganese (mg/L)	14	0.0012	0.061	0.12	0.37	1.1	2.2	1.2
Mercury (µg/L)	14	0.1	0.05	0.075	0.14	0.27	0.43	0.41
Nickel (µg/L)	14	3.5	2.5	4.7	11	28	49	40
Nitrate (mg/L)	13	0.05	0.03	0.07	0.30	1.0	2.2	2.3
pH	10	5.7			6.7			7.2
Potassium (mg/L)	14	3.4	2.8	4.3	8.2	16	23	101 ^b
Selenium (µg/L)	14	0.4	0.25	0.42	0.97	2.2	3.8	8.1
Silver (µg/L)	14	1.6	1.0	1.6	3.6	7.8	13	9.0
Sodium (mg/L)	14	17	15	18	24	33	40	39
Specific conduc-tance (µmhos/cm)	10	8 ^b	150	180	220	280	320	320
Sulfate (mg/L)	13	5.6	5.6	8.0	14	23	30	140 ^b
Thallium (µg/L)	14	0.4	0.20	0.38	1.1	2.9	5.6	5.0
Total dissolved solids (mg/L)	13	81	100	130	180	260	330	270
Vanadium (µg/L)	14	1.0	0.55	0.95	2.2	5.0	8.6	8.0
Zinc (µg/L)	14	2.9			80			37,400 ^b

^a Statistical characteristics are calculated from the population and may be smaller than the minimum value or larger than the maximum value.

^b Anomalous value that may be erroneous.

are flagged as anomalous represent either analytical errors or contamination; all other data in these tables represent the distribution of natural background concentrations.

Nearly all groundwater in the PGDP area is a calcium-sodium bicarbonate water type (Tables 5, 6, and 7). The remainder is a calcium-sodium sulfate or a sodium-calcium chloride water type. Typical Ca:Na ratio values range from 0.1 to 10 whereas typical Ca:Mg values range from 2 to 20. The ratio values for $\text{HCO}_3:\text{Cl}$ and $\text{HCO}_3:\text{SO}_4$ are <1.0 for only 5–8% of the samples. Sulfate and some calcium contents probably result from the solution of gypsum because, as noted by Freeze and Cherry (1979, pp. 241–243), gypsum is the usual source of sulfate in sedimentary rocks. Other calcium comes from the solution of calcite. Chloride and some sodium contents probably result from the solution of halite; Freeze and Cherry (1979, p. 244) point out that chloride minerals in sedimentary rocks are very soluble and that chloride concentrations at shallow depths are probably controlled by molecular diffusion from a fine-grained matrix. Other sodium contents result from ion exchange in the lattice of clay minerals because samples with a relatively high sodium content commonly have a relatively low calcium content.

The pH of the groundwater typically ranges from 5.3 to 7.9. Two samples of water from the RGA and two samples from the UCRS were reported to have pH values of 9.2, 10.5, 12.1, and 14.0. High pH values can be produced by contamination with cement grout, which was used in well construction, but the calcium, sodium, and potassium contents of these samples are near average, and only the sample from MW 131 has an unusually high alkalinity; the high pH values are probably erroneous. The median pH is 6.5 in the UCRS, 6.4 in the RGA, and 6.7 in the McN. There are no detectable relationships between pH and the aluminum, alkalinity, sulfate, and dissolved solids contents of the water or between pH and the Ca:Na ratio. Cumulative probability graphs of pH in the UCRS and RGA show two statistical populations. The average pH in the first population is 6.4 in the UCRS and 6.3 in the RGA; the average pH in the second population is 7.3 in the UCRS and 6.9 in the RGA. Water samples in the second population might represent a small amount of leachate from cement grout, but the aluminum contents and the Na:K ratios are normal in these samples. There is no obvious explanation for the differences in the populations.

Cumulative probability graphs show single statistical populations for both specific conductance (Fig. 1) and total dissolved solids (calculated as the sum of ion concentrations). The geometric mean of specific conductance at 25°C is 430 $\mu\text{S}/\text{cm}$ in the UCRS, 280 $\mu\text{S}/\text{cm}$ in the RGA, and 220 $\mu\text{S}/\text{cm}$ in the McN. The geometric mean of total dissolved solids is 290 mg/L in the UCRS, 160 mg/L in the RGA, and 180 mg/L in the McN. The ranges of specific conductance and total dissolved solids are also largest in the UCRS and smallest in the McN. Approximately 75% of the water samples from the UCRS, 95% of the samples from the RGA, and 100% of the samples from the McN have a dissolved solids content of <500 mg/L and thus meet the secondary drinking water standard.

The higher average specific conductance and dissolved solids content in the UCRS may occur because surficial loess in some areas contains soluble minerals. If geologic information is lacking at some locations in the PGDP area, relatively high values of specific conductance and dissolved solids in groundwater samples from the UCRS may indicate the occurrence of loess in the

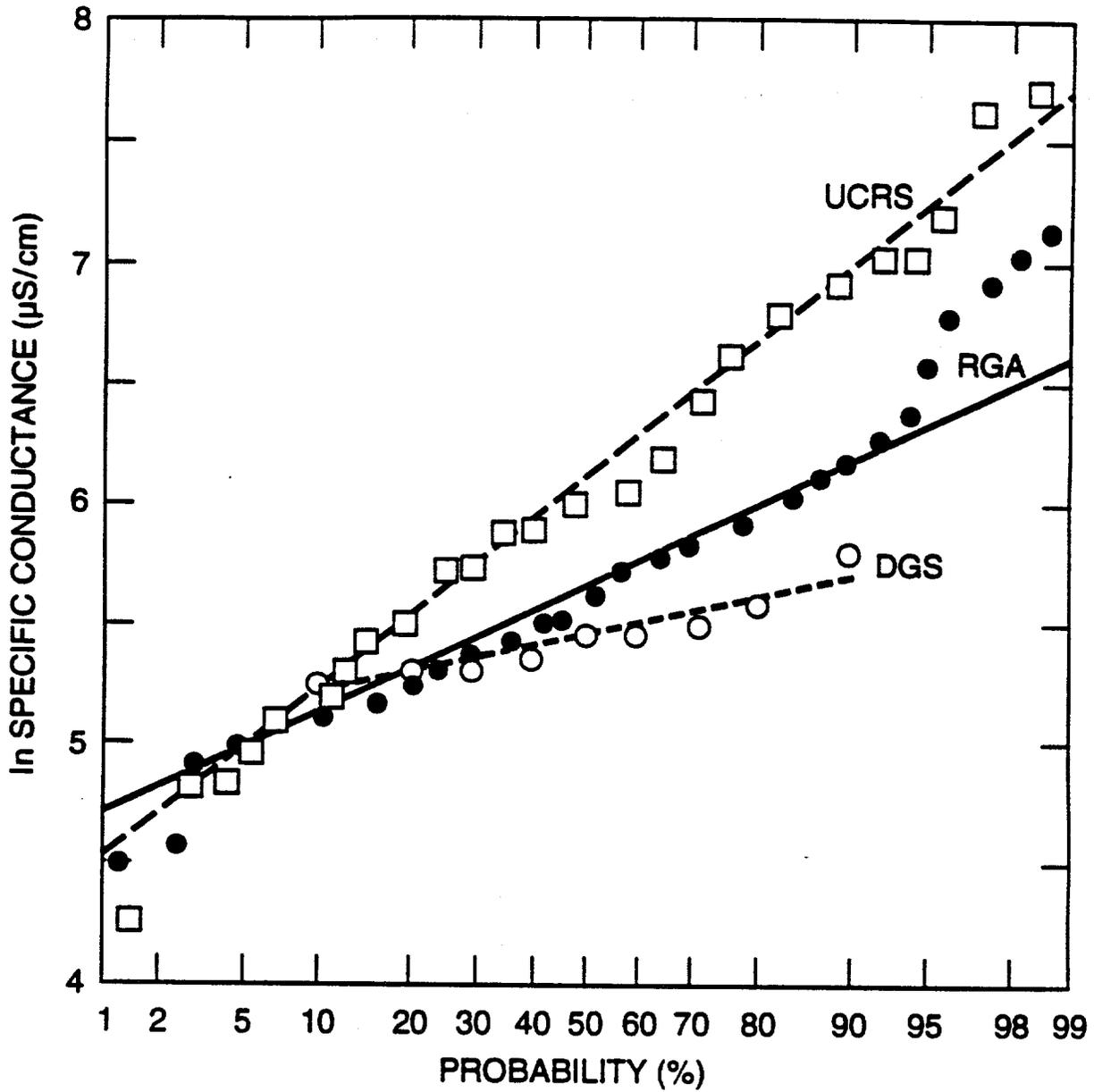


Figure 1. Cumulative probability graphs for specific conductance of groundwater near PGDP.

recharge area. Also, either unusually low or unusually high values of specific conductance and total dissolved solids in water samples from the RGA may indicate an area of downward percolation or flow from the UCRS into the RGA.

The concentrations of nearly all constituents in water samples have approximately the same ranges in the UCRS, the RGA and the McN, but the standard deviation of specific conductance is 490 $\mu\text{S}/\text{cm}$ in the UCRS, 230 $\mu\text{S}/\text{cm}$ in the RGA, and 100 $\mu\text{S}/\text{cm}$ in the McN. The decrease in the standard deviation of specific conductance with depth shows water mixing along groundwater flow paths. Thus, the source for nearly all groundwater near PGDP is recharge to the water table in the UCRS, and most solution and ion exchange apparently occur in the UCRS. A large majority of all recharge and all dissolution probably occurs on-site.

The configuration of the potentiometric surface for the McNairy Formation in western Kentucky (Clausen et al. 1992, Fig. 3.1) seems to indicate that the PGDP area is a discharge location. However, the water chemistry data indicate that groundwater locally flows from the RGA into the McN in the PGDP area, and this conclusion is supported by an interpretation of water-level fluctuations in the RGA and McN (Clausen et al. 1992, p. 15). Groundwater flows from the RGA into the McN are probably small because of the fine-grained sediments in the McN.

Dissolved oxygen was not measured for the water samples near PGDP, but the median Eh is 0.22 V, and the 10%-90% range for Eh is 0.0 to 0.34 V. These results show that most groundwater near PGDP occurs under slightly to moderately oxidizing conditions. Previously, Clausen et al. (1992, p. 74) pointed out that the occurrence and mobility of ^{99}Tc (probably as pertechnetate anions) and the low concentrations of TCE degradation products (dichloroethene and vinyl chloride) in the contaminant plumes indicate slightly oxidizing conditions. A similar conclusion can be reached from the occurrence of small to moderate amounts of nitrate and, as discussed in Section 8.17, a solubility limit of ~ 1.0 mg/L for manganese in the groundwater samples. The average dissolved oxygen content of the groundwater may be ~ 1 -3 mg/L. Recent measurements of dissolved oxygen within the screen at on-site well MW 106 were ~ 2 -4 mg/L (J. L. Clausen, PGDP, written communication, 1994).

Some of the groundwater samples were analyzed for sulfide, and $\sim 30\%$ of these samples were reported to contain 0.1-10 mg/L of sulfide. In natural waters, however, sulfide occurs only under strongly reducing conditions (sulfate reduction follows nitrate, iron, and manganese reduction). Reducing conditions are possible in local on-site areas (J. L. Clausen, PGDP, written communication, 1994), but such conditions are not shown by other CH2M HILL chemistry data. All of the sulfide concentrations are probably erroneous.

If slightly to moderately oxidizing conditions are assumed to occur in groundwater near PGDP, mercury occurs in a metallic and not a methylated form; arsenic occurs in anionic and not methylated form; and the solubility limits for iron and manganese are ~ 0.3 and 0.05-1.0 mg/L, respectively.

6.0 GENERAL RELATIONSHIPS OF SOIL AND GROUNDWATER CHEMISTRY

A comparison of geometric mean concentrations of constituents in near-surface soils and groundwater in the RGA (Table 8) shows the relative solubility of the soil minerals. Sodium, for example, is 80 times less abundant than aluminum in soils but is very soluble and has a soil:groundwater ratio of only 3. Elements with a ratio value of 130-300 include antimony, cadmium, calcium, magnesium, potassium, and selenium. The elements with a ratio value of 500-2000 are barium, beryllium, lead, mercury, silver and zinc. All other elements have a ratio value of >2000.

The concentrations of all solutes in groundwater are partly determined by the distribution and concentration of natural minerals in near-surface soils and by any additional solution along the flow paths. However, some elements, such as calcium, magnesium, and sodium, have a relatively high solubility in groundwater, whereas other constituents, such as aluminum, chromium, iron, lead, and manganese, have a relatively low solubility under the Eh-pH conditions in the PGDP area. Also, some solute concentrations are attenuated along the flow paths by dilution, by ion exchange (sodium for divalent cations), by precipitation in the presence of other constituents (sulfate for barium; chloride for silver; silica for aluminum), and by sorption and coprecipitation processes (antimony, arsenic, barium, beryllium, cadmium, cobalt, copper, lead, nickel, selenium, vanadium, and zinc), especially with iron and manganese oxyhydroxides.

Contaminants in soils may or may not have the same solubility as natural minerals, but an anomalously large soil concentration of any constituent generally produces an anomalous groundwater concentration. The groundwater concentration near the contaminant source is then attenuated along the flow path by dilution, sorption, matrix diffusion, and the same other processes that affect the natural concentrations. For these reasons, the ratios of maximum background concentrations in soil and groundwater represent the dilution and attenuation factors (DAF) that occur in the PGDP area.

The DAF can be multiplied by the MCL for drinking water to calculate the maximum soil concentration for a groundwater concentration equal to or less than the MCL and thus a soil concentration that will protect groundwater in this area (Table 9). Numbers of this type are used at many sites to determine soil cleanup levels and are commonly estimated with the Summers model (EPA 1989). The maximum soil concentrations for groundwater protection in table 9 should be much more realistic than those from the Summers model because the former represent the results of the actual physical processes for dilution and attenuation at PGDP.

The groundwater protection levels for antimony and thallium in soils (Table 9) are determined by the maximum background concentrations in groundwater because background concentrations exceed the MCLs. The background concentrations of thallium in soil and groundwater are poorly defined by the present data set, however, and the groundwater protection level is only a rough estimate. The groundwater protection level for mercury in soils is determined by the very low MCL

**Table 8. Chemical relationships of near-surface soil and water
in the regional gravel aquifer**

Constituent	Geometric mean, soil (mg/kg)	Geometric mean, water (mg/L)	Ratio ^a
Aluminum	8020	0.025	320000
Antimony	2.7	0.018	150
Arsenic	5.5	0.0025	2200
Barium	95	0.12	790
Beryllium	0.65	0.00082	790
Cadmium	0.70	0.0030	230
Calcium	3200	25	130
Chromium	15	0.0032	4700
Cobalt	8.8	0.0055	1600
Copper	13	0.0055	2400
Iron	14800	0.15	99000
Lead	17	0.0084	2000
Magnesium	1560	8.4	190
Manganese	416	0.082	5100
Mercury	0.11	0.00015	730
Nickel	15	0.0070	2100
Potassium	498	2.0	250
Selenium	0.27	0.0016	170
Silver	1.6	0.0031	520
Sodium	101	31	3
Vanadium	22	0.0031	7100
Zinc	44	0.030	1500

^a (soil concentration)/(groundwater concentration).

Table 9. Dilution and attenuation factors (DAF) and groundwater protection levels for soil concentrations

Metal	Max back-ground in soils (mg/kg)	Max back-ground in water (mg/L)	Ratio (DAF) ^a	MCL for water (mg/L)	Maximum soil concentration for groundwater protection ^b (mg/kg)
Antimony	45	0.050	900	0.005	45 ^c
Arsenic	20	0.023	900	0.05	45
Barium	360	0.15	2400	2.0	4800
Beryllium	30	0.003	10000	0.004	40
Cadmium	12	0.005	2400	0.005	12
Chromium	160	0.040	4000	0.1	400
Cobalt	70	0.010	7000		
Copper	63	0.090	700	1.3	910
Lead	130	0.015	8700	0.015	130
Mercury	2.5	0.0002	12000	0.00002	2.5 ^c
Nickel	100	0.009	11000	0.10	1100
Selenium	4.0	0.001	4000	0.05	200
Silver	10	0.010	1000	0.050	50
Sodium	900	200	4.5		
Thallium	2.8	0.012	230	0.002	2.8 ^c
Vanadium	70	0.010	7000		
Zinc	190	0.6	320	5.0	1600

^a (Maximum soil concentration) / (Maximum groundwater concentration)

^b (Ratio) x (MCL), except as indicated.

^c Derived from the maximum background concentrations for soil and groundwater.

for methyl mercury even though mercury occurs in metallic form near PGDP. Whether or not the groundwater protection levels for soil constituents will be applicable for remedial actions at PGDP will need to be negotiated with the regulators.

7.0 DATA ACCURACY AND PRECISION

The accuracy of the soils chemistry data near PGDP can only be checked by comparing the analyses of duplicate samples. For the purposes of this report, duplicate samples in which the Table 9 Dilution and attenuation factors (DAF) and groundwater protection levels for soil concentrations higher concentration is within 20% of the lower concentration can be classed as good; differences of 21-100% can be classed as fair; and differences of >100% can be classed as poor. The best results were those for aluminum, barium, beryllium, calcium, magnesium, sodium, and vanadium because >50% of the comparisons are in the good class, and <10% are in the poor class. The analyses for chromium, iron, nickel, and zinc were only slightly less accurate because >40% of the comparisons are in the good class, and <12% are in the poor class. For arsenic, copper, and potassium, 33-37% of the comparisons are in the good class, and 4-15% are in the poor class. The worst results were those for cobalt, lead, and manganese, which have a nearly equal number of comparisons in the good and poor classes. The other constituents (antimony, cadmium, mercury, selenium, silver, and thallium) are below detection limits in most samples, and comparisons of analytical accuracy cannot be made.

The water chemistry data for wells near PGDP include some errors, but this is not unusual. As reported by Hem (1985, p. 163), for example, a comparison of the results obtained by different laboratories in several studies showed that 8% of the values were grossly in error. A more significant determination is whether or not the errors produce a bias toward high or low values.

A comparison of a few analyses in CH2M HILL (1991, 1992) with those in Kearl (1993) and Lindquist and Bohac (1989) for the same wells do not show consistent differences in the analytical results for major ions. However, the average ratio of specific conductance and total dissolved solids is 1.7 for chemical analyses by U.S. Geological Survey (USGS; Davis et al. 1973, Table 2) on samples from private wells near PGDP but only 1.5 for the PGDP analyses. As stated by Hem (1985, p. 165) the ratio should be in the range 1.3 to 1.8 for waters of ordinary composition, and a water in which most anions are bicarbonate should be near the high end of the range. The USGS data fit this criterion, but the PGDP data do not. Also, ~75% of the water samples at PGDP have an acceptable charge balance (Table 10), but only 0-20% of the samples, depending on hydrologic unit, have an anion or cation sum [calculated as $100 \times (\text{meq/L})$] that is within 10% of the specific conductance ($\mu\text{S/cm}$). In the samples with an unacceptable charge balance, 70-100% of either anions or cations are too high when compared with specific conductance. These results indicate that the concentrations of major ions in the PGDP data are more likely to be too high than too low.

Table 10. Accuracy checks on water analyses near PGDP.

Percent of Water Samples ^a			
	<u>McN</u>	<u>RGA</u>	<u>UCRS</u>
Acceptable Results:			
Charge Balance ($\pm 20\%$) ^b	60	74	73
Total Anions ($\pm 10\%$) ^c	0	15	20
Total Cations ($\pm 10\%$) ^c	0	12	13
Anions, Cations, & Balance ($\pm 20\%$)	0	4	8
Unacceptable Results:			
Charge Balance			
Excess anions	29	39	39
Excess cations	21	27	24
Total Anions ^c			
Too Low	10	13	10
Too High	90	72	70
Total Cations ^c			
Too Low	0	6	3
Too High	100	81	84

^a Percent of water samples for which all indicated data are available.

^b WATEQ method for cation-anion balance calculation; major ions only.

^c Assumes correct specific conductance.

Water analyses were also checked by comparing concentrations in multiple samples obtained over a 2-year period. Lateral groundwater velocities in the UCRS and RGA are estimated to range from <1 mm/year to ~25 m/year (CH2M HILL 1992, p. 3-36), and nearly all groundwater should be a few months to a few decades old. Also, because nearly all solutes are dissolved from near-surface soils during periods of aquifer recharge, temporal changes of constituent concentration at all deeper levels should be small. Thus, the reported concentration should be nearly the same as the actual concentration. Hem (1985, p. 163) stated that the difference between the actual and the reported concentration of any solute in a water sample should be within 10% of the actual value, although concentrations below 1 mg/L commonly have a larger error.

For multiple samples from wells near PGDP, the maximum concentrations of barium, bicarbonate, calcium, chloride, magnesium, sodium, and sulfate were within 20% of the minimum concentrations for >50% of the wells. However, the maximum concentrations of aluminum, antimony, arsenic, cobalt, copper, chromium, iron, lead, potassium, and zinc were within 20% of the minimum value in <20% of the wells. These results show that the minor and trace elements are more likely to include errors than are the major ions.

Solubility calculations using the WATEQ model (Ball and Nordstrom 1992) show that several aluminum minerals are supersaturated in most water samples and that some samples are supersaturated with silver metal, barite (barium sulfate) and goethite (iron hydroxide). If a silica content in the 8-18 mg/L range of the USGS data (Davis et al. 1973, Table 2) is included in the WATEQ model, some samples are also supersaturated with kaolinite (a clay mineral). Both barium and silver occur in higher concentrations in clay than in other sediments. Thus, the WATEQ results show that the groundwater analyses represent both dissolved species and the ion contents of colloidal particles; trace elements that are sorbed by or coprecipitated with the colloidal particles are likely to be too high in some analyses.

Solubility calculations also show that 57% of the water samples from the UCRS are supersaturated with barite but that only 20% of the samples from the RGA and 8% of the samples from the McN are supersaturated with this mineral. The barite probably occurs as colloidal particles, and the relative amounts of these particles may show that most colloidal transport occurs in the UCRS as vertical flows from the UCRS into the RGA under relatively large hydraulic gradients. The higher concentrations of aluminum, beryllium, and chromium are also apparently associated with colloidal particulates, and more samples from the UCRS seem to exceed the solubility limits for these constituents than do samples from the RGA and McN.

The results of the evaluations and comparisons of groundwater chemistry data at PGDP indicate that some of the reported concentrations are too high and that, for wells with multiple samples, the minimum concentration is a more reliable indicator of the actual concentration than is the maximum concentration.

Comparisons of the geometric means and standard deviations for unflagged (highest reliability) and flagged data (CH2M HILL 1991, 1992) did not show significant differences, and the data were combined for analysis and interpretation purposes. For the same purposes, detection limits were used for constituents with lower concentrations in both soils and groundwater. This procedure may have contributed to irregularity in the data distribution at the low end of the ranges but did not produce anomalies in the cumulative probability graphs. Any bias is toward higher concentrations and is thus conservative.

8.0 ELEMENT CONCENTRATIONS

8.1 ALUMINUM

Cumulative probability graphs of aluminum concentrations in near-surface soils and in soil borings show two populations. The transition to the upper population, which apparently represents a larger clay content, begins at a concentration of 4500 mg/kg. Approximately 90% of the near-surface samples but only 60% of the samples from soil borings fall within the upper population. Also, the geometric mean concentration of aluminum is ~8000 mg/kg in near-surface soils but only ~4800 mg/kg in the soil borings (Tables 1 and 2). Aluminum concentrations of 19,000–43,000 mg/kg in near-surface samples collected from test pits 2 and 3 in the C-747-A area are anomalous and may represent contamination. The maximum background concentration of aluminum in soils is ~18,000 mg/kg. All aluminum concentrations in sediment samples are within the normal range for other soil samples.

Aluminum has a solubility of ~20–40 $\mu\text{g/L}$ in natural waters at a nearly neutral pH, but solubility is decreased by the presence of silica, which causes precipitation as a clay mineral (Hem 1985, pp. 73–75). Cumulative probability graphs of aluminum concentrations in water samples near PGDP show two populations (Fig. 2). The first population has a geometric mean of ~20 $\mu\text{g/L}$ in the UCRS, RGA, and McN. The transition to the second, upper population begins at a concentration of 25 $\mu\text{g/L}$.

As shown in Tables 5, 6, and 7; the maximum aluminum concentrations in the water samples are 21 mg/L in the UCRS, 66 mg/L in the RGA, and 1.9 mg/L in the McN; these concentrations exceed the solubility limits for aluminum. Also, as noted previously; WATEQ models show that aluminum is supersaturated with respect to several minerals in at least some of the samples that plot in the upper populations on the probability graphs. If all concentrations of >25 $\mu\text{g/L}$ (the intersection of the population lines on the graphs) are assumed to exceed solubility limits, 82% of the samples from the UCRS, 64% of the samples from the RGA, and 40% of the samples from the McN exceed the solubility limits for aluminum. These samples probably included colloidal particulates that passed through the filter pad and were dissolved by acidification. There is no drinking water limit for aluminum.

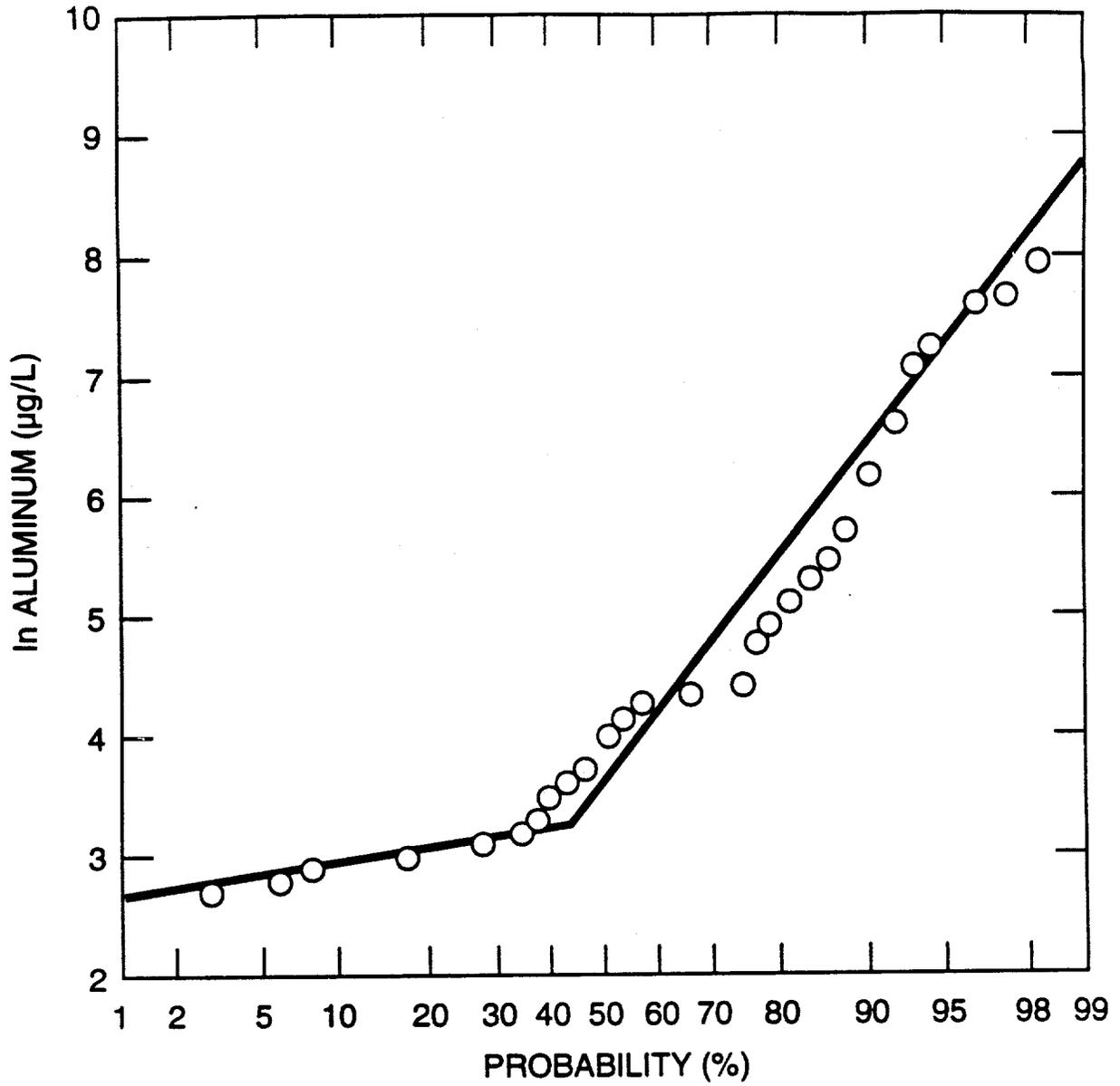


Figure 2. Cumulative probability graph showing two statistical populations for aluminum in water samples from the RGA.

8.2 ANTIMONY

Cumulative probability graphs for antimony in near-surface soils and soil borings are irregular but have a similar slope (approximately the same standard deviation). All of these samples apparently represent background concentrations near PGDP; the maximum concentration is ~21 mg/kg in soil borings and 45 mg/kg in near-surface soils. Sediment samples fall within this range except for two duplicate samples from WMU 17, which have concentrations of 352 and 425 mg/kg of antimony; these data are anomalous and apparently represent contamination.

Little is known about the occurrence of antimony in groundwater; the average concentration in U.S. streams is <1 $\mu\text{g/L}$, but larger amounts may occur in groundwater (Hem 1985, p. 145). If antimony behaves like arsenic in natural waters, it occurs as an anion, and metallic compounds of antimony may be sorbed by hydrous iron and manganese oxide particles. The cumulative probability graphs for antimony are irregular but seem to show a single population in all hydrologic units.

The drinking water limit for antimony is 5 $\mu\text{g/L}$. All samples of groundwater near PGDP exceed this standard. The geometric mean concentrations are 22 $\mu\text{g/L}$ in the UCRS, 18 $\mu\text{g/L}$ in the RGA, and 23 $\mu\text{g/L}$ in the McN; the maximum background concentration is ~50 $\mu\text{g/L}$. Only two samples contain >55 $\mu\text{g/L}$ of antimony; the maximum reported concentration is 66 $\mu\text{g/L}$. Also, in all cases where multiple samples of water were obtained from a well, only one of the samples contains >50 $\mu\text{g/L}$ of antimony. Only one sample of water was obtained from well MW 52 in the RGA and from wells MW 23 and MW 27 in the McN; all three wells were reported to contain 52 $\mu\text{g/L}$ of antimony.

The maximum background concentration for antimony in near-surface soils near PGDP is 45 mg/kg, and the maximum background concentration in groundwater, as discussed above, is ~50 $\mu\text{g/L}$. For these conditions, the maximum soil concentration for groundwater protection is 45 mg/kg (Table 9). Only the sediment samples from WMU 17 exceed this limit.

8.3 ARSENIC

The cumulative probability graph for samples from soil borings shows a single population for arsenic concentrations, but the graph for near-surface samples shows anomalous values above a concentration of ~20 mg/kg. The anomalous samples, which contain 20–46 mg/kg of arsenic, were obtained from test pit 3 in the C-747-A area and from sites H351 and H352 in WMU 97. Also, sediment samples from WMUs 17, 18, and 19 contain 20–27 mg/kg of arsenic; one sediment sample from site 7 on Little Bayou Creek contains 22 mg/kg; and site 1 on the N-S ditch contains 34 mg/kg. If the maximum background concentration of arsenic in soils at PGDP is 20 mg/kg, all of these samples represent analytical errors or low levels of contamination.

Arsenic occurs in water as an arsenate or arsenite (anions), and the presence of copper may limit the solubility of arsenic to ~200–400 $\mu\text{g/L}$; the sorption of metal arsenates on iron and manganese particles may also limit arsenic solubility (Hem 1985, p. 144). The geometric mean concentrations of arsenic in filtered water samples near PGDP are 3.5 $\mu\text{g/L}$ in the UCRS, 2.5 $\mu\text{g/L}$ in the RGA, and 6.5 $\mu\text{g/L}$ in the McN. The arsenic in the water samples is probably dissolved because the cumulative probability graphs show a single statistical population and because there are no detectable correlations of arsenic content with pH or with concentrations of copper, iron, and manganese.

The drinking water limit for arsenic is 50 $\mu\text{g/L}$, and with the exception of one well, all arsenic concentrations are less than half of this limit. Two filtered water samples from well MW 186 in the UCRS near the northwest corner of PGDP showed arsenic concentrations of 280 and 330 $\mu\text{g/L}$. These high concentrations plot above the population line on a cumulative probability graph and are clearly anomalous. Also, the arsenic concentrations in MW 186 are an order of magnitude higher than those observed elsewhere; the next highest concentration is 23 $\mu\text{g/L}$ in MW 192. Wells near MW 186 in both the UCRS and the RGA have low concentrations of arsenic, however. Any contamination is limited to the UCRS in the area near MW 186, and there is no detectable contaminant plume.

The maximum background concentrations of arsenic are ~20 mg/kg in soils and 23 $\mu\text{g/L}$ in groundwater. The maximum soil concentration for groundwater protection is ~45 mg/kg (Table 9), and all soil samples are at or below this limit.

8.4 BARIUM

The cumulative probability graph for barium concentrations in soil borings shows a single statistical population, but the graph for samples from near-surface soils shows anomalous values above a concentration of ~360 mg/kg. Barium concentrations of 386–657 mg/kg occur in samples from test pits 2 and 3 in the C-747-A area. For sediment samples, the WMU 19 site contains 464 mg/kg of barium, and site 1 on the N-S ditch contains 922 mg/kg of barium. If the maximum background concentration of barium is 360 mg/kg for soils near PGDP, the higher values represent analytical errors or low levels of contamination.

The solubility of barium in natural waters is commonly determined by that of barite and is ~14 $\mu\text{g/L}$ for 100 mg/L of sulfate and 140 $\mu\text{g/L}$ for 10 mg/L of sulfate (Hem 1985, p. 136). Barium may also be sorbed by or coprecipitated with iron and manganese oxides and hydroxides. Cumulative probability graphs for the samples near PGDP show single populations and the geometric mean concentrations of barium are 120 $\mu\text{g/L}$ for the UCRS and RGA and 130 $\mu\text{g/L}$ for the McN. Solubility calculations, as mentioned previously, show that 57% of the water samples from the UCRS and 20% of the samples from the RGA are supersaturated with respect to barite. These points on the cumulative probability graphs represent a solubility limit of ~150 $\mu\text{g/L}$. Water samples with relatively high concentrations of barium thus include barite or other particulates that were dissolved

by acidification. The primary drinking water limit for barium is 2.0 mg/L, which is much higher than the solubility limit near PGDP. None of the water samples exceed the drinking water limit.

The maximum background concentration of barium in soils is ~360 mg/kg and the solubility limit in groundwater is ~150 µg/L. For an MCL of 2.0 mg/L, the maximum soil concentration for groundwater protection is 4800 mg/kg of barium (Table 9). All soil samples have <25% of this concentration.

8.5 BERYLLIUM

The cumulative probability graph for beryllium in soil borings shows a single population, but ~25% of the samples from near-surface soils fall into a second population, which includes concentrations of >3 mg/kg. These higher concentrations apparently show that beryllium minerals are associated with clay minerals in near-surface soils. The maximum concentration of beryllium in the soil borings is 2.6 mg/kg, but the maximum concentration in near-surface soils is 25 mg/kg, nearly an order of magnitude larger. Approximately 75% of the sediment samples have concentrations of >3 mg/kg; the maximum concentration is 29 mg/kg from site 5 on Little Bayou Creek. These results suggest that most sediment samples have a relatively high clay content. All beryllium concentrations are apparently in the background range; there is no evidence for contamination.

Maximum beryllium concentrations in natural waters are ~1–100 µg/L, but beryllium minerals are rare, and beryllium is strongly sorbed by clays, and by iron and manganese particles (Hem 1985, p. 134). The MCL for beryllium in drinking water is 4.0 µg/L. One sample from the RGA slightly exceeds this limit, but another sample from the same well contains only 0.4 µg/L. Cumulative probability graphs of beryllium concentrations show two populations in the UCRS and the RGA; the inflection points for the connecting "s" curves occur at concentrations of 0.4 and 0.8 µg/L. As noted above, beryllium concentrations may be higher in clays than in coarser-grained sediments, and ~72% of the samples from the UCRS but only 50% of the samples from the RGA fall in the upper population. For purposes of this report, all beryllium concentrations are assumed to be in solution and the maximum background concentration is ~3 µg/L.

For an MCL in groundwater of 4 µg/L for beryllium, the maximum concentration in soils for groundwater protection would be 40 mg/kg (Table 9). All soil samples are below this level.

8.6 BICARBONATE

Carbonate concentrations were not measured for soils. In groundwater, the geometric mean concentrations of bicarbonate are 190 mg/L in the UCRS, 120 mg/L in the RGA, and 170 mg/L in the McN. The standard deviation of bicarbonate concentration is highest in the UCRS and lowest in the McN. These results apparently show the locations and effects of recharge. The three UCRS wells with the lowest bicarbonate contents are on the banks of Bayou Creek, and the 19 RGA wells

with the lowest bicarbonate contents occur mostly in the C404 area of PGDP and in the area of the TVA Shawnee Steam Plant. Faster vertical flow rates or waters with smaller than normal amounts of bicarbonate may occur in these areas. There is not a drinking water limit for bicarbonate; the maximum background concentration in groundwater near PGDP is 670 mg/L.

8.7 CADMIUM

Cumulative probability graphs for cadmium in soils are irregular below the detection limit of ~1.0 mg/kg. Above this limit, samples from near-surface soils seem to represent a statistical population that has somewhat higher concentrations and a larger standard deviation, than does the population for samples from soil borings. This result may show a correlation between the occurrences of cadmium minerals and clay minerals.

One soil sample from a depth of 10-15 ft in MW 175 was reported to have a cadmium concentration of 13 mg/kg, but this value is probably erroneous; all other shallower and deeper samples from MW 175 have concentrations of <1.5 mg/kg of cadmium. Except for this one sample, the maximum concentration of cadmium in soil borings is 5.6 mg/kg. Sediment samples have a maximum concentration of 7.2 mg/kg for cadmium, and near-surface soil samples have a maximum background concentration of ~12 mg/kg. Near-surface samples from test pit 3 in the C-747-A area contain concentrations, which are clearly anomalous, of 56 to 235 mg/kg.

The water chemistry of cadmium is similar to that of zinc, but cadmium minerals are less common; few streams contain >10 µg/L of cadmium (Hem 1985, p. 142). Cadmium is sorbed by hydrous iron and manganese oxide particles and may coprecipitate with manganese, but the PGDP data show no apparent correlations between cadmium and zinc, iron, or manganese contents. The cumulative probability graphs for cadmium in the UCRS and the RGA show two populations. The intersections of the population lines on the graph occur at a concentration of 2.7-3.0 µg/L. These intersections might show a solubility limit, but, for purposes of this report, all cadmium is assumed to be in solution.

The MCL for cadmium in drinking water is 5 µg/L. The single water samples from wells RW 54 and RW 72 in the RGA were reported to contain 22 and 24 mg/L of cadmium, but both wells are in remote locations, and the analyses are obviously erroneous. Two water samples from the McN and one sample from the UCRS were reported to exceed the MCL, but other samples from two of these wells are below the MCL. The sample from the McN well, MW 27, was reported to contain 18 µg/L of cadmium, but the well is in an upgradient, background location, and the high concentration is apparently erroneous or caused by colloidal particles. There is no evidence for contamination by cadmium in the wells near PGDP.

The maximum background concentration of cadmium in soils near PGDP is ~12 mg/kg, and the maximum background concentration in groundwater is ~5 µg/L. For an MCL of 5 µg/L, the maximum soil concentration of cadmium for groundwater protection would be the same as the

maximum background concentration (Table 9). Only the samples from test pit 3 in the C-747-A area exceed this limit.

8.8 CALCIUM

Cumulative probability graphs for calcium concentrations in soils show two or three different statistical populations. The maximum calcium concentration in soil borings is 27,000 mg/kg, but only 5% of the samples exceed a concentration of 2600 mg/kg. For near-surface soils, 20% of the samples belong to a population that has a minimum concentration of ~15,000 mg/kg and a maximum concentration of ~300,000 mg/kg (30% calcium). Analytical errors are possible, but 5-10% of the near-surface samples apparently were obtained from a fine-grained material, such as unweathered loess, that exceeds 100,000 mg/kg of calcium. Sediment samples have calcium concentrations within these ranges; the maximum concentration is 47,400 mg/kg, but only 5% of the samples exceed a concentration of 20,000 mg/kg. Calcium in soils is not hazardous.

The geometric mean concentrations of calcium in water samples are 32 mg/L in the UCRS, 25 mg/L in the RGA, and 21 mg/L in the McN. The McN data plot as a single population on a cumulative probability graph but data from the UCRS and RGA show two populations. For the UCRS and RGA samples, 18 of the 42 wells with the highest calcium concentrations are among the 42 wells that have the highest sulfate concentrations. The second population thus may result from the solution of gypsum, which may occur in fine-grained sediments of the UCRS. Some of the RGA wells that have relatively high concentrations of calcium are in the area of the PGDP, but others are near the Shawnee Steam Plant and the Ohio River. There is not a drinking water limit for calcium. Maximum concentrations are 210 mg/L in the UCRS, 200 mg/L in the RGA, and 49 mg/L in the McN.

8.9 CHLORIDE

The only chloride analyses were those for groundwater. The geometric mean concentrations are 28 mg/L in the UCRS, 26 mg/L in the RGA, and 11 mg/L in the McN. Cumulative probability graphs are somewhat irregular but seem to show a single population in each hydrologic unit. The standard deviation of chloride concentration is largest in the UCRS, and most chloride may derive from the solution of halite in fine-grained sediments of the UCRS. The secondary drinking water limit for chloride is 250 mg/L because larger amounts can be tasted by some people. None of the samples from the RGA and McN exceed this limit. In the UCRS, two samples of water from MW 127 contain 340 and 350 mg/L, and one sample from MW 186 was reported to contain 790 mg/L. Another sample from well MW 186 contains only 98 mg/L of chloride, however, and the higher concentration is probably erroneous. The reason for the high concentration of chloride in well MW 127 is unknown. This well is downgradient of PGDP, but the only UCRS well between MW 127 and the PGDP site is MW 198, which contains only 7 mg/L of chloride. The chloride source for well MW 127 is apparently local.

8.10 CHROMIUM

Cumulative probability graphs for chromium in soils show that the maximum background concentration is ~160 mg/kg and that larger concentrations are clearly anomalous. Samples from test pit 3 in the C-747-A area have chromium concentrations of 337-505 mg/kg. One near-surface sample from site H210 in the C-747-C area was reported to contain 258 mg/kg, but an integrated sample from 0-5 ft depth contains only 65 mg/kg of chromium. A low level of chromium contamination is possible at this location, but the analysis might be erroneous.

Sediment samples from sites 5, 7, and 9 on Little Bayou Creek contain 195-260 mg/kg of chromium, and two duplicate samples from site 2 on the N-S ditch contain 155-221 mg/kg of chromium; low levels of contamination are possible at these sites. A sediment sample from WMU 18 contains 1960 mg/kg of chromium, however, and two duplicate samples from WMU 17 contain 17,000-22,100 mg/kg of chromium; higher levels of contamination are indicated for these locations.

Chromium in natural waters usually occurs as chromate anions; concentrations are generally <10 µg/L (Hem 1985, p. 138). The geometric mean concentrations in the water samples near PGDP are 4.1 µg/L in the UCRS, 3.2 µg/L in the RGA, and 3.3 µg/L in the McN. Cumulative probability graphs show a single population in the UCRS and the McN, but two populations in the RGA. The break in the slope of the graph for water samples from the RGA occurs at a concentration of 9 µg/L, which is near the upper limit noted by Hem (1985, p. 138); larger concentrations may exceed the solubility limit and may represent the contributions of colloidal particles. Approximately 20% of the UCRS samples and 10% of the RGA and McN samples have a chromium content of >9 µg/L. For the purposes of this report, however, all chromium is assumed to be in solution.

The MCL for chromium in drinking water is 100 µg/L. Water samples from the UCRS and the McN do not exceed this limit, but three water samples from MW 70 in the RGA have a chromium content of 65-107 µg/L. Well MW 70 is in the C404 area of the PGDP, and contamination is possible at this location. However, other nearby wells in the RGA have only normal concentrations of chromium, and any contamination is local. In other RGA wells, the maximum chromium content is ~40 µg/L.

The maximum background concentration of chromium in soils is ~160 mg/kg, and the maximum background concentration, which may exceed the solubility limit, in groundwater is ~40 µg/L. These values indicate that the maximum chromium content in soils for groundwater protection is ~400 mg/kg (Table 9). Only the samples from test pit 3 in the C-747-A area exceed this level.

8.11 COBALT

The cumulative probability graph for cobalt in soil borings shows a single statistical population; the maximum concentration is 48 mg/kg. The graph for cobalt in near-surface soils is irregular, but

there are no apparent anomalies. The maximum cobalt concentrations in sediment samples and near-surface soil samples are 62 and 69 mg/kg, respectively.

The solubility limit for cobalt may be ~6–10 µg/L, but cobalt coprecipitates with manganese and is strongly sorbed by iron and manganese oxides (Hem 1985, p. 138). The geometric mean concentrations of cobalt in the PGDP water samples are 6.0 µg/L in the UCRS, 5.5 µg/L in the RGA, and 6.7 µg/L in the McN. Cumulative probability graphs are irregular, but seem to show single populations in all three hydrologic units. Approximately 30% of the samples in each hydrologic unit have concentrations of >10 µg/L, which apparently exceeds the solubility limit for cobalt and probably indicates the occurrence of colloidal iron or manganese particles. Cobalt is associated with nickel, and 66% of the water samples have a Co:Ni ratio of 0.5–2.0.

Two samples of water from well TVA 9 have cobalt concentrations of 100 and 140 µg/L, and three samples of water from well TVA 14 have cobalt concentrations of 48–55 µg/L. These water samples also have large concentrations of aluminum, iron, manganese, and nickel, which are probably natural, and if contamination has occurred, it is unlikely that the source is the PGDP. There is not an MCL for cobalt.

The maximum background concentration for cobalt in soils is ~70 mg/kg, and the solubility limit for groundwater in the PGDP area is probably ~10 µg/L. These data represent a dilution and attenuation factor of 7000 (Table 9).

8.12 COPPER

A cumulative probability graph for copper in soil borings shows a single statistical population, and the maximum concentration is 63 mg/kg. Approximately 7% of the samples from near-surface soils, however, fall in a second population that exceeds this level and apparently represents contamination. Samples from test pit 3 in the C-747-A area, for example, contain 8240–18,700 mg/kg of copper. Lower levels of contamination by copper also might be indicated by concentrations of 231 mg/kg in the surface sample from boring H210 in the C-747-C area and by concentrations of 141 mg/kg and 175 mg/kg in samples from test pits 1 and 2 in the C-747-A area. For sediment samples, low levels of contamination by copper are probably indicated by concentrations of 122–134 mg/kg at sites 1 and 2 on the N-S ditch, and by concentrations of 136–335 mg/kg in samples from WMUs 17, 18, and 19.

Copper may have a solubility limit of ~10 µg/L in natural waters because copper is sorbed by and coprecipitates with iron oxyhydroxides (Hem 1985, p. 141). Approximately 10% of the water samples from the UCRS, 20% of the samples from the RGA, and 35% of the samples from the McN have concentration of >10 µg/L and may include colloidal particles of iron or copper minerals. These results also suggest that copper minerals, like iron and manganese minerals, are more common in the deeper hydrologic units. The cumulative probability graphs are somewhat irregular but seem to show a single population in each hydrologic unit; the maximum background concentration is ~90

$\mu\text{g/L}$, which apparently exceeds the solubility limit. For the purposes of this report, however, all copper is assumed to be in solution. The secondary drinking water standard for copper is 1.3 mg/L; none of the samples exceed this limit.

The maximum background concentrations for copper in soils and groundwater are ~ 63 mg/kg and 90 $\mu\text{g/L}$. For a secondary drinking water limit of 1.3 mg/L, the maximum soil concentration for groundwater protection is 910 mg/kg of copper (Table 9). Only the samples from test pit 3 in the C-747-A area exceed this limit.

8.13 CYANIDE

All analyses for cyanide in soils near PGDP were below detection limits, but low levels were reported in some groundwater samples. The occurrence of cyanide in water samples is commonly considered to be an indication of contamination by industrial processes (Hem 1985, pp. 124, 154). However, relatively large concentrations of cyanide and cyanate have been observed (by the author) in the spring runoff from animal feed pens in the upper Midwest, and some farm wells near the feed pens contain tens of micrograms per liter of these ions. The MCL for cyanide in drinking water is 200 $\mu\text{g/L}$. Geometric mean concentrations in the water samples near PGDP are 5.0 $\mu\text{g/L}$ in the UCRS and RGA and 3.3 $\mu\text{g/L}$ in the McN. One water sample from well MW 12 in the RGA was reported to contain 410 $\mu\text{g/L}$ of cyanide, but other samples from the same well contain only 3 $\mu\text{g/L}$ and 5 $\mu\text{g/L}$ of cyanide. Maximum concentrations in other wells are <25 $\mu\text{g/L}$ and are probably not indicative of industrial contamination.

8.14 IRON

Cumulative probability graphs show that the maximum background concentration of iron in soil samples near PGDP is $\sim 52,000$ mg/kg. Near-surface samples from test pit 3 in the C-747-A area contain $\sim 75,000$ – $98,000$ mg/kg of iron and are clearly anomalous on the graph. Also, two duplicate sediment samples from WMU 17 contain 100,000–132,000 mg/kg of iron. These results indicate contamination, but iron in soils is not hazardous.

The geometric mean concentrations of iron in groundwater are 0.27 mg/L in the UCRS, 0.15 mg/L in the RGA, and 2.2 mg/L in the McN. This result might show that iron compounds occur in larger concentrations in the McN or might show only the inclusion of more colloidal particles of iron oxyhydroxide in samples from the McN. The ranges in iron content are 4.5 $\mu\text{g/L}$ to 74 mg/L in the UCRS, 0.6 $\mu\text{g/L}$ to 74 mg/L in the RGA, and 20 $\mu\text{g/L}$ to 17 mg/L in the McN. WATEQ models show that some water samples are supersaturated with respect to goethite, but the cumulative probability graphs show single populations.

The secondary drinking water limit for iron is 0.3 mg/L because larger concentrations can precipitate under oxidizing conditions; larger amounts are not harmful. Groundwater apparently occurs under mildly oxidizing conditions in the PGDP area, as discussed previously, and

concentrations of >0.3 mg/L may represent the inclusion of dissolved colloidal particles of hydrous iron oxide. If so, $\sim 30\%$ of the water samples from the UCRS and RGA and 85% of the samples from the McN contained these particles. There is no detectable correlation of iron content with manganese content or pH, but some of the samples with a high iron content also have relatively high concentrations of cobalt and nickel; these metals may have been sorbed on iron particles in the samples. There is no reason to believe that any of the high iron contents in groundwater indicate contamination.

8.15 LEAD

Cumulative probability graphs show that the maximum background concentration of lead in soil borings and near-surface soils is ~ 130 mg/kg. An anomalous concentration of 323 mg/kg of lead was reported for the surface sample from boring H210 in the C-747-C area, but the integrated sample for a depth of 0–5 ft from this boring contains only 70 mg/kg, and all other samples from deeper levels contain <35 mg/kg of lead. Lead concentrations in samples from test pit 3 in the C-747-A area are also anomalous and range from 503–1160 mg/kg. All sediment samples are within the background range for lead.

The solubility of lead is probably <50 $\mu\text{g/L}$, and lead can be sorbed by particulates and may coprecipitate with manganese (Hem 1985, pp. 143–144). The geometric mean concentrations are 1.6 $\mu\text{g/L}$ in the UCRS, 8.4 $\mu\text{g/L}$ in the RGA, and 1.0 $\mu\text{g/L}$ in the McN. The cumulative probability graphs are irregular but apparently show single statistical populations.

The MCL for lead is 15 $\mu\text{g/L}$. None of the McN samples exceed this standard. Two samples of water from the UCRS were reported to contain 18 $\mu\text{g/L}$, but other samples from the same wells contain <6 $\mu\text{g/L}$ of lead. For the RGA, six water samples were reported to contain 17 – 28 $\mu\text{g/L}$, one sample was reported to contain 80 $\mu\text{g/L}$, and one sample was reported to contain 97 $\mu\text{g/L}$ of lead, but other water samples from these same wells contain <4 $\mu\text{g/L}$ of lead. Only one sample was collected from privately-owned well RW 113 in the RGA and was reported to contain 106 $\mu\text{g/L}$ of lead. This well is located near the northwest corner of the PGDP site, where contamination is possible, but there is no detectable contaminant plume, and any contamination is local. The maximum background concentration in groundwater is apparently ~ 15 $\mu\text{g/L}$, the same as the MCL.

The maximum background concentrations of lead in soils and groundwater are ~ 130 mg/kg and 15 $\mu\text{g/L}$. The maximum soil concentration for groundwater protection is the same as the maximum background concentration (Table 9). The surface sample from boring H210 and near-surface samples from test pit 3 exceed this limit.

8.16 MAGNESIUM

Cumulative probability graphs show that all magnesium concentrations in soils are in the background range, The maximum concentrations are 3250 mg/kg in soil borings, 12,600 mg/kg in

near-surface samples, and 4460 mg/kg in sediments. The larger concentrations in near-surface soils probably show that magnesium minerals are more abundant in the fine-grained soils of the UCRS. Magnesium in soils is not hazardous.

The geometric mean concentrations of magnesium are 11 mg/L in the UCRS, 8.4 mg/L in the RGA, and 7.8 mg/L in the McN. Cumulative probability graphs for the UCRS and the McN show a single population, but RGA data plot as an "s" curve with a central plateau. Sulfate data show a similar plot and there seems to be a correlation of magnesium and sulfate values for data points in the plateaus on these graphs. Thus, some of the magnesium minerals may be in a sulfate rather than a carbonate form. Ca:Mg ratios commonly decrease along groundwater flow paths, but the ratio values in the PGDP area do not show a pattern. The maximum background concentration in groundwater is ~74 mg/L. There is not a drinking water limit for magnesium.

8.17 MANGANESE

Cumulative probability graphs show that maximum background concentrations of manganese are ~2900 mg/kg in the soil borings and ~3400 mg/kg in near-surface soils. One sample from test pit 2 in the C-747-A area contains 8090 mg/kg, and sediment samples from site 1 on Little Bayou Creek and site 1 on the N-S ditch contain 4020 and 4150 mg/kg of manganese. These concentrations might indicate low levels of contamination, but manganese in soils is not hazardous.

Manganese, like iron, has a large range in concentration for the water samples near PGDP. The geometric means are 120 µg/L in the UCRS, 82 µg/L in the RGA, and 370 µg/L in the McN. This order, in which the McN has the largest average concentration and the RGA has the least, is the same as that for iron. Also, the average iron concentrations in the hydrologic units are all higher than the average manganese concentrations, but the ratio values are different, and, otherwise, there is no apparent correlation between iron and manganese contents. The secondary drinking water standard for manganese is 50 µg/L because larger amounts may precipitate under oxidizing conditions; larger amounts are not harmful.

Groundwater from alluvial aquifers may contain ~1.0 mg/L of manganese in some areas (Hem 1985, p. 89), and the cumulative probability graphs for the PGDP samples show a flatter slope for concentrations of >1.0 mg/L. Approximately 15% of the samples from each of the hydrologic units at PGDP have manganese concentrations of >1.0 mg/L; part of the manganese in these samples probably occurred in particulate form and was dissolved by acidification.

8.18 MERCURY

Approximately 80% of the analyses for mercury in soils were below detection limits. The cumulative probability graphs are irregular, but maximum background concentrations are estimated to be ~1.1 mg/kg in samples from soil borings and 2.5 mg/kg in samples from near-surface soils. Sediment samples have a maximum concentration of 1.3 mg/kg of mercury. The surface sample

from boring H210 in the C-747-C area contains 7.7 mg/kg of mercury, but the integrated sample from a depth of 0–5 ft contains only 0.28 mg/kg, and deeper samples from this boring were below the detection limit of ~0.12 mg/kg of mercury. Also, the near-surface sample from H382 in WMU 26 contains 12 mg/kg of mercury, but samples H380 and H381 from the same WMU contain only 0.1 mg/kg.

The stable form of mercury in natural waters is the free metal, but mercury minerals are rare. Concentrations in natural waters rarely exceed a few tenths of a microgram per liter; mercury concentrations also have a strong correlation with particulates (Hem 1985, p. 142). The geometric mean concentration in the PGDP samples is 0.15 µg/L in the UCRS, RGA, and McN. The MCL for methyl mercury is 0.02 µg/L, but mercury can be assumed to be in the metallic form except under strongly reducing conditions, and nearly all groundwater near PGDP occurs under slightly to moderately oxidizing conditions. The old MCL for metallic mercury was 2 µg/L.

The detection limit for the water analyses was ~0.1 µg/L of mercury, and background wells were reported to contain as much as 0.2 µg/L of mercury. One water sample from well MW 162 in the UCRS was reported to contain 0.38 µg/L, and one sample from well MW 133 in the McN was reported to contain 0.41 µg/L of mercury. For the RGA wells, samples from MW 156, MW 66, and MW 185 were reported to contain 0.45, 0.90, and 1.8 µg/L of mercury, respectively. Other samples from all five wells contain only 0.1–0.2 µg/L of mercury, however.

Because maximum background concentrations in soil and groundwater are 2.5 mg/kg and 0.2 µg/L of mercury and because the MCL in water is 0.02 µg/L for methyl mercury, the maximum soil concentration for groundwater protection purposes is that of the maximum background concentration (Table 9); only two near-surface samples, as noted above, exceed this limit, and these analyses may be erroneous.

8.19 NICKEL

Cumulative probability graphs show a single population for 85% (near-surface soils) to 99% (soil borings) of the samples, but the remaining samples constitute a second population and a few anomalous points at the top of the concentration range. The maximum background concentration was selected at the top of the range for the main population and is ~100 mg/kg. The deepest sample from MW 132 was reported to contain 122 mg/kg of nickel, but this result is almost certainly erroneous; all shallower samples from this well contain <20 mg/kg of nickel. One sample from test pit 2 in the C-747-A area contains 132 mg/kg and the sediment sample from WMU 18 contains 220 mg/kg of nickel; these results might show a low level of contamination. Similarly, near-surface sample sites H382 and H380 in WMU 26 were reported to contain 102 and 264 mg/kg of nickel.

Higher levels of contamination were found in test pit 3 in the C-747-A area where samples contain, respectively 4880–12,300 mg/kg of nickel.

Nickel concentrations in natural waters may be controlled by coprecipitation with manganese and by sorption on hydrous iron and manganese oxide particles; nickel is generally associated with cobalt in water samples, but nickel concentrations are larger than those of cobalt; the median concentration of nickel in surface streams is $\sim 10 \mu\text{g/L}$ (Hem 1985, p 139). Geometric mean concentrations in groundwater samples near PGDP are $9.0 \mu\text{g/L}$ in the UCRS, $7.0 \mu\text{g/L}$ in the RGA, and $11 \mu\text{g/L}$ in the McN.

Cumulative probability graphs of nickel in groundwater show two statistical populations; the transition to the second population occurs at a concentration of $\sim 9 \mu\text{g/L}$. Approximately 50% of the samples from the UCRS and 40% of the samples from the RGA fall in the second population, which has a maximum concentration of $\sim 180 \mu\text{g/L}$ and probably exceeds the solubility limit for nickel. For the purposes of this report, all nickel concentrations of $>9 \mu\text{g/L}$ are assumed to represent the contributions of particulates. This assumption can be checked by resampling.

The MCL for nickel in drinking water is $100 \mu\text{g/L}$. Four water samples from the UCRS and three samples from the RGA exceed this limit, but, with one exception, other samples from the same wells are below the limit. The two water samples from well MW 182 were reported to contain 155 and $166 \mu\text{g/L}$ of nickel. Contamination at this location, which is near a landfill and near the northeast corner of the PGDP is possible. However, contamination is unlikely because nearby wells in the UCRS contain much lower concentrations of nickel and because of the apparent association of high nickel and particle concentrations.

The maximum background concentration of nickel in soil is $\sim 100 \text{mg/kg}$, and the solubility limit in groundwater is assumed to be $\sim 9 \mu\text{g/L}$. For groundwater protection, the maximum soil concentration would be $\sim 1100 \text{mg/kg}$ (Table 9). Only the samples from test pit 3 in the C-747-A area exceed this limit.

8.20 NITRATE

Nitrate concentrations were measured only for groundwater. The geometric mean concentrations of nitrate are 2.1mg/L in the UCRS, 2.4mg/L in the RGA, and 0.3mg/L in the McN. The drinking water limit for nitrate is 45mg/L . All eight water samples above this limit are from wells within the PGDP site, but other samples from the same wells contain $<45 \text{mg/L}$ of nitrate with two exceptions. The two samples from well MW 94 in the UCRS contain 69mg/L , and the two samples from well MW 12 in the RGA contain 64 and 78mg/L of nitrate.

The cumulative probability graphs for nitrate show single populations in the RGA and McN but two populations in the UCRS. The transition to the second population begins at a concentration of $\sim 10 \text{mg/L}$. All nitrate concentrations of $>10 \text{mg/L}$ in wells near PGDP might represent contamination. Based on this standard, nitrate contamination might have occurred near UCRS wells MW 64, MW 94, MW 143, MW 167, and MW 170 as well as near RGA wells MW 12, MW 66, MW 137, MW 191, RW 2, RW 16, RW 21, RW 53, and RW 294. The relatively high

concentrations of nitrate in wells MW 12, MW 64, MW 66, MW 94, MW 167, MW 170, and RW 2 might come from on-site sources at PGDP. However, there is not a detectable plume, and any contamination is local. Wells MW 143, MW 191, RW 21, RW 53, and RW 294 are in background locations, and any contamination is local. PGDP is also not the source for wells MW 137 and RW 16.

8.21 POTASSIUM

The maximum background concentration of potassium in soils, as shown by cumulative probability graphs, is ~2000 mg/kg although one sample from the McN in boring H206 contains 3290 mg/kg of potassium. All sediment samples fall in the background range. However, samples from test pit 3 in the C-747-A area contain 10,200–25,000 mg/kg of potassium, and these results probably indicate contamination. Potassium in soils is not hazardous.

There is not a drinking water limit for potassium. In most natural waters, potassium concentrations are a tenth to a half that of sodium, and potassium concentrations do not exceed a few tens of milligrams per liter (Hem 1985, p. 105). The cumulative probability graphs for groundwater near PGDP show two populations, which cannot be explained, in the UCRS and the RGA. Geometric mean concentrations of potassium in the groundwater samples near PGDP are 1.5 mg/L in the UCRS, 2.0 mg/L in the RGA, and 8.2 mg/L in the McN, but potassium contents have ranges of ~0.45–52 mg/L in the UCRS, 0.15–120 mg/L in the RGA, and 3.4–100 mg/L in the McN. Also, Na/K ratios have a range of 0.43–270 in the UCRS, 0.17–130 in the RGA, and 0.25–10 in the McN. The highest potassium concentrations and the lowest Na:K ratios do not necessarily correspond with a relatively high pH, and contamination of water in these wells by cement grout is unlikely. The highest and lowest ratio values are also unlikely, however, and potassium concentrations of >50 mg/L might be caused by errors in the chemical analyses. For wells with multiple samples, the maximum value for potassium is within 20% of the minimum value for only 18% of the wells, and the data have a poor precision.

8.22 SELENIUM

The cumulative probability graphs for near-surface soils and borehole samples show a single population and only one anomalously high value; the maximum background concentration of selenium is ~4.0 mg/kg. Sediment samples from site 1 in the N-S ditch and from WMU 18 contain slightly elevated concentrations of 6.2 and 6.4 mg/kg of selenium. Also, the surface sample at H352 in WMU 97 was reported to contain 25 mg/kg of selenium, but this result may be erroneous because two duplicate samples from H351 in the same WMU contain only 2.6 and 2.9 mg/kg of selenium.

Selenium occurs as an anion in natural waters and rarely exceeds a concentration of 1 µg/L because selenium is associated with iron and is sorbed by ferric oxyhydroxide particles (Hem 1985, pp. 145–146). If iron particles are dissolved by acidification of the samples, selenium contents can be higher, and this may be the case for groundwater samples near PGDP. The cumulative

probability graphs show single populations in which the geometric mean concentrations are 1.6 $\mu\text{g/L}$ in the UCRS and the RGA and 1.0 $\mu\text{g/L}$ in the McN. The maximum concentrations are 8.1 $\mu\text{g/L}$ in the McN and 12 $\mu\text{g/L}$ in the UCRS and RGA. For the purposes of this report, concentrations above 1.0 $\mu\text{g/L}$ are assumed to exceed the solubility limit.

The MCL for selenium is 50 $\mu\text{g/L}$. None of the water samples exceed this limit. For a maximum background concentration of 4.0 mg/kg in the soils and a solubility limit of 1.0 $\mu\text{g/L}$ in groundwater, the maximum soil concentration for groundwater protection would be 200 mg/kg (Table 9); all soil concentrations are below this limit.

8.23 SILVER

Only ~10–30% of the analyses for silver in soil samples are above detection limits, but cumulative probability graphs show little scatter. The maximum background concentration is ~10 mg/kg. The surface sample from boring H210 in the C-747-C area is anomalous and contains 42 mg/kg of silver, but the integrated sample from a depth of 0–5 ft contains only 14 mg/kg, and deeper samples contain <6 mg/kg of silver. Only one sediment sample is anomalous; a concentration of 79 mg/kg of silver was found in the sample from WMU 19. These few anomalous values may indicate low levels of contamination or analytical errors.

The solubility of silver is determined by that of the free metal or by silver chloride in most natural waters, and concentrations are generally <10 $\mu\text{g/L}$ (Hem 1985, p. 141). There is not a current federal MCL for silver, but some states retain the old MCL of 50 $\mu\text{g/L}$. The geometric mean concentrations of silver in the water samples near PGDP are 3.7 $\mu\text{g/L}$ in the UCRS, 3.1 $\mu\text{g/L}$ in the RGA, and 3.6 $\mu\text{g/L}$ in the McN. Almost all samples contain <10 $\mu\text{g/L}$ of silver, and WATEQ models show that samples are supersaturated with the free metal where concentrations are as low as 4–9 $\mu\text{g/L}$. Thus, approximately half of the samples contain most silver in particulate form. One sample from well MW 58 in the UCRS has a silver content that exceeds 50 $\mu\text{g/L}$, but another sample from this well contains only 11 $\mu\text{g/L}$ of silver.

The maximum background concentration for silver is ~10 mg/kg in soils and is assumed to be ~10 $\mu\text{g/L}$ in groundwater. For an MCL of 50 $\mu\text{g/L}$, the maximum soil concentration for groundwater protection would be 50 mg/kg (Table 9); only the sediment sample from WMU 19 is above this level.

8.24 SODIUM

As shown by cumulative probability graphs, the maximum background concentration of sodium is ~600 mg/kg in near-surface soils and ~900 mg/kg in soil borings. Anomalous concentrations of 1530–1770 mg/kg occur in two duplicate sediment samples from WMU 17, and concentrations of 2830–8170 mg/kg of sodium occur in near-surface samples from test pit 3 in the C-747-A area; these results might indicate contamination.

The geometric mean concentrations of sodium in the water samples are 56 mg/L in the UCRS, 31 mg/L in the RGA, and 24 mg/L in the McN. Maximum concentrations are 320 mg/L in the UCRS, 150 mg/L in the RGA, and 39 mg/L in the McN. The cumulative probability graphs show single statistical populations in which the standard deviation is largest in the UCRS and lowest in the McN. These results probably indicate that the source for most sodium is fine-grained sediments in the UCRS. Some of the sodium may come from the solution of halite and some from ion exchange with calcium. Ca:Na ratios range from ~0.1-10.

There is not an MCL for sodium in drinking water, but two samples from well MW 186 in the UCRS exceed 200 mg/L, which is the highest concentration for all other samples. This well is located near the northwest corner of the PGDP site; contamination is possible at this location, but the samples do not plot as anomalous values on the cumulative probability graph. For maximum background concentrations of 900 mg/kg in soil and ~200 mg/L in groundwater, the dilution and attenuation factor for sodium is only 4.5 (Table 9).

8.25 SULFATE

Sulfate concentrations were measured only for groundwater. The geometric mean concentrations are 34 mg/L in the UCRS, 12 mg/L in the RGA, and 14 mg/L in the McN. The cumulative probability graphs for sulfate are unusual. The McN samples seem to show a single population with a small standard deviation (a shallow slope on the graph). This same population seems to occur in the center of the range for the RGA samples and at the high end of the range for the UCRS samples. Other RGA and UCRS samples plot as populations that have a larger standard deviation. There is some association of sulfate and calcium values, which may occur because of the solution of gypsum, but both Ca:SO₄ and Na:SO₄ ratios, in units of equivalents per million, range from ~0.15-150. There is no apparent reason for the different slopes on the cumulative probability graphs, and laboratory errors in the analysis of sulfate are possible.

The secondary drinking water standard for sulfate is 250 mg/L. With one exception, none of the wells exceed this limit in two or more samples. Well TVA 9 was reported to contain 460 and 520 mg/L of sulfate; this well is close to the ash ponds at the Shawnee Steam Plant. Contamination may have occurred near this location but the source is not PGDP.

8.26 THALLIUM

Only one soil sample, which was obtained from a depth of 4 ft in boring H253, was above detection limits for the analysis of thallium; the sample contains 13 mg/kg of thallium. The range for thallium concentrations in U.S. soils was given as 0.02-2.8 mg/kg by Kabata-Pendias and Pendias (1984). Because boring H253 is in the C-747-A area, the sample might represent contamination, and resampling should be considered.

Thallium is a transition metal and may occur as an anion in natural waters, but nothing is known about the solubility limit. The MCL for drinking water is 2.0 $\mu\text{g/L}$. Approximately 50% of the samples from the UCRS, and 40% of the samples from the RGA and McN exceed the MCL, but none of the data plot as anomalies on the cumulative probability graphs. The thallium contents of the samples apparently are natural.

The maximum thallium content of soils for groundwater protection purposes is that of the maximum background concentration, possibly ~ 2.8 mg/kg (Table 9), because ~ 40 – 50% of the groundwater samples exceed the MCL. If thallium contamination might have occurred at PGDP, however, new soil samples and groundwater samples are needed to better define the natural background concentrations.

8.27 VANADIUM

Cumulative probability graphs for vanadium concentrations in soils are smooth and regular; the maximum background concentration in both near-surface soils and in soil borings is 70 mg/kg. Only the sediment sample from site 1 on the N-S ditch contains a slightly anomalous concentration of 81 mg/kg of vanadium.

In natural waters, vanadium generally occurs as an anion; solubility may be controlled by that of iron vanadate; vanadium minerals are rare, and concentrations rarely exceed 10 $\mu\text{g/L}$ (Hem 1985, p. 138). The geometric mean concentrations for the samples near PGDP are 3.9 $\mu\text{g/L}$ in the UCRS, 3.1 $\mu\text{g/L}$ in the RGA, and 2.2 $\mu\text{g/L}$ in the McN. The cumulative probability graphs are irregular but show single statistical populations. Only two of the wells with multiple samples have vanadium concentrations of >10 $\mu\text{g/L}$ in all samples: wells MW 197 and MW 201 have vanadium concentrations of 11–25 $\mu\text{g/L}$. The maximum background concentration may be ~ 10 $\mu\text{g/L}$. There is not an MCL for drinking water.

8.28 ZINC

Cumulative probability graphs show a single population and a maximum concentration of 190 mg/kg in soil borings but two populations and a maximum concentration of 1130 mg/kg in near-surface soils. Near-surface samples containing 800–1130 mg/kg of zinc were obtained from test pit 3 in the C-747-A area. Lower concentrations of 317 and 390 mg/kg of zinc were reported for the near-surface samples from H56 and H210. One sample from H257 contains 387 mg/kg, but a duplicate sample contains only 197 mg/kg of zinc. The sediment sample from WMU 18 contains 504 mg/kg, and the two duplicate samples from WMU 17 contain 3240–4170 mg/kg of zinc. If the maximum background concentration is assumed to be that of samples from soil borings, all of the higher results from near-surface soils and sediments are anomalous.

Zinc minerals are more soluble than those of nickel and copper; the solubility of zinc may be controlled by that of a silicate mineral or by sorption, ion exchange, and coprecipitation processes

(Hem 1985, p. 142). The geometric mean concentrations in the samples near PGDP are 27 $\mu\text{g/L}$ in the UCRS, 30 $\mu\text{g/L}$ in the RGA, and 80 $\mu\text{g/L}$ in the McN. The average concentration of iron is also much higher in the McN than in the other hydrologic units. These results suggest that the higher concentrations of zinc are associated with colloidal particles of hydrous iron oxide. Cumulative probability graphs show single populations in the UCRS and RGA, but the plot for the McN is irregular. The maximum background concentration in both the UCRS and the RGA is $\sim 600 \mu\text{g/L}$.

The secondary drinking water standard for zinc is 5 mg/L; larger amounts can be tasted by some people, but probably are not harmful. The only sample from privately-owned well RW 113 in the RGA was reported to contain 5.1 mg/L of zinc. This well is near the northwest corner of the PGDP, where pollution is possible, but there is not a plume of high concentrations, and the sample also contains high concentrations of aluminum and iron, which probably occur in particulate form. The only samples from wells MW 23 and MW 27 in the McN were reported to contain 31 mg/L and 37 mg/L of zinc. Both wells are in upgradient, background locations, however, and the high concentrations are either erroneous or are caused by colloidal particles in the samples.

The maximum background concentrations for zinc in soil and groundwater are $\sim 190 \text{ mg/kg}$ and 0.6 mg/L; for groundwater protection, the maximum soil concentration would be $\sim 1600 \text{ mg/kg}$ (Table 9); only the samples from WMU 17 exceed this limit.

9.0 CONCLUSIONS

Only the near-surface and sediment samples from the PGDP area show any evidence of contamination. The soil samples from test pit 3 in the C-747-A exceed the maximum concentration for groundwater protection purposes in arsenic, cadmium, chromium, copper, lead, and nickel; the same samples show lower levels of contamination for aluminum, barium, iron, potassium, and zinc. However, samples from test pit 2 in the same area show only low levels of contamination for aluminum, barium, copper, manganese, and nickel; samples from test pit 1 show only a low level of contamination for copper. If soil contamination has occurred in this WMU, it is apparently localized and does not extend very far either laterally or vertically. Similarly, the surface sample from boring H210 in the C-747-C area exceeds groundwater protection levels for lead and mercury and has lower, but anomalous levels of chromium, copper, silver, and zinc. These results might be erroneous, however, because the integrated sample from a depth of 0-5 ft contains only background levels of all constituents. In WMU 97, near-surface samples from borings H351 and H352 exceed the groundwater protection level for arsenic. The same sample from boring H352 also has an anomalous concentration of selenium, and the sample from boring H353 in WMU 97 has an anomalous concentration of thallium. The near-surface sample from boring H382 in WMU 26 exceeds the groundwater protection level for mercury, and samples from both H380 and H382 contain lower but anomalous levels of nickel. Finally, the near-surface sample from boring H56 (WMU 79) shows an anomalous level of zinc. However, none of the results for WMUs 26, 79, and

97 are confirmed by high concentrations at deeper depths. These results show that if contamination has occurred, it is localized and does not extend below a depth of ~1-2 m.

Sediment samples from WMUs 17, 18, and 19 contain the largest number of anomalous concentrations. Soil concentration levels for groundwater protection are exceeded for antimony and zinc in WMU 17 and for silver in WMU 19. Lower but anomalous levels of arsenic, barium, chromium, copper, iron, and nickel also occur in one or more of these samples. Possible contamination also was found in sediments from the N-S ditch and Little Bayou Creek. Samples from site 1 on the N-S ditch and from site 7 on Little Bayou Creek have anomalous concentrations of arsenic. Anomalous levels of barium, copper, manganese, selenium, and vanadium were also found at site 1 on the N-S ditch, and anomalous levels of chromium and copper were found at site 2. On Little Bayou Creek, an anomalous level of manganese occurs at site 1, and anomalous levels of chromium occur at sites 5, 7, and 9. Most anomalous concentrations in the sediments seem to represent local hot spots.

The soils data contain errors, and multiple errors for the same sample or for the same batch of samples are possible. If there is a question as to whether or not soil contamination has occurred, the CH2M HILL data should be checked by resampling.

There are not detectable contaminant plumes for any of the inorganic constituents of the groundwater samples, and the concentrations of these constituents within the TCE and ⁹⁹Tc plumes are no higher than elsewhere in the area. Also, with one exception, groundwater samples contain only background concentrations of metals near WMUs where soil contamination may have occurred. The one exception is well MW 186, which contains anomalous concentrations of sodium and arsenic in the C-747-A area where both constituents have high concentrations in the soil samples from test pit 3. Nevertheless, only background concentrations of other test-pit constituents occur in groundwater at MW 186. These results show that if soils contamination has occurred in other areas, groundwater contamination is unlikely.

Despite the poor correlation of anomalously high concentrations in soils and groundwater, low levels of nitrate contamination in groundwater have apparently occurred near a few on-site and off-site wells, and contamination is possible for antimony at well MW 52, for chromium at well MW 70, for chloride at well MW 127, for nickel at well MW 182, for sulfate at well TVA 9, and for lead and zinc at well RW 113.

All groundwater samples exceed the drinking water limit for antimony, and some samples exceed the MCLs for mercury and thallium. However, all of these concentrations are probably natural. The MCL for methyl mercury is 0.02 µg/L, but background wells were reported to contain as much as 0.2 µg/L of mercury. Also, nearly all groundwater near PGDP occurs under slightly to moderately oxidizing conditions, and mercury almost certainly occurs in the metallic form, not the methyl form. Any remaining concerns about contamination near PGDP will require new samples.

The concentrations of nearly all constituents in the water samples have approximately the same ranges in the UCRS, the RGA, and the McN. This result indicates a single source for both the water and the solutes. Similarly, the decrease in the standard deviations of specific conductance, total dissolved solids, and several major constituents from the UCRS to the RGA and the McN shows mixing along groundwater flow paths. Thus, the source for all groundwater near PGDP is recharge to the water table in the UCRS, and minerals in the fine-grained sediments of the UCRS are the main source for the major ions and most trace elements. Copper, iron, manganese, and zinc, however, have larger average concentrations in the McN than in the RGA and UCRS.

Either relatively low or relatively high values of specific conductance, dissolved solids, and major-ion concentrations in the RGA may show areas of downward percolation from the UCRS into the RGA. These data should be useful for an interpretation of potentiometric maps.

There is conclusive evidence that the filtered groundwater samples near PGDP contained colloidal particles of clay, and hydrous iron and manganese oxides and that minor constituents were dissolved or stripped from these particles by acidification of the samples. Nearly all of the anomalous or highest concentrations of aluminum, barium, chromium, cobalt, copper, iron, manganese, nickel, selenium, silver, and zinc can be explained by this process.

Solubility calculations show that ~60% of the water samples from the UCRS, 20% of the water samples from the RGA, and 10% of the water samples from the McN are supersaturated with barite. The barite apparently occurs as colloidal particles that passed through the filter pads. Relatively high concentrations of aluminum and chromium are also more common in the UCRS than in the RGA. These results may show an association of colloidal transport with vertical flows from the UCRS into the RGA under hydraulic gradients of up to 1.0. The lateral hydraulic gradient in the RGA is only ~0.0001–0.003 (Clausen et al. 1992, Drawing SK-3), and less colloidal transport would be expected for these conditions.

The interpretations of inorganic water chemistry in CH2M HILL (1991, 1992) were based mostly on unfiltered water samples, whereas all interpretations in the present report are based on data from filtered samples. The smaller concentrations of most constituents in most filtered samples show that the unfiltered samples are mixtures of water and soil particles. Except for colloids, these particles are immobile in the RGA aquifer. Also, if few colloids are transported laterally through the aquifer, future water samples should be collected without disturbing the smaller particles in the aquifer matrix and in the well. This objective will require changes in the purging and sampling procedures. Karl (1993, pp. 24–32) obtained good ion balances and consistent concentrations of both inorganic and organic constituents in multiple, unfiltered samples by pumping at rates of only 100 mL/min.

10.0 REFERENCES

- Ball, J. W., and D. K. Nordstrom. 1992. User's manual for WATEQ4F: with revised thermodynamic database and test cases for calculating speciation of major, trace, and redox elements in natural waters. U.S. Geol. Sur. Open-File Rep. 91-183.
- Carlson, T. 1994. Background levels at Lawrence Livermore National Laboratory, site 300. Abstract. p.2. In Abstracts of the Sixth National Technology Information Exchange (TIE) Workshop. U.S. Department. of Energy, Office of Environmental Restoration, Kennewick, Wash.
- CH2M HILL. 1991. Results of the site investigation, phase I, at the Paducah Gaseous Diffusion Plant, Paducah, Kentucky. PGDP/KY/ER-4.
- CH2M HILL. 1992. Results of the site investigation, phase II, at the Paducah Gaseous Diffusion Plant, Paducah, Kentucky. PGDP/KY/SUB/13B-97777C P-03/1991/1.
- Clausen, J. L., J. W Douthitt, K. R. Davis, and B. E. Phillips. 1992. Report of the Paducah Gaseous Diffusion Plant groundwater investigation, phase III. PGDP/KY/E-150
- Davis, R. W., T. W. Lambert, and A. J. Hansen, Jr. 1973. Subsurface geology and ground-water resources of the Jackson Purchase region, Kentucky. U.S. Geol. Surv. Water-Supply Pap. No. 1987.
- Fleischhauer, H. L., and N. Korte. 1990. Formulation of cleanup standards for trace elements with probability plots. *Environ. Manage.*, 14(1):95-105.
- Freeze R. A., and J. A. Cherry. 1979. *Groundwater*. Prentice-Hall, Englewood Cliffs, N. J.
- Gilbert, R. O. 1987. *Statistical methods for environmental pollution monitoring*. Van Nostrand Reinhold, New York.
- Goodrich, R. D. 1927. Straight line plotting of skew frequency data. *Am. Soc. Civ. Eng. Trans.* 91:1-118.
- Hem, J. D. 1985. Study and interpretation of the chemical characteristics of natural water. U.S. Geol. Sur. Water-Supply Pap. No. 2254, 3rd ed.
- Kabata-Pendias, A. and H. Pendias. 1984. *Trace elements in soils and plants*. CRC Press, Boca Raton, Fla.
- Kearl, P. M. 1993. Colloidal borescope investigation at Paducah Gaseous Diffusion Plant. ORNL internal report - Contract DE-AC05-84OR21400. Oak Ridge National Laboratory.
- Lepeltier, C. 1969. A simplified treatment of geochemical data by graphical representation. *Econ. Geol* 64:538-550.
- Lindquist, K. F., and C. E. Bohac. 1989. Shawnee groundwater assessment, phase I. Tennessee Valley Authority Engineering Laboratory Report. WR28-2-35-110.
- Lindsay, W. L. 1979. *Chemical equilibria in soils*. John Wiley, New York.
- Myers, J. 1994. Background concentrations of naturally occurring constituents of concern at Sandia National Laboratory. Abstract. p.4. In Abstracts of the Sixth National Technology Information Exchange (TIE) Workshop. U.S. Department of Energy, Office of Environmental Restoration, Kennewick, Wash.
- Otto, G. H. 1939. A modified logarithmic probability graph for the interpretation of mechanical analysis of sediments. *Jour. Sed. Pet.* 9:62-76.

- Petersen, S. W. 1994. Determination of soil and ground water background for radionuclides at the Hanford site. Abstract. p. 25. In Abstracts of the Sixth National Technology Information Exchange (TIE) Workshop. U.S. Department of Energy, Office of Environmental Restoration, Kennewick, Wash.
- Shaw, D. M. 1961. Element distribution laws in geochemistry. *Geochim. Cosmochim. Acta* 3:116-134.
- Sinclair, A. J. 1976. Applications of probability graphs in mineral exploration. *Assoc. Explor. Geochem. Special Vol. 4*
- Tennant, C. B., and M. L. White. 1959. Study of the distribution of some geochemical data. *Econ. Geol.* 54:1281-1290.
- U.S. Environmental Protection Agency. 1989. Determining soil response action levels based on potential contaminant migration to groundwater. EPA/540/2-89/057, Washington, D.C.
- U.S. Environmental Protection Agency. 1991. GAO-EAS 1.2.1 Geostatistical environmental assessment software, user's guide. EPA 600/8-91/008. Environmental Monitoring Systems Laboratory, Las Vegas, Nev.
- Winters, S. L. 1994. Background groundwater quality characterization of the Department of Energy Oak Ridge Reservation, Oak Ridge, Tennessee, preliminary analysis. Abstract. p. 23. In Abstracts of the Sixth National Technology Information Exchange (TIE) Workshop. U.S. Department of Energy, Office of Environmental Restoration, Kennewick, Wash.

INTERNAL DISTRIBUTION

- | | | |
|---------------------|---------------------|---------------------------------|
| 1. F.A. Anderson | 24. J.T. Grumski | 47. W.L. Richards |
| 2. L.V. Asplund | 25. C.S. Haase | 48. C.T. Rightmire |
| 3. R.O. Barnett | 26. S.J. Hildebrand | 49. T.H. Row |
| 4. L.D. Bates | 27. R.K. Holmes | 50. W.E. Sanford |
| 5. F.P. Baxter | 28. D.D. Huff | 51. F.E. Sharples |
| 6. D.T. Bell | 29. L.P. Hull | 52. D.S. Shriner |
| 7. B.A. Berven | 30. G.K. Jacobs | 53. E.D. Smith |
| 8. H.L. Boston | 31. W.K. Jago | 54. S.H. Stow |
| 9. R.B. Clapp | 32. P. Kanciriuk | 55. L.E. Toran |
| 10. K.W. Cook | 33. R.H. Ketelle | 56. L.O. Vaughan |
| 11. R.B. Cook | 34. H.L. King | 57. D.B. Watson |
| 12. T.K. Cothron | 35. A.J. Kuhaida | 58. S.H. Welch |
| 13. J.H. Cushman | 36. P.J. Lemiszki | 59. R.K. White |
| 14. V.H. Dale | 37. J.M. Loar | 60. S.L. Winters |
| 15. F. P. Delozier | 38. C.J. Marshall | 61. T.F. Zondlo |
| 16. A.F. Diefendorf | 39. G.R. Miller | 62. Central Research Library |
| 17. R. B. Dreier | 40. G.R. Moline | 63-77. ESD Library |
| 18. T. O. Early | 41. G.K. Moore | 78-79. Laboratory Records Dept. |
| 19. N.T. Edwards | 42. C.A. Motley | 80. Laboratory Records, ORNL-RC |
| 20. J.M. Forstrom | 43. J.B. Murphy | 81. ORNL Patent Section |
| 21. D.E. Fowler | 44. M.J. Norris | 82. ORNL Y-12 Technical Library |
| 22. C.W. Gehrs | 45. R.S. Poling | 83-107. PGDP/KEVIL Library |
| 23. P.A. Gourieux | 46. D.E. Reichle | |

EXTERNAL DISTRIBUTION

108. D.W. Dollins, U.S. Department of Energy, Paducah Site Office, P.O. Box 1410, Paducah, KY 42002-1410
109. R.C. Edwards, U.S. Department of Energy, Paducah Site Office, P.O. Box 1410, Paducah, KY 42002-1410
110. R. N. Farvolden, Professor, Department of Earth Sciences, University of Waterloo, Waterloo, Ontario N2L 3G1 Canada
111. D.W. Freckman, Director, College of Natural Resources, 101 Natural Resources Building, Colorado State University, Fort Collins, CO 80523

112. G. Y. Jordy, Director, Office of Program Analysis, Office of Energy Research, ER-30, G-226, U.S. Department of Energy, Washington, DC 20545
113. S.L. Lankford, U.S. Department of Energy, Oak Ridge Operations Office, IRC Building, P.O. Box 2001, Oak Ridge, TN 37838-8541
114. E.R. Meehan, U.S. Department of Energy, Portsmouth Site Office, P.O. Box 628, Piketon, OH 45661-7550
115. A. Patrinos, Director, Environmental Sciences Division, Office of Health and Environmental Research, ER-74, U.S. Department of Energy, Washington, DC 20585
116. M.E. Redfield, U.S. Department of Energy, Paducah Site Office, P.O. Box 1410, Paducah, KY 42002-1410
117. G. S. Sayler, Professor, 10515 Research Drive, Suite 100, The University of Tennessee, Knoxville, TN 37932-2567
118. J.T. Sweeney, U.S. Department of Energy, Oak Ridge Operations Office, IRC Building, P.O. Box 2001, Oak Ridge, TN 37838-8541
119. F. J. Wobber, Environmental Sciences Division, Office of Health and Environmental Research, ER-74, U.S. Department of Energy, Washington, DC 20585
120. Office of Assistant Manager for Energy Research and Development, U.S. Department of Energy Oak Ridge Operations, P.O. Box 2001, Oak Ridge, TN 37831-8600
- 121-122. Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831

APPENDIX A
CUMULATIVE PROBABILITY PLOTS
AND STATISTICAL TABLES
FOR SOILS AND GROUNDWATER ANALYSES

APPENDIX A.1	NEAR-SURFACE SOILS	A-3
APPENDIX A.2	BOREHOLE SAMPLES	A-31
APPENDIX A.3	SEDIMENT SAMPLES.....	A-59
APPENDIX A.4	GROUNDWATER SAMPLES FROM UPPER CONTINENTAL RECHARGE SYSTEM.	A-87
APPENDIX A.5	GROUNDWATER SAMPLES FROM REGIONAL GRAVEL AQUIFER	A-119
APPENDIX A.6	GROUNDWATER SAMPLES FROM McNAIRY FORMATION	A-151

This page left intentionally blank.

APPENDIX A.1
CUMULATIVE PROBABILITY PLOTS AND STATISTICAL TABLES
FOR NEAR-SURFACE SOILS

This page left intentionally blank.

>STATS
 >STATS AGMGKG ALMGKG ASMGKG BAMGKG BEMGKG CAMGKG CDMGKG CHMGKG CNMGKG ,
 >COMGKG CUMGKG FEMGKG HMGKG KMGKG MGMGKG MNMGKG NAMGKG NIMGKG PBMGKG ,
 >SBMGKG SEMGKG TLMGKG VMGKG ZNMGKG / Mean Min Max SD CV Kurtosis Median ,
 >Range SEM Skewness Sum Variance N

FRI 11/04/94 1:13:20 PM D:\WORK\SURFSOIL\TOPSOIL.SYS

TOTAL OBSERVATIONS: 146

	AGMGKG	ALMGKG	ASMGKG	BAMGKG	BEMGKG
N OF CASES	146	146	146	146	146
MINIMUM	0.360	1120.000	0.240	14.000	0.170
MAXIMUM	42.000	43100.000	46.000	657.000	25.000
RANGE	41.640	41980.000	45.760	643.000	24.830
MEAN	2.158	9284.466	6.889	115.527	3.947
VARIANCE	12.885	.364164E+08	44.790	8850.485	38.236
STANDARD DEV	3.590	6034.597	6.693	94.077	6.183
STD. ERROR	0.297	499.427	0.554	7.786	0.512
SKEWNESS (G1)	9.578	3.469	3.903	3.544	1.680
KURTOSIS (G2)	102.633	15.571	17.467	15.168	1.743
SUM	315.080	1355532.000	1005.820	16867.000	576.230
C.V.	1.663	0.650	0.971	0.814	1.567
MEDIAN	1.750	8435.000	5.400	96.500	0.620

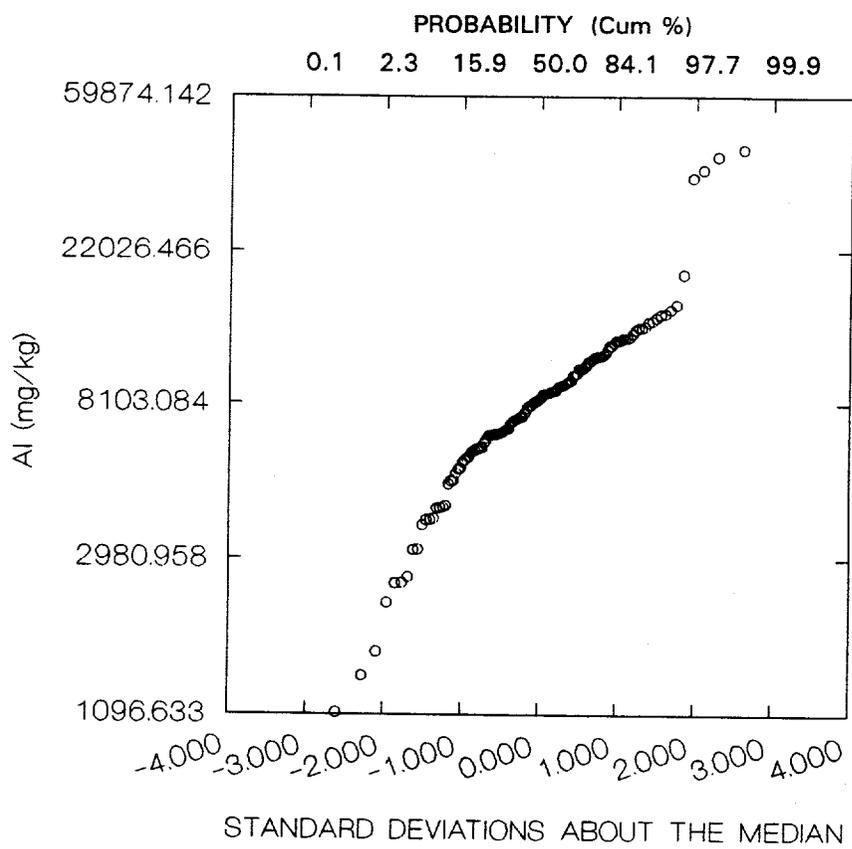
	CAMGKG	CDMGKG	CHMGKG	CNMGKG	COMGKG
N OF CASES	146	146	146	143	146
MINIMUM	235.000	0.250	2.600	0.210	1.200
MAXIMUM	293000.000	235.000	505.000	1.700	69.000
RANGE	292765.000	234.750	502.400	1.490	67.800
MEAN	20500.233	5.201	30.160	0.537	9.151
VARIANCE	.213532E+10	572.582	4672.880	0.036	87.784
STANDARD DEV	46209.526	23.929	68.358	0.190	9.369
STD. ERROR	3824.328	1.980	5.657	0.016	0.775
SKEWNESS (G1)	3.459	7.834	5.084	1.457	4.229
KURTOSIS (G2)	13.268	65.517	26.477	9.023	20.314
SUM	2993034.000	759.380	4403.400	76.820	1336.100
C.V.	2.254	4.601	2.267	0.354	1.024
MEDIAN	2545.000	0.805	14.000	0.590	6.650

	CUMGKG	FEMGKG	HMGKG	KMGKG	MGMGKG
N OF CASES	146	146	146	146	146
MINIMUM	2.500	3500.000	0.038	110.000	257.000
MAXIMUM	18700.000	97600.000	12.000	25000.000	12600.000
RANGE	18697.500	94100.000	11.962	24890.000	12343.000
MEAN	416.838	17098.151	0.268	1026.274	1820.897
VARIANCE	6093829.854	.171205E+09	1.391	9993810.200	2596763.762
STANDARD DEV	2468.568	13084.528	1.179	3161.299	1611.448
STD. ERROR	204.300	1082.883	0.098	261.631	133.364
SKEWNESS (G1)	6.342	4.019	8.591	6.418	3.318
KURTOSIS (G2)	39.637	19.571	76.072	41.253	15.226
SUM	60858.400	2496330.000	39.180	149836.000	265851.000
C.V.	5.922	0.765	4.394	3.080	0.885
MEDIAN	13.000	14300.000	0.100	474.500	1410.000

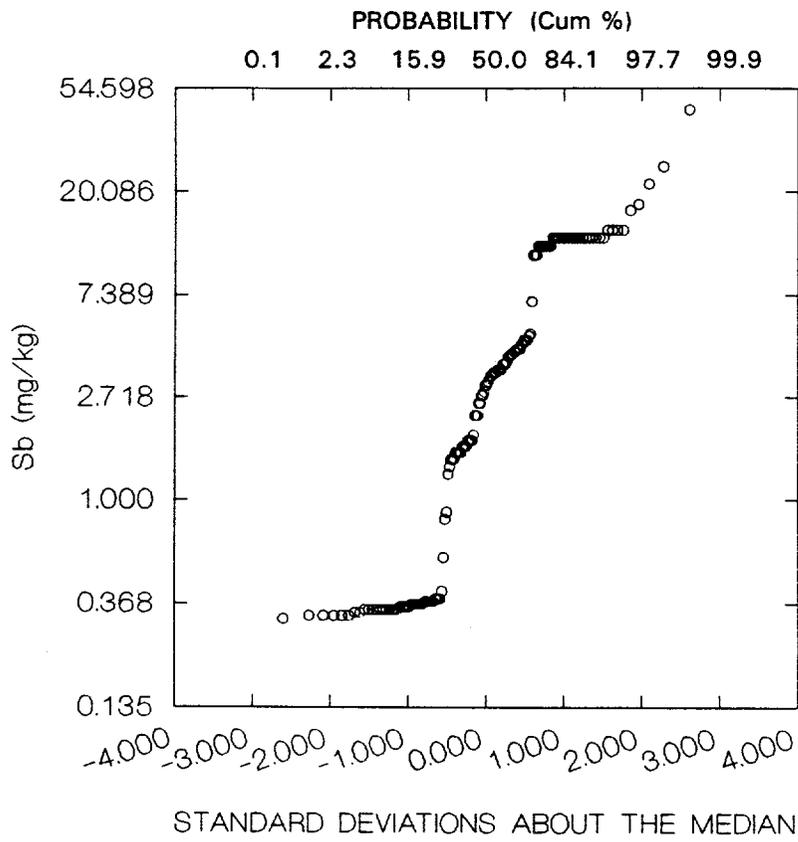
	MNMGKG	NAMGKG	NIMGKG	PBMGKG	SBMGKG
N OF CASES	146	146	146	146	146
MINIMUM	25.000	24.000	2.800	1.600	0.320
MAXIMUM	8090.000	8170.000	12300.000	1160.000	45.000
RANGE	8065.000	8146.000	12297.200	1158.400	44.680
MEAN	570.664	270.233	279.403	47.565	5.349
VARIANCE	634574.790	932705.283	2639385.641	23129.014	41.363
STANDARD DEV	796.602	965.767	1624.619	152.082	6.431
STD. ERROR	65.927	79.927	134.454	12.586	0.532
SKEWNESS (G1)	6.462	6.657	6.522	5.624	2.264
KURTOSIS (G2)	54.080	45.326	42.295	32.616	8.835
SUM	83317.000	39454.000	40792.800	6944.500	780.970
C.V.	1.396	3.574	5.815	3.197	1.202
MEDIAN	357.500	86.000	14.000	15.000	3.100

	SEMGKG	TLMGKG	VMGKG	ZNMGKG
N OF CASES	146	146	146	146
MINIMUM	0.110	0.220	2.300	12.000
MAXIMUM	25.000	13.000	70.000	1130.000
RANGE	24.890	12.780	67.700	1118.000
MEAN	0.581	1.205	23.214	86.390
VARIANCE	4.282	6.252	99.058	30174.198
STANDARD DEV	2.069	2.500	9.953	173.707
STD. ERROR	0.171	0.207	0.824	14.376
SKEWNESS (G1)	11.385	3.622	1.147	4.982
KURTOSIS (G2)	131.673	11.617	4.148	25.593
SUM	84.870	175.940	3389.200	12613.000
C.V.	3.560	2.075	0.429	2.011
MEDIAN	0.300	0.575	23.000	42.000

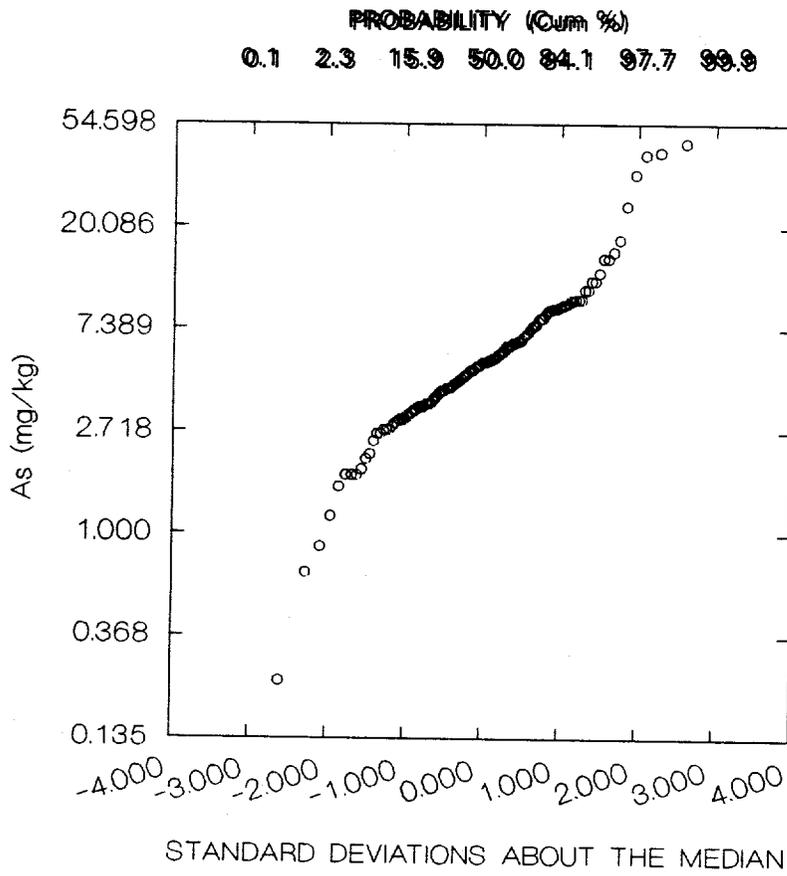
Near-Surface Soils: Cumulative Probability Graph, Aluminum



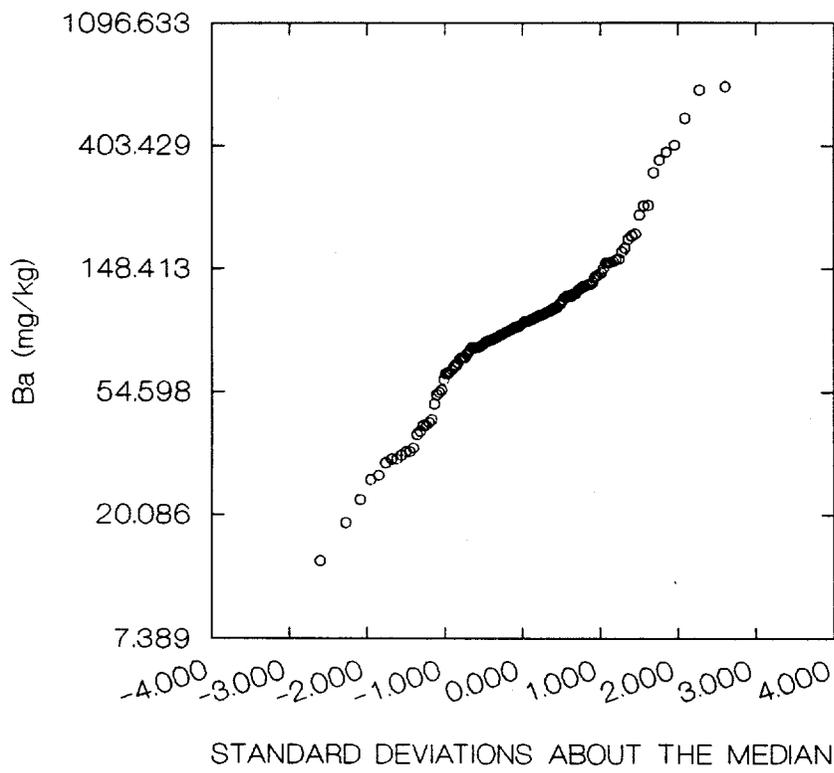
Near-Surface Soils: Cumulative Probability Graph, Antimony



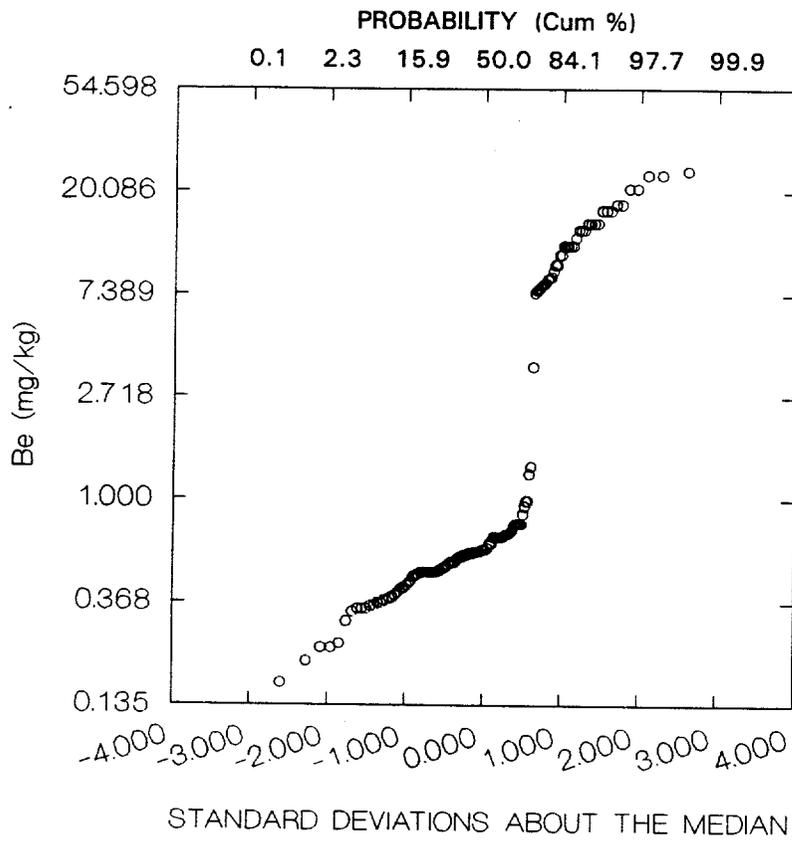
Near-Surface Soils: Cumulative Probability Graph, Arsenic



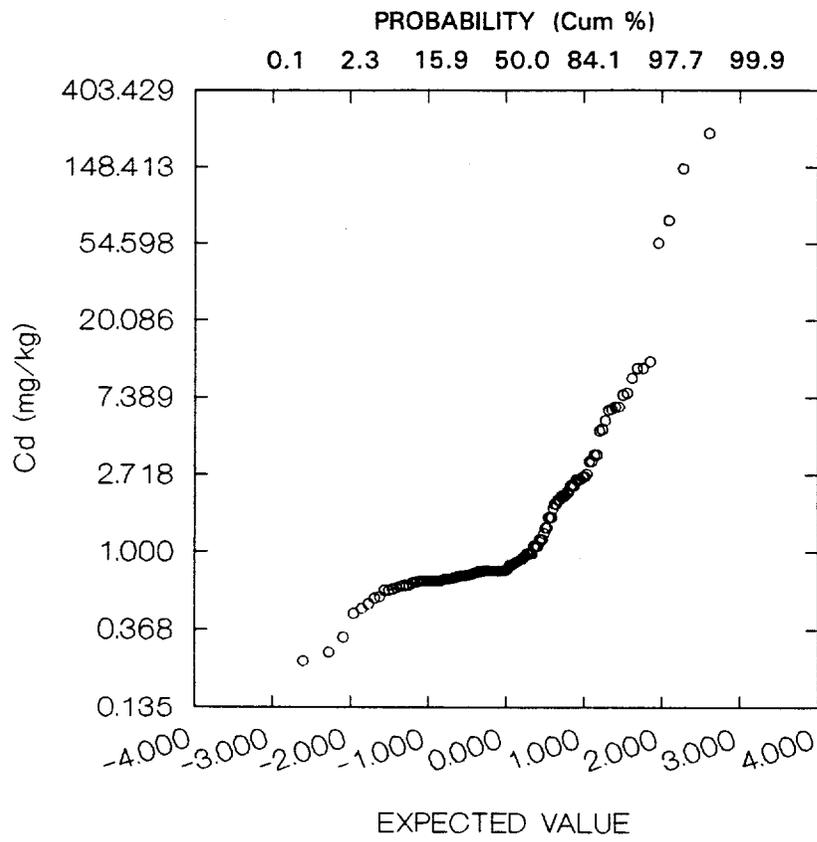
Near-Surface Soils: Cumulative Probability Graph, Barium



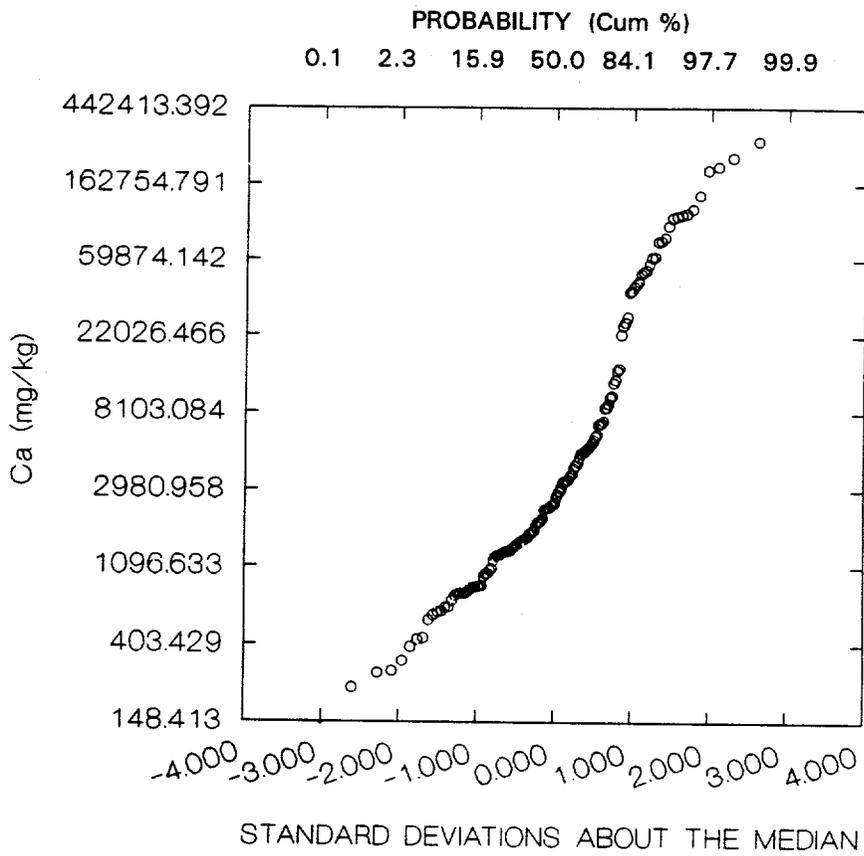
Near-Surface Soils: Cumulative Probability Graph, Beryllium



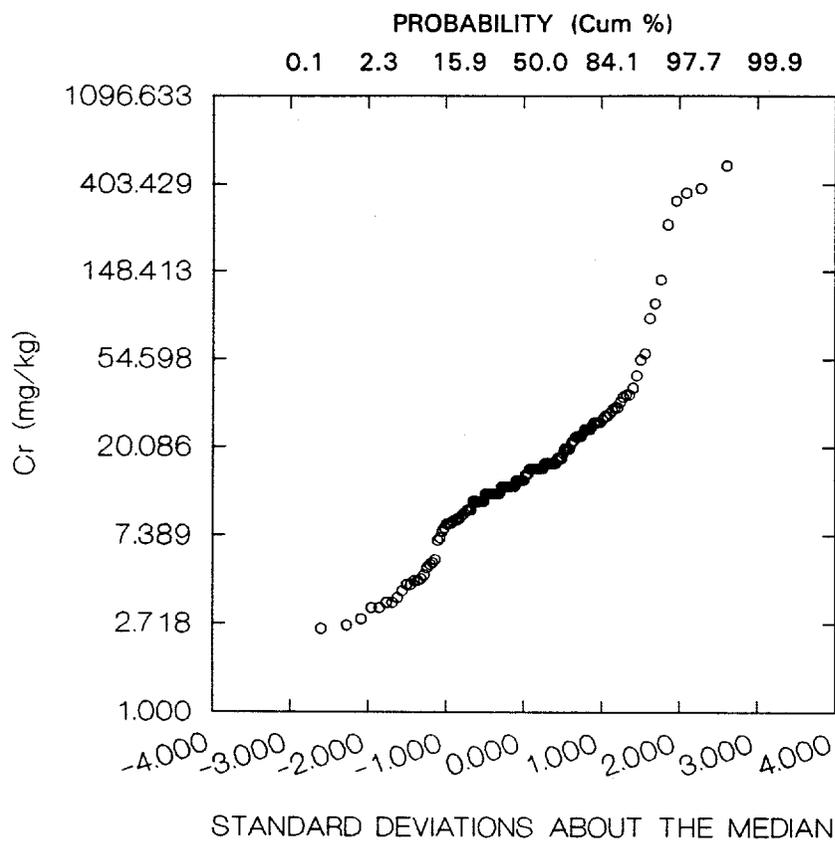
Near-Surface Soils: Cumulative Probability Graph, Cadmium



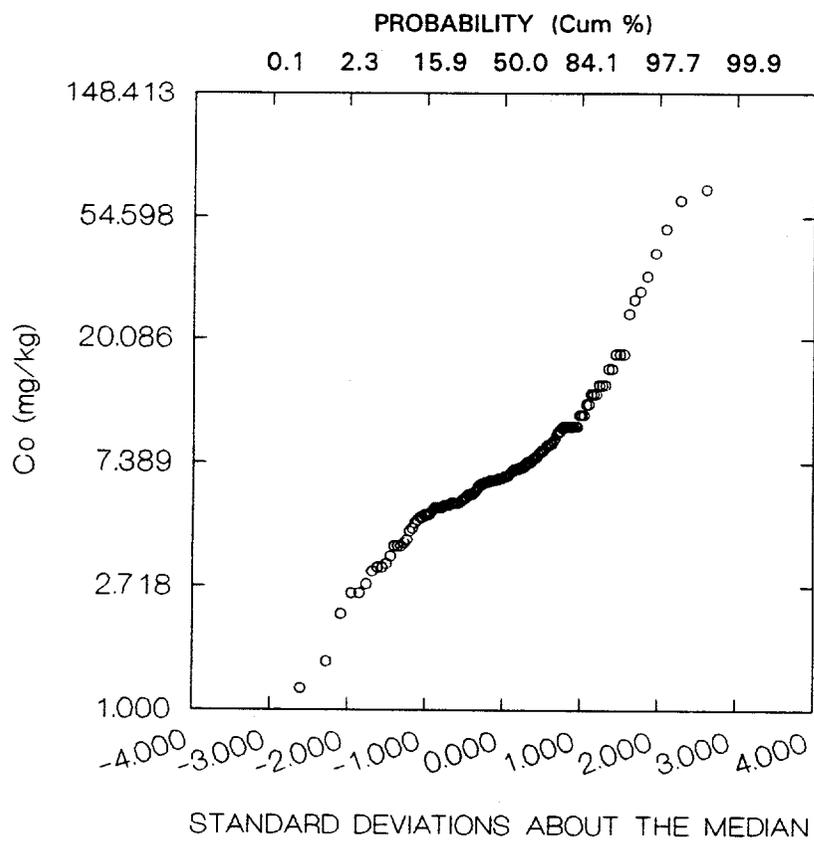
Near-Surface Soils: Cumulative Probability Graph, Calcium



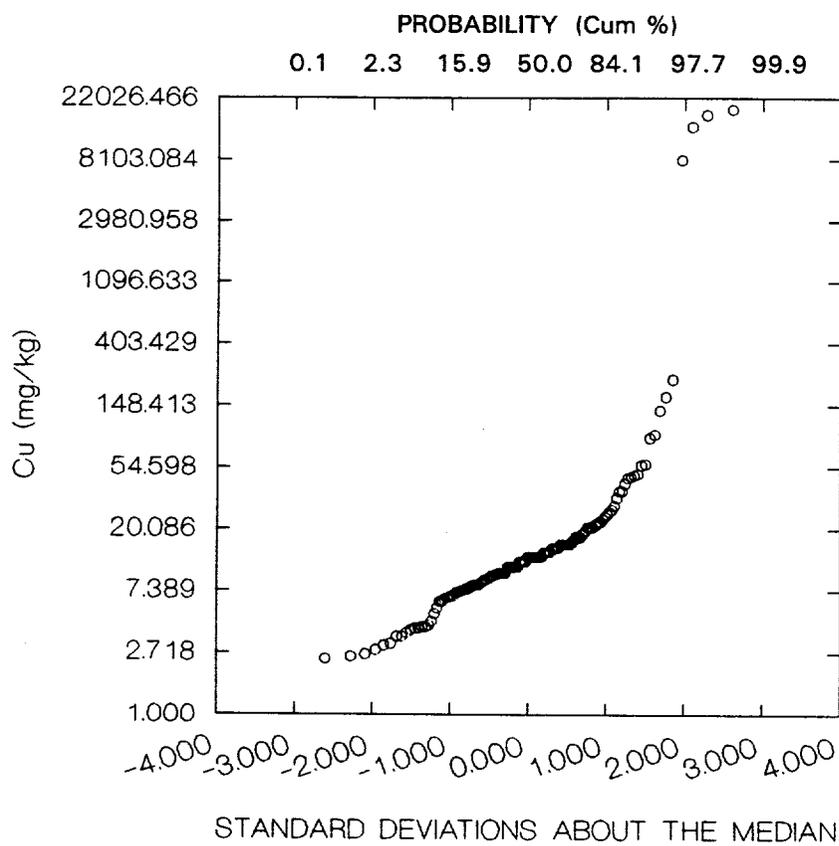
Near-Surface Soils: Cumulative Probability Graph, Chromium



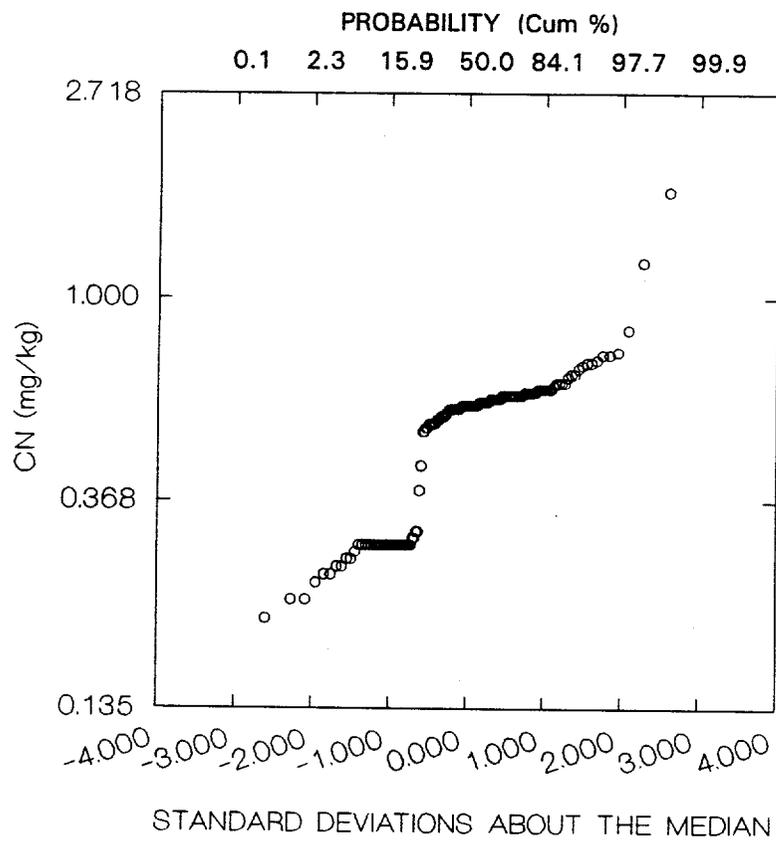
Near-Surface Soils: Cumulative Probability Graph, Cobalt



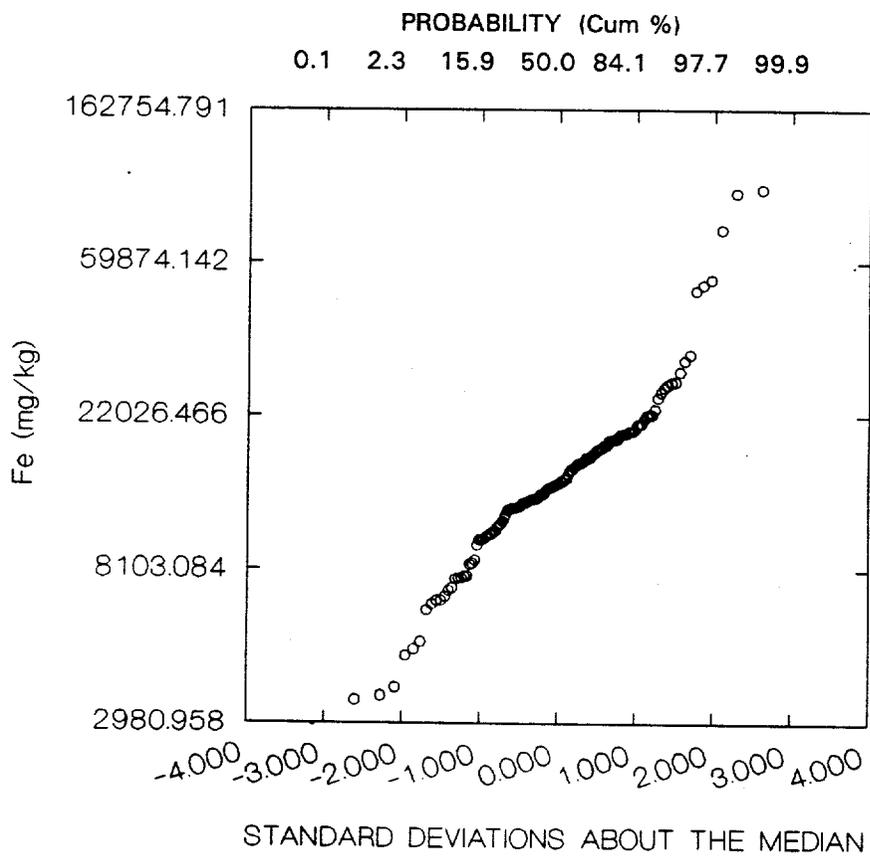
Near-Surface Soils: Cumulative Probability Graph, Copper



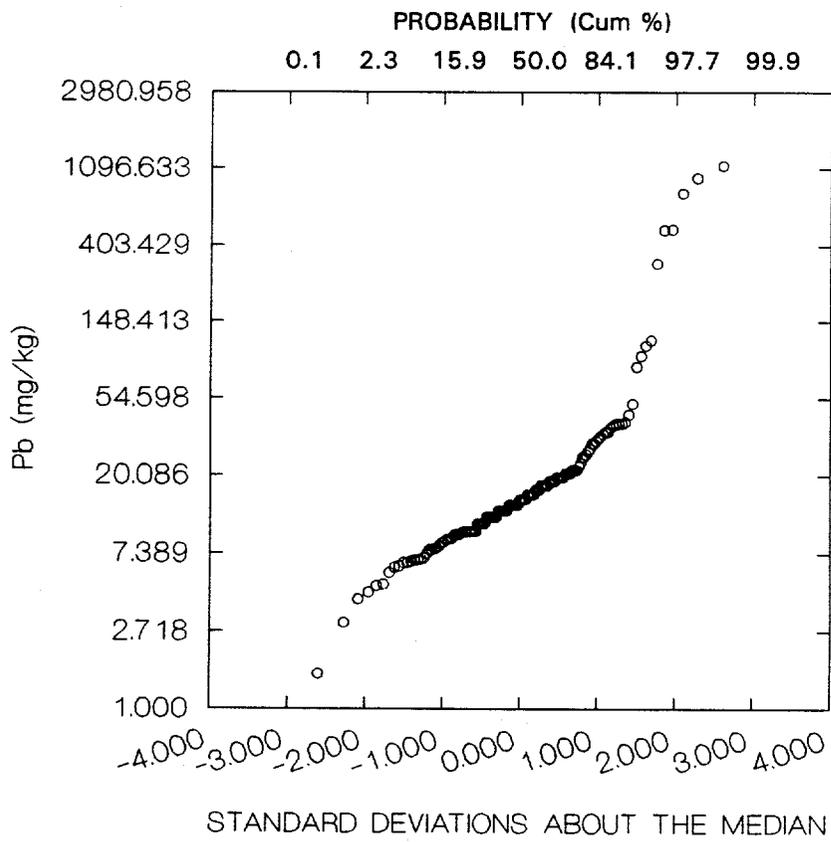
Near-Surface Soils: Cumulative Probability Graph, Cyanide



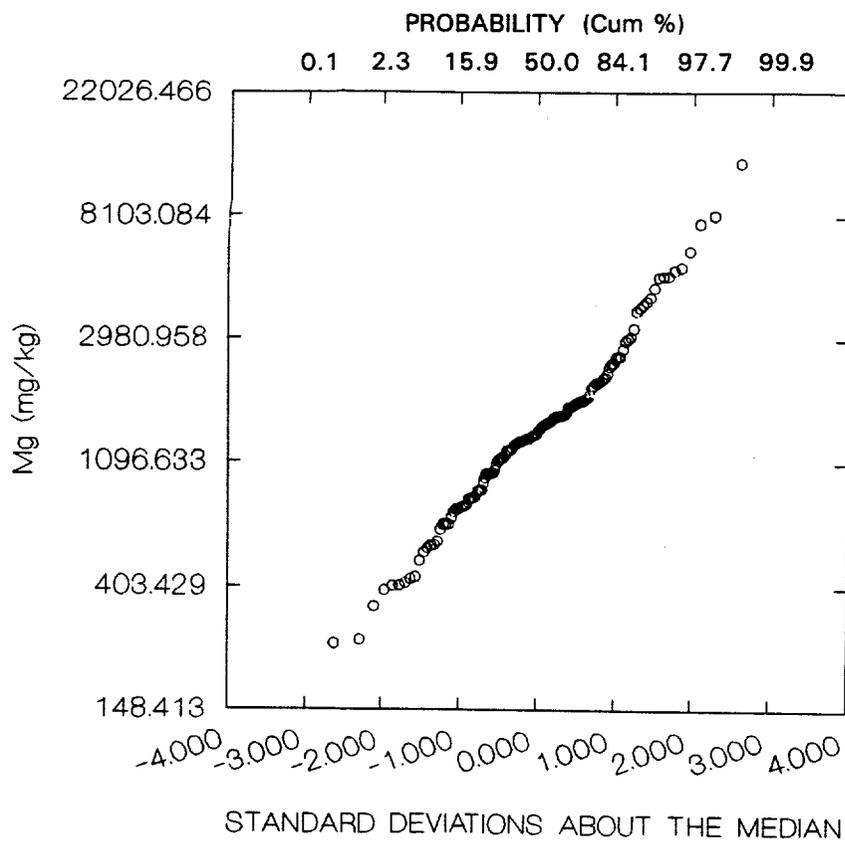
Near-Surface Soils: Cumulative Probability Graph, Iron



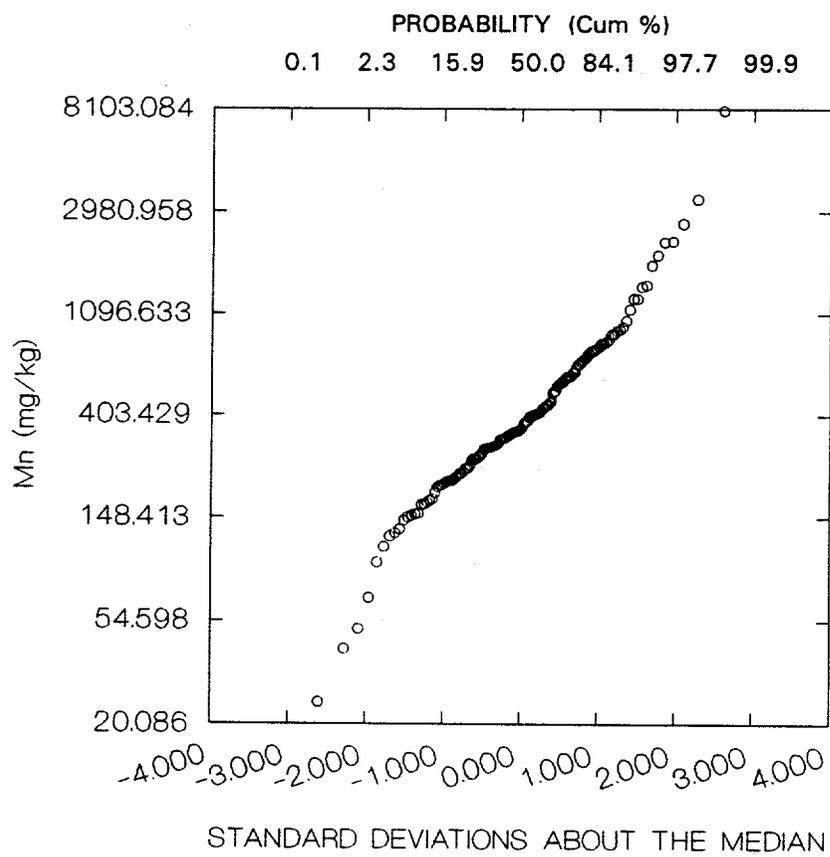
Near-Surface Soils: Cumulative Probability Graph, Lead



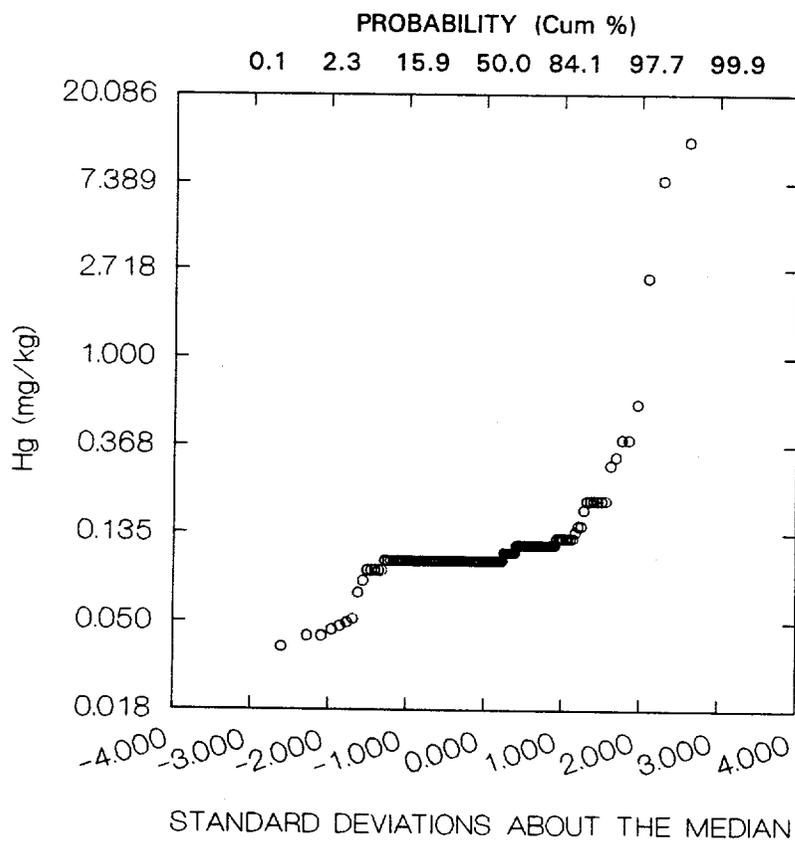
Near-Surface Soils: Cumulative Probability Graph, Magnesium



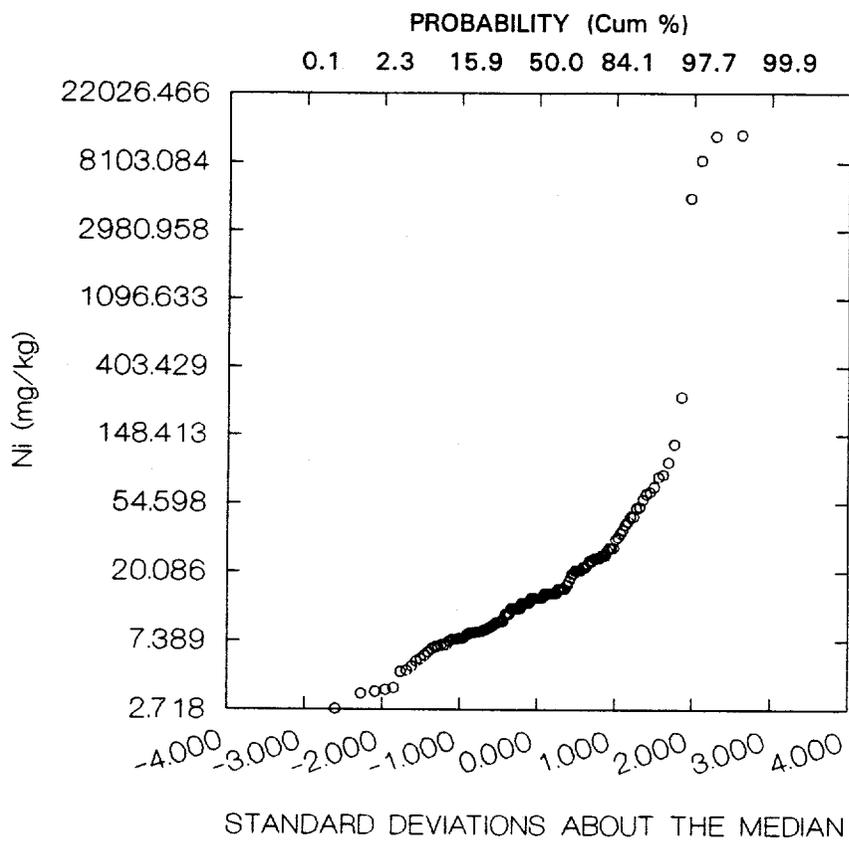
Near-Surface Soils: Cumulative Probability Graph, Manganese



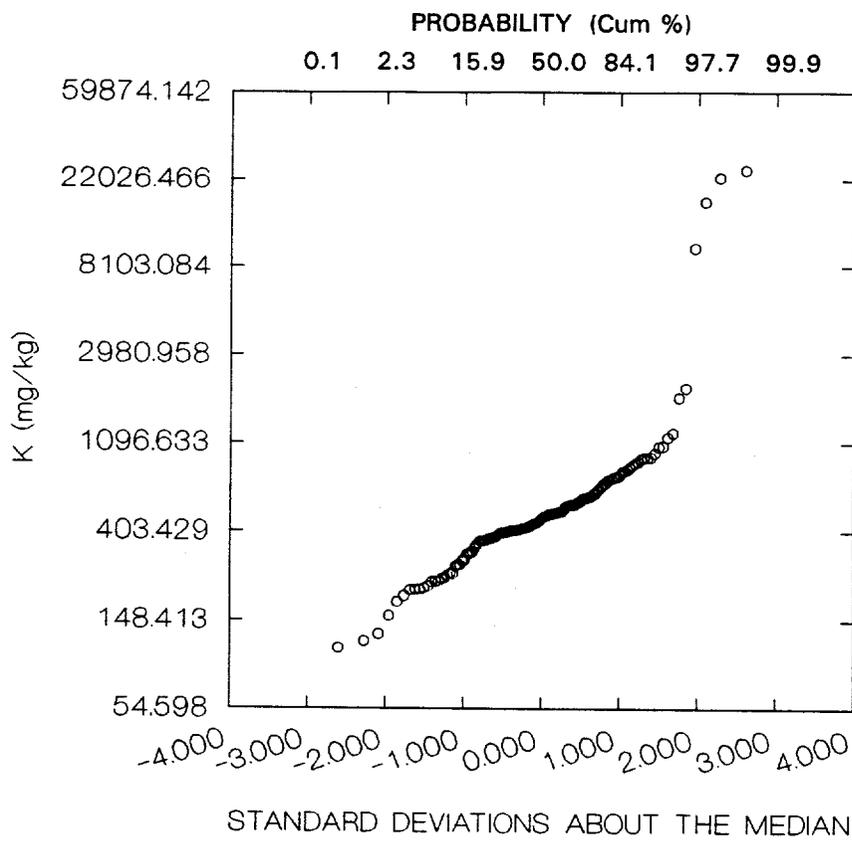
Near-Surface Soils: Cumulative Probability Graph, Mercury



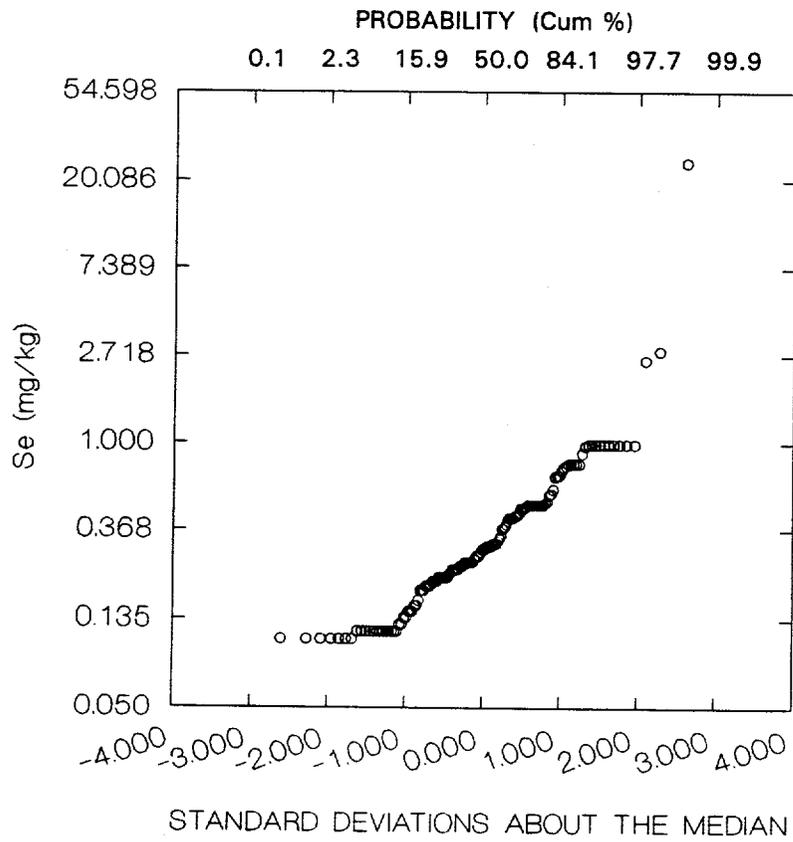
Near-Surface Soils: Cumulative Probability Graph, Nickel



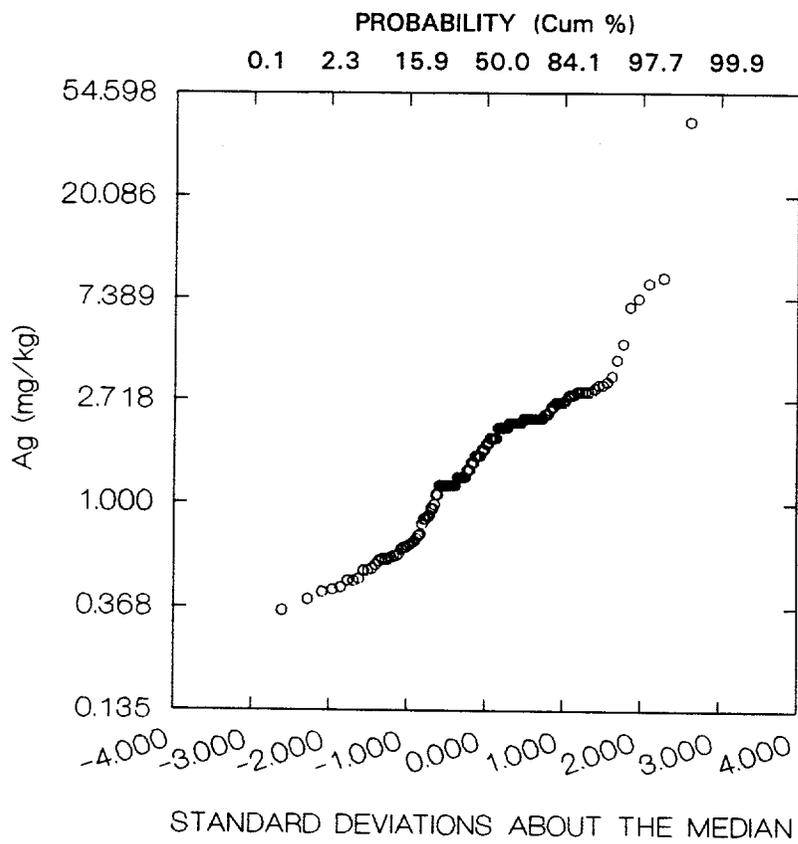
Near-Surface Soils: Cumulative Probability Graph, Potassium



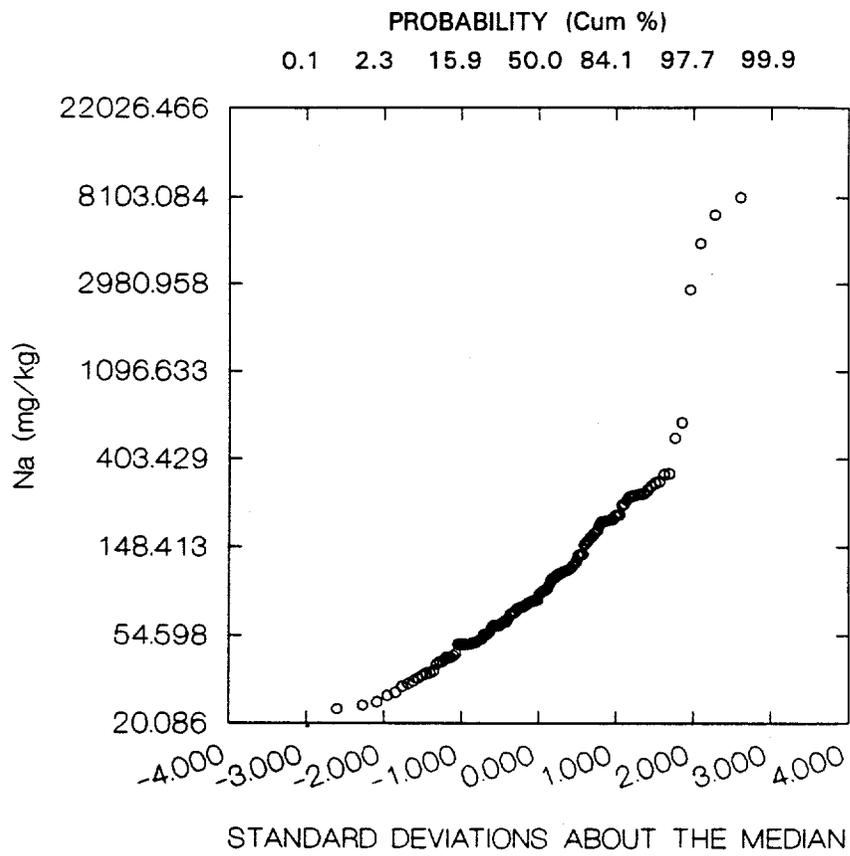
Near-Surface Soils: Cumulative Probability Graph, Selenium



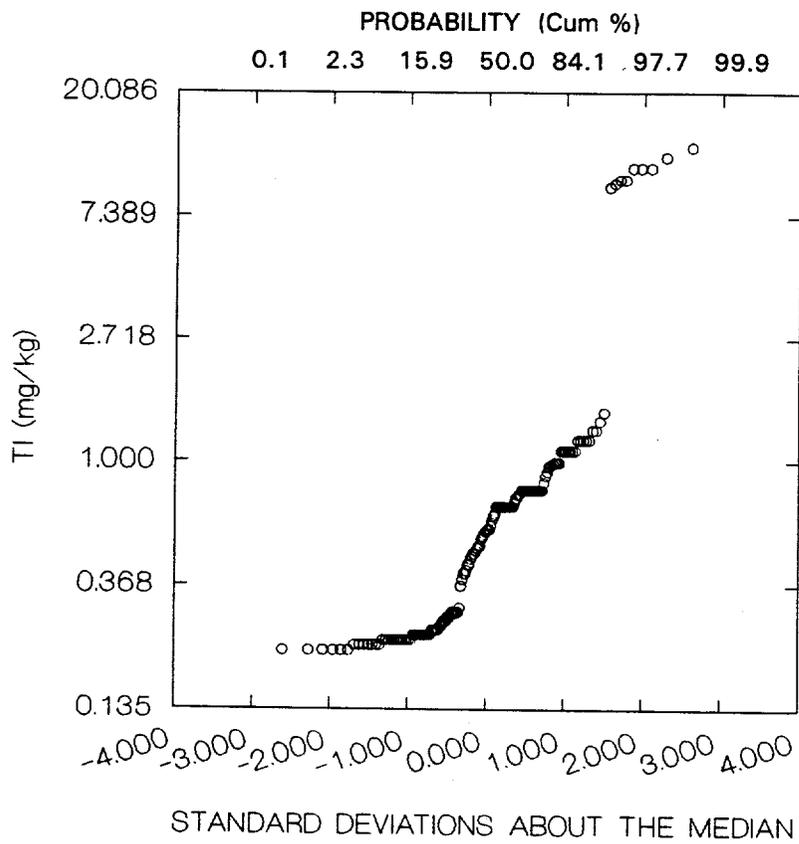
Near-Surface Soils: Cumulative Probability Graph, Silver



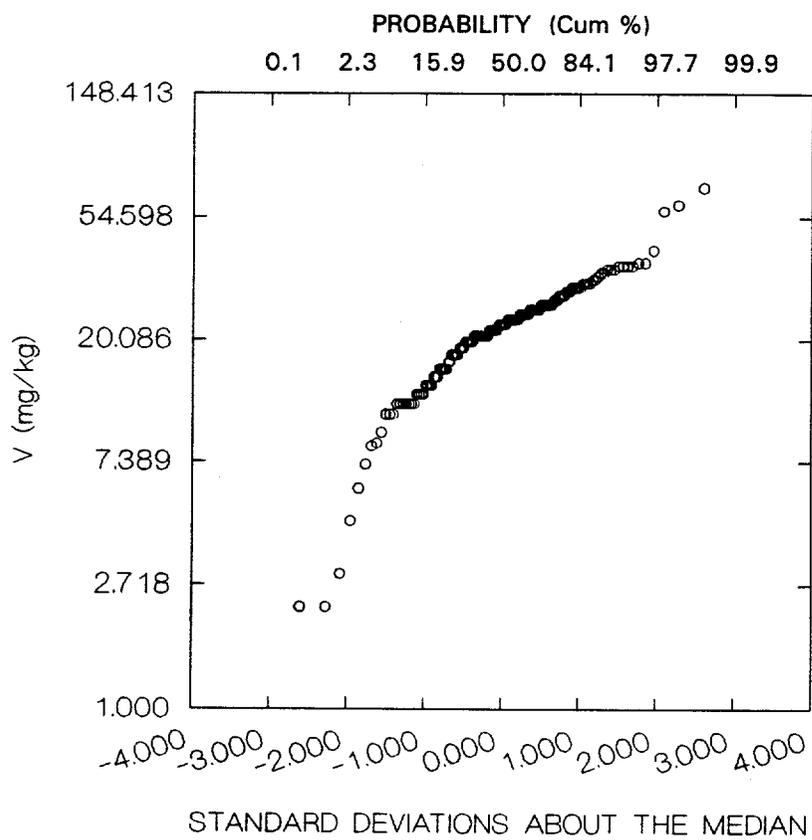
Near-Surface Soils: Cumulative Probability Graph, Sodium



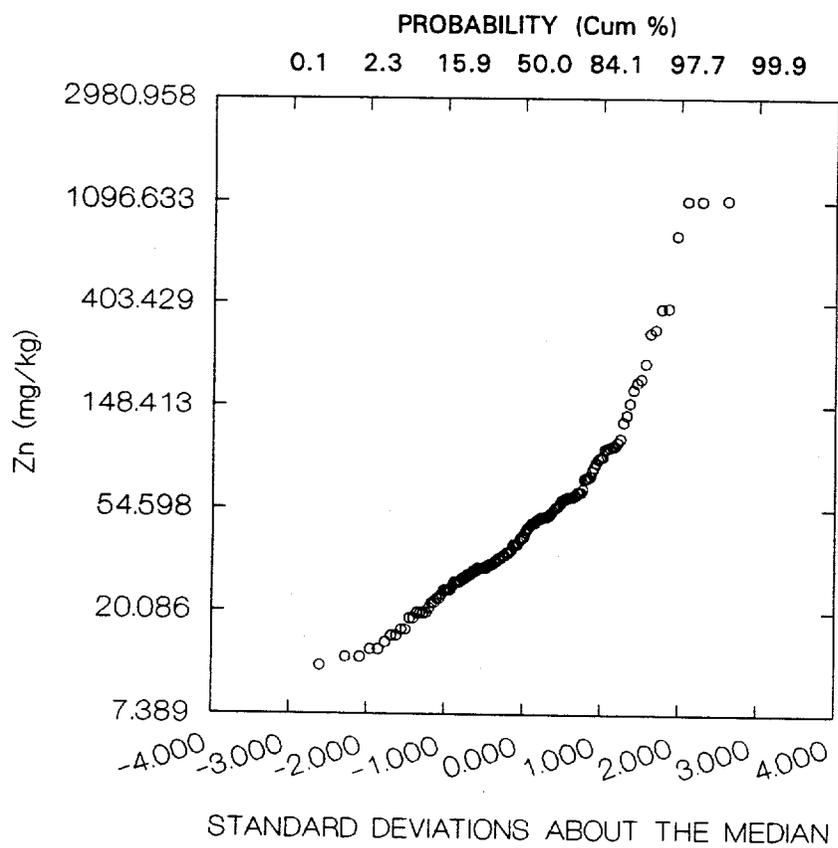
Near-Surface Soils: Cumulative Probability Graph, Thallium



Near-Surface Soils: Cumulative Probability Graph, Vanadium



Near-Surface Soils: Cumulative Probability Graph, Zinc



APPENDIX A.2

**CUMULATIVE PROBABILITY PLOTS AND STATISTICAL TABLES
FOR BOREHOLE SAMPLES**

This page left intentionally blank.

>STATS AGMGKG ALMGKG ASMGKG BAMGKG BEMGKG CAMGKG CDMGKG CHMGKG CNMGKG ,
 >COMGKG CUMGKG FEMGKG / Mean Min Max SD CV Kurtosis Median Range SEM ,
 >Skewness Sum Variance N

FRI 11/04/94 1:25:12 PM D:\WORK\SUBSOILS\SUBSOIL.SYS

TOTAL OBSERVATIONS: 597

	AGMGKG	ALMGKG	ASMGKG	BAMGKG	BEMGKG
N OF CASES	597	597	597	597	597
MINIMUM	0.280	159.000	0.160	2.000	0.005
MAXIMUM	14.000	18200.000	18.700	341.000	2.600
RANGE	13.720	18041.000	18.540	339.000	2.595
MEAN	1.185	5217.075	2.366	53.327	0.578
VARIANCE	0.848	.113465E+08	4.361	2441.569	0.096
STANDARD DEV	0.921	3368.454	2.088	49.412	0.310
STD. ERROR	0.038	137.862	0.085	2.022	0.013
SKEWNESS(G1)	6.088	0.725	2.209	1.934	1.690
KURTOSIS(G2)	68.057	0.191	8.532	5.060	5.516
SUM	707.517	3114594.000	1412.481	31836.500	345.214
C.V.	0.777	0.646	0.883	0.927	0.535
MEDIAN	0.953	4680.000	1.800	36.000	0.520

	CAMGKG	CDMGKG	CHMGKG	CNMGKG	COMGKG
N OF CASES	597	597	597	589	597
MINIMUM	1.720	0.130	0.484	0.120	0.580
MAXIMUM	27200.000	12.800	161.000	1.400	48.000
RANGE	27198.280	12.670	160.516	1.280	47.420
MEAN	1304.817	0.922	13.940	0.561	5.550
VARIANCE	4800694.424	0.582	233.619	0.050	23.379
STANDARD DEV	2191.049	0.763	15.285	0.225	4.835
STD. ERROR	89.674	0.031	0.626	0.009	0.198
SKEWNESS(G1)	7.354	7.684	3.779	0.422	3.126
KURTOSIS(G2)	65.071	101.656	22.296	0.308	16.046
SUM	778975.920	550.711	8322.350	330.361	3313.270
C.V.	1.679	0.827	1.096	0.400	0.871
MEDIAN	923.000	0.790	11.000	0.577	4.300

	CUMGKG	FEMGKG
N OF CASES	597	597
MINIMUM	0.640	545.000
MAXIMUM	61.500	47400.000
RANGE	60.860	46855.000
MEAN	8.050	12636.452
VARIANCE	60.832	.525370E+08
STANDARD DEV	7.799	7248.240
STD. ERROR	0.319	296.651
SKEWNESS(G1)	2.885	0.988
KURTOSIS(G2)	12.228	1.607
SUM	4806.103	7543962.000
C.V.	0.969	0.574
MEDIAN	5.700	11800.000

>STATS HGMGKG KMGKG MGMGKG MNMGKG NAMGKG NIMGKG PBMGKG SBMGKG SEMGKG ,
 >TLMGKG VMGKG ZNMGKG / Mean Min Max SD CV Kurtosis Median Range SEM ,
 >Skewness Sum Variance N

FRI 11/04/94 1:26:18 PM D:\WORK\SUBSOILS\SUBSOIL.SYS

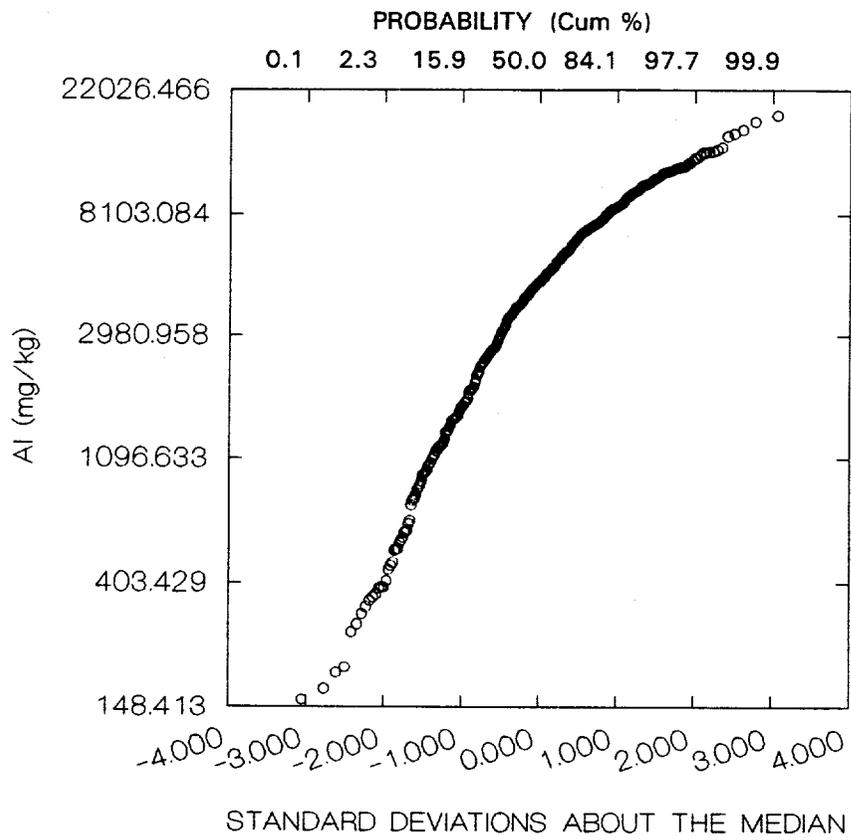
TOTAL OBSERVATIONS: 597

	HGMGKG	KMGKG	MGMGKG	MNMGKG	NAMGKG
N OF CASES	597	597	597	597	597
MINIMUM	0.010	36.000	16.600	1.700	3.100
MAXIMUM	1.060	3290.000	3250.000	2920.000	882.000
RANGE	1.050	3254.000	3233.400	2918.300	878.900
MEAN	0.089	326.725	711.339	188.798	180.624
VARIANCE	0.004	76444.903	344662.964	67857.062	13003.090
STANDARD DEV	0.061	276.487	587.080	260.494	114.031
STD. ERROR	0.003	11.316	24.028	10.661	4.667
SKEWNESS(G1)	8.073	3.551	1.305	4.164	1.215
KURTOSIS(G2)	111.746	24.630	1.555	27.750	3.276
SUM	53.313	195055.000	424669.100	112712.400	107832.700
C.V.	0.688	0.846	0.825	1.380	0.631
MEDIAN	0.093	238.000	525.000	108.000	181.000

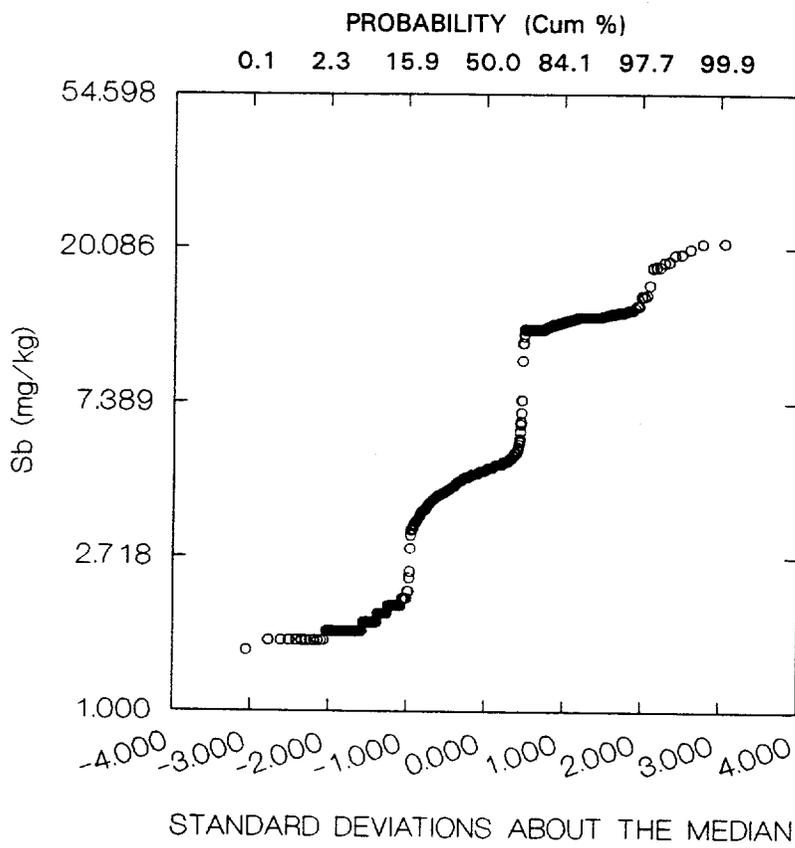
	NIMGKG	PBMGKG	SBMGKG	SEMGKG	TLMGKG
N OF CASES	597	597	597	597	597
MINIMUM	0.840	0.484	1.500	0.086	0.160
MAXIMUM	122.000	133.000	21.000	3.800	9.600
RANGE	121.160	132.516	19.500	3.714	9.440
MEAN	8.606	8.303	6.787	0.359	0.625
VARIANCE	70.317	91.009	19.697	0.093	0.881
STANDARD DEV	8.386	9.540	4.438	0.305	0.939
STD. ERROR	0.343	0.390	0.182	0.012	0.038
SKEWNESS(G1)	6.147	6.019	0.774	4.707	7.451
KURTOSIS(G2)	67.408	57.543	-0.648	38.099	60.169
SUM	5137.870	4956.989	4051.800	214.396	372.885
C.V.	0.974	1.149	0.654	0.849	1.503
MEDIAN	7.300	6.700	4.810	0.300	0.540

	VMGKG	ZNMGKG
N OF CASES	597	597
MINIMUM	0.712	0.830
MAXIMUM	68.900	190.000
RANGE	68.188	189.170
MEAN	18.551	22.754
VARIANCE	98.395	330.522
STANDARD DEV	9.919	18.180
STD. ERROR	0.406	0.744
SKEWNESS(G1)	0.914	2.410
KURTOSIS(G2)	1.604	13.255
SUM	11074.833	13584.230
C.V.	0.535	0.799
MEDIAN	17.000	17.800

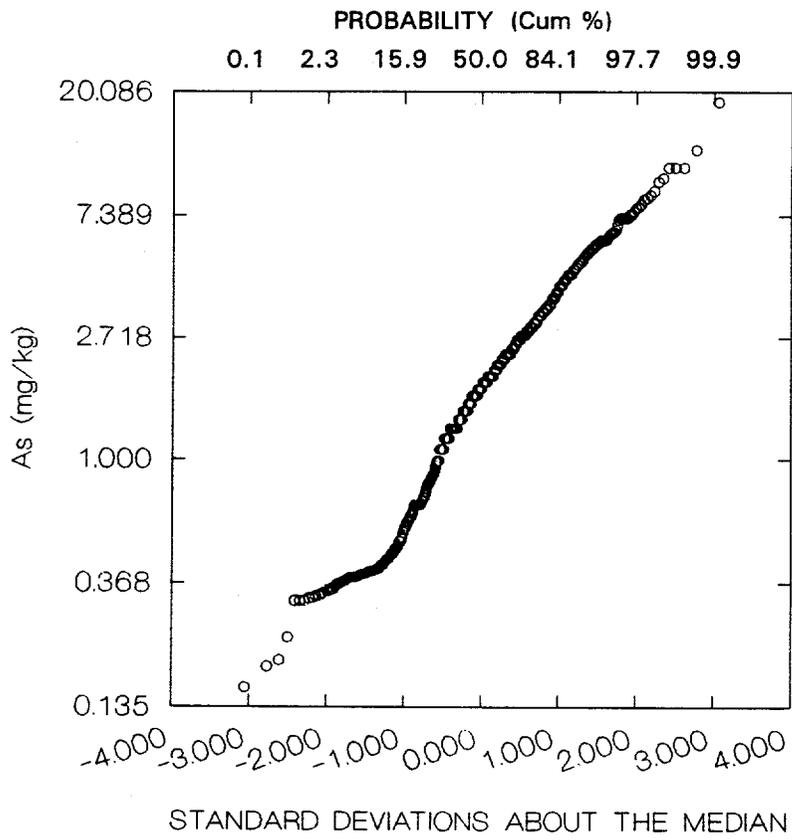
Subsoil: Cumulative Probability Graph, Aluminum



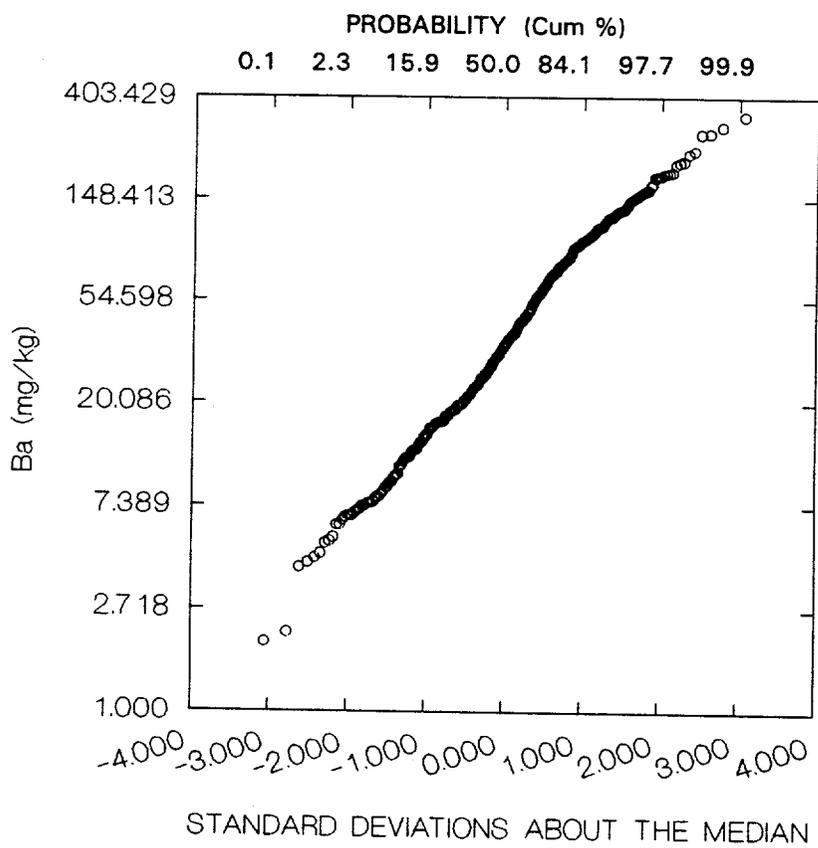
Subsoil: Cumulative Probability Graph, Antimony



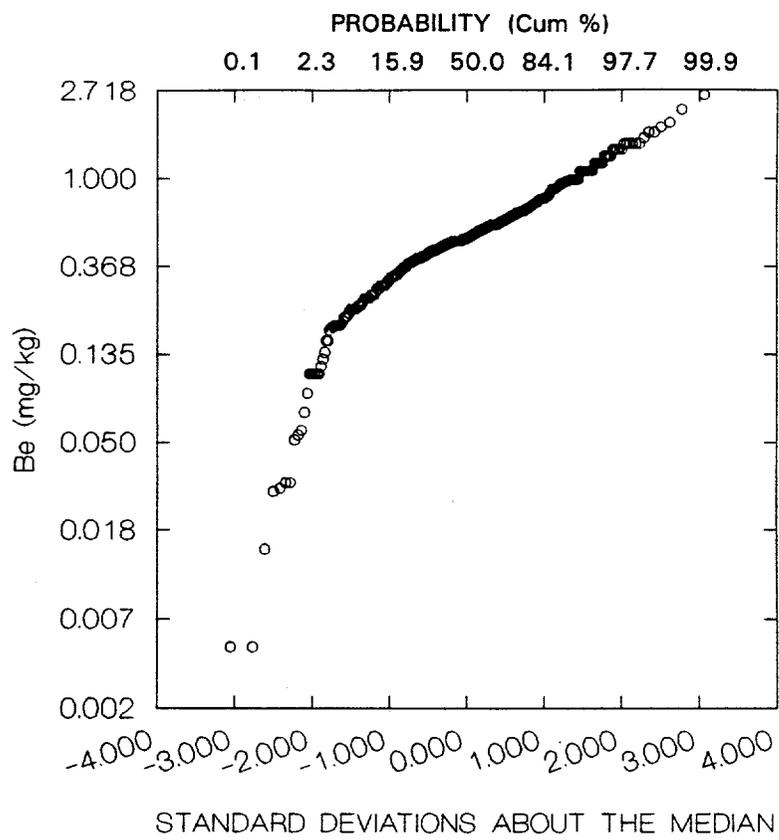
Subsoil: Cumulative Probability Graph, Arsenic



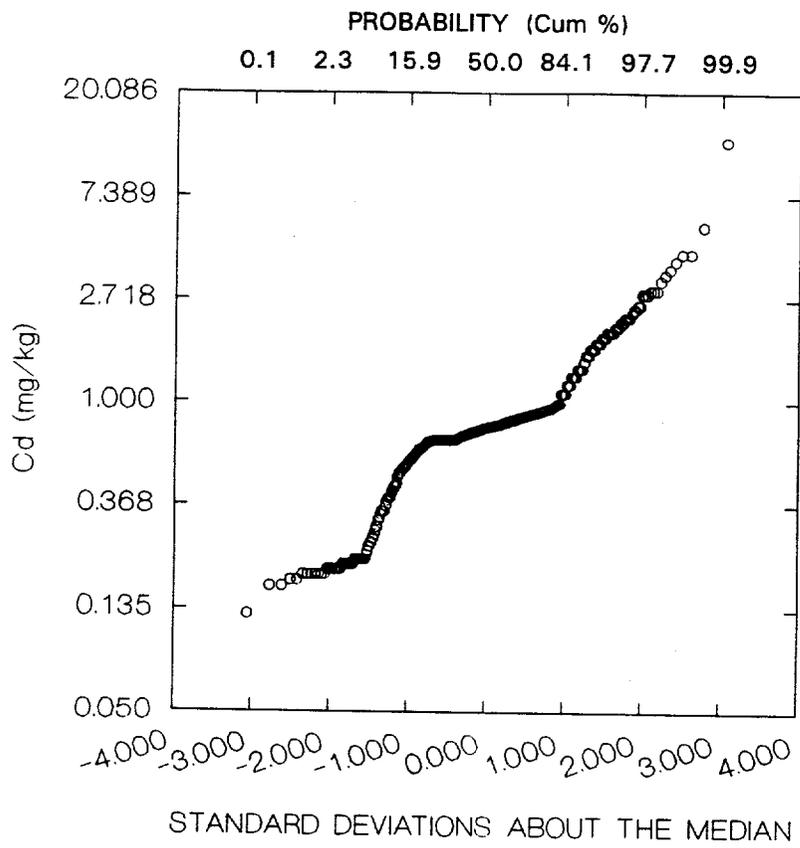
Subsoil: Cumulative Probability Graph, Barium



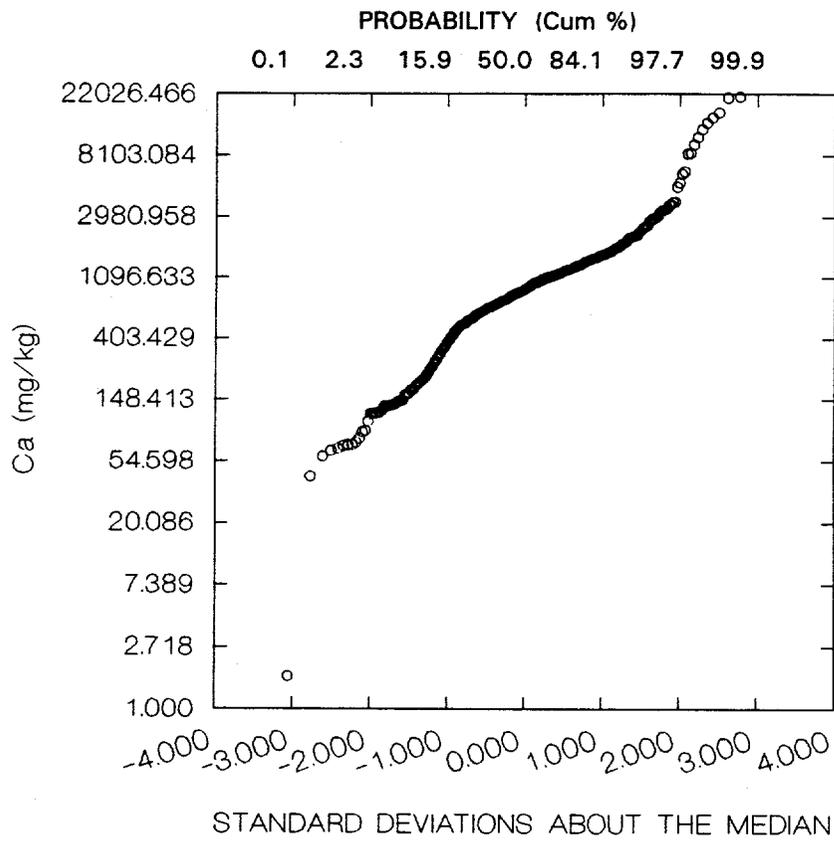
Subsoil: Cumulative Probability Graph, Beryllium



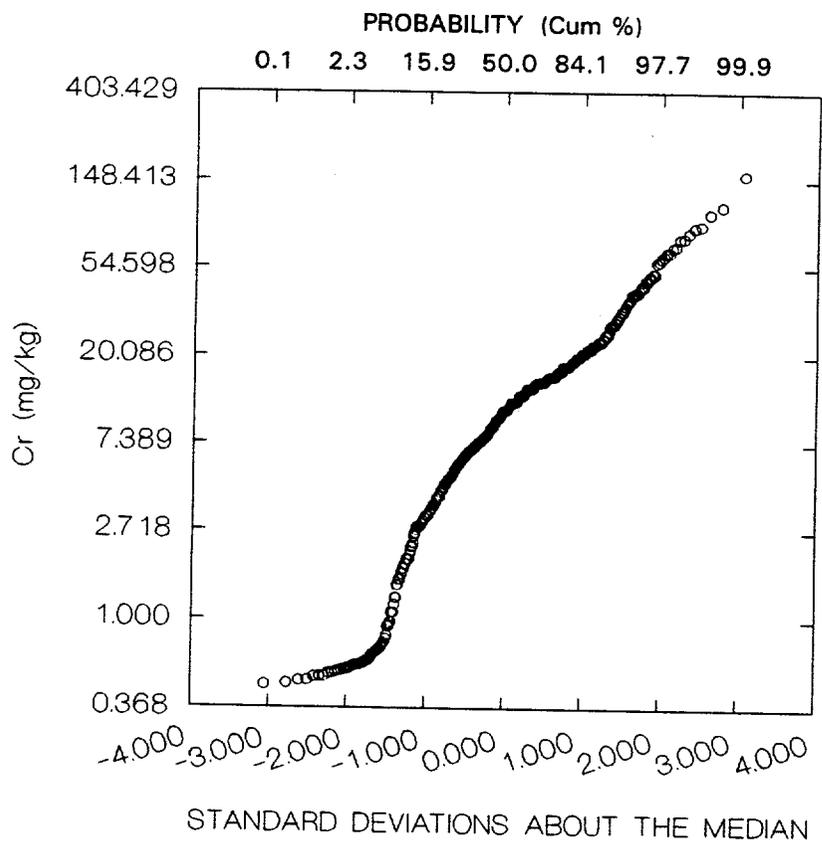
Subsoil: Cumulative Probability Graph, Cadmium



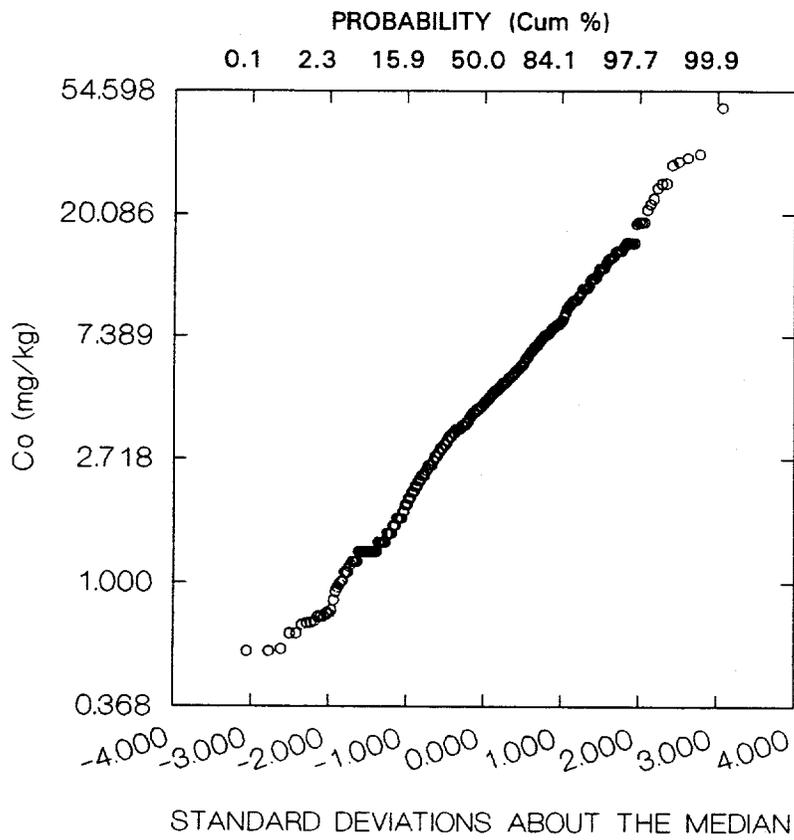
Subsoil: Cumulative Probability Graph, Calcium



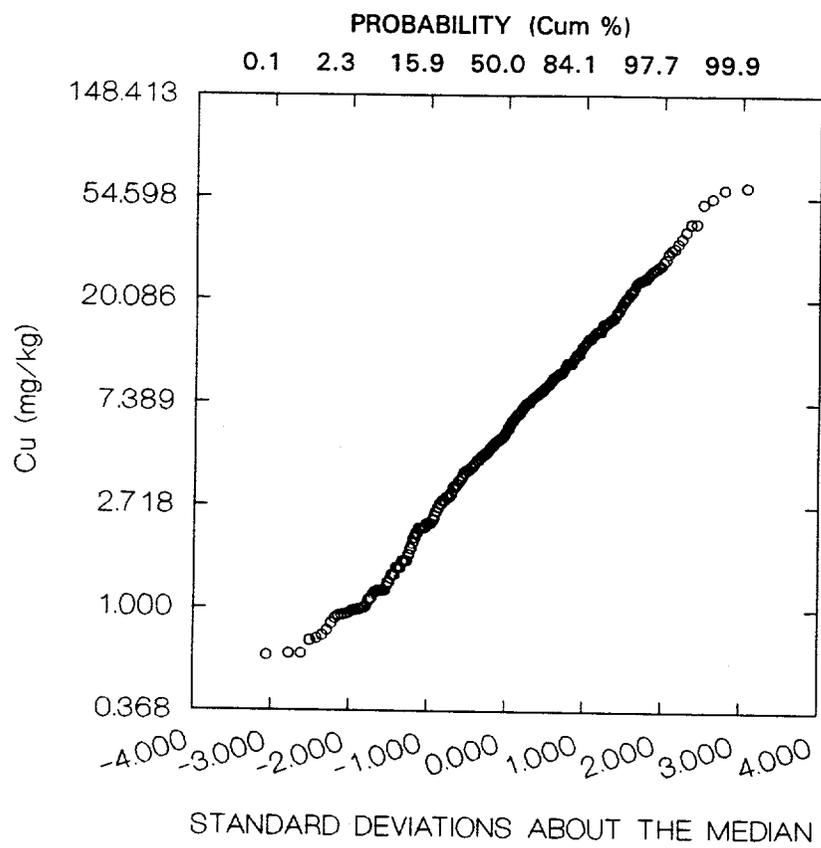
Subsoil: Cumulative Probability Graph, Chromium



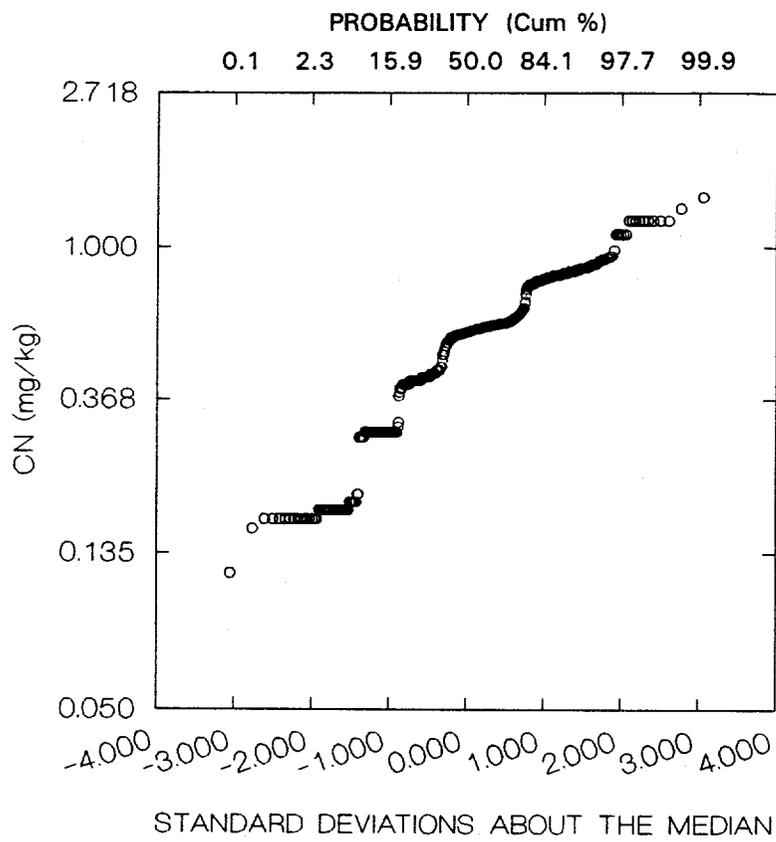
Subsoil: Cumulative Probability Graph, Cobalt



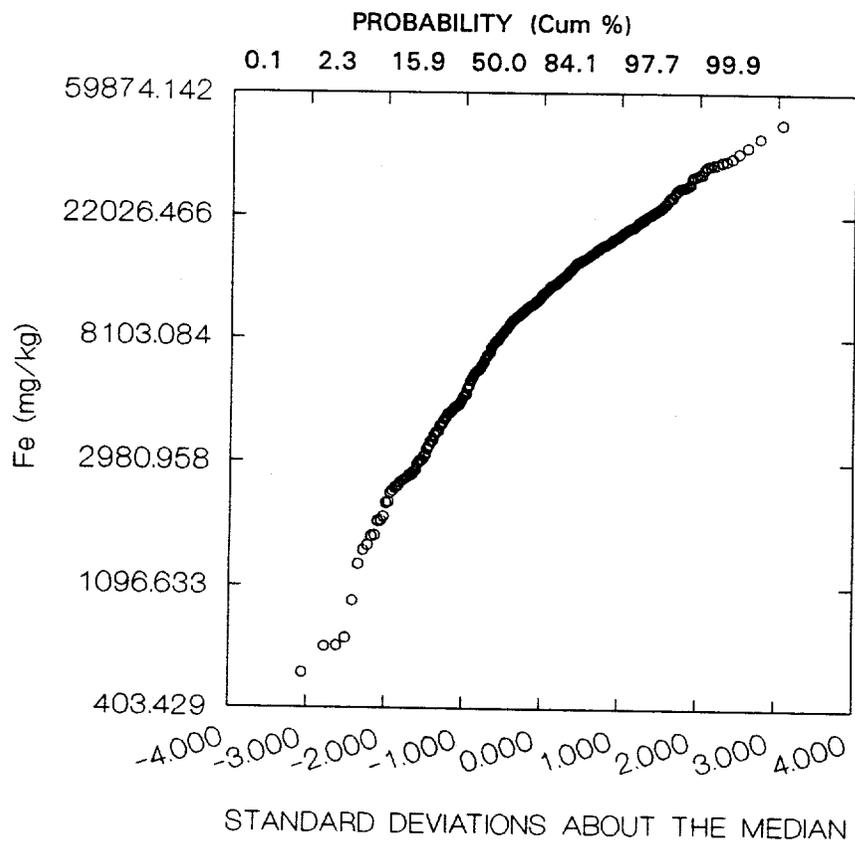
Subsoil: Cumulative Probability Graph, Copper



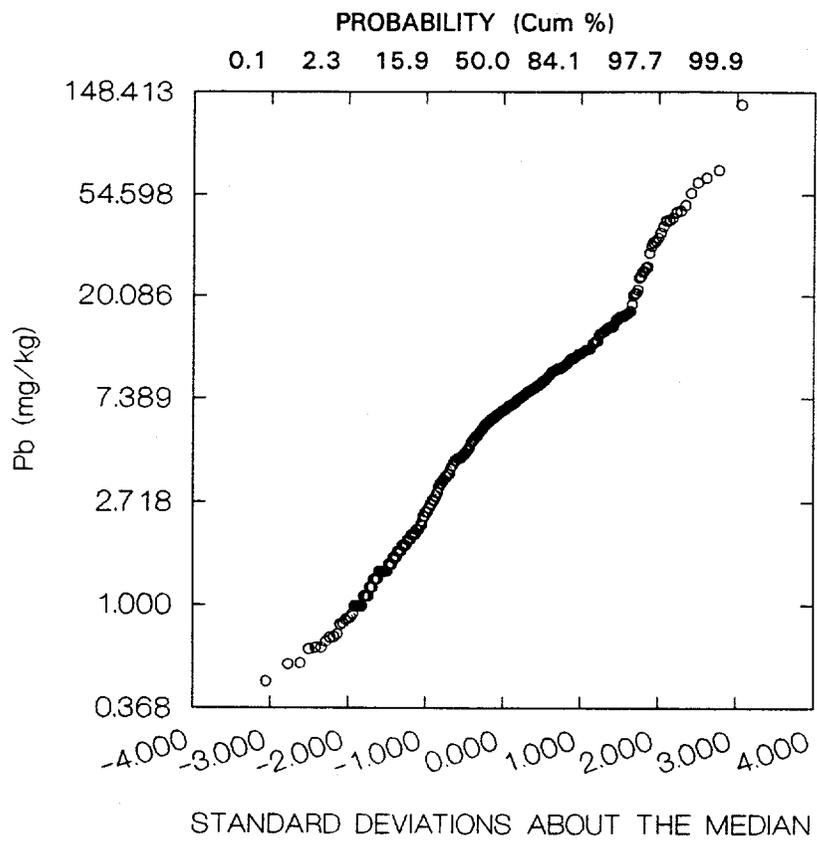
Subsoil: Cumulative Probability Graph, Cyanide



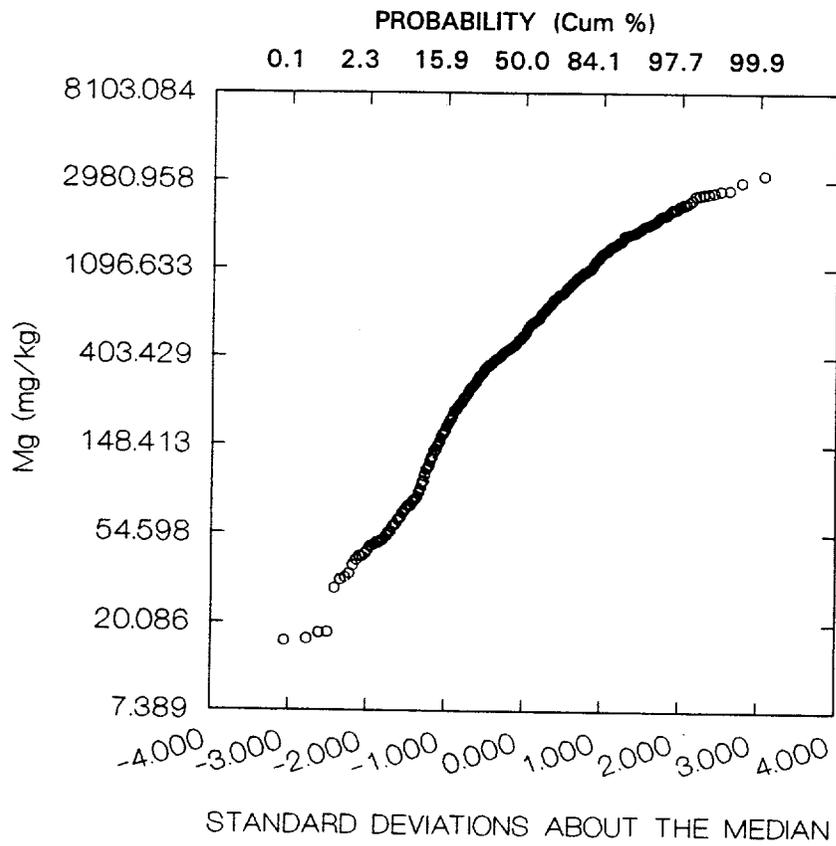
Subsoil: Cumulative Probability Graph, Iron



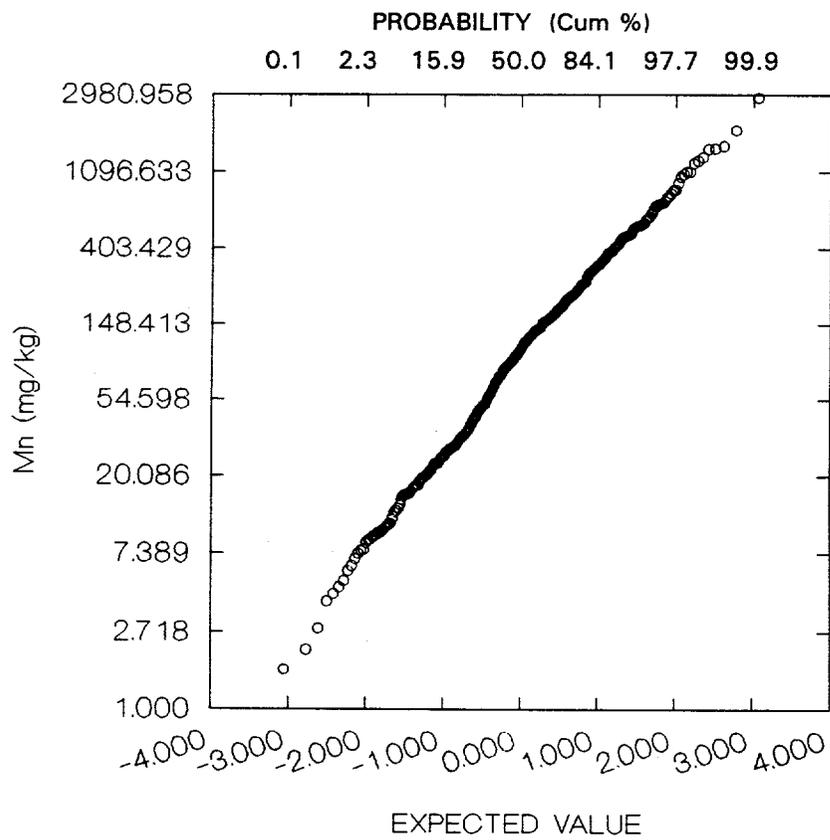
Subsoil: Cumulative Probability Graph, Lead



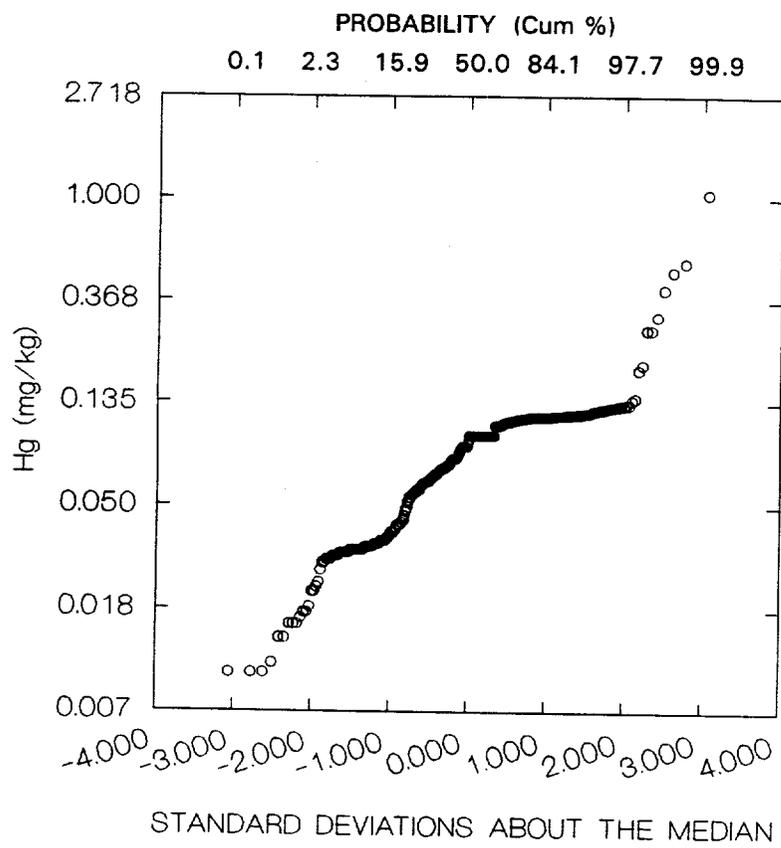
Subsoil: Cumulative Probability Graph, Magnesium



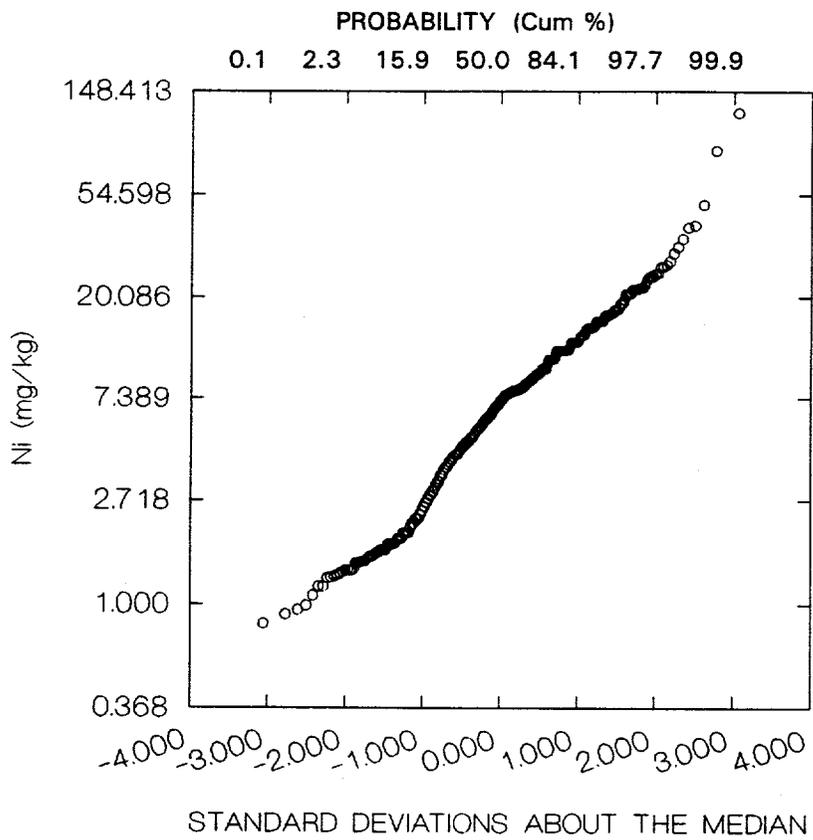
Subsoil: Cumulative Probability Graph, Manganese



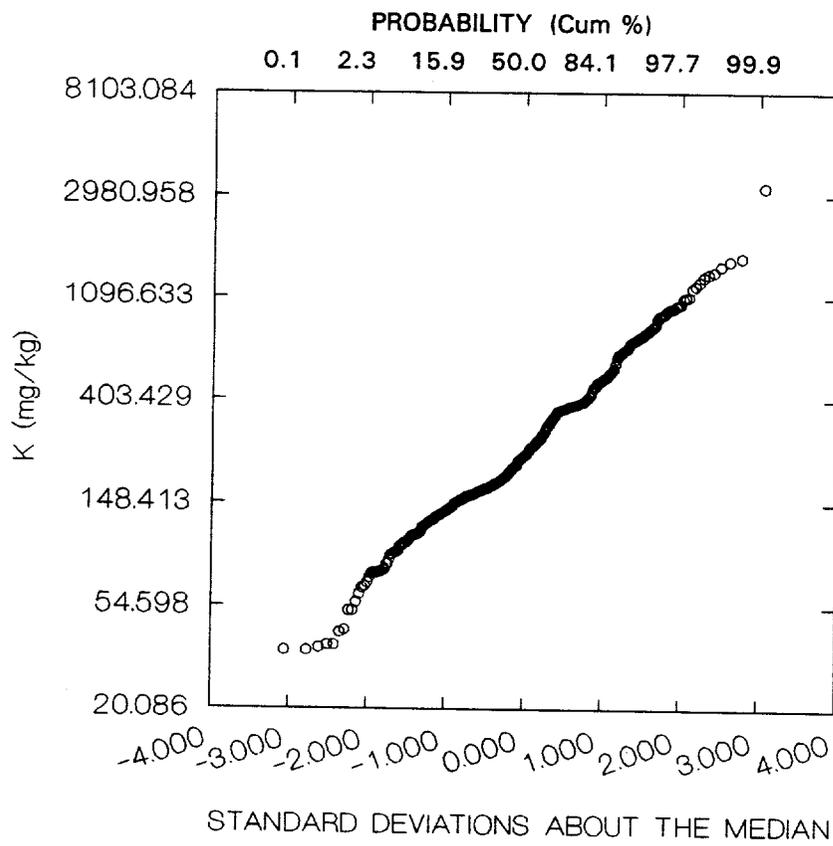
Subsoil: Cumulative Probability Graph, Mercury



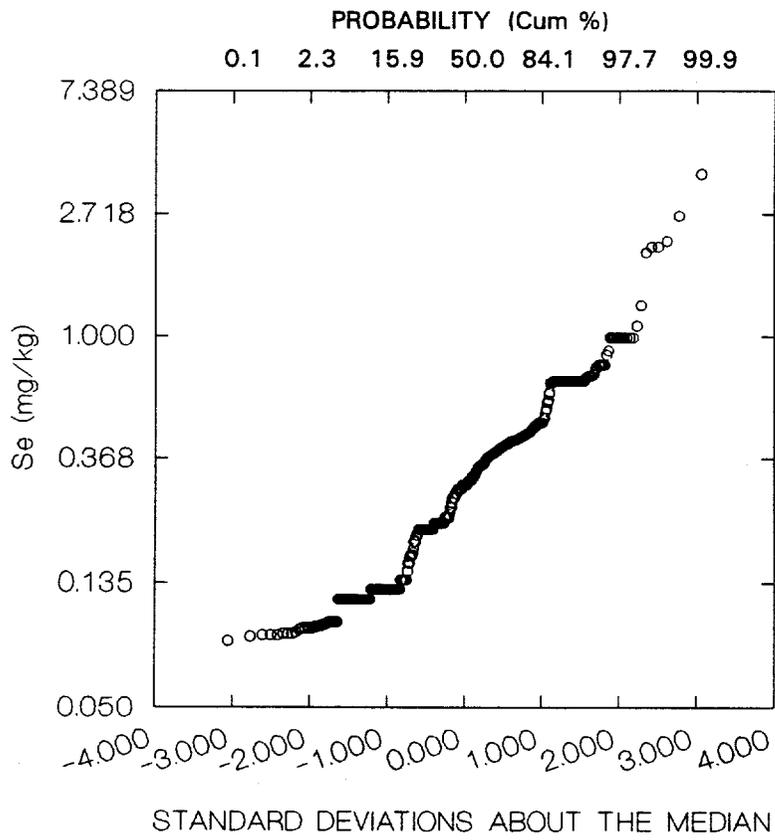
Subsoil: Cumulative Probability Graph, Nickel



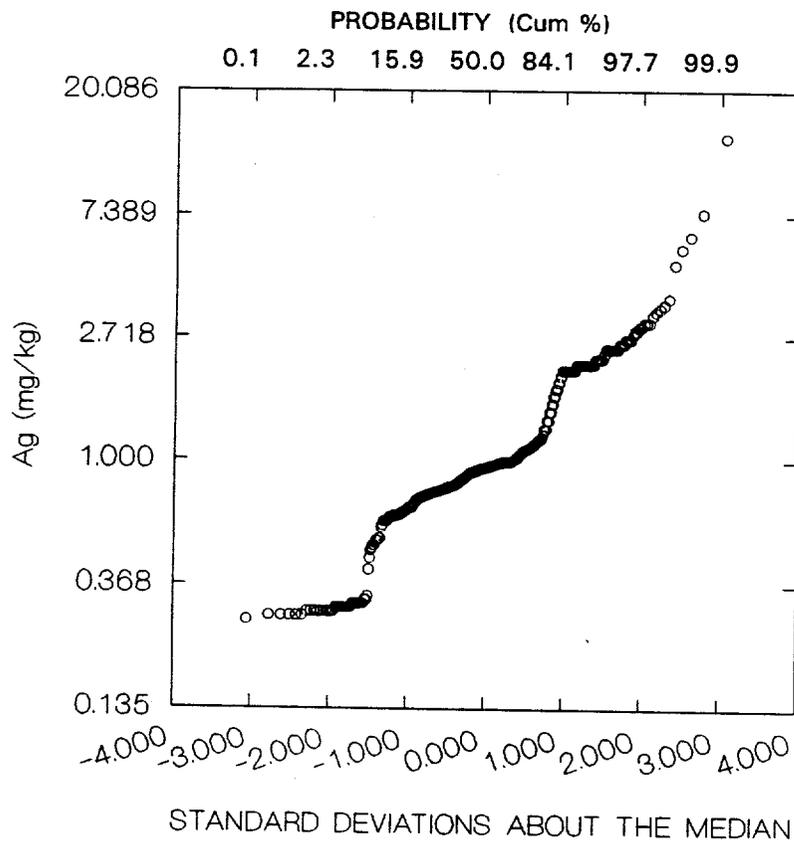
Subsoil: Cumulative Probability Graph, Potassium



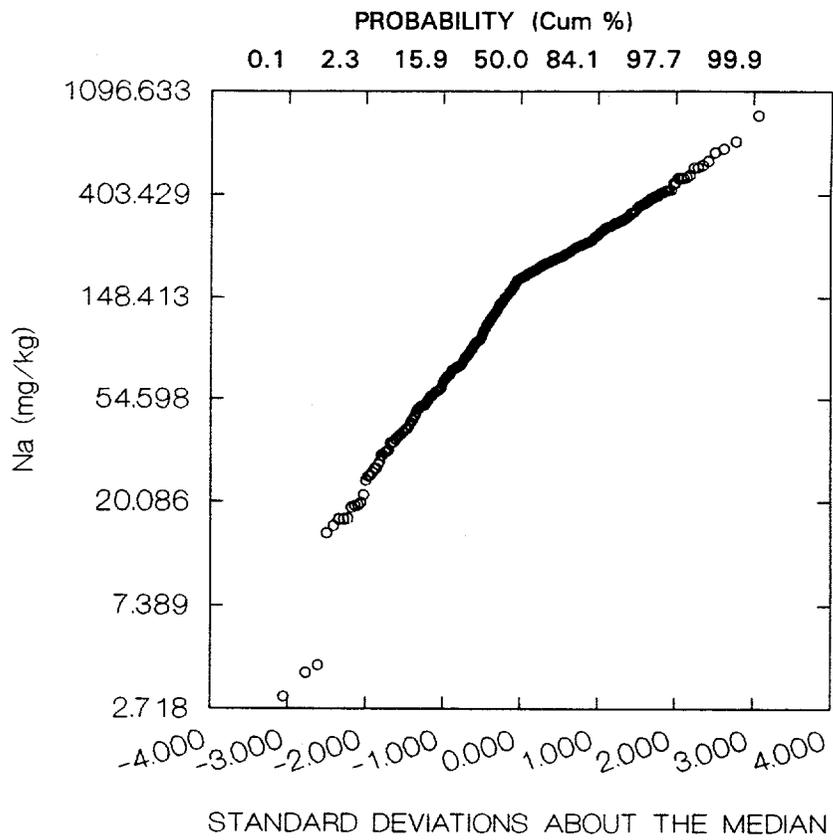
Subsoil: Cumulative Probability Graph, Selenium



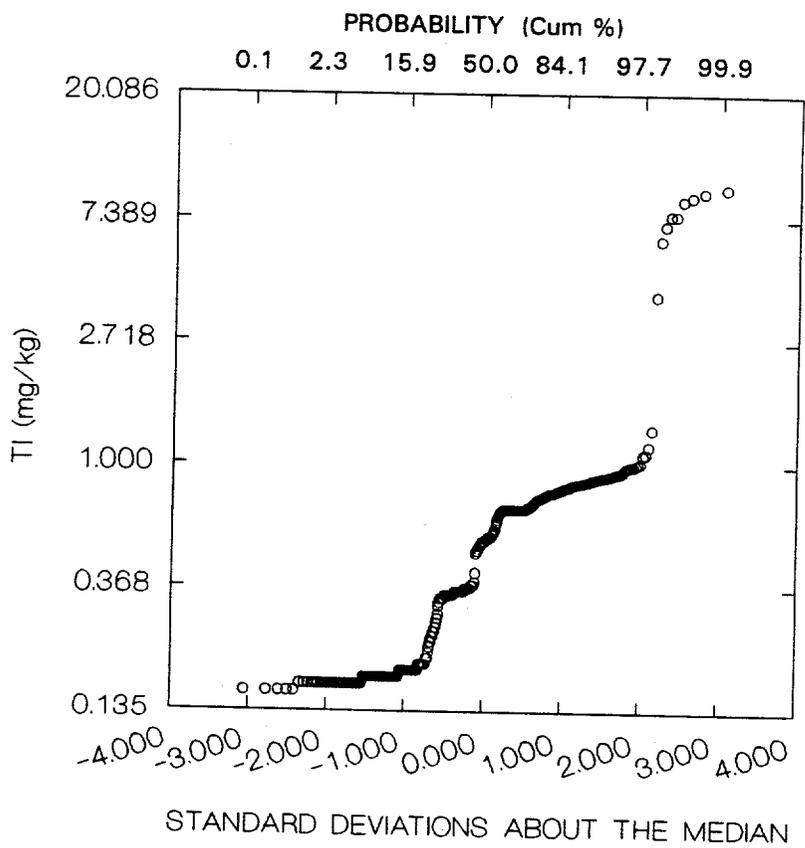
Subsoil: Cumulative Probability Graph, Silver



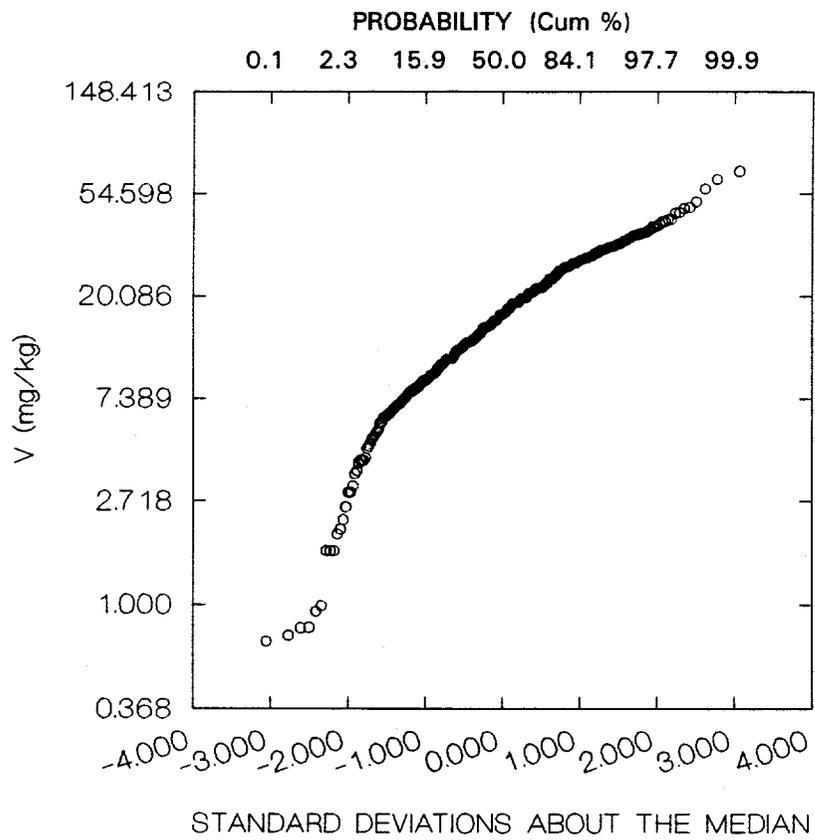
Subsoil: Cumulative Probability Graph, Sodium



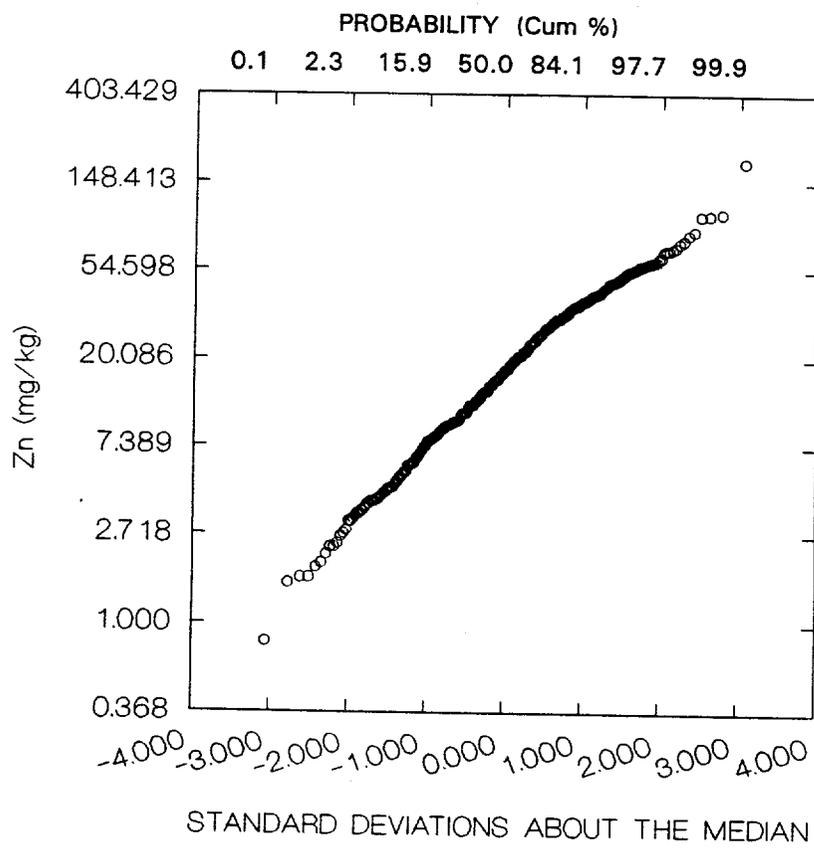
Subsoil: Cumulative Probability Graph, Thallium



Subsoil: Cumulative Probability Graph, Vanadium



Subsoil: Cumulative Probability Graph, Zinc



APPENDIX A.3

**CUMULATIVE PROBABILITY PLOTS AND STATISTICAL TABLES
FOR SEDIMENT SAMPLES**

This page left intentionally blank.

>STATS AGMGKG ALMGKG ASMGKG BAMGKG BEMGKG CAMGKG CDMGKG CHMGKG CNMGKG ,
 >COMGKG CUMGKG FEMGKG HMGKG KMGKG MGMGKG MNMGKG NAMGKG NIMGKG PBMGKG ,
 >SBMGKG SEMGKG TLMGKG VMGKG ZNMGKG / Mean Min Max SD CV Kurtosis Median ,
 >Range SEM Skewness Sum Variance N

FRI 11/04/94 12:07:24 PM D:\WORK\SEDIMNT.SYS

TOTAL OBSERVATIONS: 59

	AGMGKG	ALMGKG	ASMGKG	BAMGKG	BEMGKG
N OF CASES	59	59	59	59	59
MINIMUM	0.360	687.000	0.690	7.400	0.180
MAXIMUM	79.200	17500.000	33.700	922.000	29.400
RANGE	78.840	16813.000	33.010	914.600	29.220
MEAN	3.411	7385.186	8.339	103.117	6.315
VARIANCE	104.631	.204168E+08	48.811	17579.700	26.356
STANDARD DEV	10.229	4518.491	6.987	132.588	5.134
STD. ERROR	1.332	588.257	0.910	17.262	0.668
SKEWNESS(G1)	7.073	0.135	1.718	4.520	1.918
KURTOSIS(G2)	49.862	-1.086	2.571	23.782	5.643
SUM	201.250	435726.000	491.990	6083.900	372.560
C.V.	2.999	0.612	0.838	1.286	0.813
MEDIAN	1.400	7350.000	5.600	83.800	5.400

	CAMGKG	CDMGKG	CHMGKG	CNMGKG	COMGKG
N OF CASES	59	59	59	59	59
MINIMUM	125.000	0.250	7.100	0.210	3.000
MAXIMUM	47400.000	7.210	22100.000	5.300	62.100
RANGE	47275.000	6.960	22092.900	5.090	59.100
MEAN	4015.678	1.587	740.822	0.876	9.763
VARIANCE	.806532E+08	1.733	.129171E+08	0.757	100.122
STANDARD DEV	8980.713	1.316	3594.041	0.870	10.006
STD. ERROR	1169.189	0.171	467.904	0.113	1.303
SKEWNESS(G1)	3.684	2.633	5.254	3.777	3.741
KURTOSIS(G2)	13.622	8.320	26.225	14.476	15.226
SUM	236925.000	93.610	43708.500	51.670	576.000
C.V.	2.236	0.830	4.851	0.994	1.025
MEDIAN	1350.000	1.200	20.500	0.650	7.000

	CUMGKG	FEMGKG	HMGKG	KMGKG	MGMGKG
N OF CASES	59	59	59	59	59
MINIMUM	1.100	4380.000	0.038	123.000	68.400
MAXIMUM	335.000	132000.000	1.340	1910.000	4460.000
RANGE	333.900	127620.000	1.302	1787.000	4391.600
MEAN	34.025	18559.153	0.167	562.203	1103.249
VARIANCE	4834.408	.404814E+09	0.056	167462.234	754864.058
STANDARD DEV	69.530	20119.997	0.236	409.221	868.829
STD. ERROR	9.052	2619.400	0.031	53.276	113.112
SKEWNESS(G1)	3.108	4.296	3.675	1.057	1.353
KURTOSIS(G2)	9.058	19.597	13.141	0.825	2.893
SUM	2007.500	1094990.000	9.830	33170.000	65091.700
C.V.	2.043	1.084	1.414	0.728	0.788
MEDIAN	12.200	15200.000	0.100	492.000	1040.000

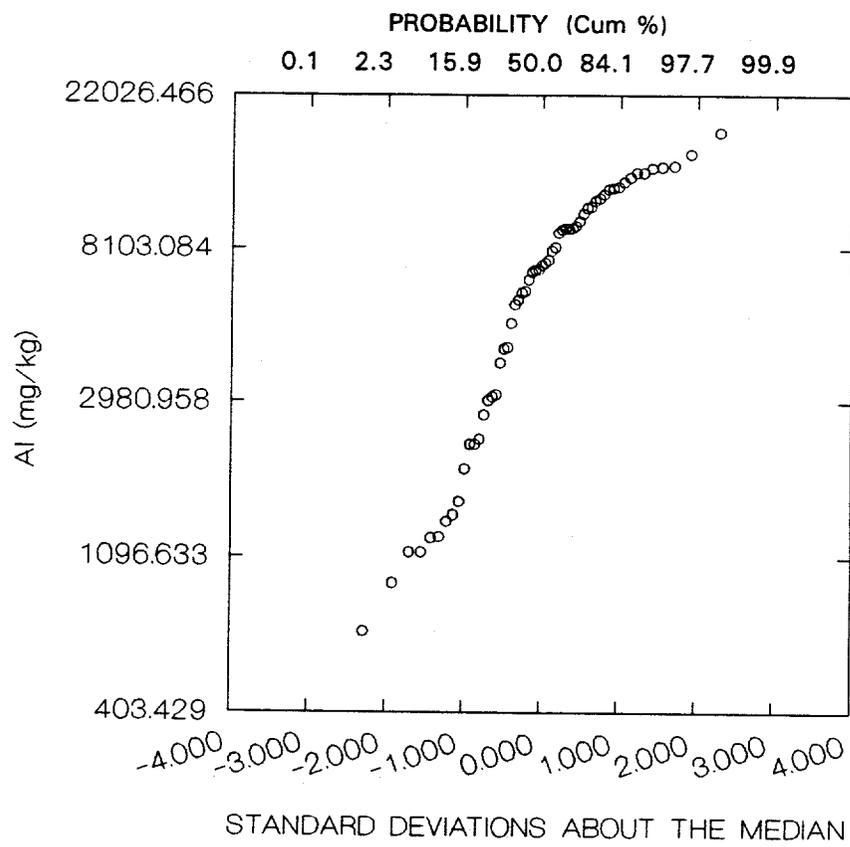
MNMGKG NAMGKG NIMGKG PBMGKG SBMGKG

N OF CASES	59	59	59	59	59
MINIMUM	62.400	23.000	2.900	3.200	0.340
MAXIMUM	4150.000	1770.000	220.000	36.500	425.000
RANGE	4087.600	1747.000	217.100	33.300	424.660
MEAN	623.576	148.925	24.166	14.605	14.868
VARIANCE	559979.279	99337.845	1116.325	66.618	5050.702
STANDARD DEV	748.318	315.179	33.411	8.162	71.068
STD. ERROR	97.423	41.033	4.350	1.063	9.252
SKEWNESS (G1)	3.472	4.038	3.893	0.951	5.191
KURTOSIS (G2)	13.250	16.215	18.482	0.119	25.336
SUM	36791.000	8786.600	1425.800	861.700	877.220
C.V.	1.200	2.116	1.383	0.559	4.780
MEDIAN	365.000	59.900	13.300	12.600	0.420

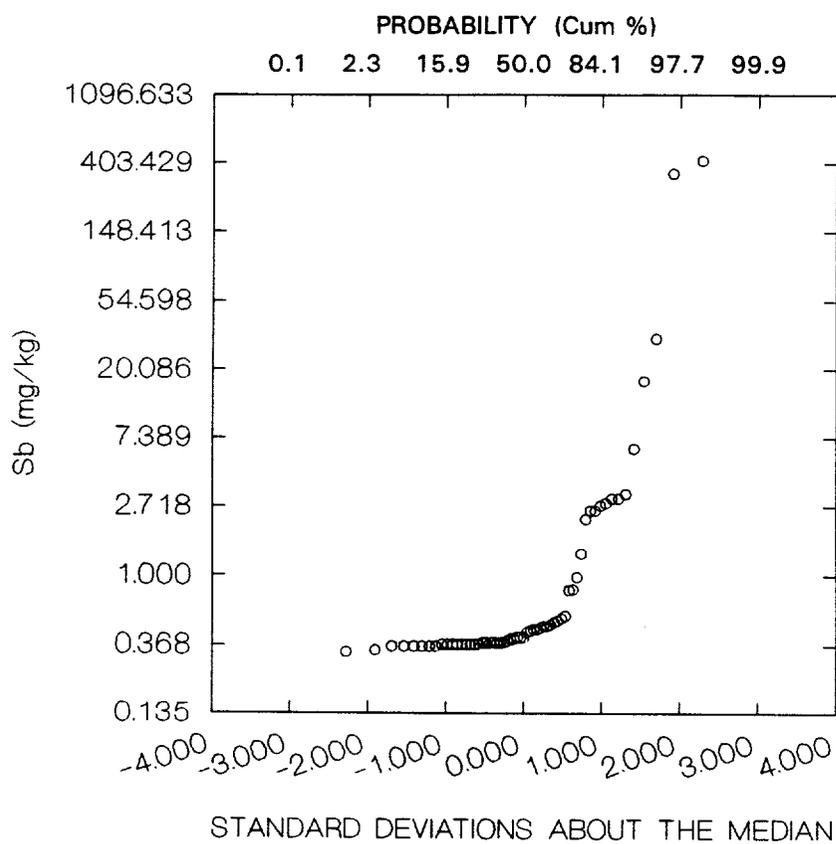
	SEMGKG	TLMGKG	VMGKG	ZNMGKG
N OF CASES	59	59	59	59
MINIMUM	0.120	0.220	1.400	5.900
MAXIMUM	6.400	7.810	80.700	4170.000
RANGE	6.280	7.590	79.300	4164.100
MEAN	0.604	0.592	27.576	186.741
VARIANCE	1.511	1.466	217.629	454613.633
STANDARD DEV	1.229	1.211	14.752	674.250
STD. ERROR	0.160	0.158	1.921	87.780
SKEWNESS (G1)	3.847	4.720	1.134	5.193
KURTOSIS (G2)	14.253	22.862	1.756	25.741
SUM	35.630	34.900	1627.000	11017.700
C.V.	2.035	2.047	0.535	3.611
MEDIAN	0.220	0.270	24.300	46.600

>

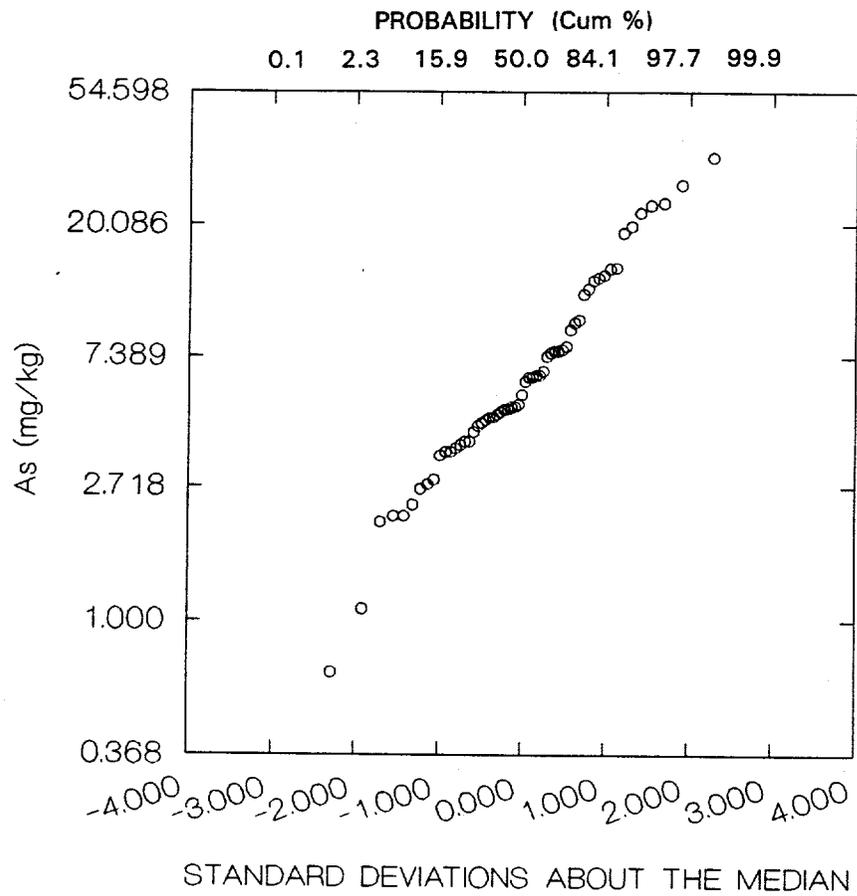
Sediment: Cumulative Probability Graph, Aluminum



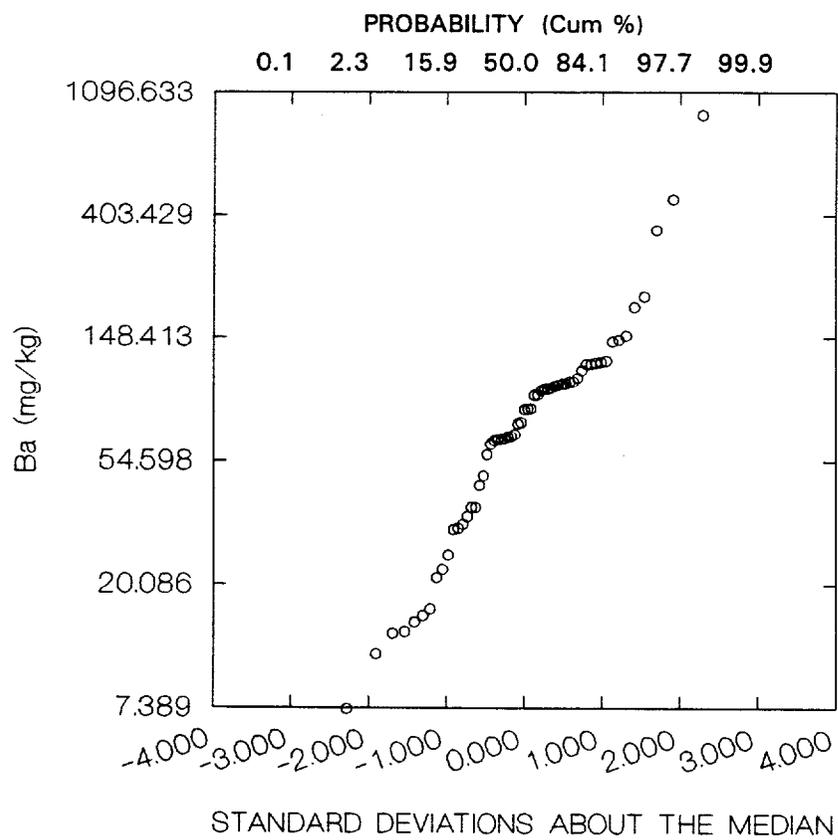
Sediment: Cumulative Probability Graph, Antimony



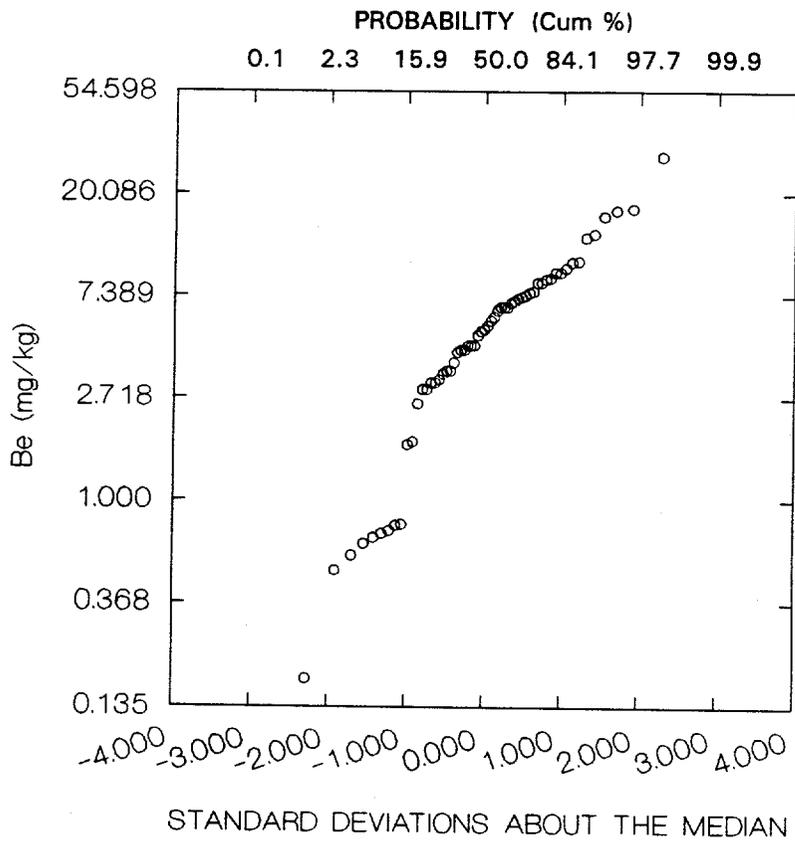
Sediment: Cumulative Probability Graph, Arsenic



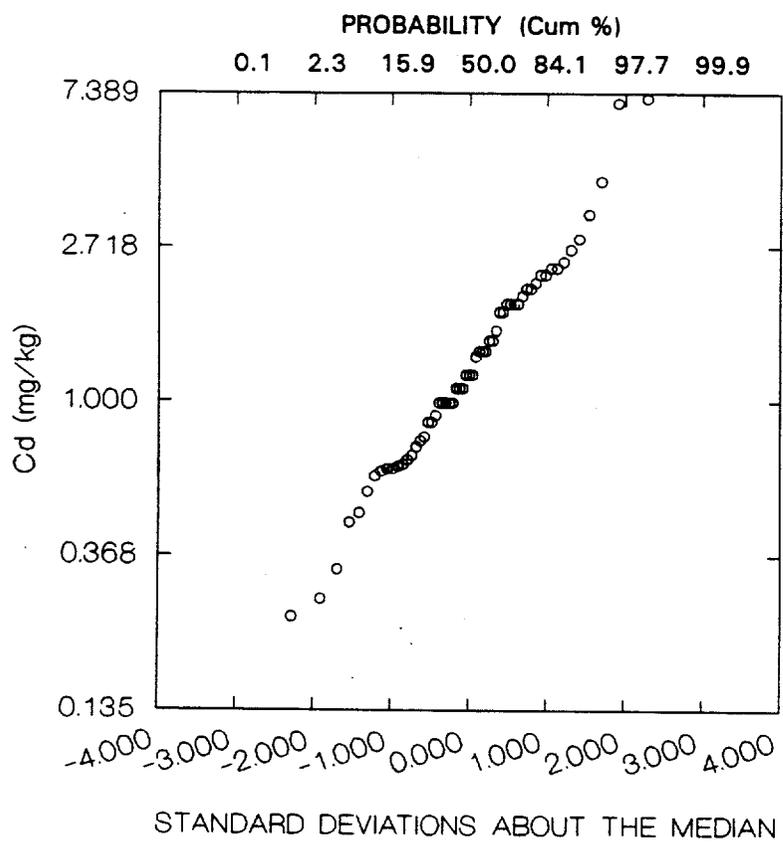
Sediment: Cumulative Probability Graph, Barium



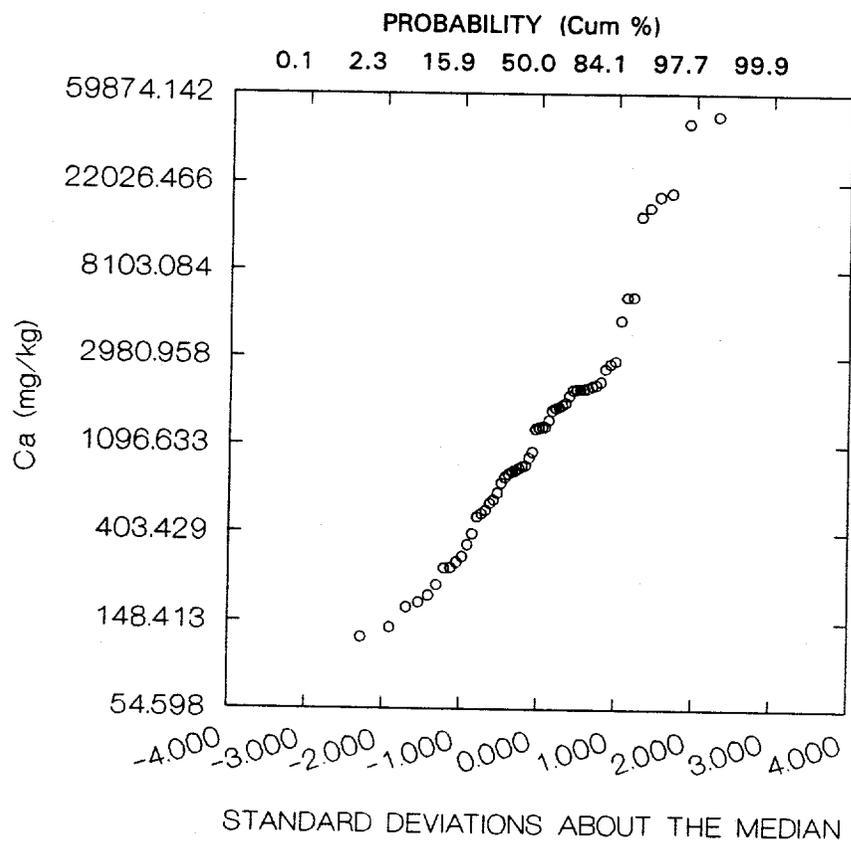
Sediment: Cumulative Probability Graph, Beryllium



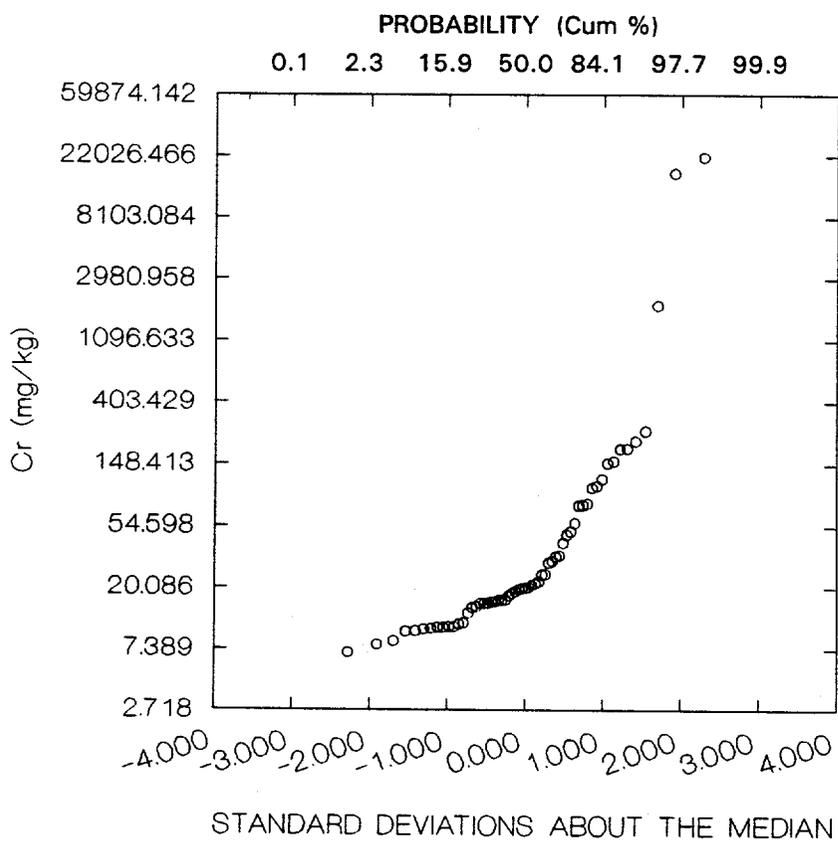
Sediment: Cumulative Probability Graph, Cadmium



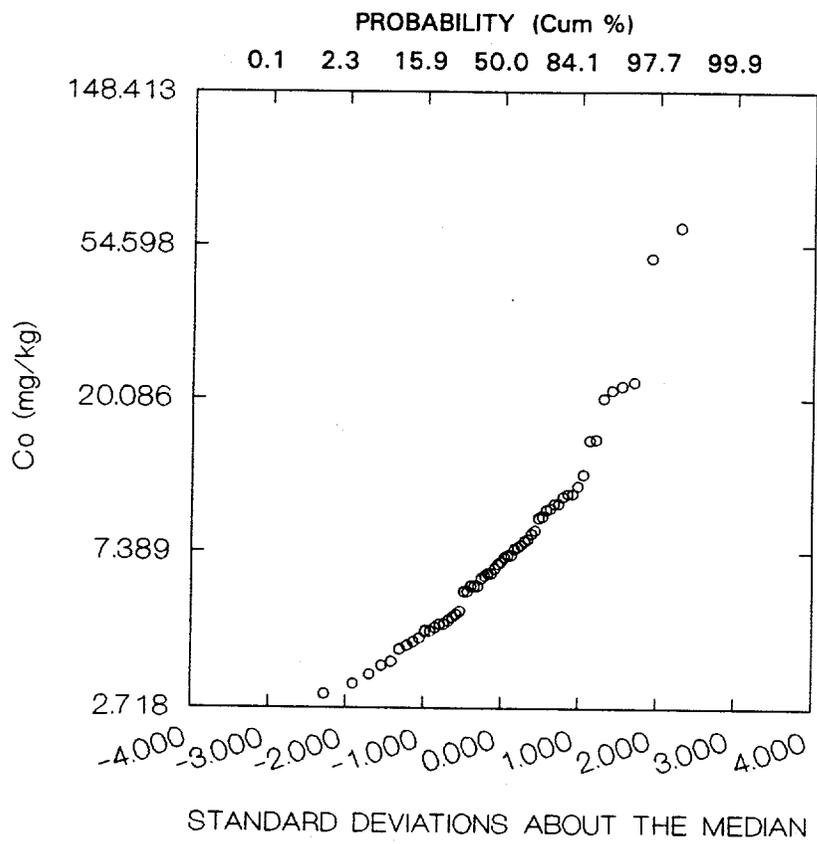
Sediment: Cumulative Probability Graph. Calcium



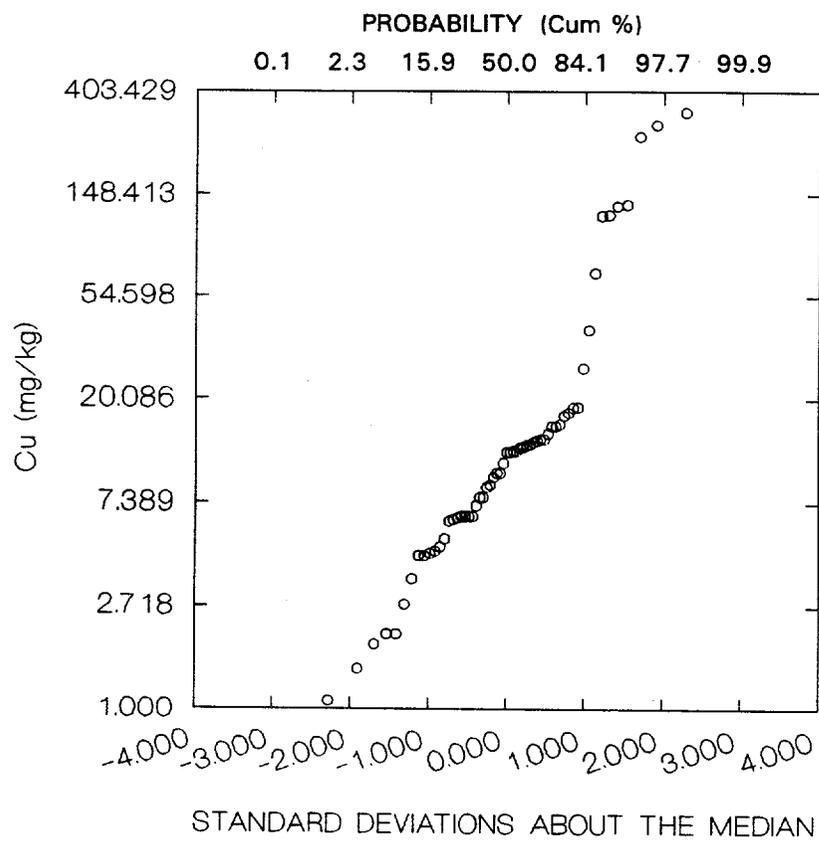
Sediment: Cumulative Probability Graph, Chromium



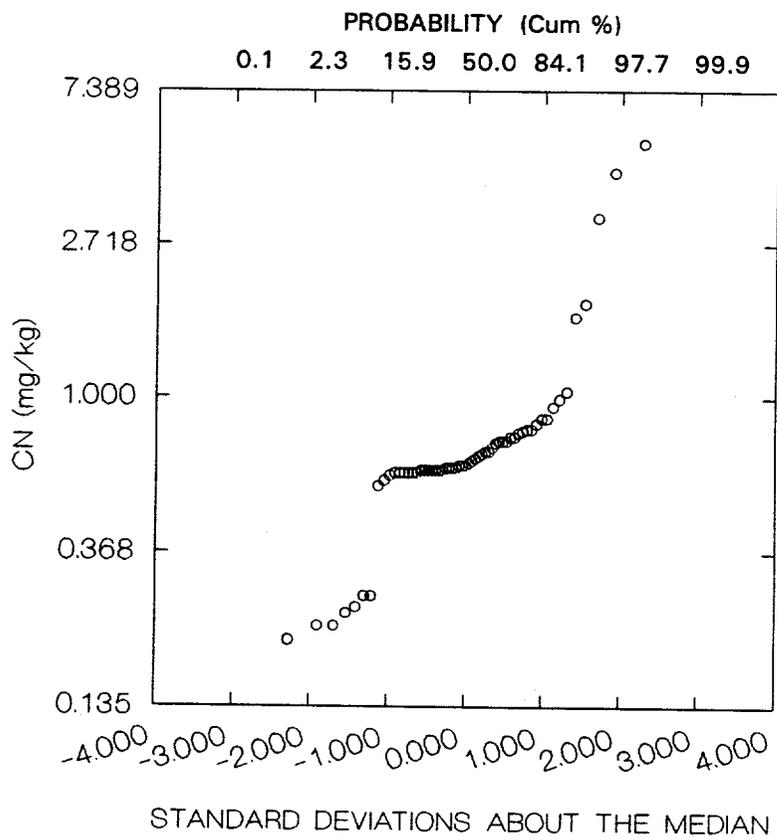
Sediment: Cumulative Probability Graph, Cobalt



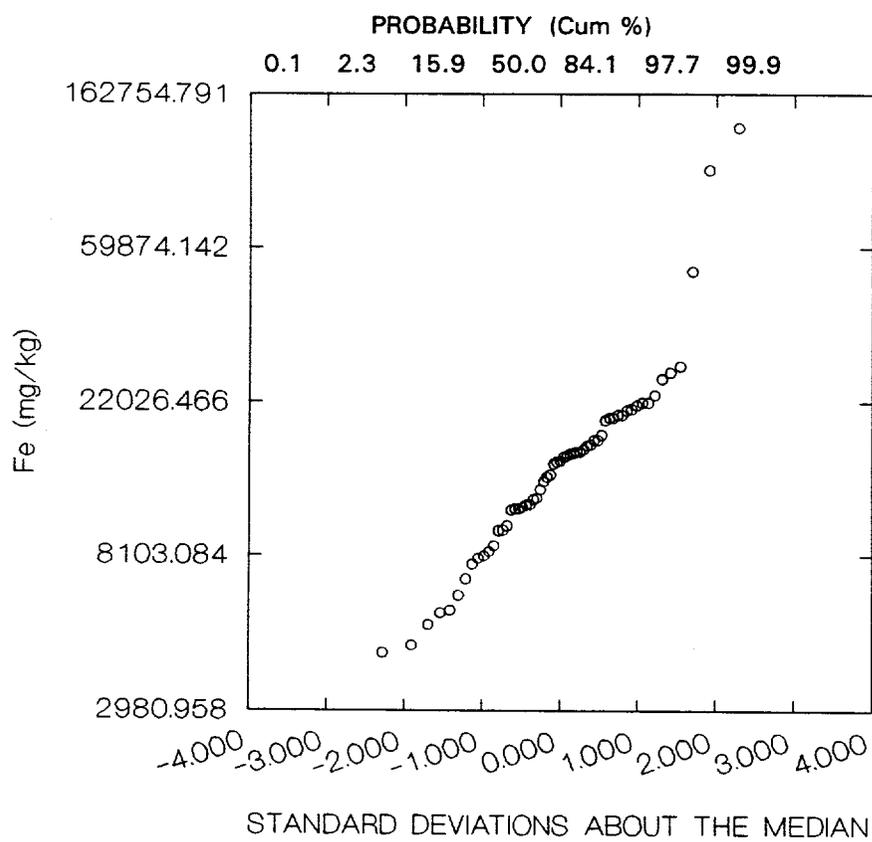
Sediment: Cumulative Probability Graph, Copper



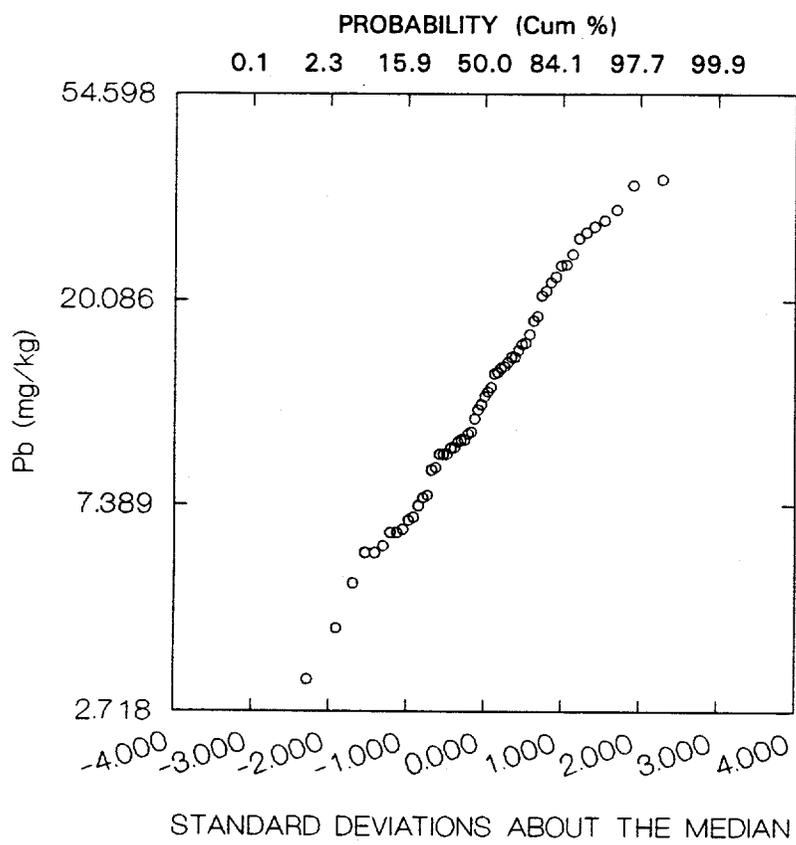
Sediment: Cumulative Probability Graph, Cyanide



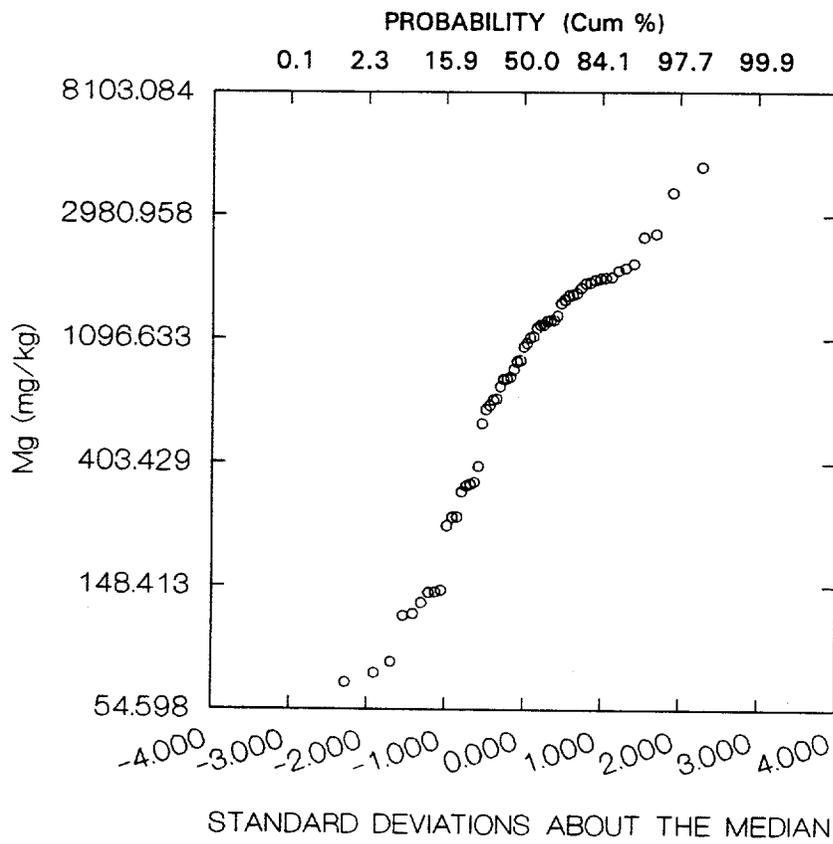
Sediment: Cumulative Probability Graph, Iron



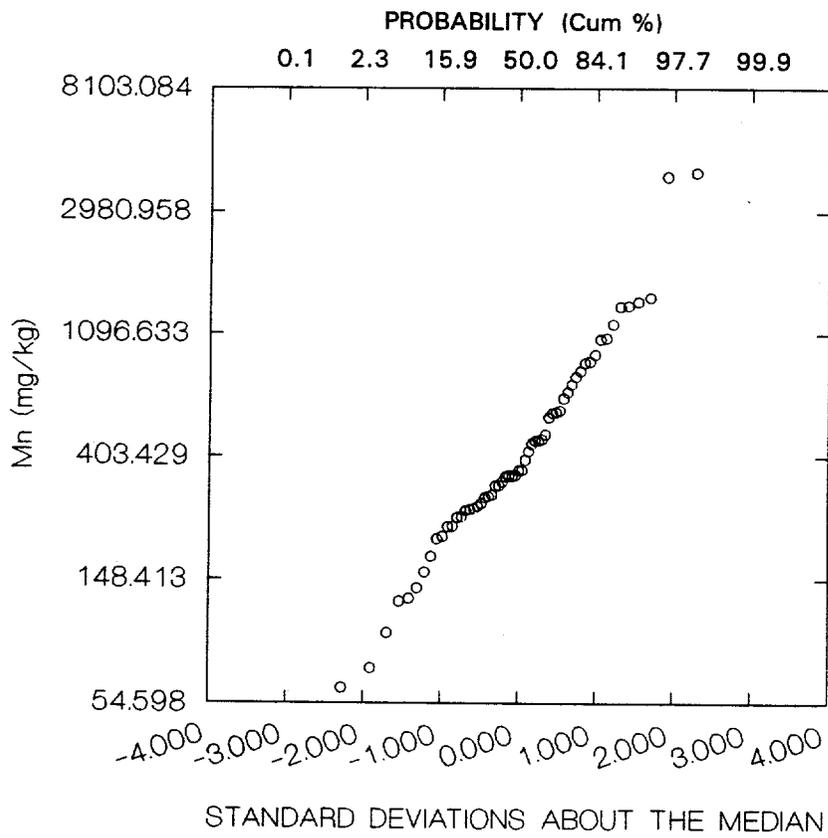
Sediment: Cumulative Probability Graph, Lead



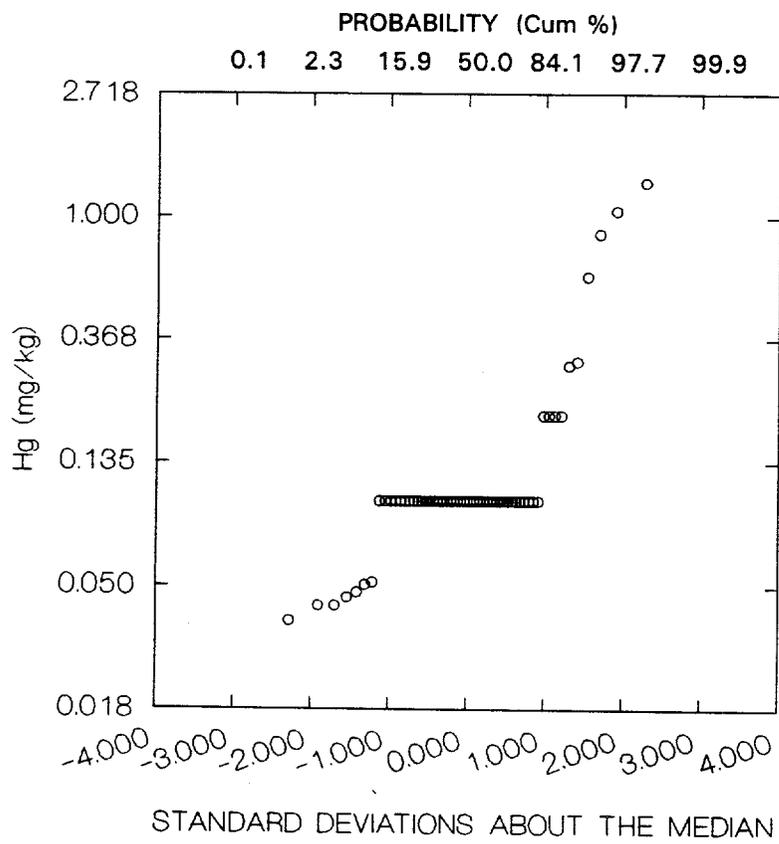
Sediment: Cumulative Probability Graph, Magnesium



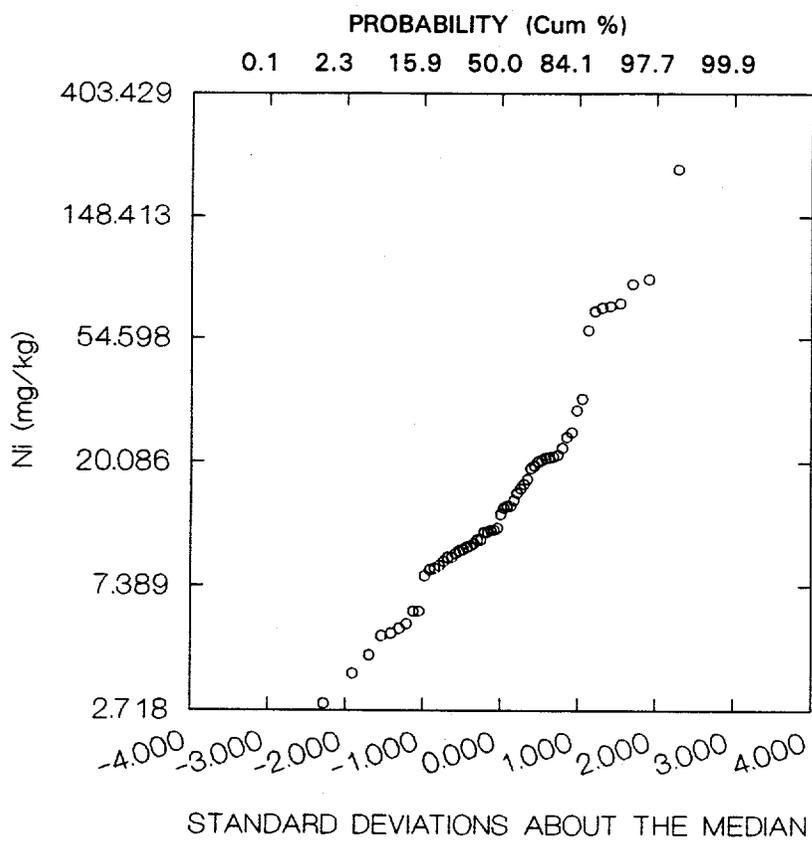
Sediment: Cumulative Probability Graph, Manganese



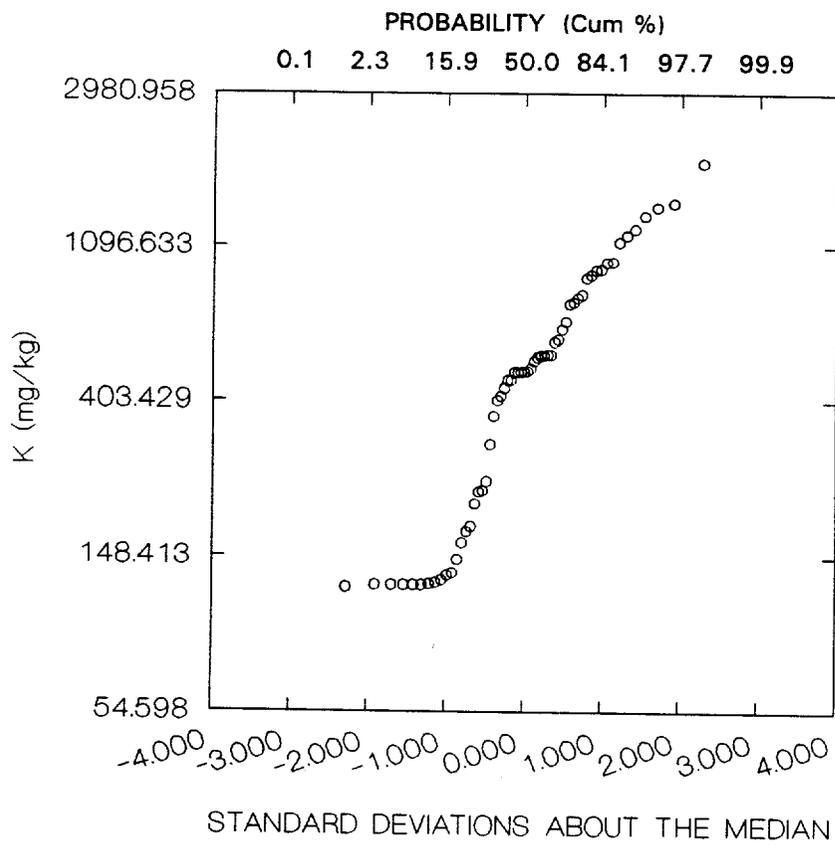
Sediment: Cumulative Probability Graph, Mercury



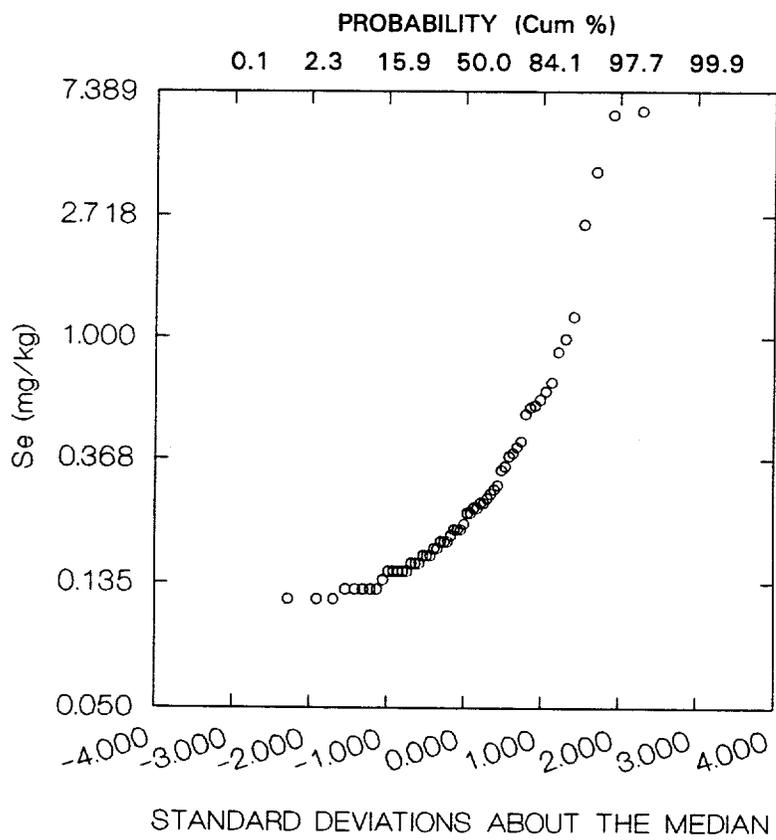
Sediment: Cumulative Probability Graph, Nickel



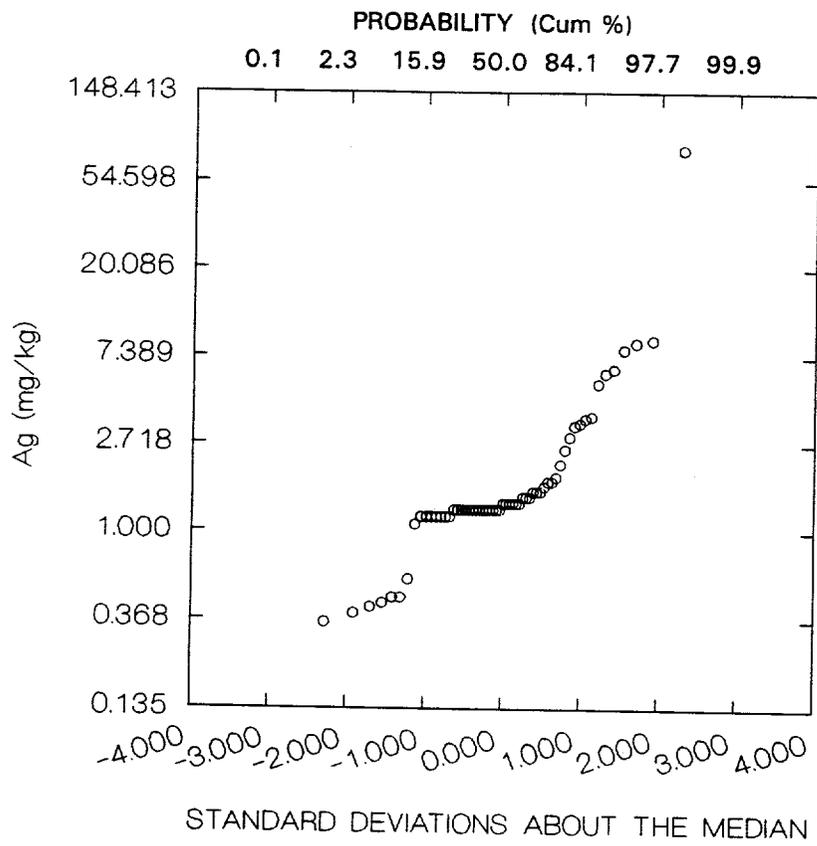
Sediment: Cumulative Probability Graph, Potassium



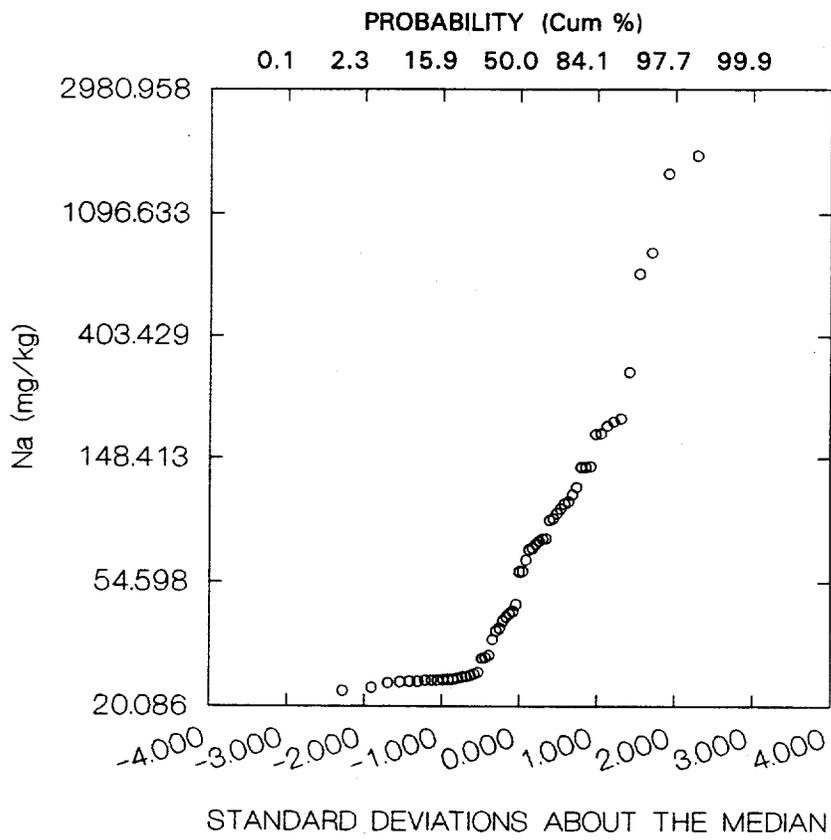
Sediment: Cumulative Probability Graph, Selenium



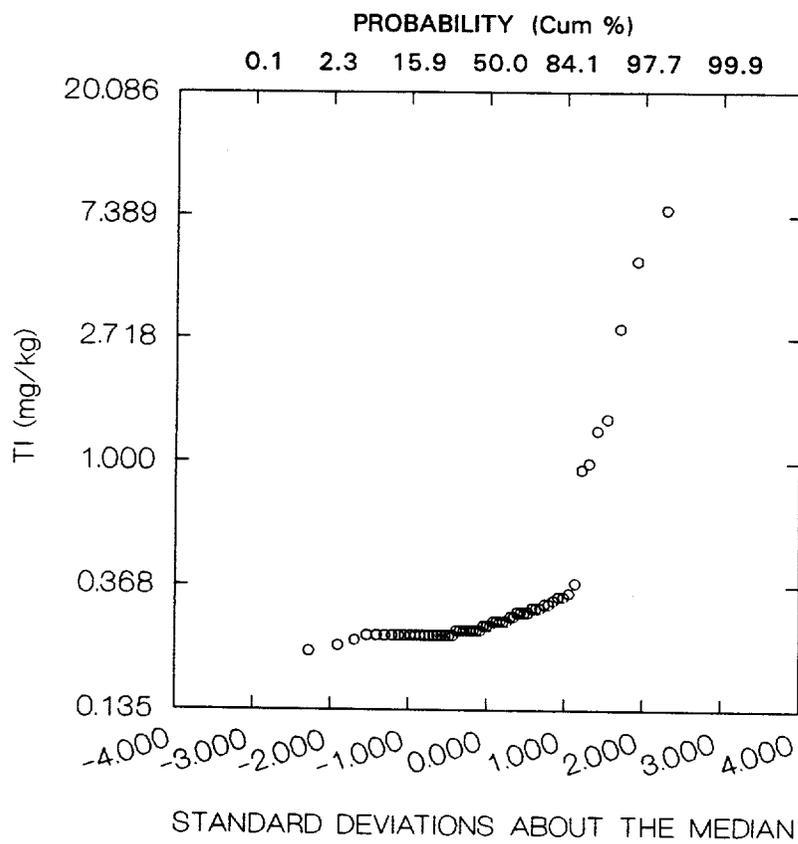
Sediment: Cumulative Probability Graph, Silver



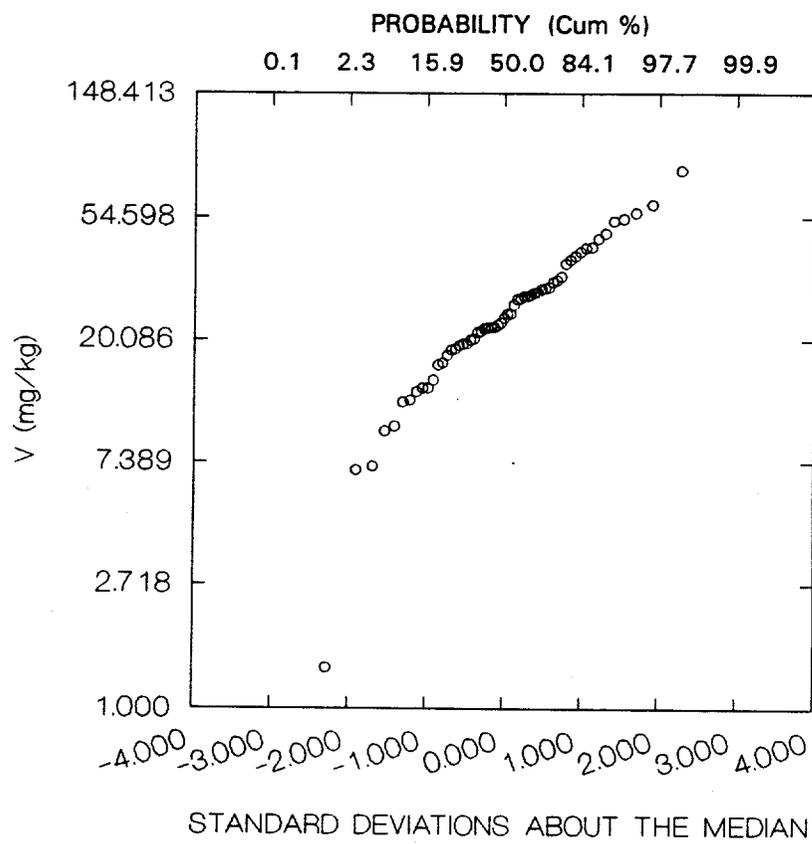
Sediment: Cumulative Probability Graph, Sodium



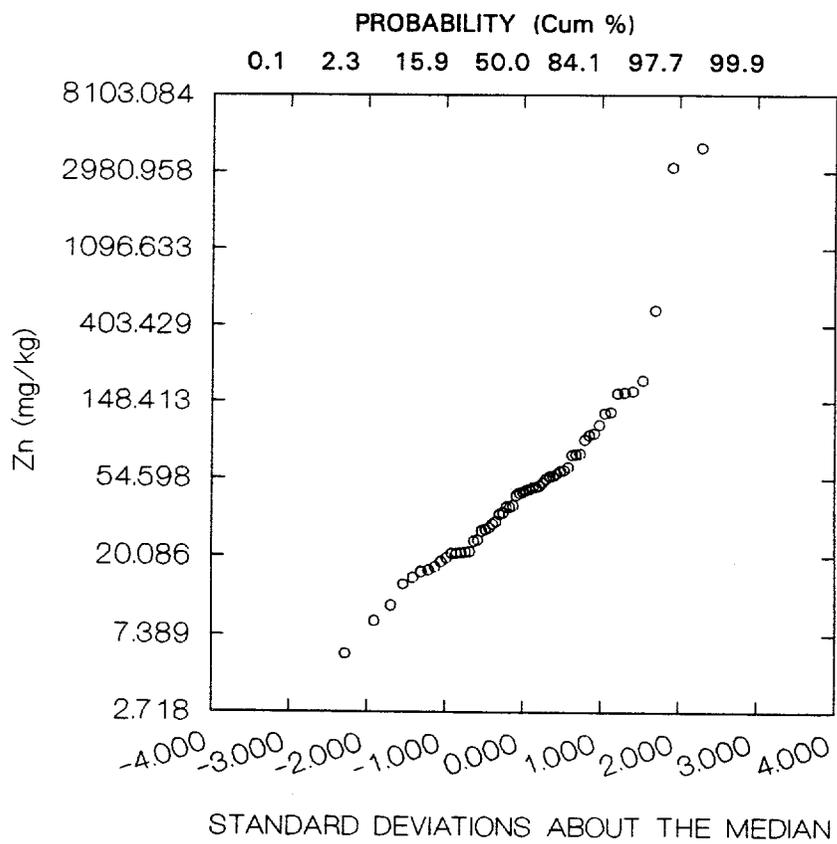
Sediment: Cumulative Probability Graph, Thallium



Sediment: Cumulative Probability Graph, Vanadium



Sediment: Cumulative Probability Graph, Zinc

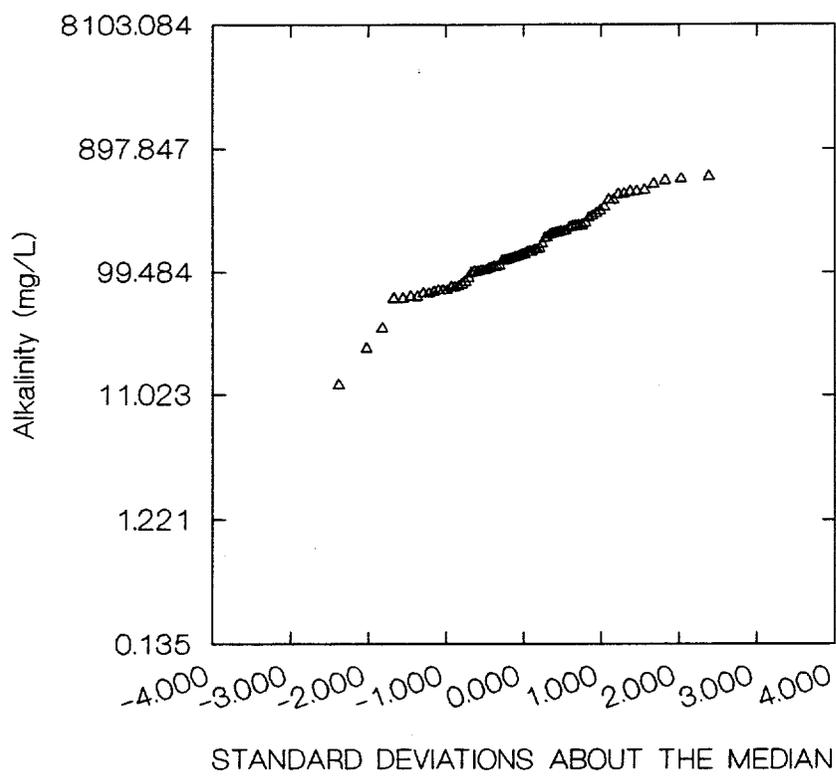


APPENDIX A.4

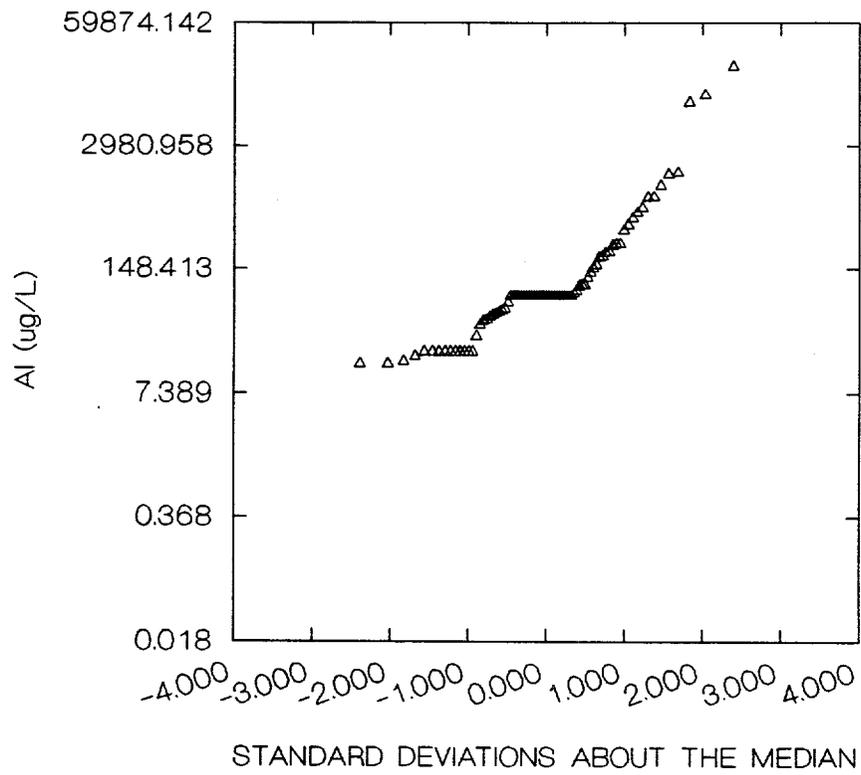
**CUMULATIVE PROBABILITY PLOTS
FOR GROUNDWATER SAMPLES FROM
UPPER CONTINENTAL RECHARGE SYSTEM**

This page left intentionally blank.

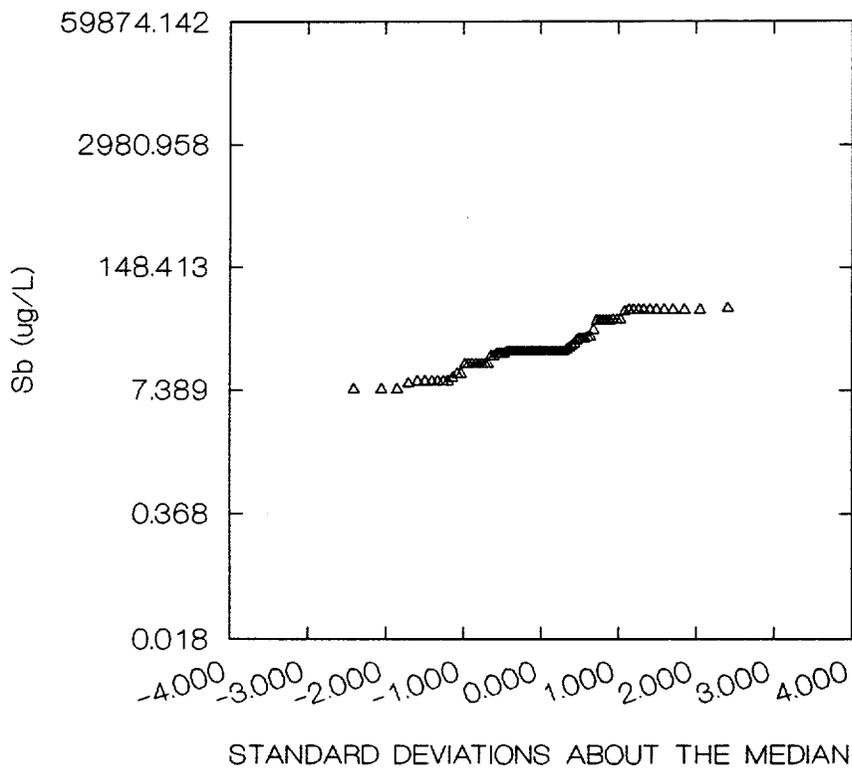
UCRS Groundwater: Cumulative Probability Graph, Alkalinity



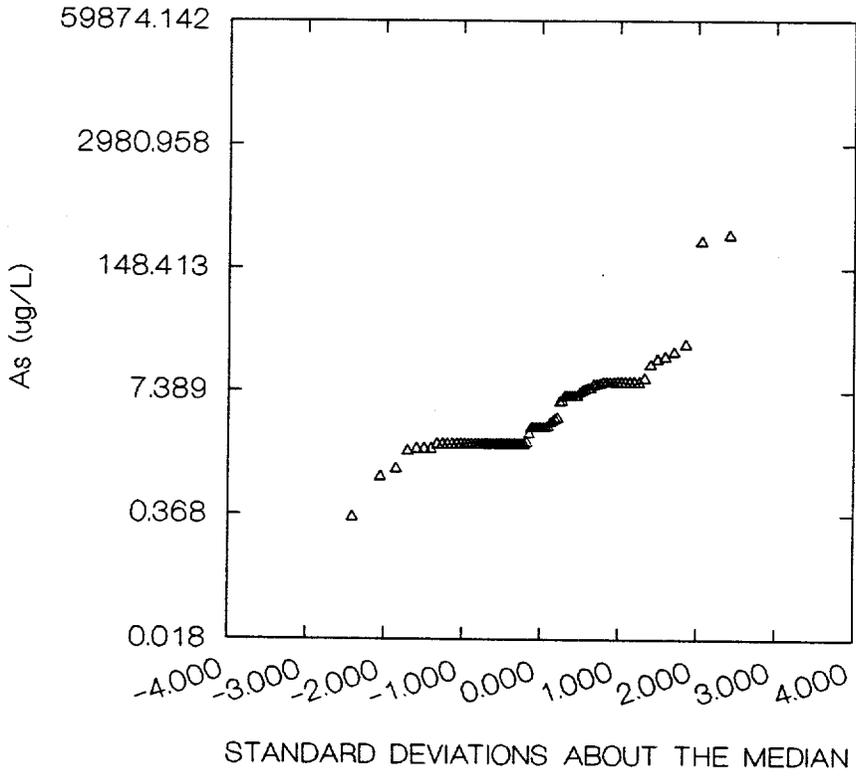
UCRS Groundwater: Cumulative Probability Graph, Aluminum



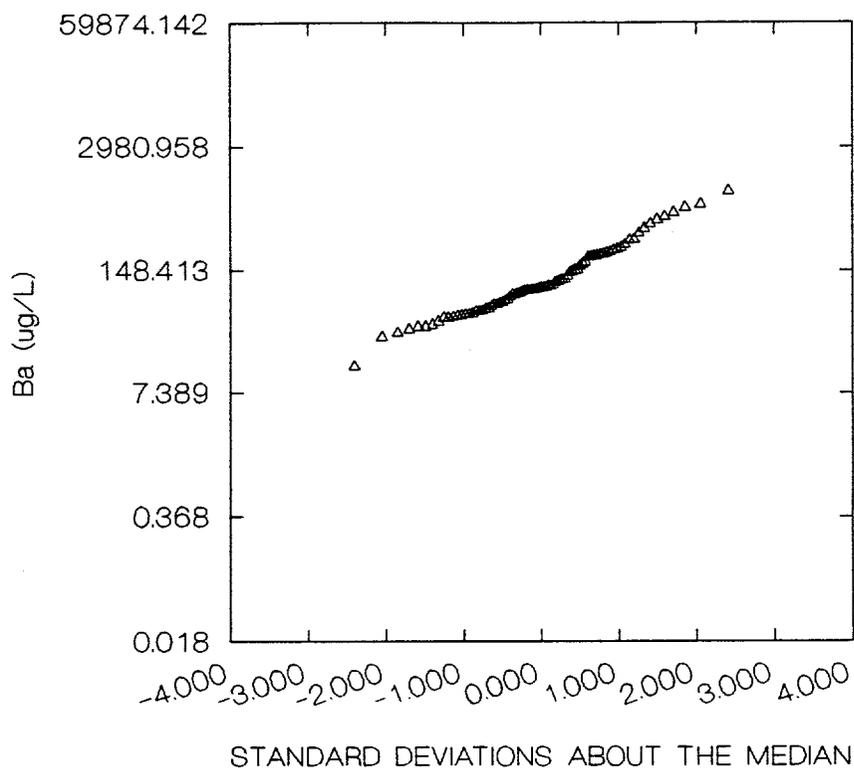
UCRS Groundwater: Cumulative Probability Graph, Antimony



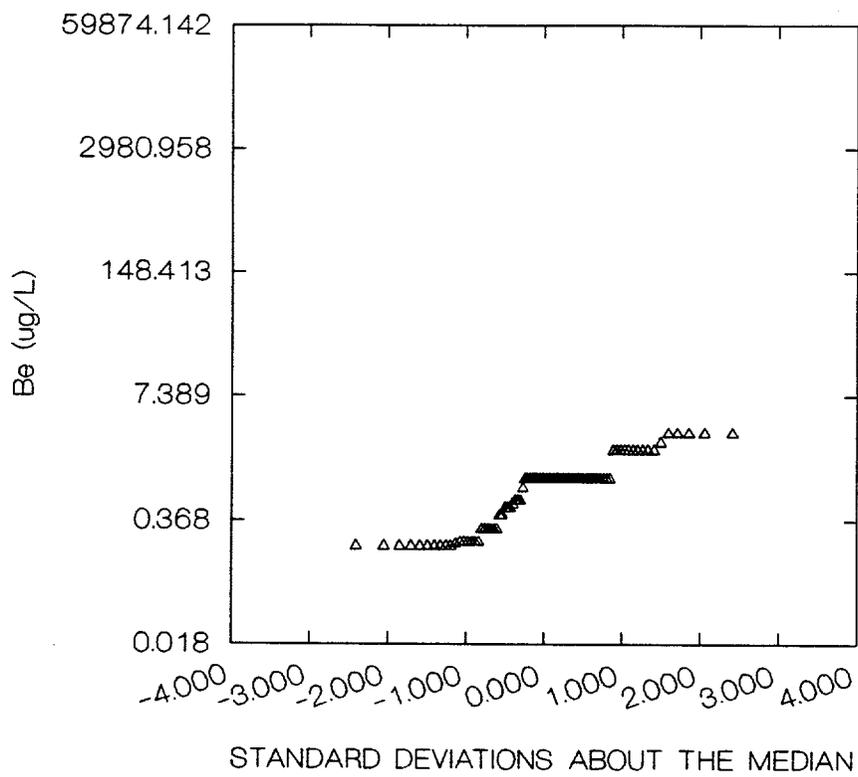
UCRS Groundwater: Cumulative Probability Graph, Arsenic



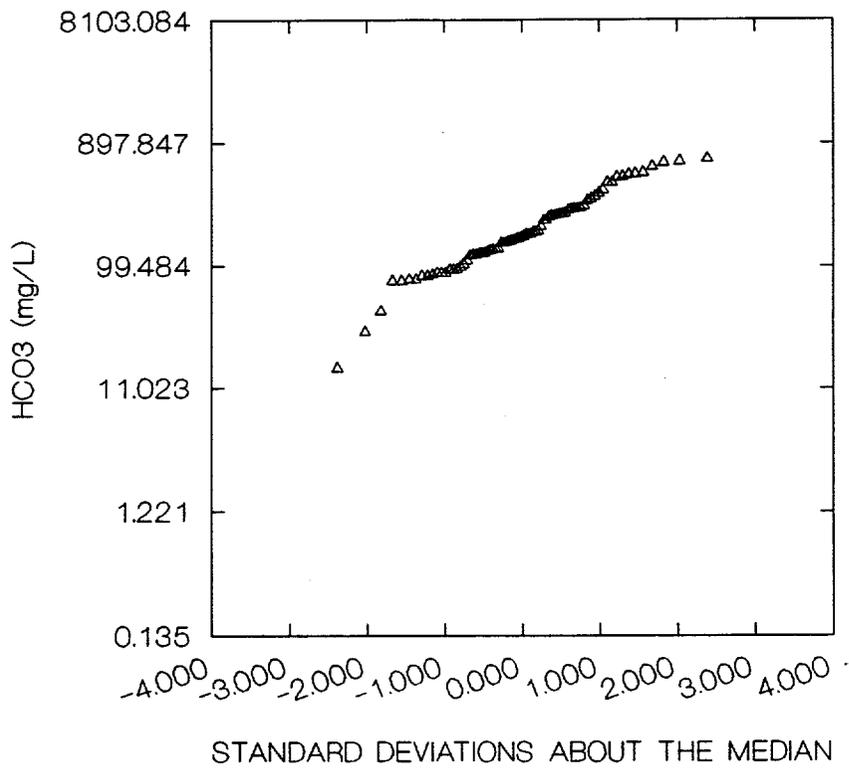
UCRS Groundwater: Cumulative Probability Graph, Barium



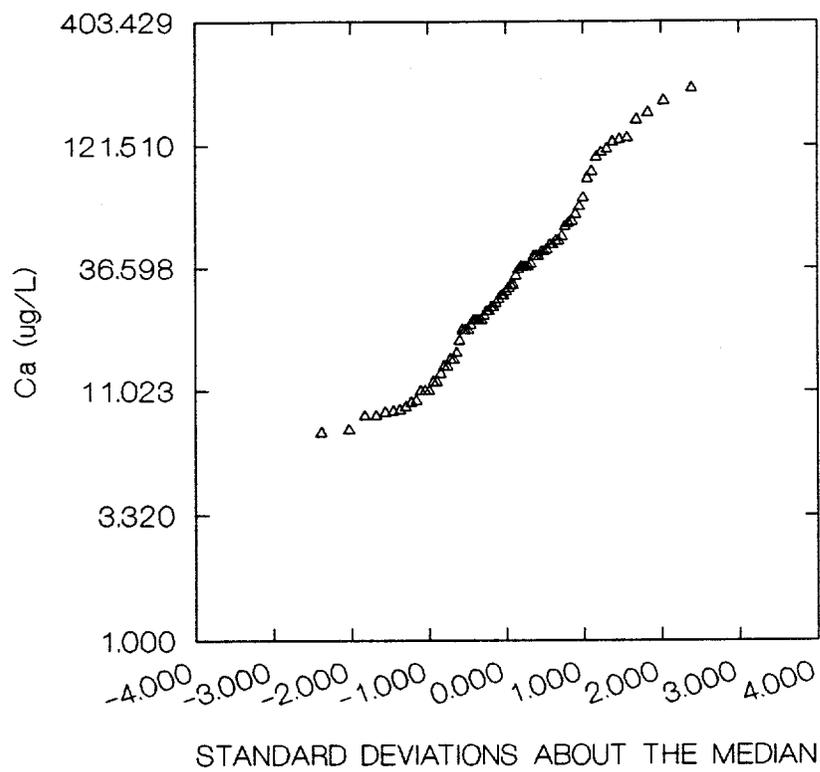
UCRS Groundwater: Cumulative Probability Graph, Beryllium



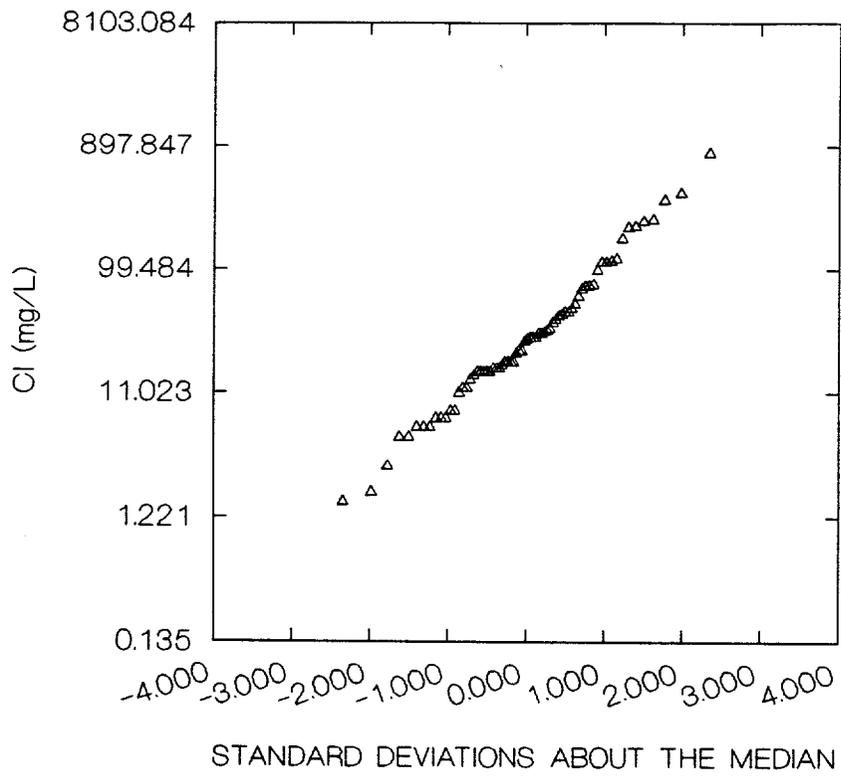
UCRS Groundwater: Cumulative Probability Graph, Bicarbonate



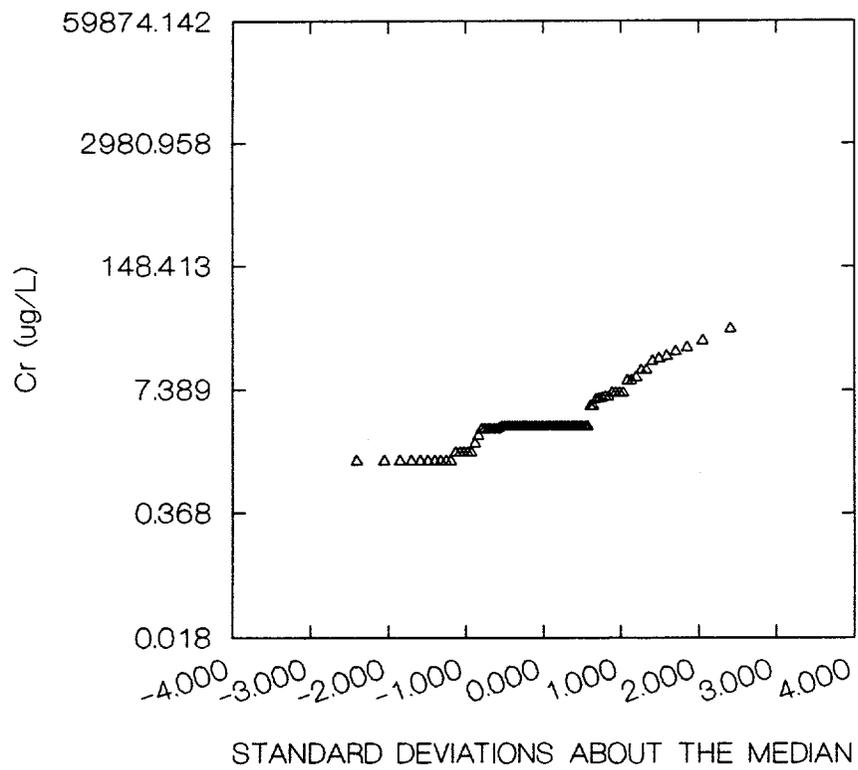
UCRS Groundwater: Cumulative Probability Graph, Calcium



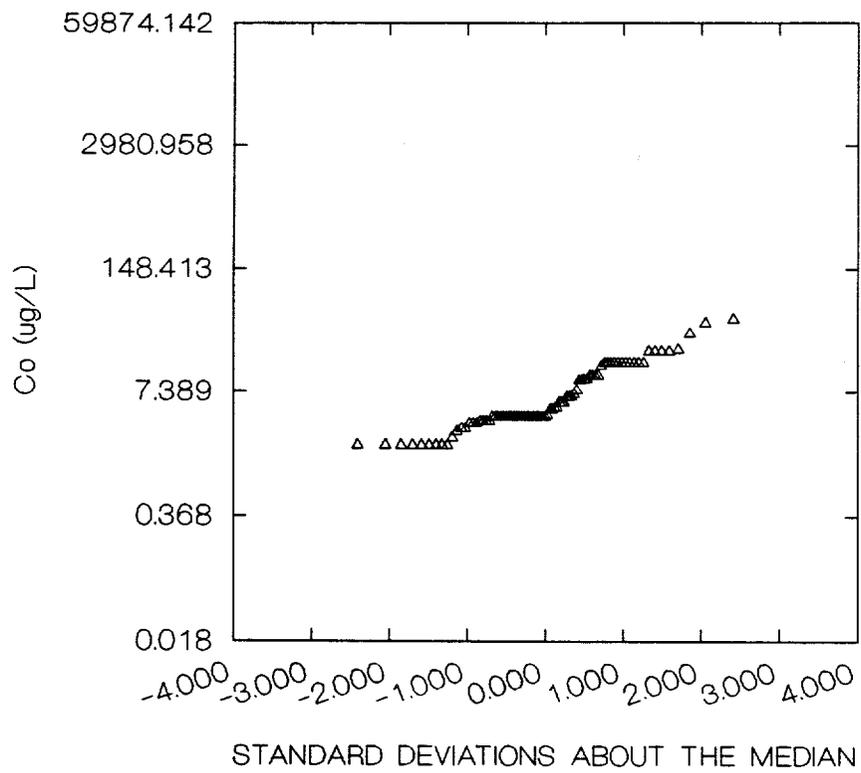
UCRS Groundwater: Cumulative Probability Graph, Chloride



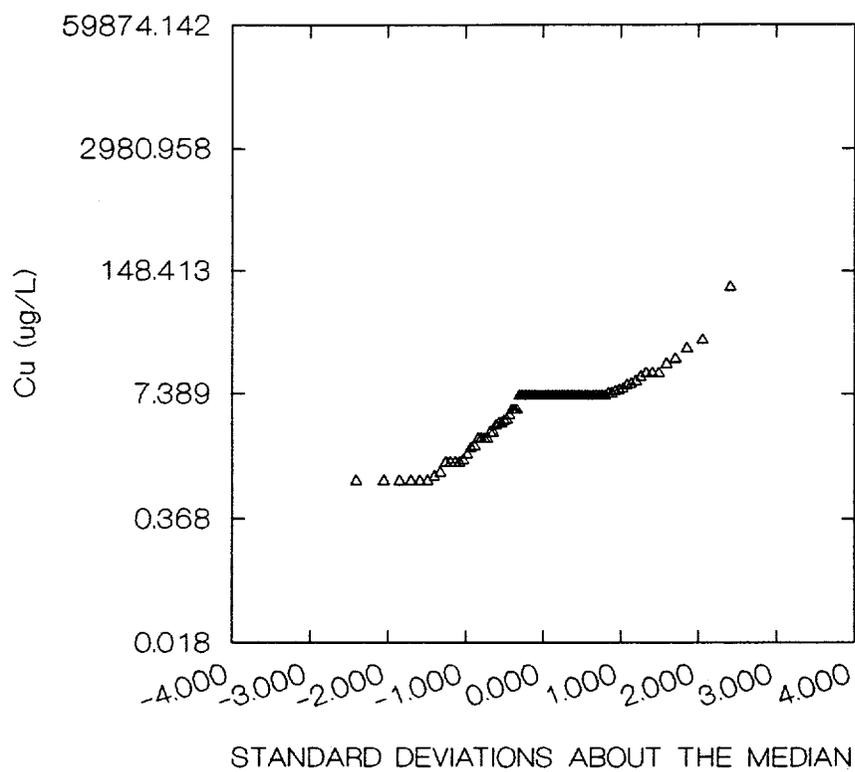
UCRS Groundwater: Cumulative Probability Graph, Chromium



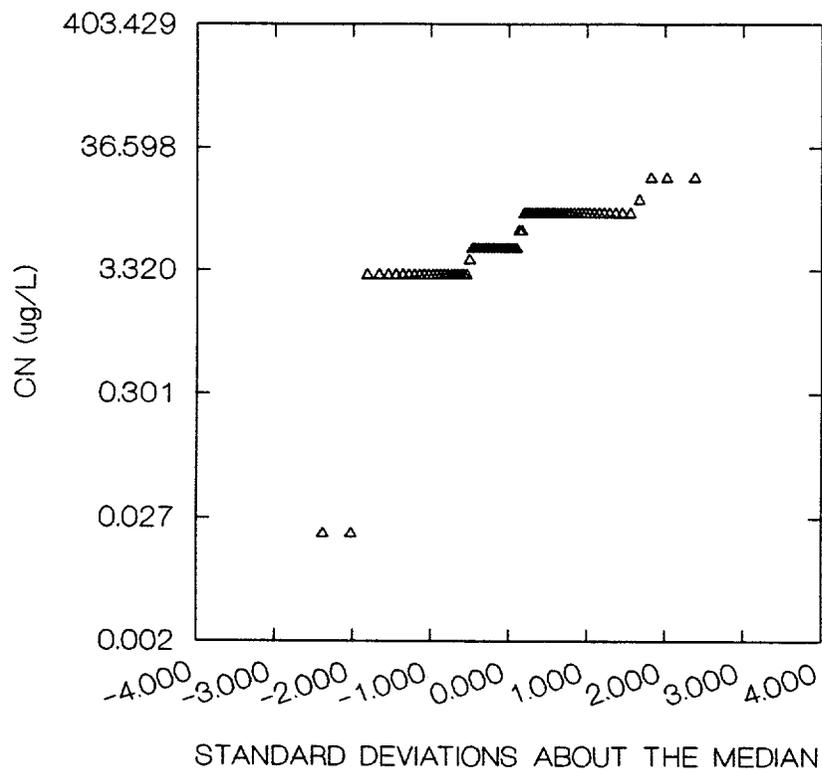
UCRS Groundwater: Cumulative Probability Graph, Cobalt



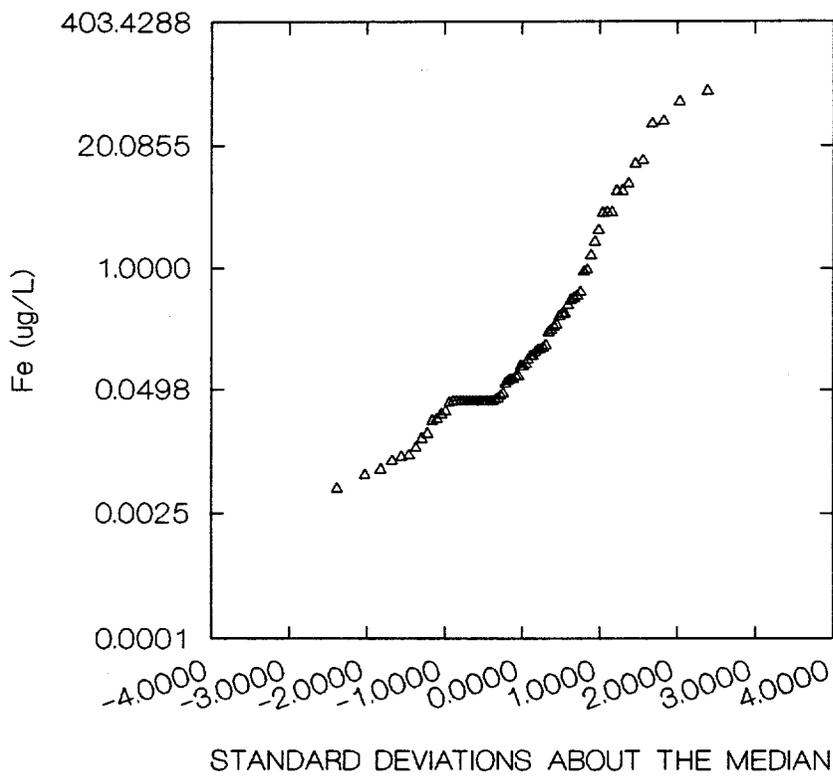
UCRS Groundwater: Cumulative Probability Graph, Copper



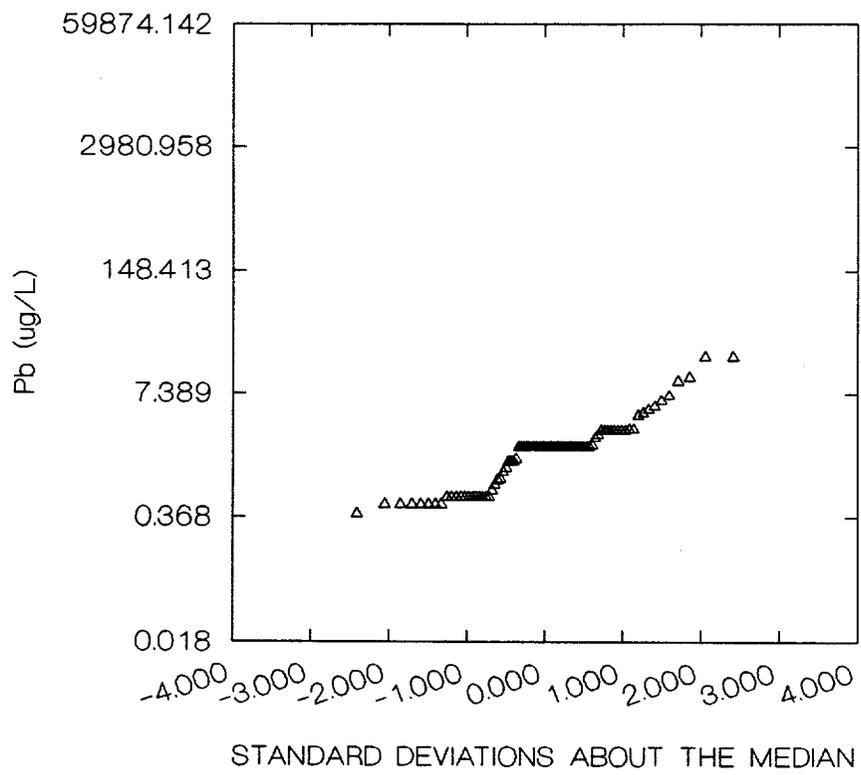
UCRS Groundwater: Cumulative Probability Graph, Cyanide



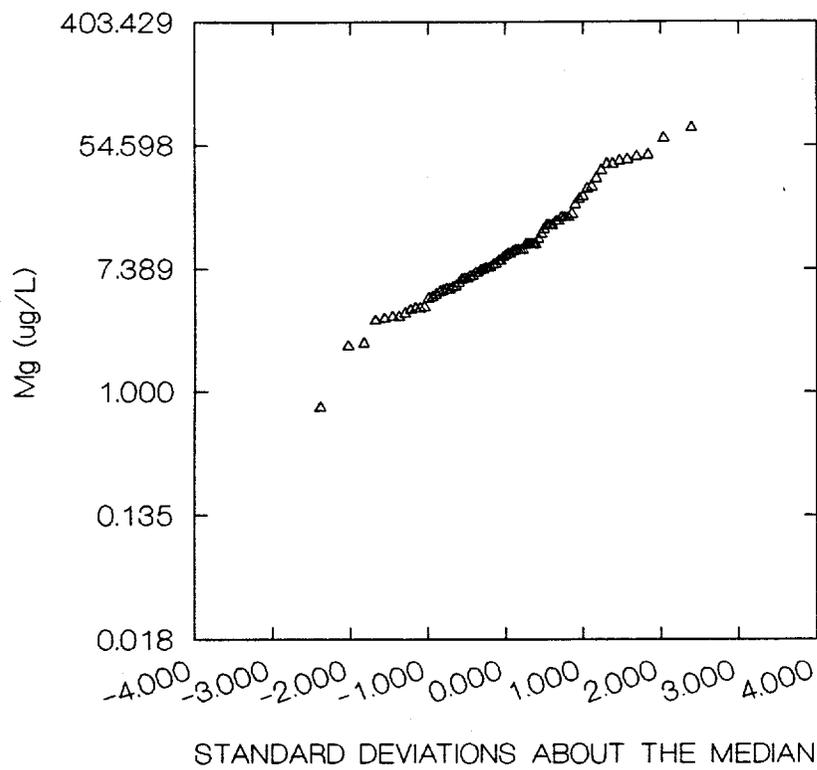
UCRS Groundwater: Cumulative Probability Graph, Iron



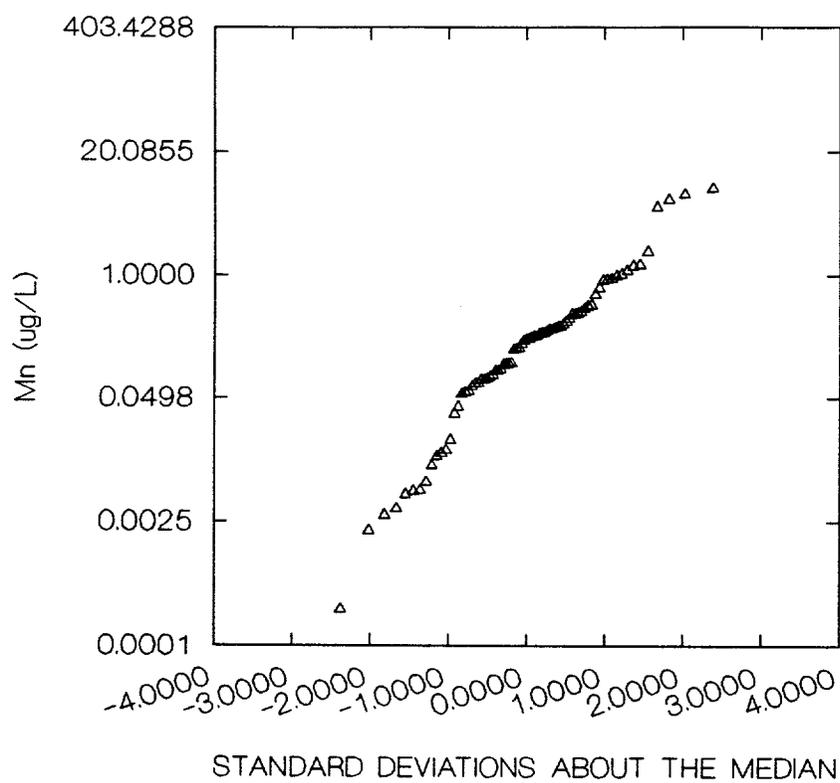
UCRS Groundwater: Cumulative Probability Graph, Lead



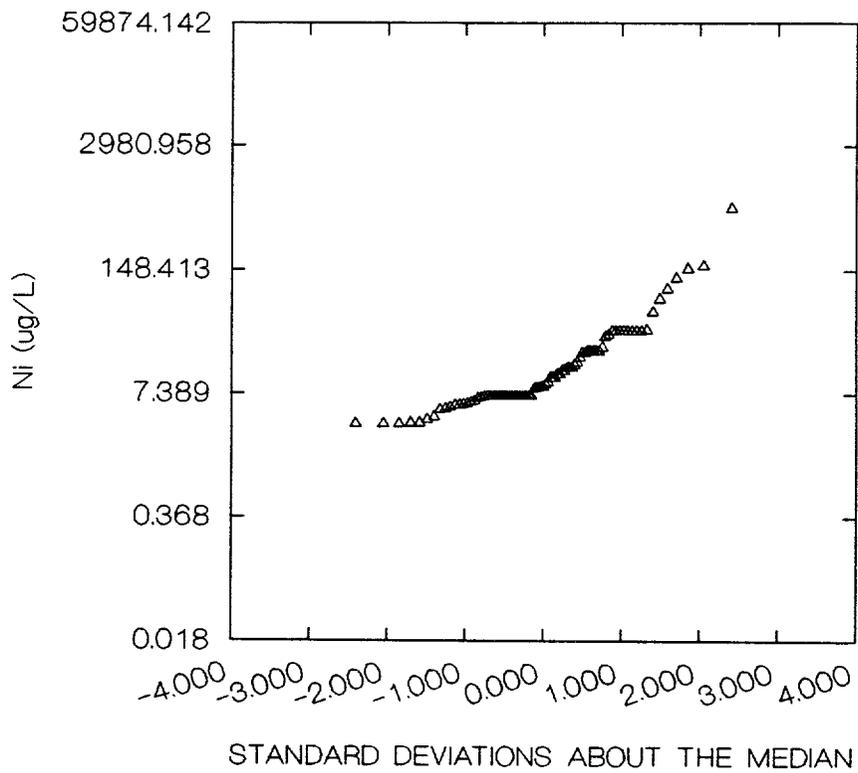
UCRS Groundwater: Cumulative Probability Graph, Magnesium



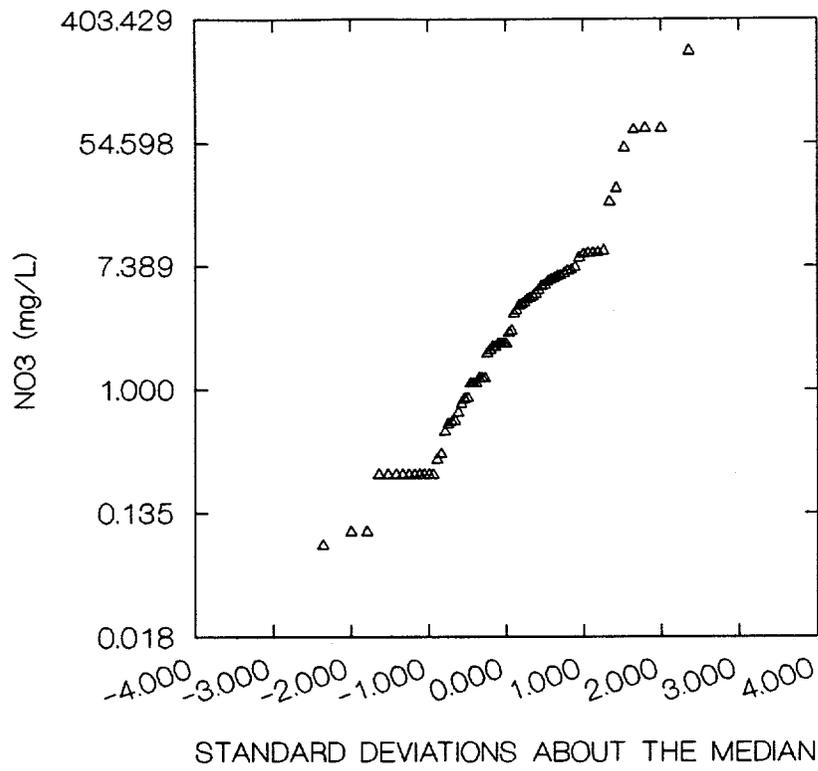
UCRS Groundwater: Cumulative Probability Graph, Manganese



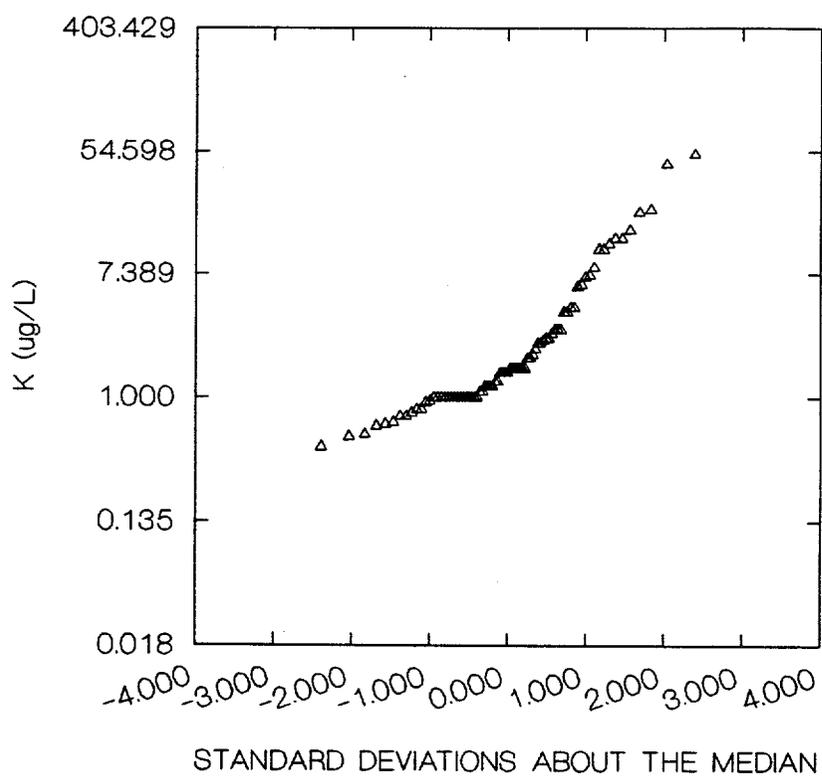
UCRS Groundwater: Cumulative Probability Graph, Nickel



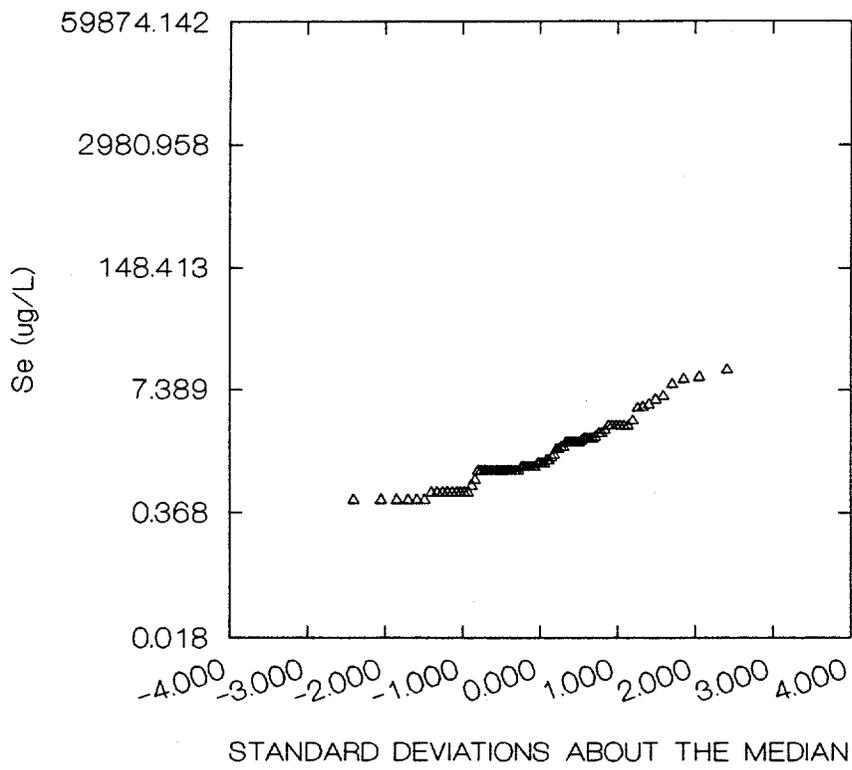
UCRS Groundwater: Cumulative Probability Graph, Nitrate



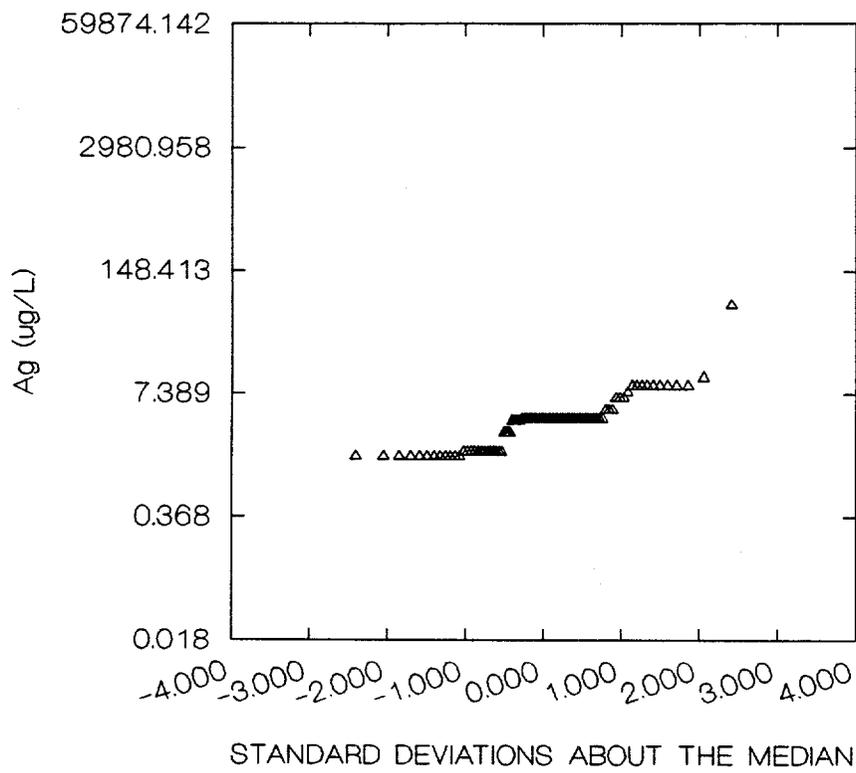
UCRS Groundwater: Cumulative Probability Graph, Potassium



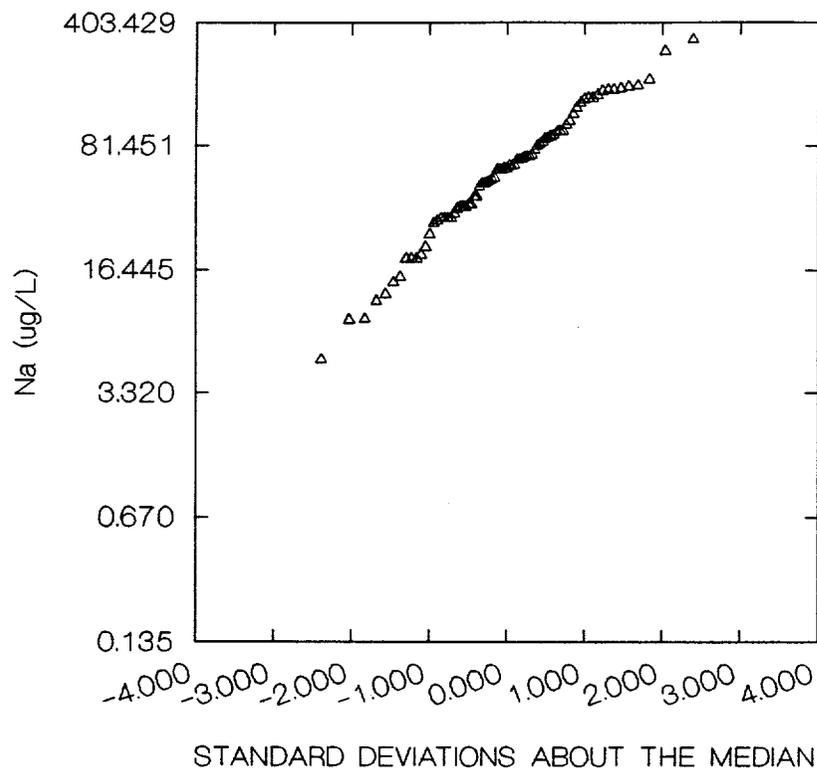
UCRS Groundwater: Cumulative Probability Graph, Selenium



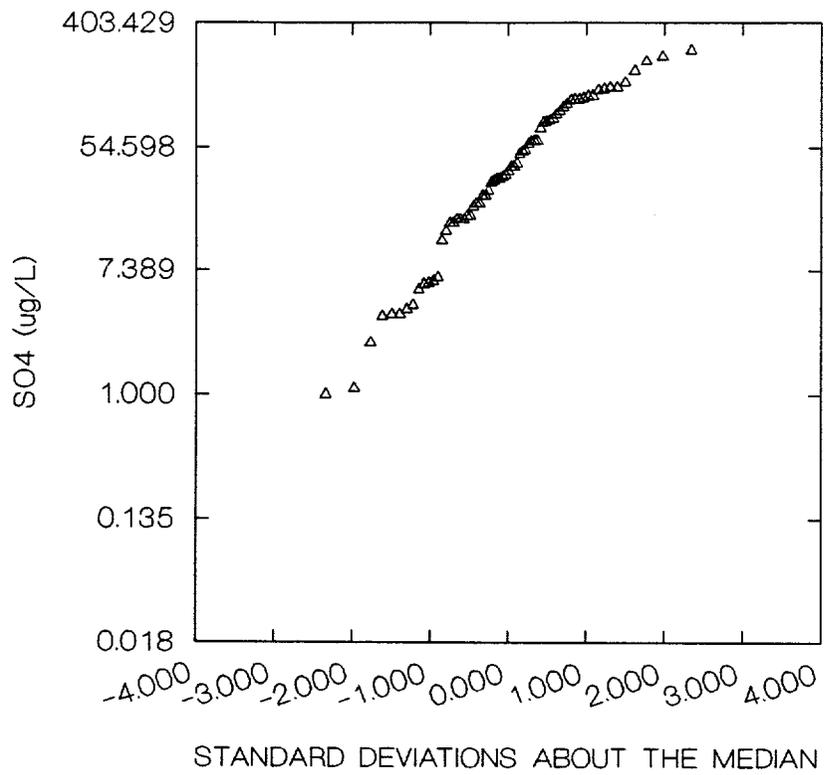
UCRS Groundwater: Cumulative Probability Graph, Silver



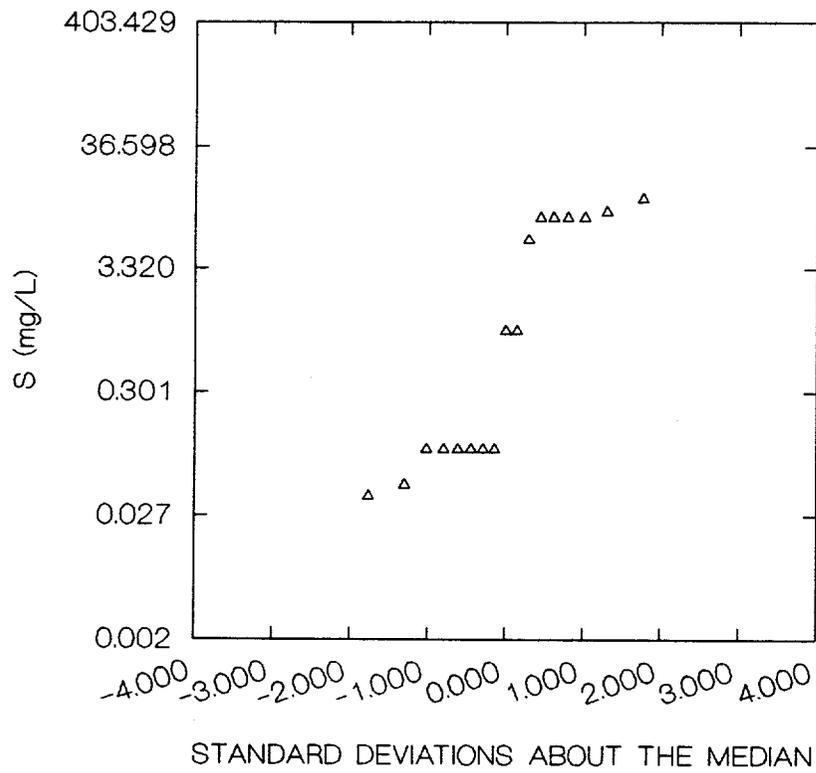
UCRS Groundwater: Cumulative Probability Graph, Sodium



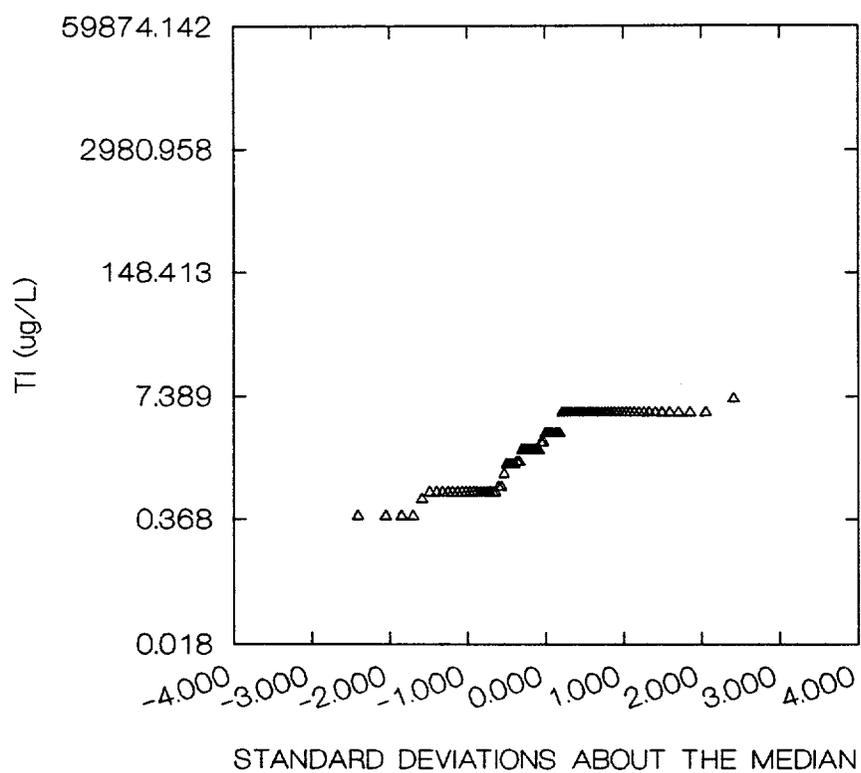
UCRS Groundwater: Cumulative Probability Graph, Sulfate



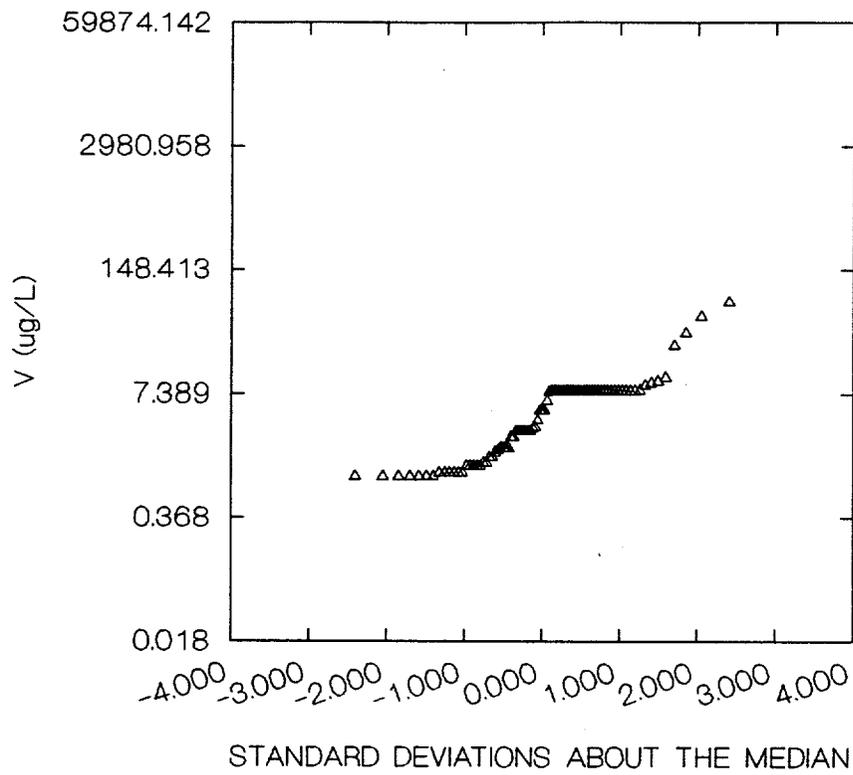
UCRS Groundwater: Cumulative Probability Graph, S



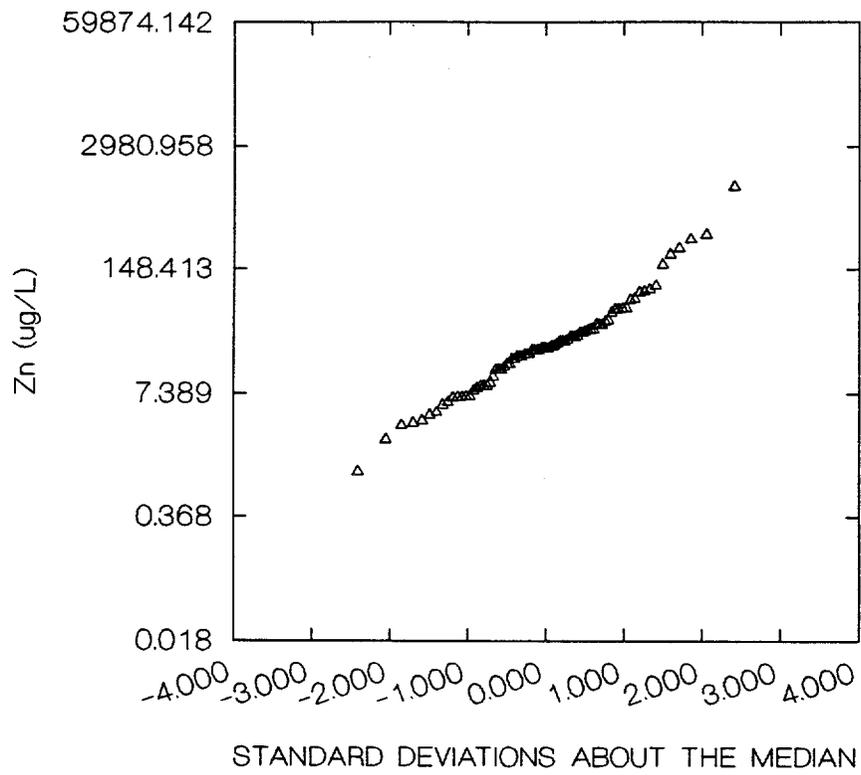
UCRS Groundwater: Cumulative Probability Graph, Thallium



UCRS Groundwater: Cumulative Probability Graph, Vanadium



UCRS Groundwater: Cumulative Probability Graph, Zinc

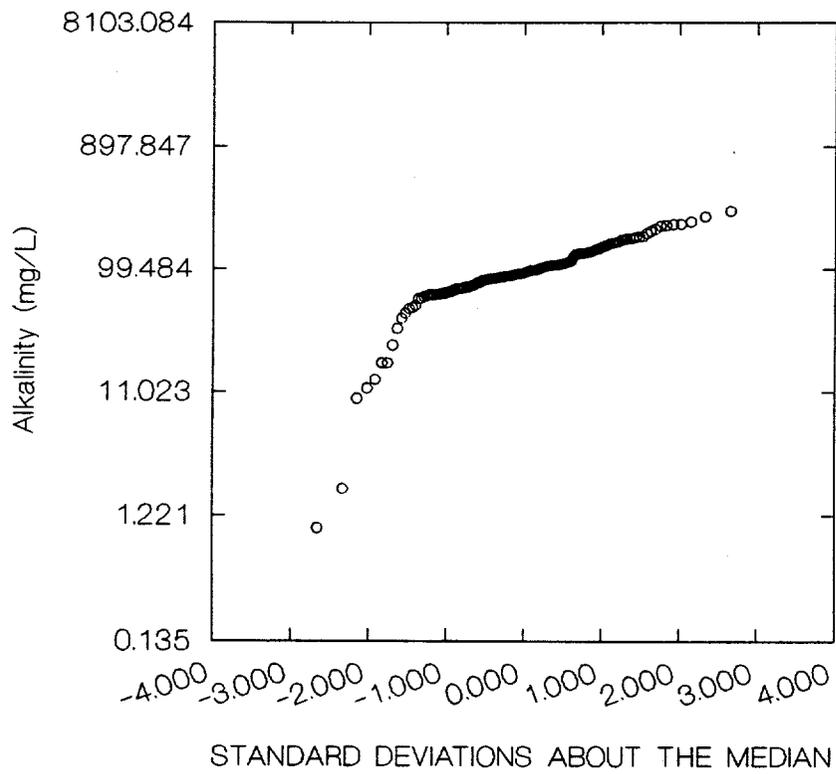


APPENDIX A.5

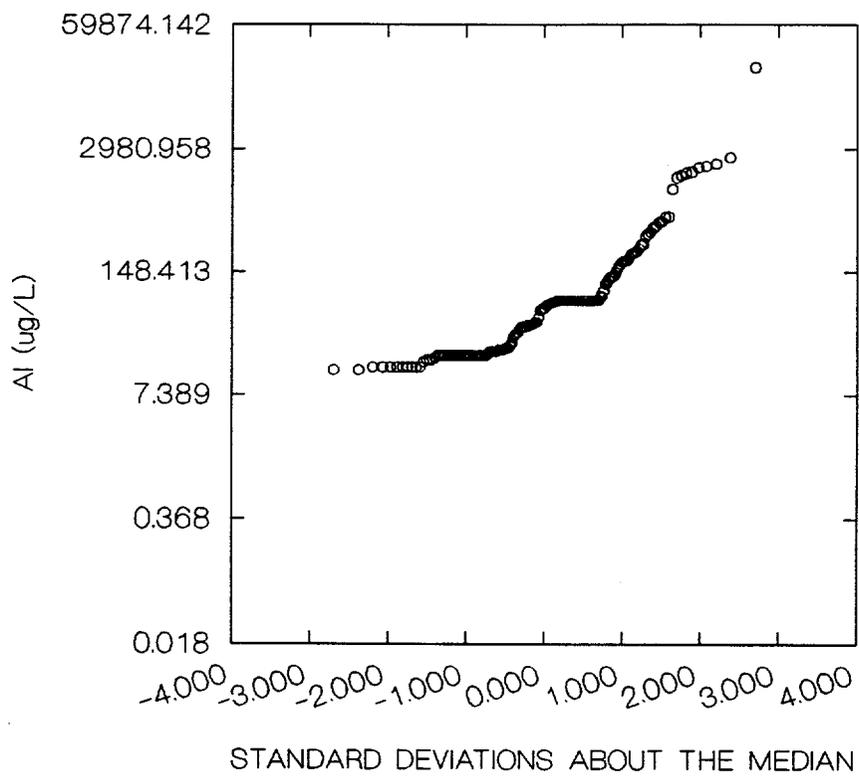
**CUMULATIVE PROBABILITY PLOTS
FOR GROUNDWATER SAMPLES FROM
REGIONAL GRAVEL AQUIFER**

This page left intentionally blank.

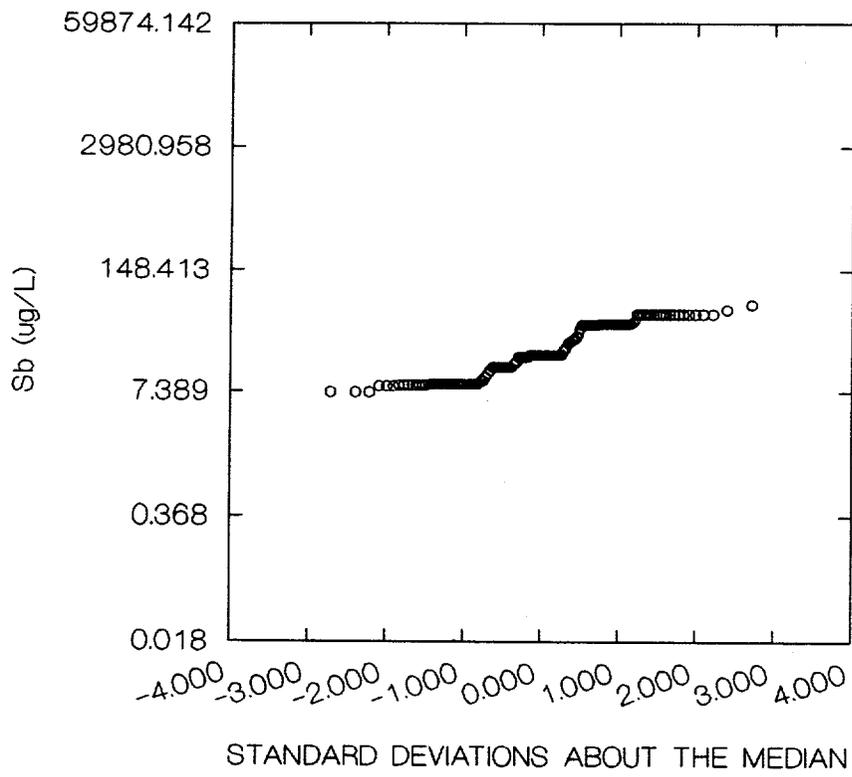
RGA Groundwater: Cumulative Probability Graph, Alkalinity



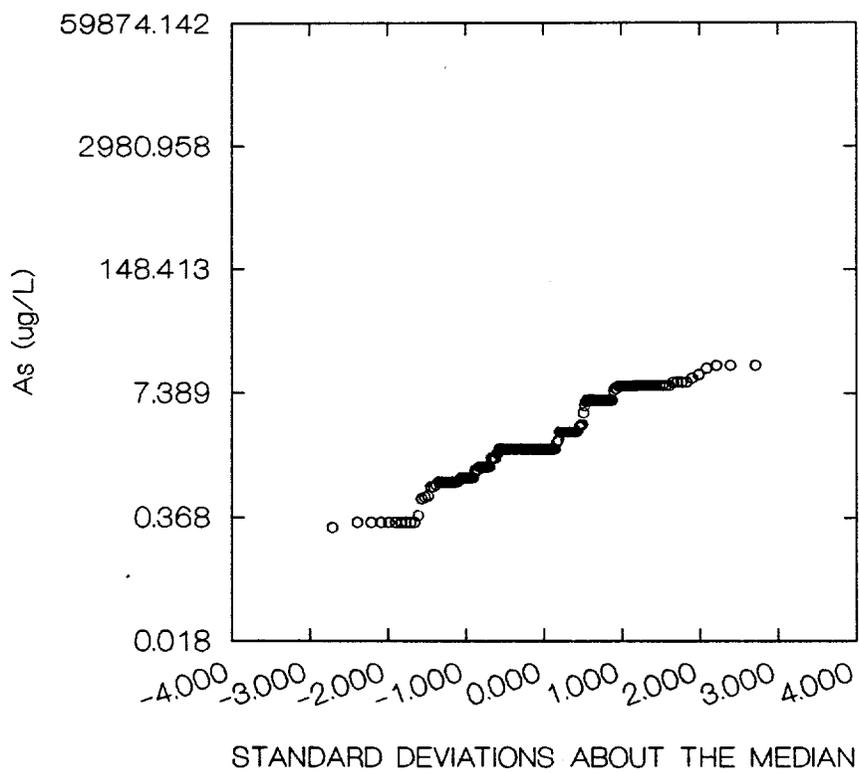
RGA Groundwater: Cumulative Probability Graph, Aluminum



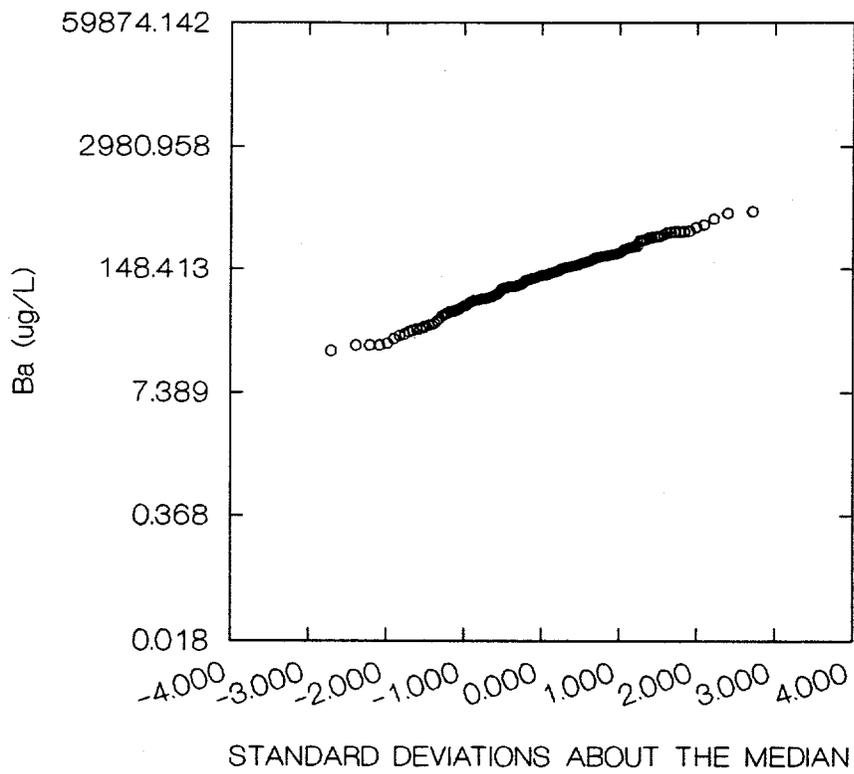
RGA Groundwater: Cumulative Probability Graph, Antimony



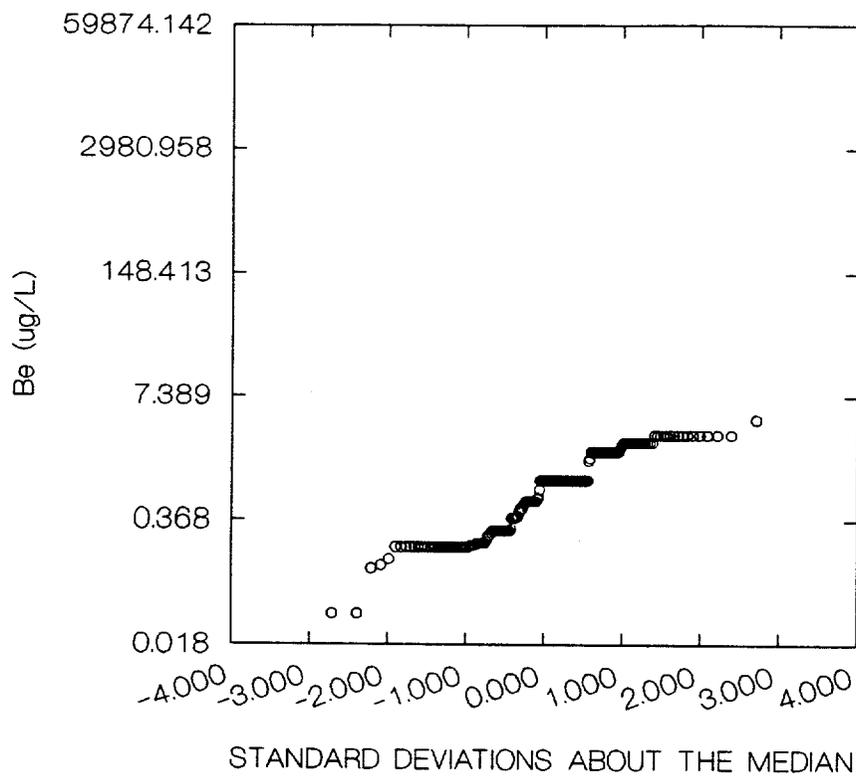
RGA Groundwater: Cumulative Probability Graph, Arsenic



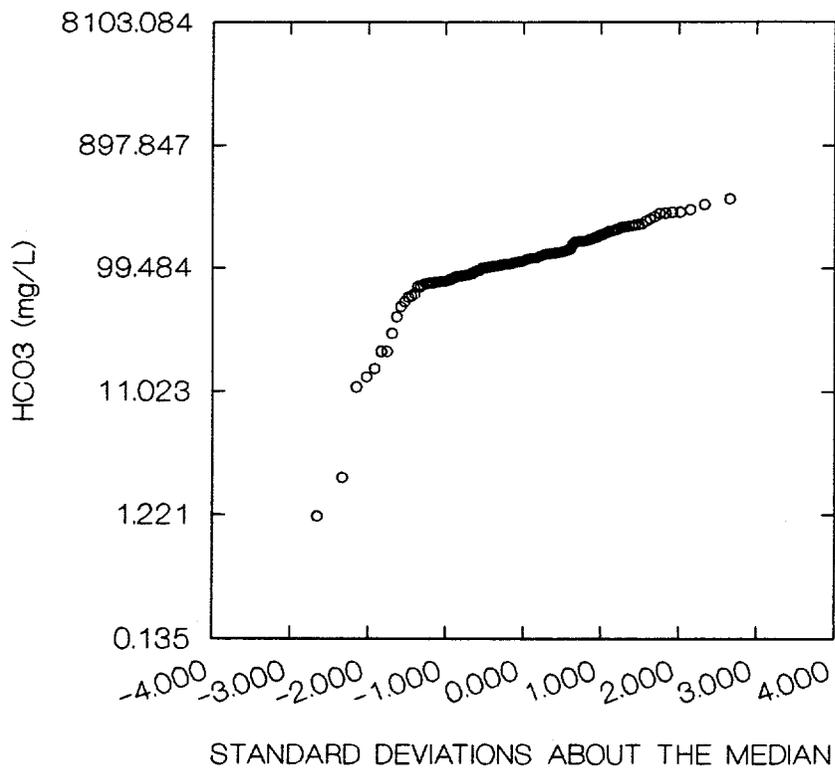
RGA Groundwater: Cumulative Probability Graph, Barium



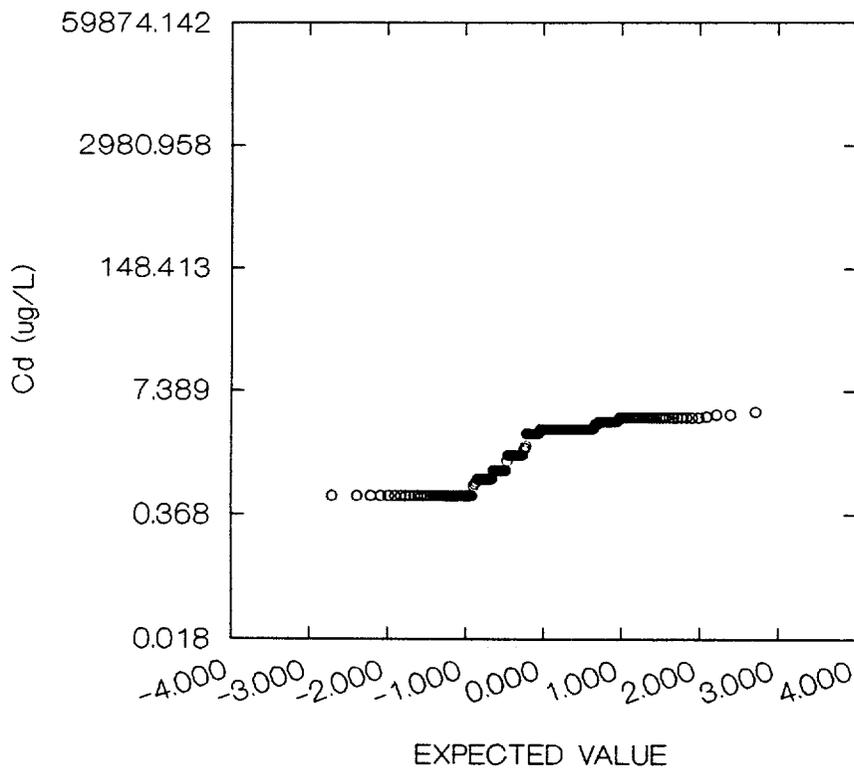
RGA Groundwater: Cumulative Probability Graph, Beryllium



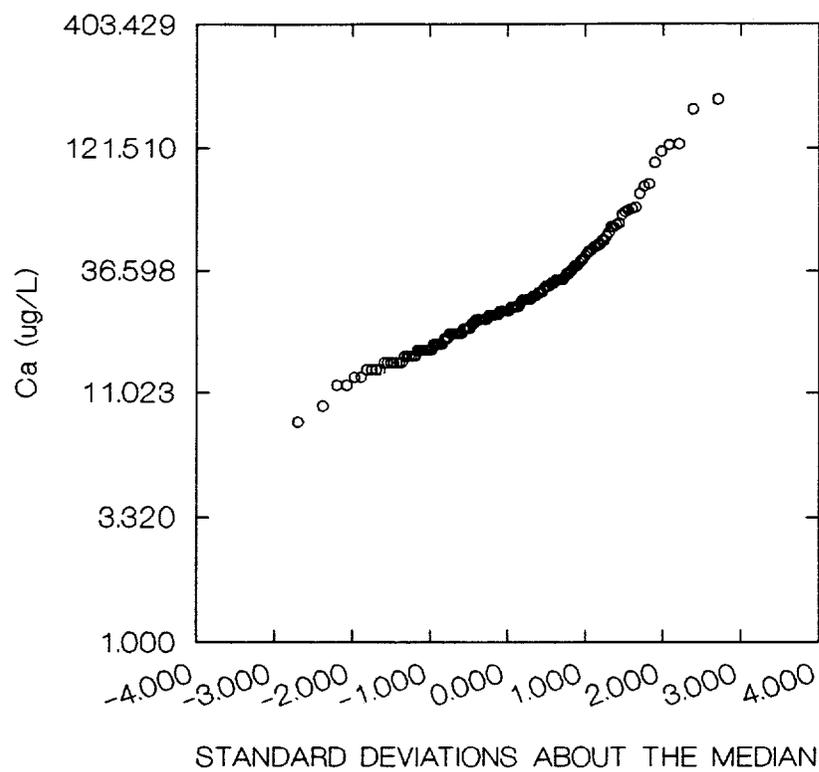
RGA Groundwater: Cumulative Probability Graph, Bicarbonate



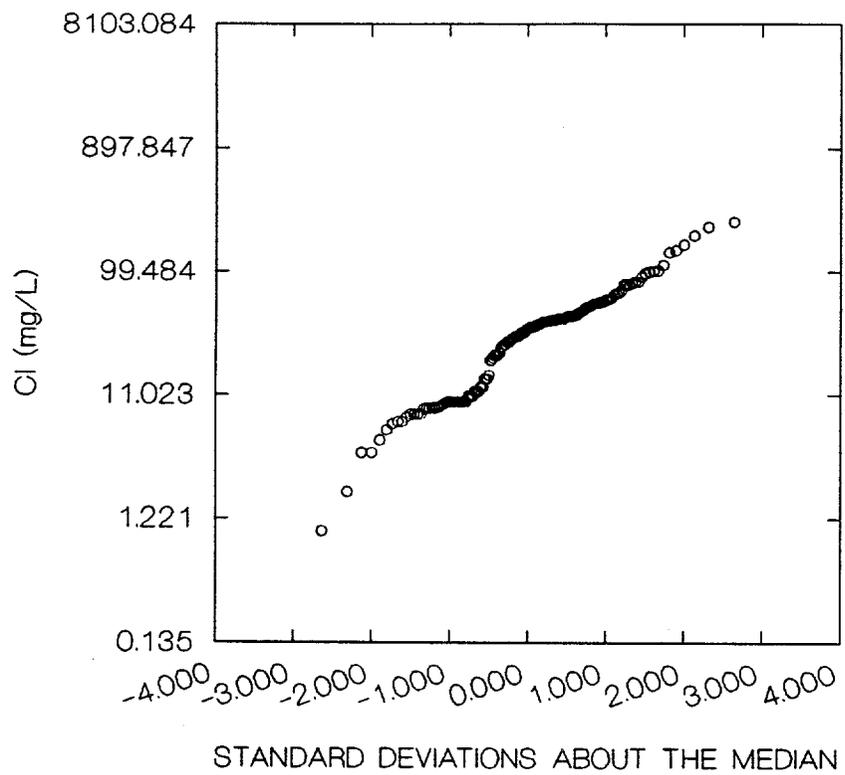
RGA Groundwater: Cumulative Probability Graph, Cadmium



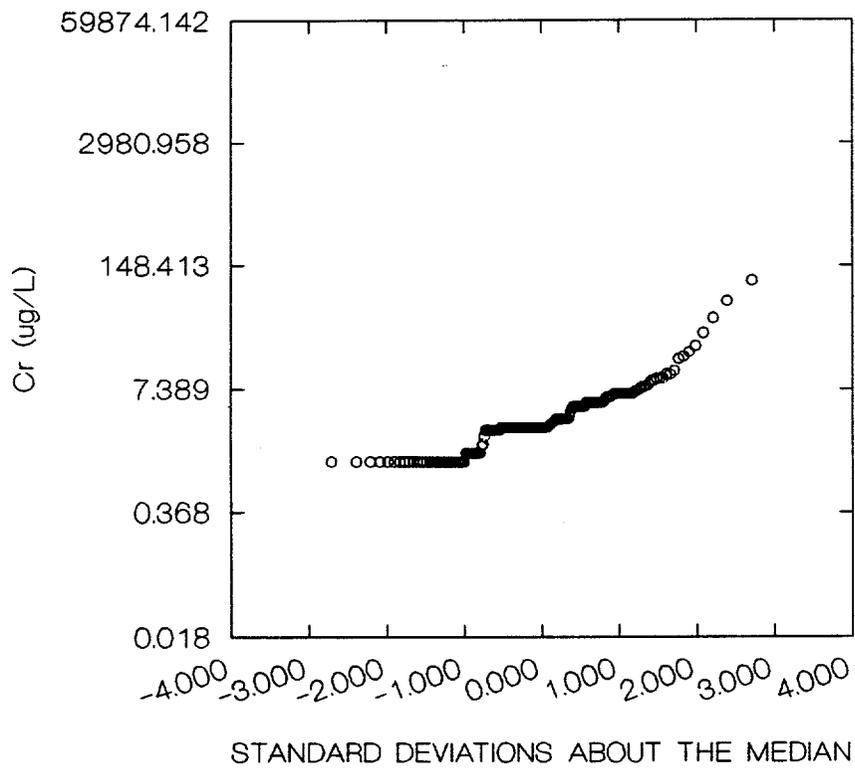
RGA Groundwater: Cumulative Probability Graph, Calcium



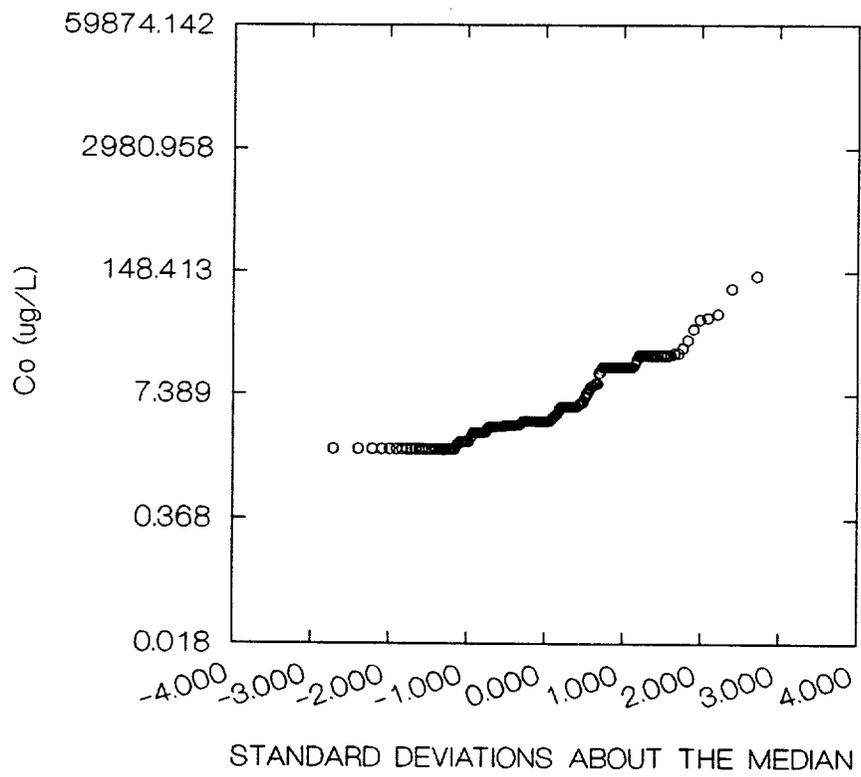
RGA Groundwater: Cumulative Probability Graph, Chloride



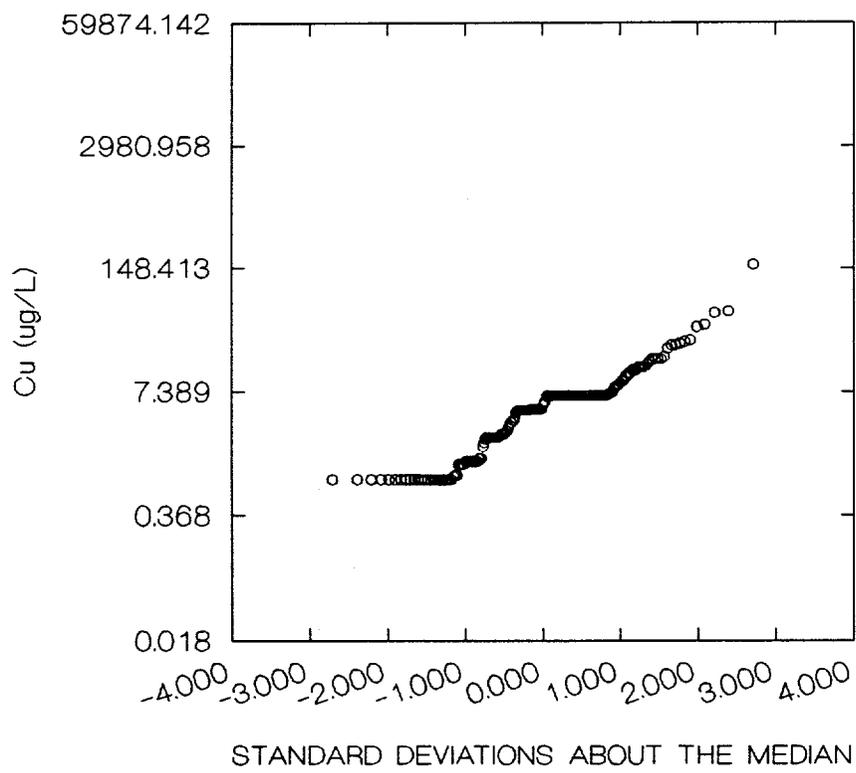
RGA Groundwater: Cumulative Probability Graph, Chromium



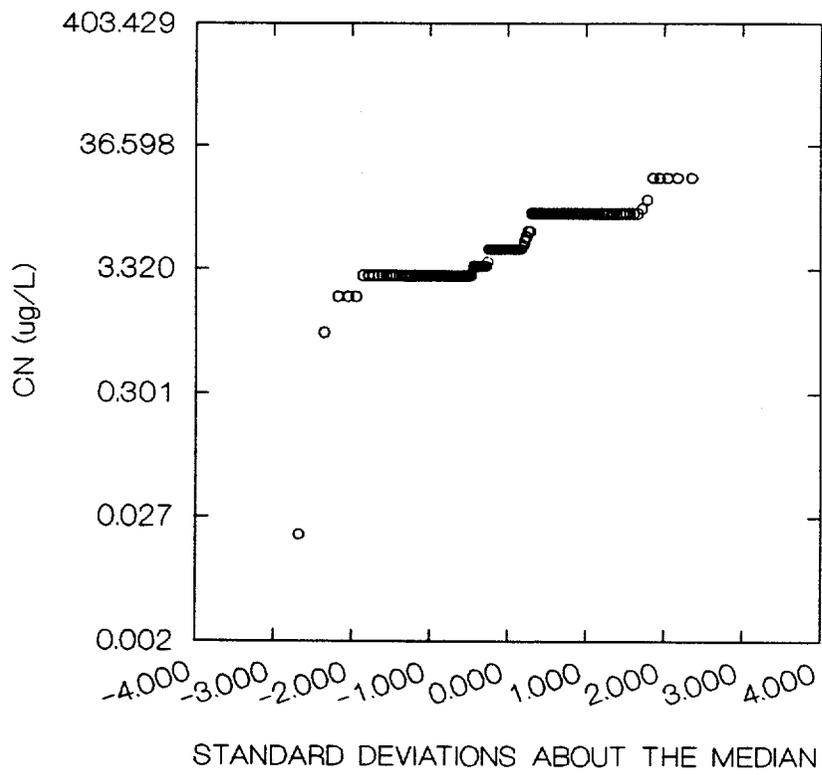
RGA Groundwater: Cumulative Probability Graph, Cobalt



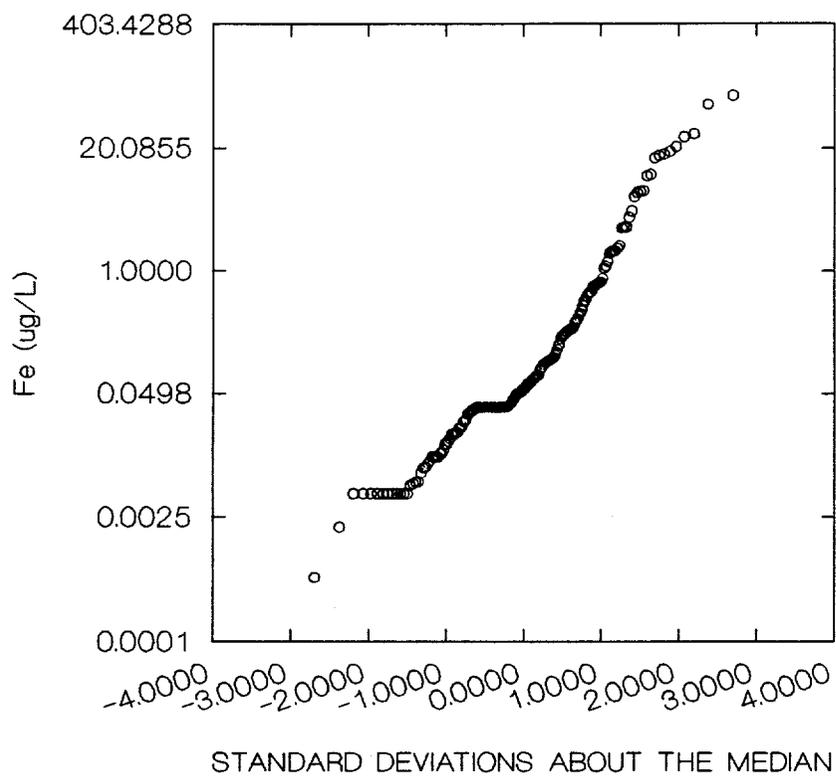
RGA Groundwater: Cumulative Probability Graph, Copper



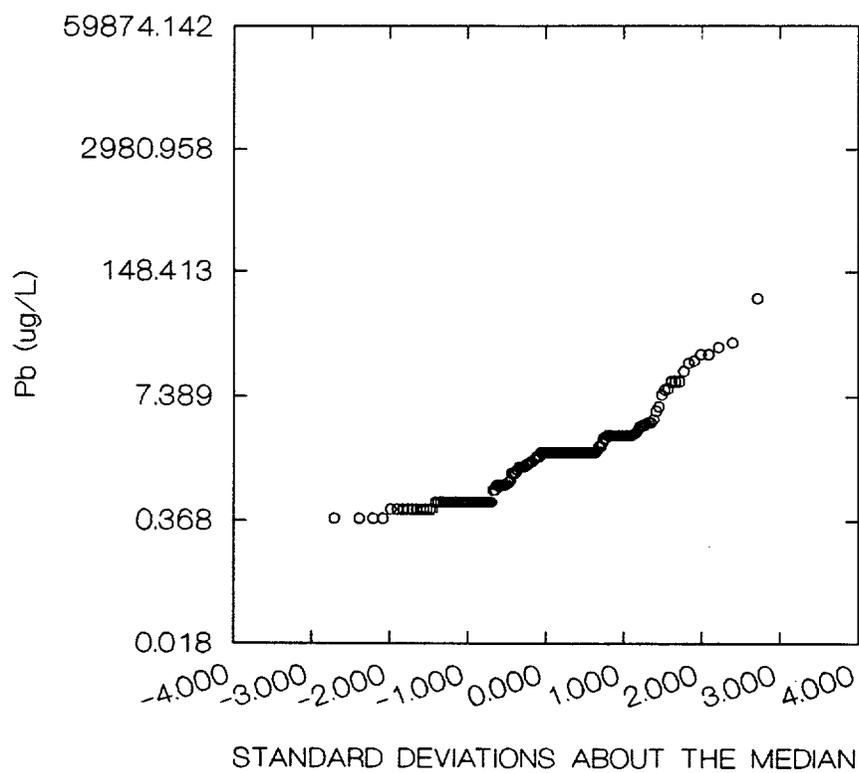
RGA Groundwater: Cumulative Probability Graph, Cyanide



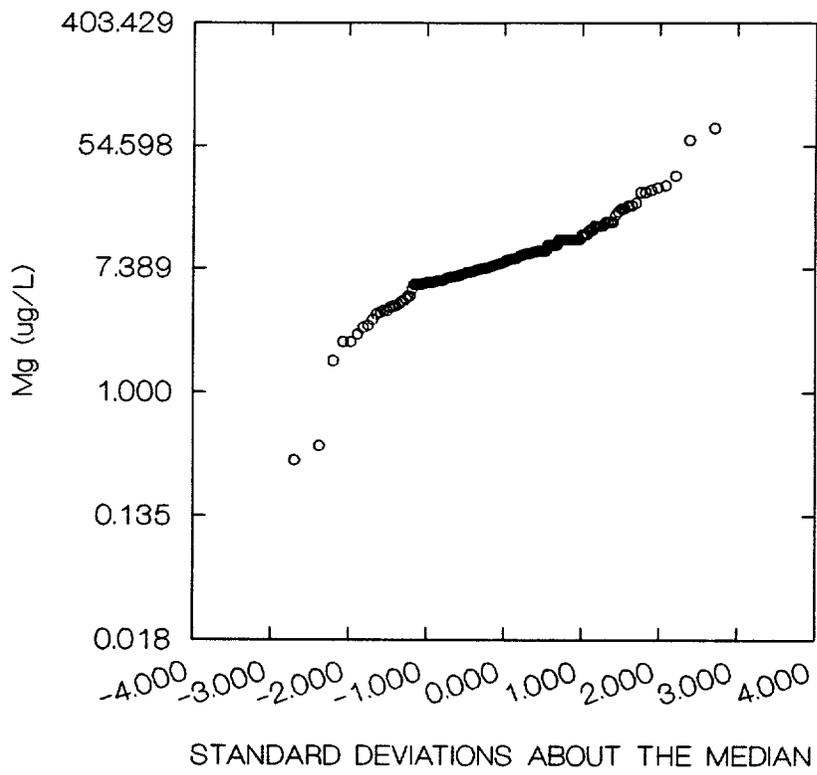
RGA Groundwater: Cumulative Probability Graph, Iron



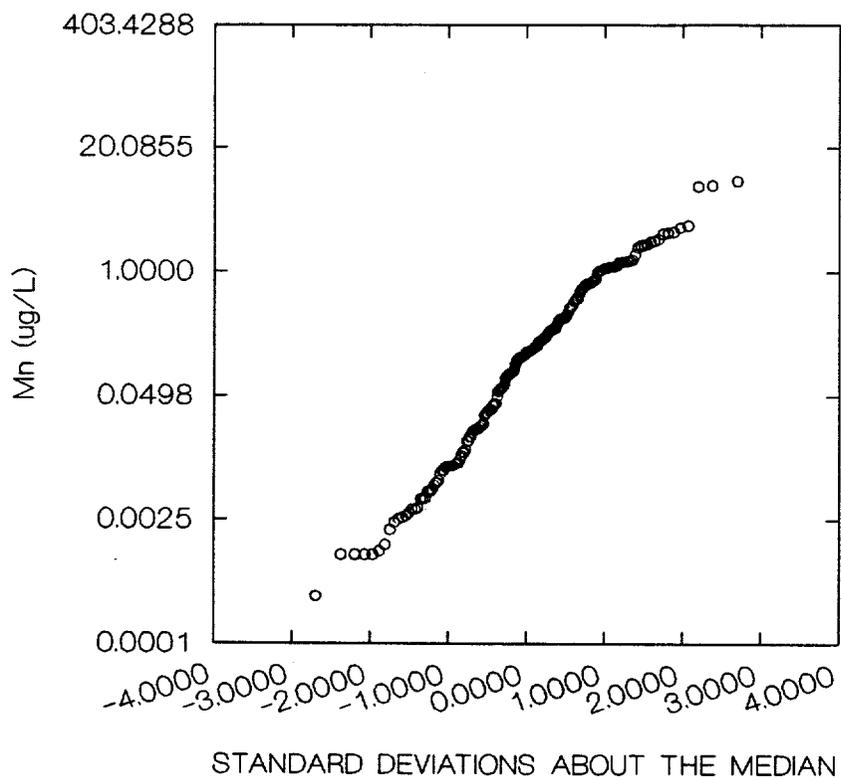
RGA Groundwater: Cumulative Probability Graph, Lead



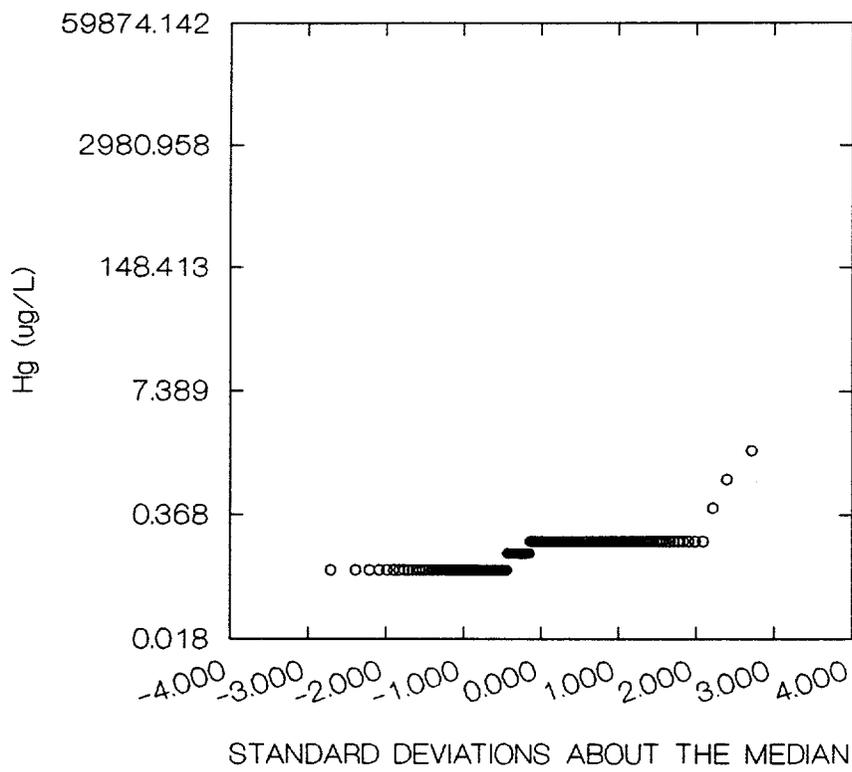
RGS Groundwater: Cumulative Probability Graph, Magnesium



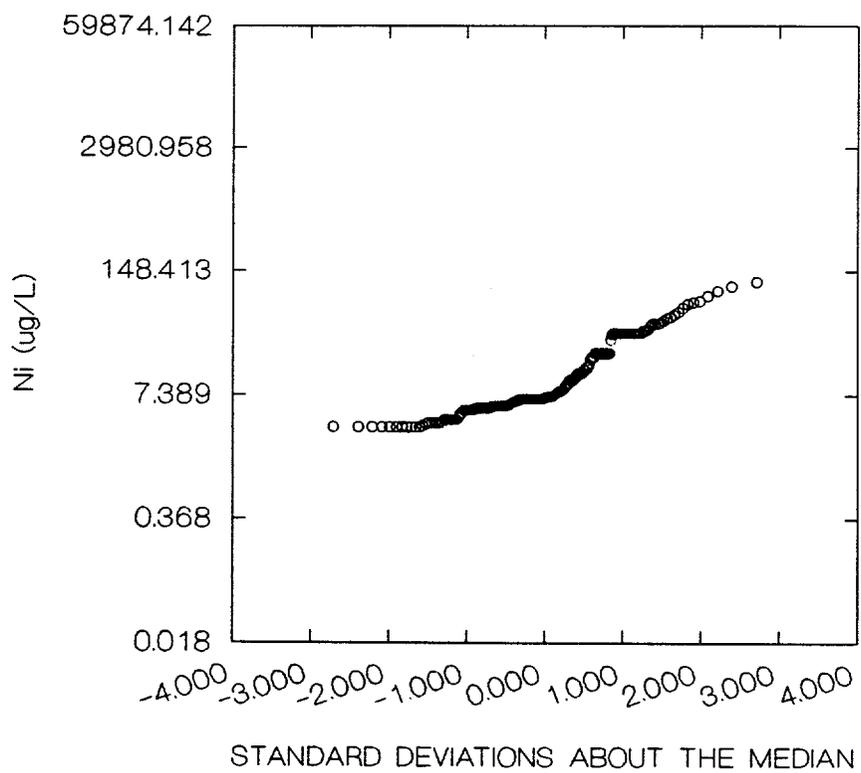
RGA Groundwater: Cumulative Probability Graph, Manganese



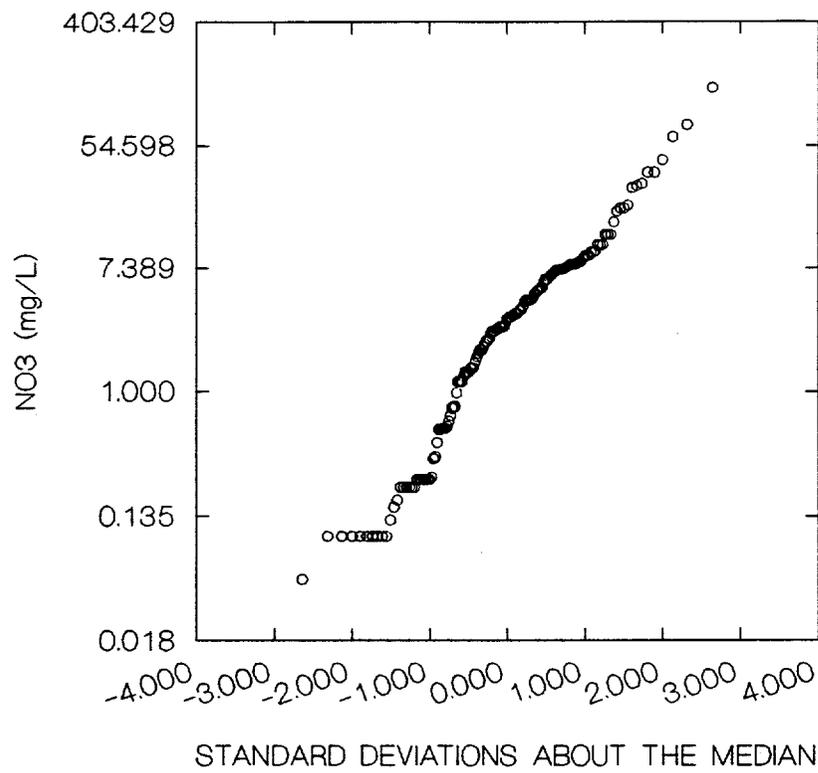
RGA Groundwater: Cumulative Probability Graph, Mercury



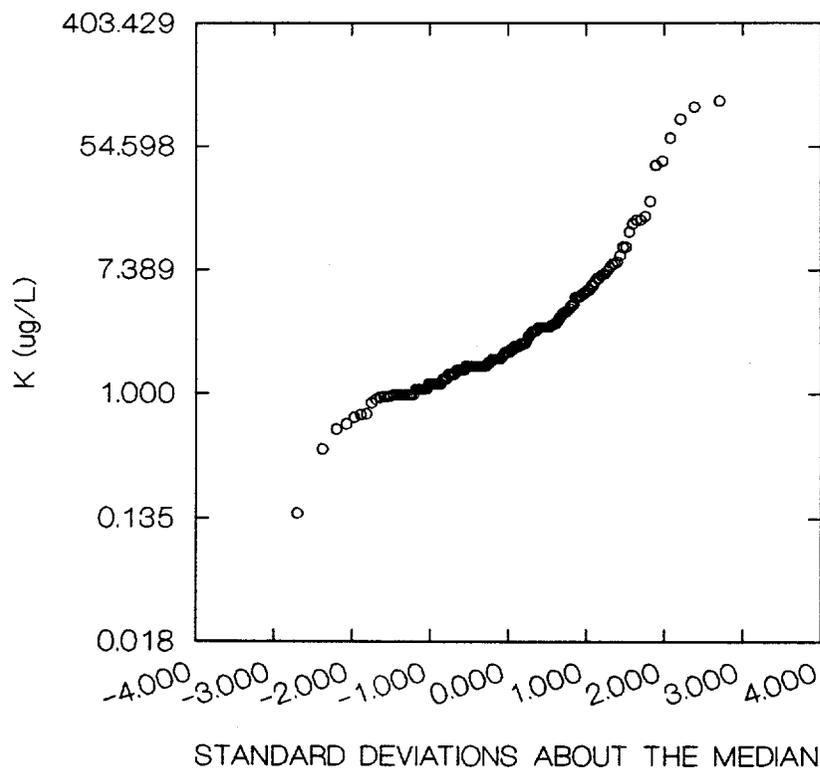
RGA Groundwater: Cumulative Probability Graph, Nickel



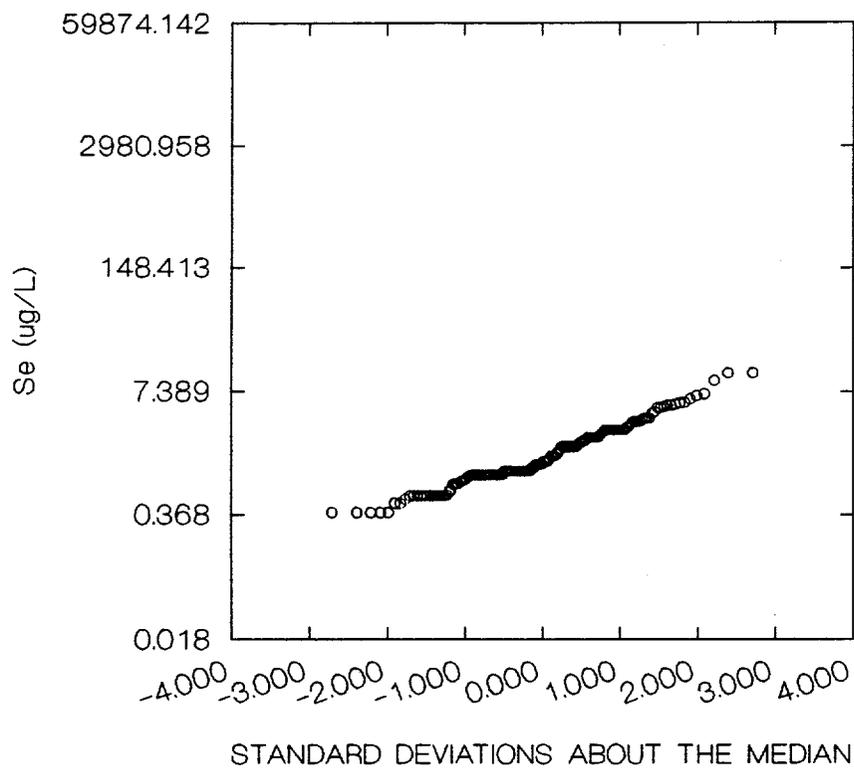
RGA Groundwater: Cumulative Probability Graph, Nitrate



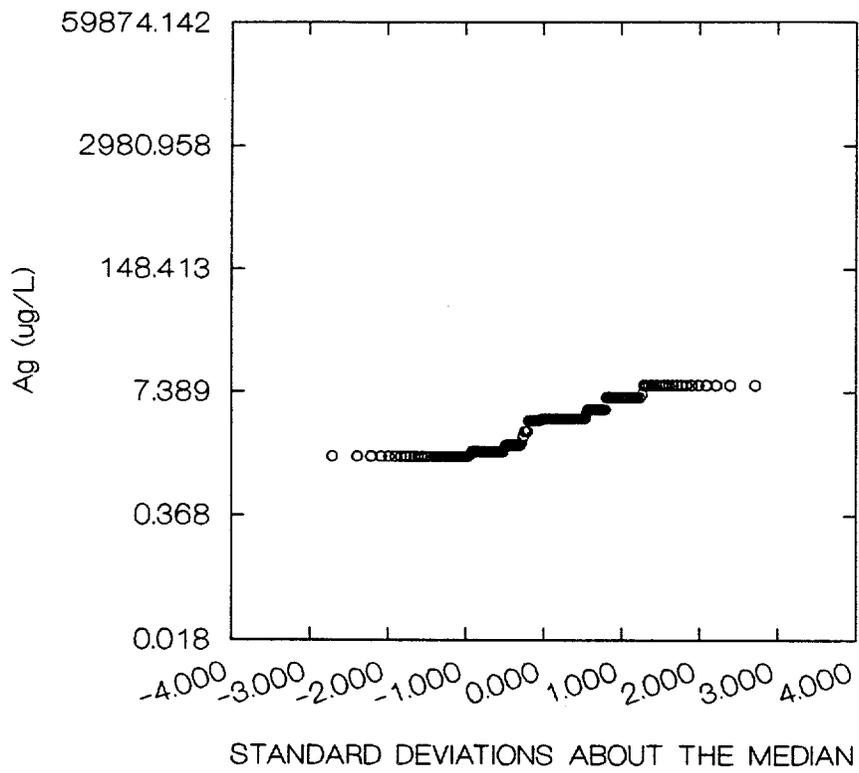
RGA Groundwater: Cumulative Probability Graph, Potassium



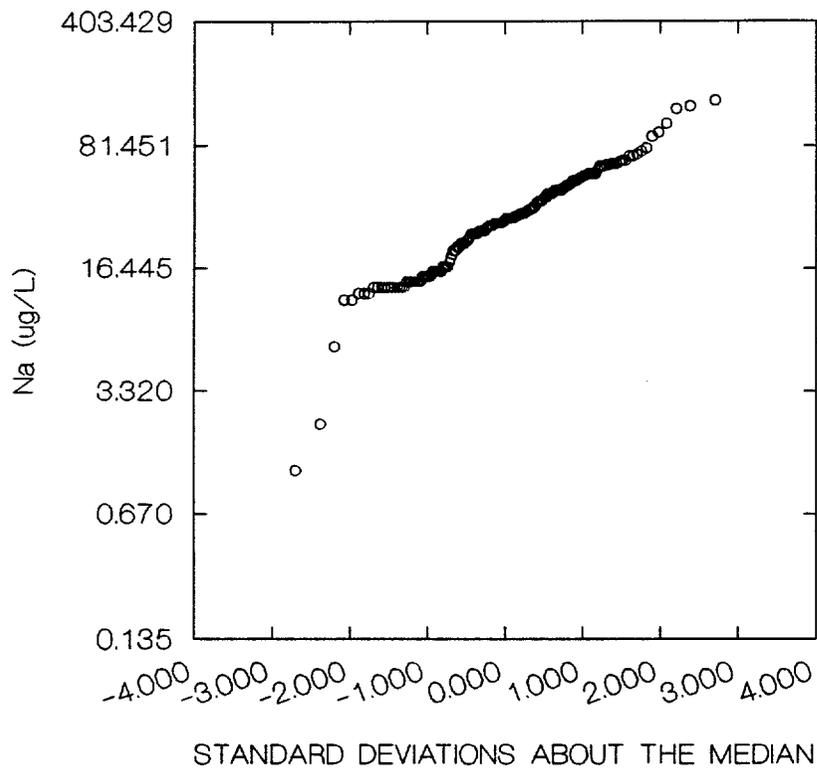
RGA Groundwater: Cumulative Probability Graph, Selenium



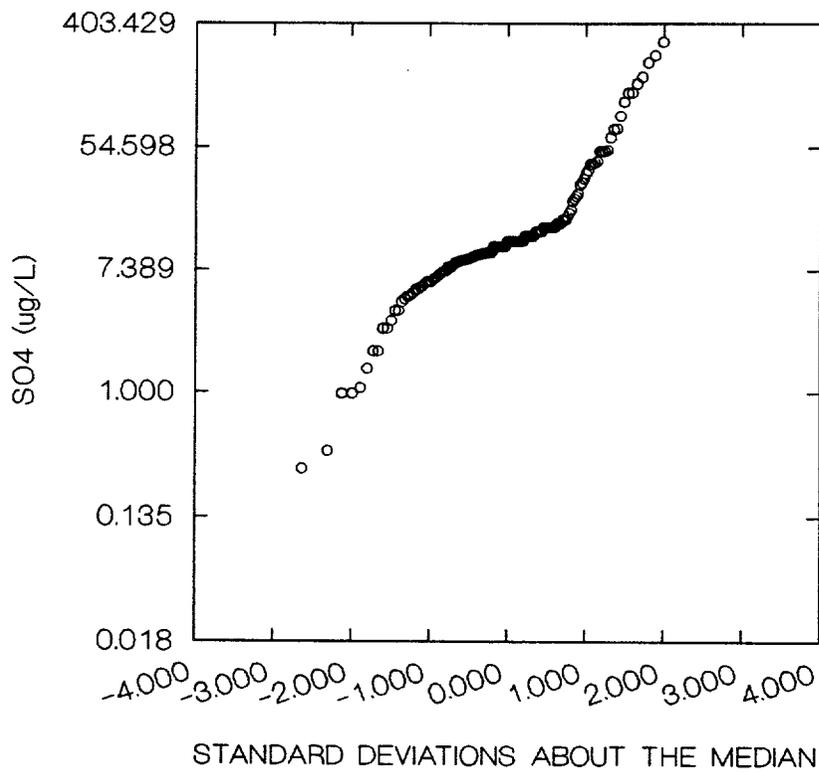
RGA Groundwater: Cumulative Probability Graph, Silver



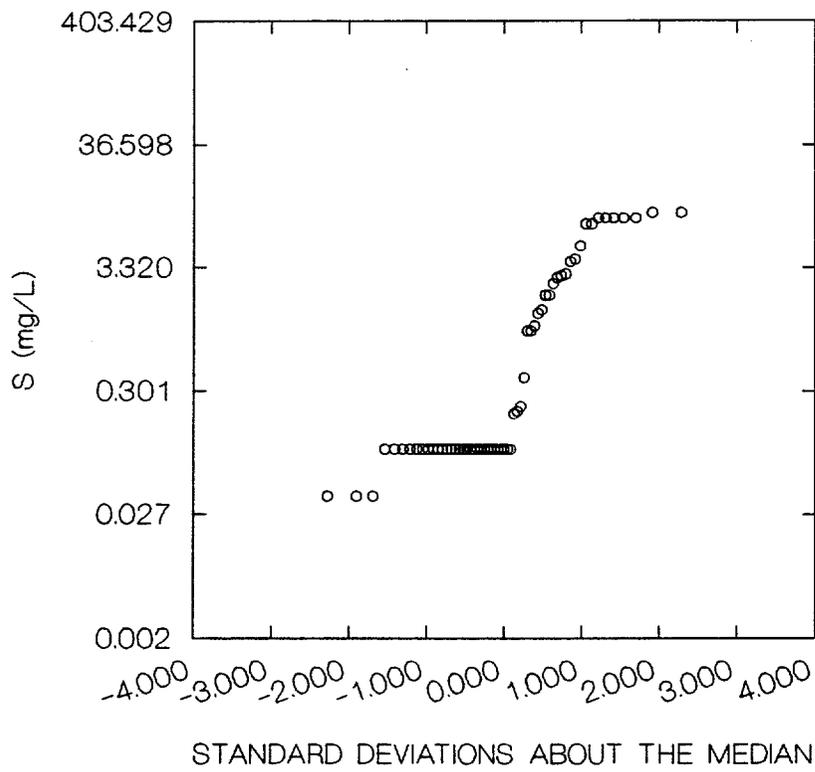
RGA Groundwater: Cumulative Probability Graph, Sodium



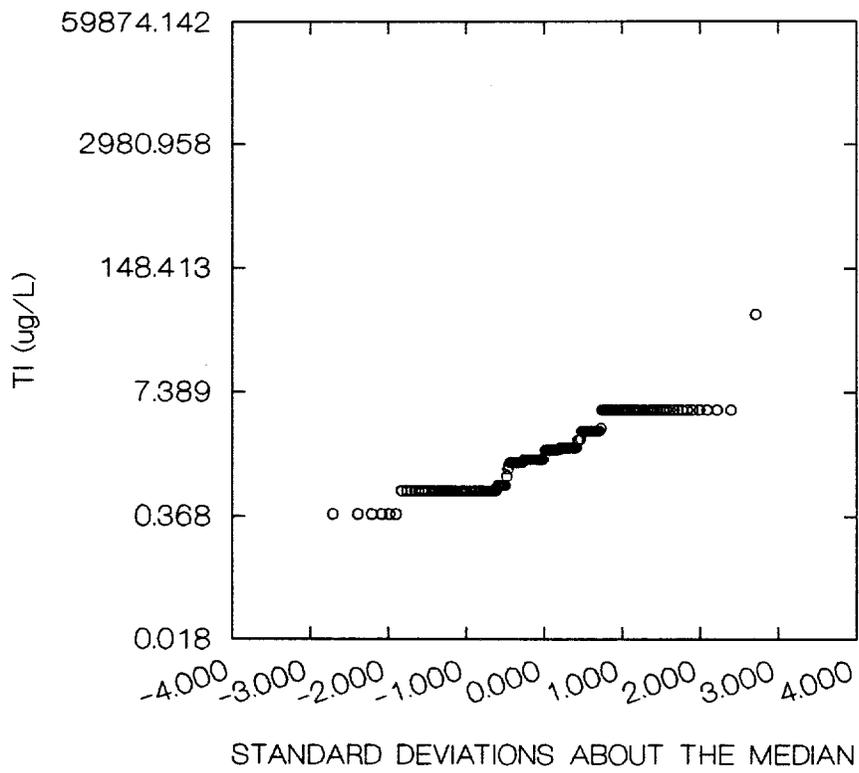
RGA Groundwater: Cumulative Probability Graph, Sulfate



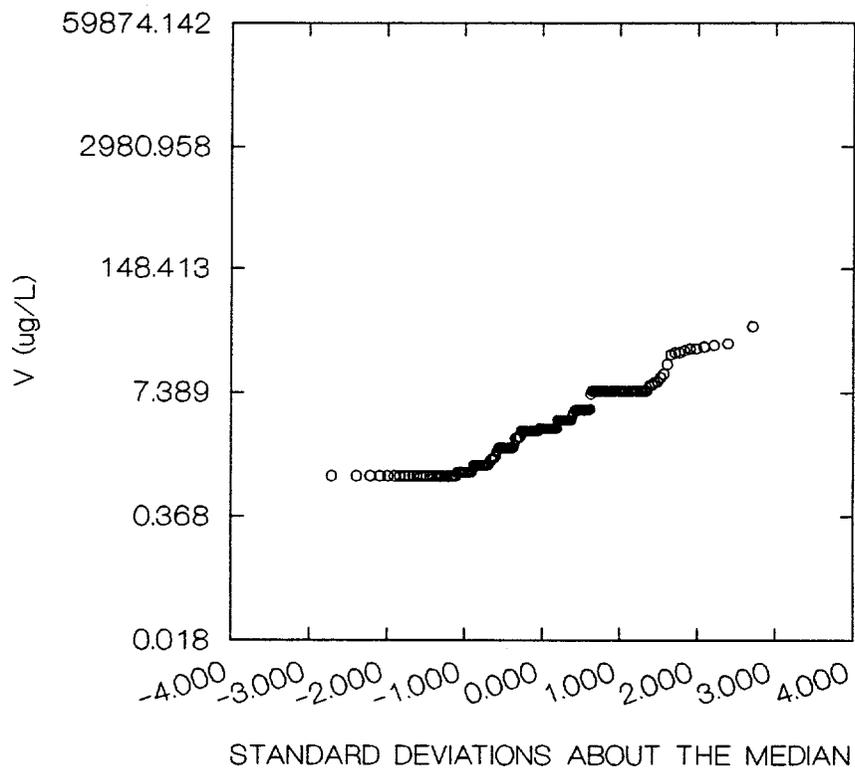
RGA Groundwater: Cumulative Probability Graph, S



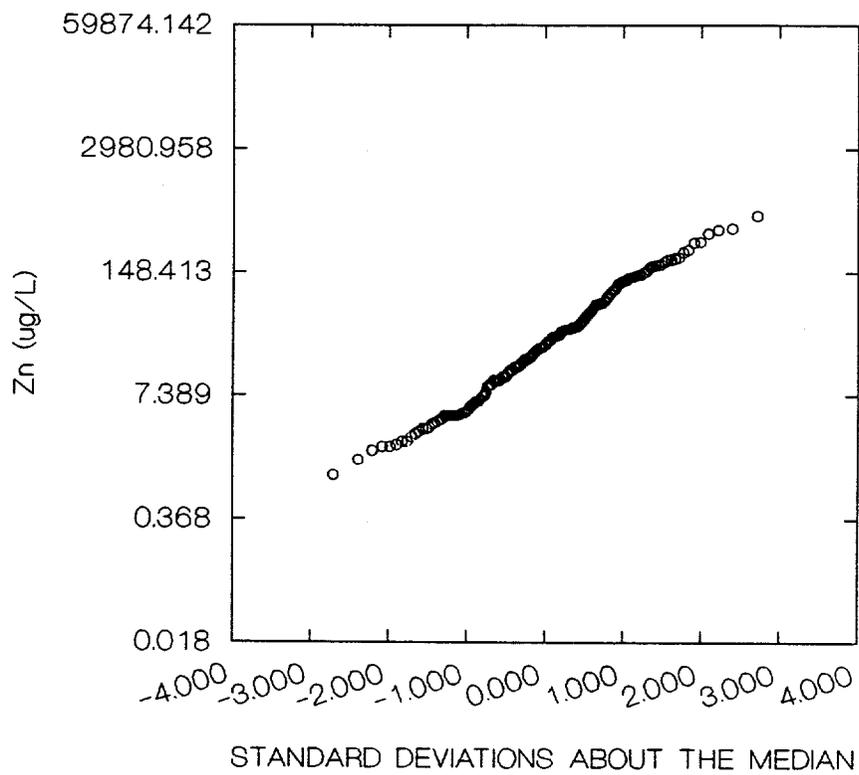
RGA Groundwater: Cumulative Probability Graph, Thallium



RGA Groundwater: Cumulative Probability Graph, Vanadium



RGA Groundwater: Cumulative Probability Graph, Zinc

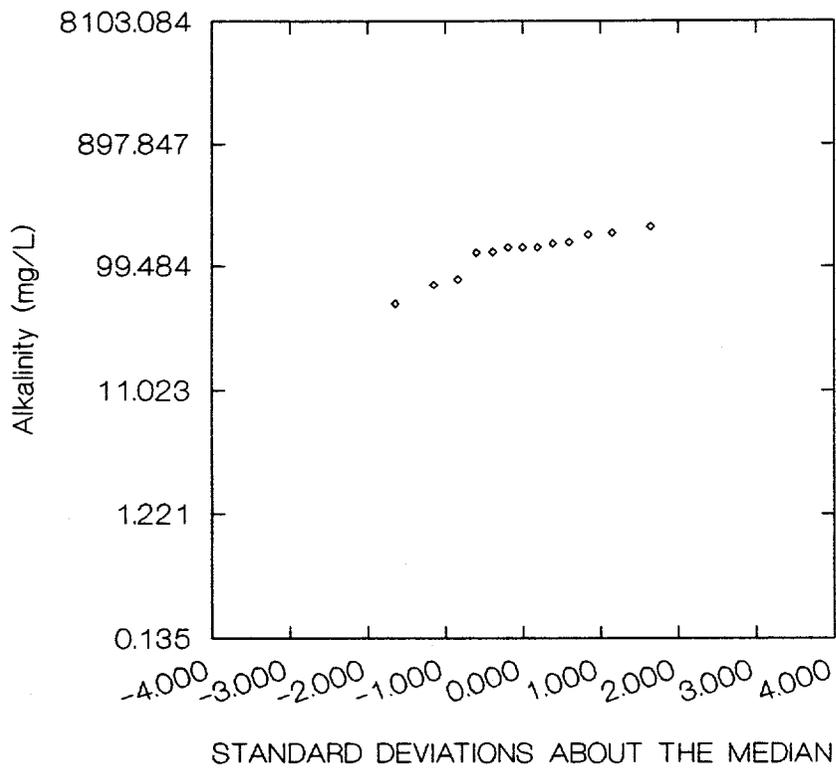


APPENDIX A.6

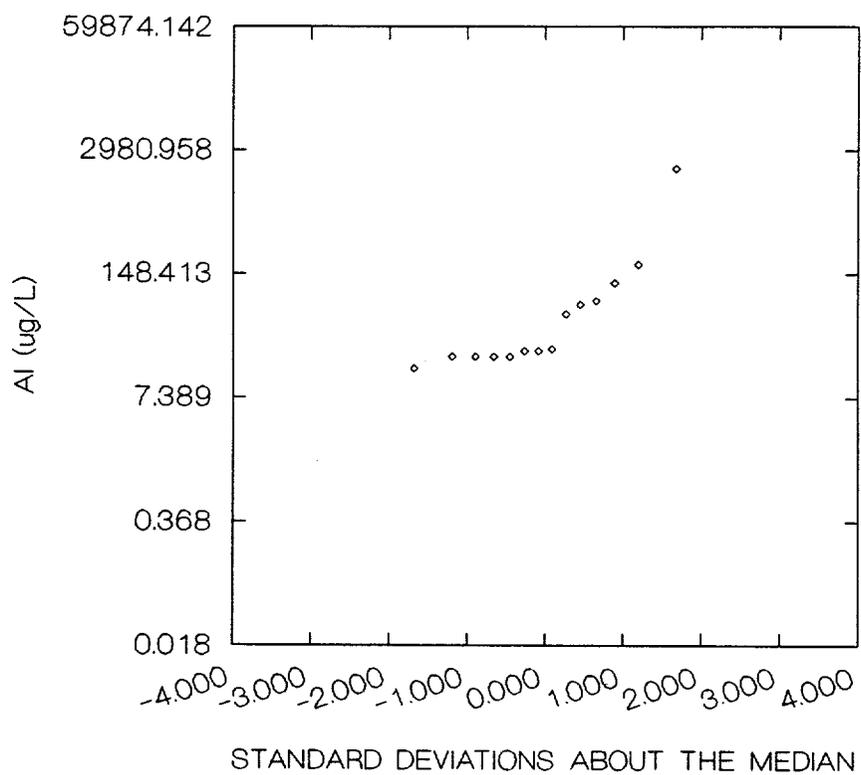
**CUMULATIVE PROBABILITY PLOTS
FOR GROUNDWATER SAMPLES FROM
MCNAIRY FORMATION**

This page left intentionally blank.

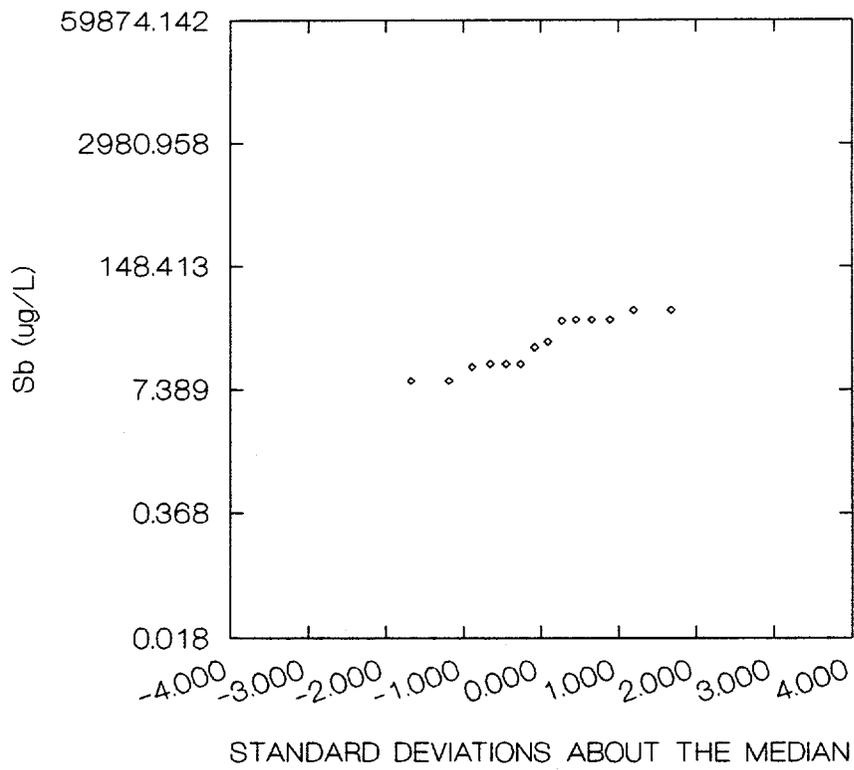
McNairy Groundwater: Cumulative Probability Graph, Alkalinity



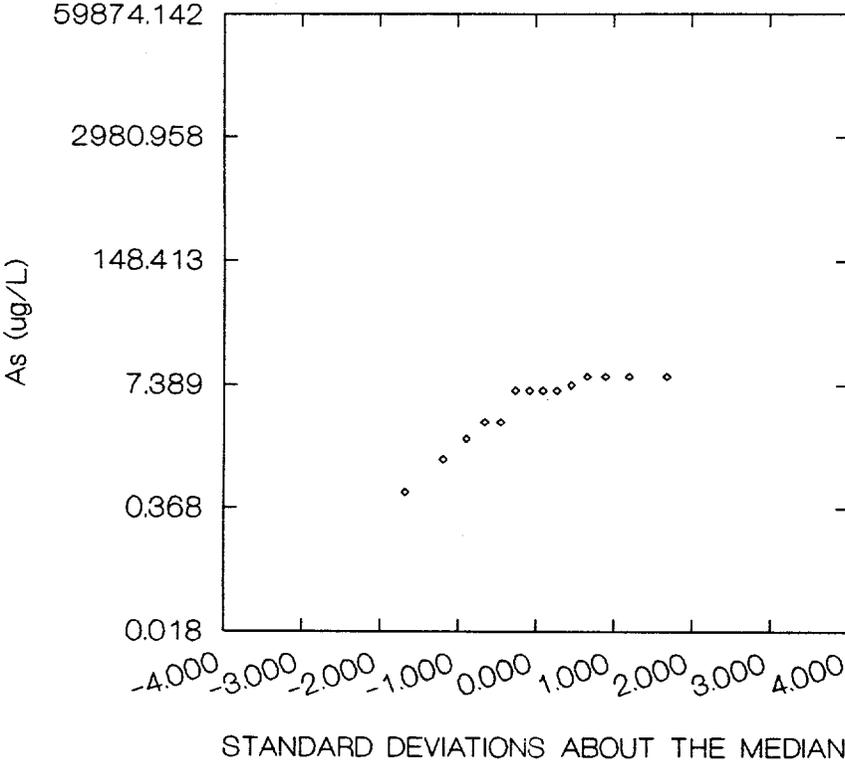
McNairy Groundwater: Cumulative Probability Graph, Aluminum



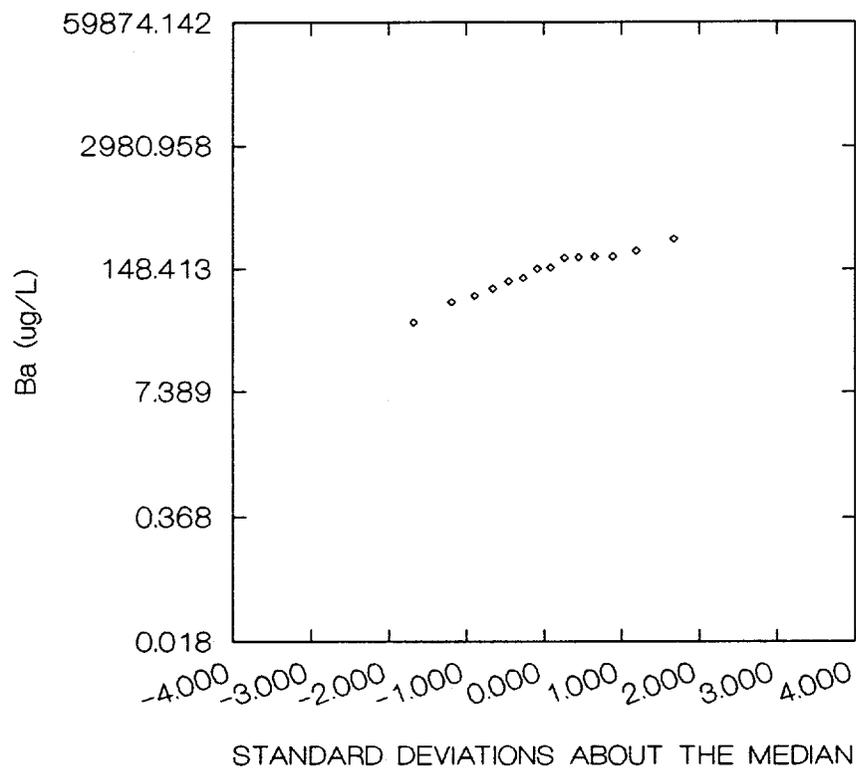
McNairy Groundwater: Cumulative Probability Graph, Antimony



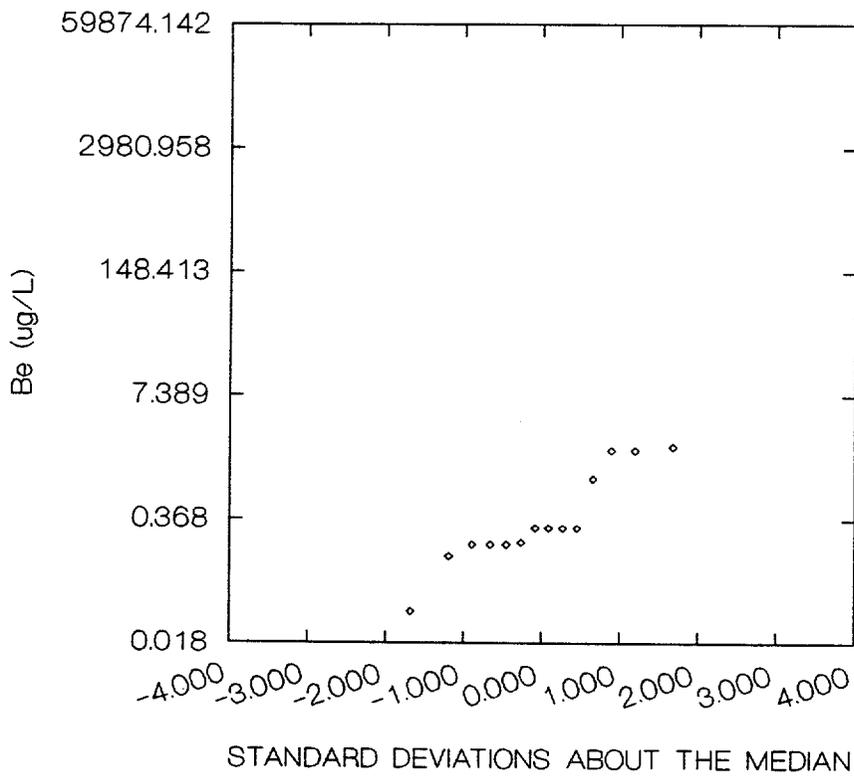
McNairy Groundwater: Cumulative Probability Graph, Arsenic



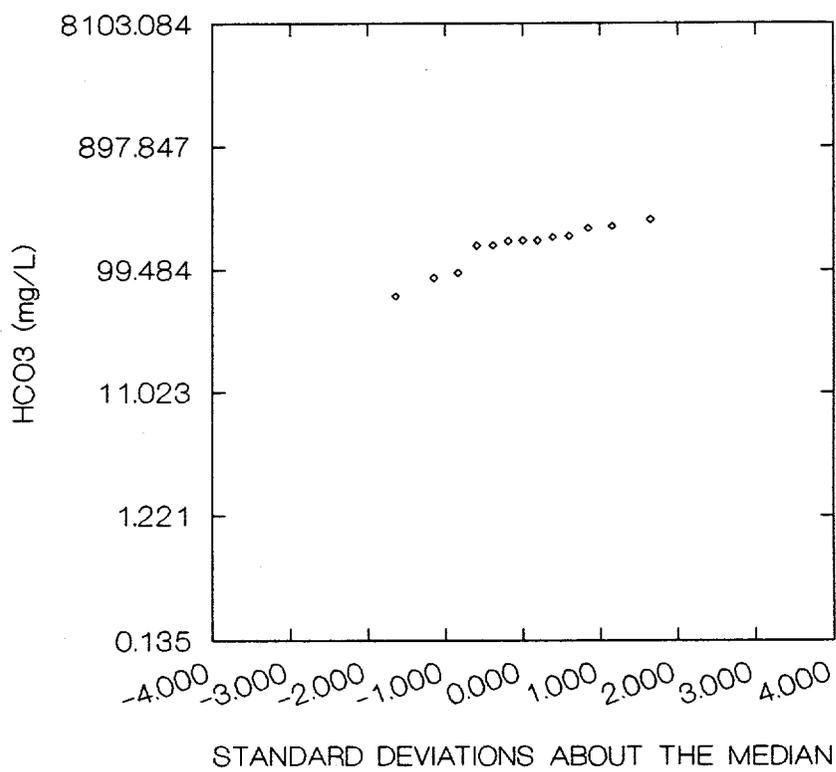
McNairy Groundwater: Cumulative Probability Graph, Barium



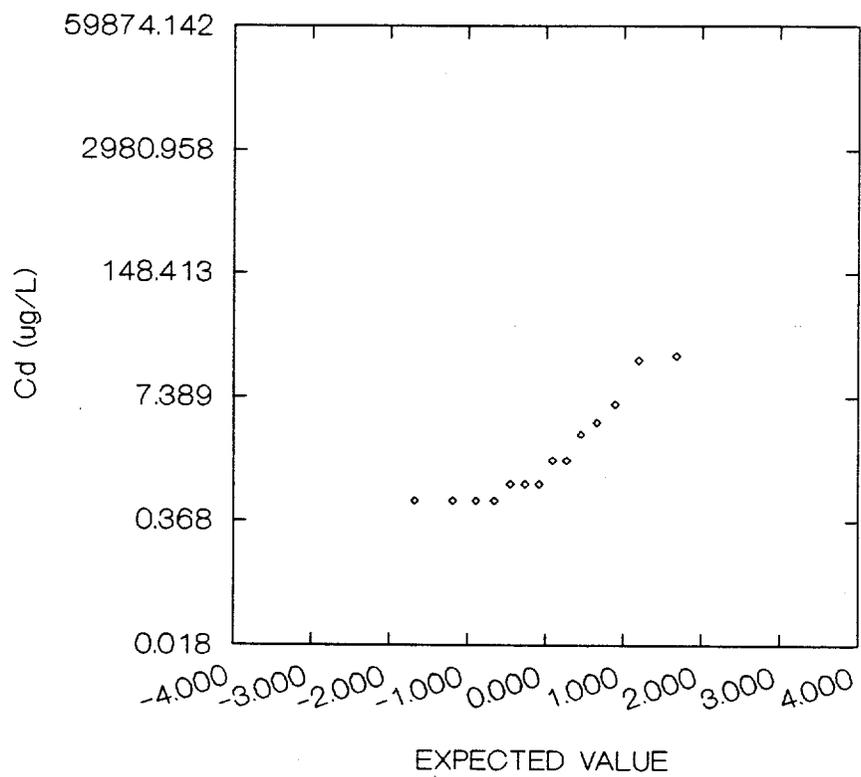
McNairy Groundwater: Cumulative Probability Graph, Beryllium



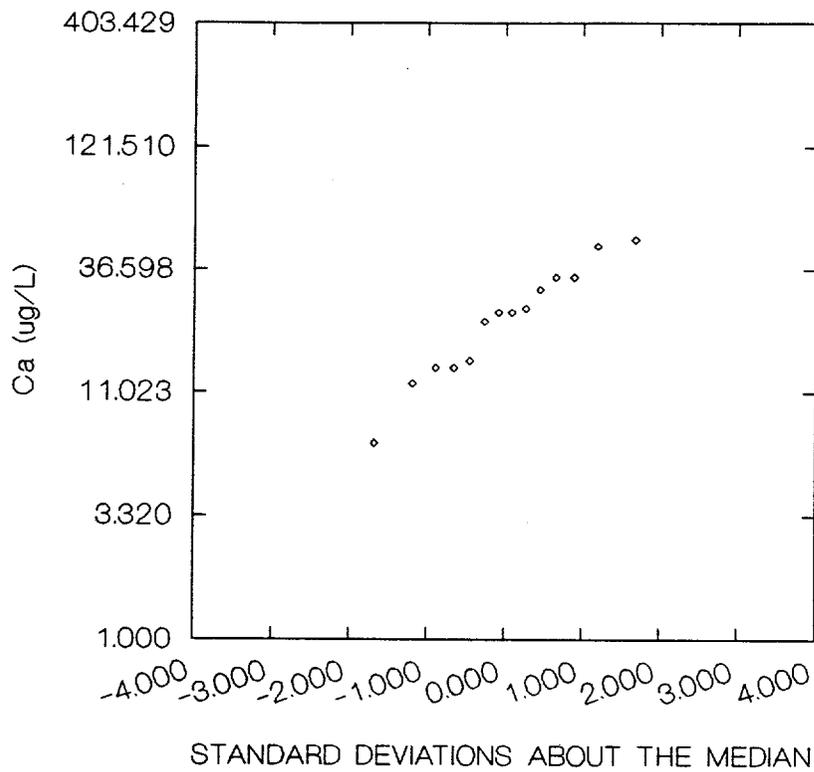
McNairy Groundwater: Cumulative Probability Graph, Bicarbonate



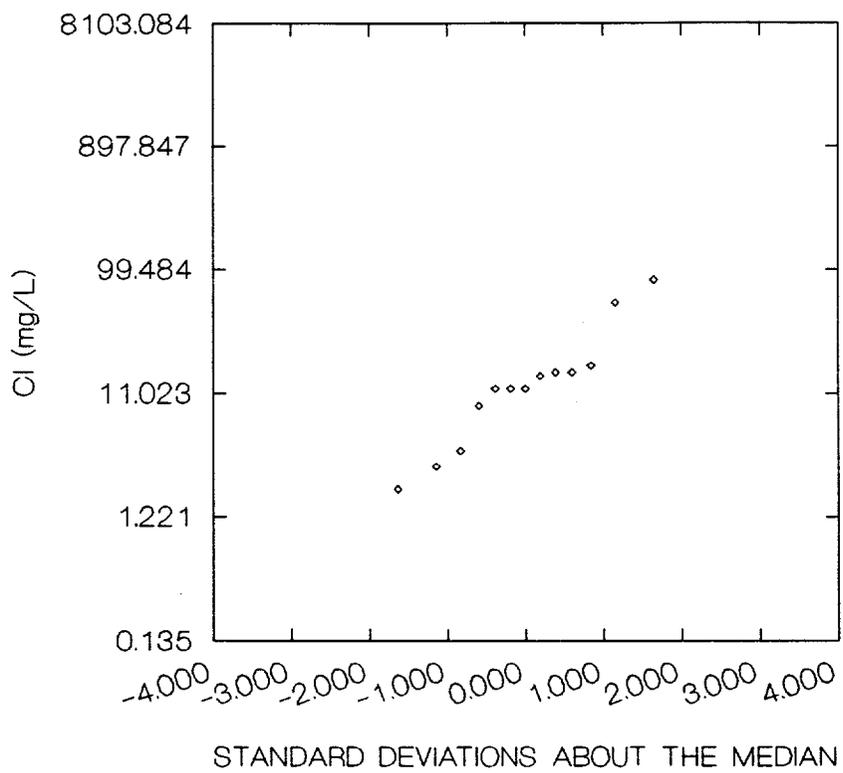
McNairy Groundwater: Cumulative Probability Graph, Cadmium



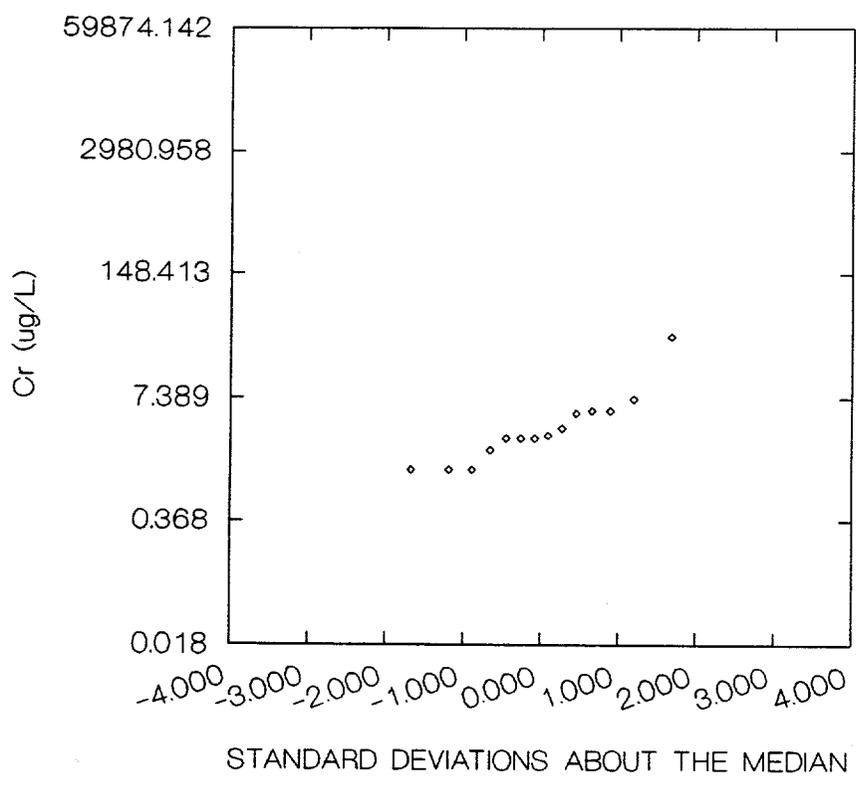
McNairy Groundwater: Cumulative Probability Graph, Calcium



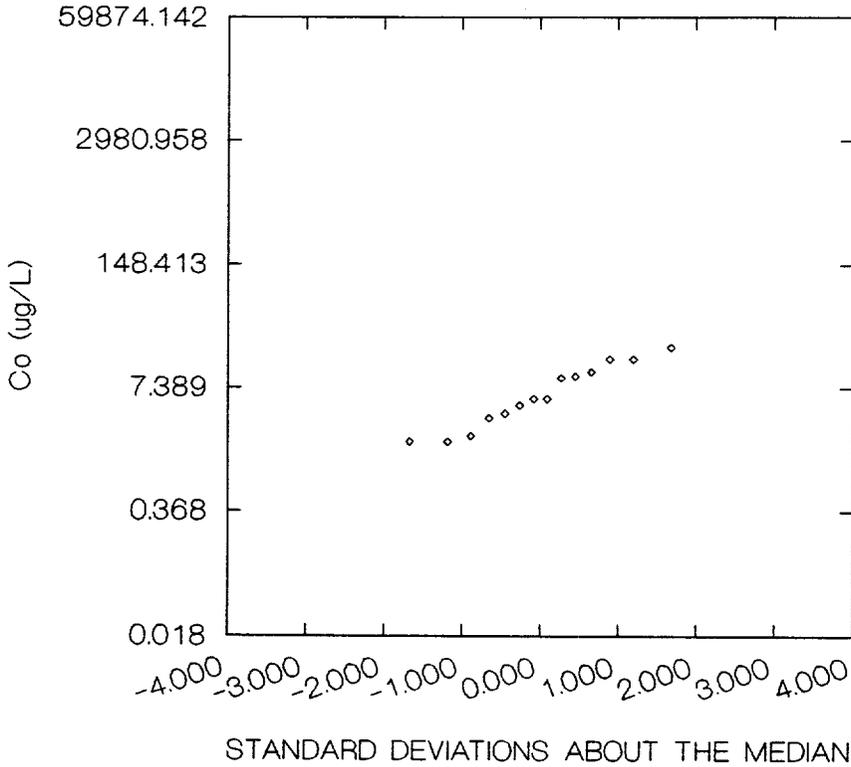
McNairy Groundwater: Cumulative Probability Graph, Chloride



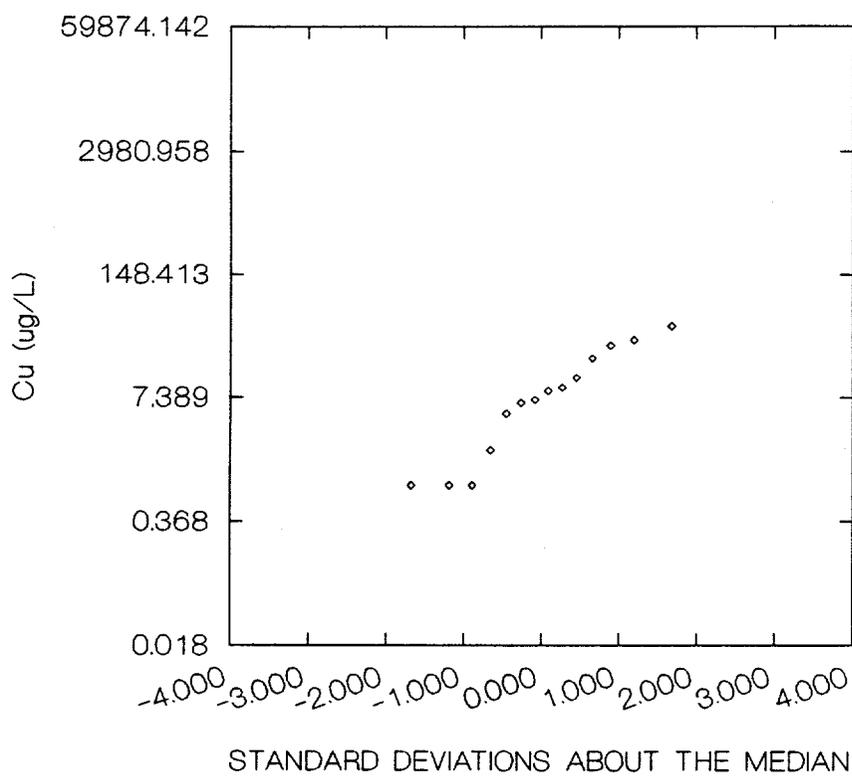
McNairy Groundwater: Cumulative Probability Graph, Chromium



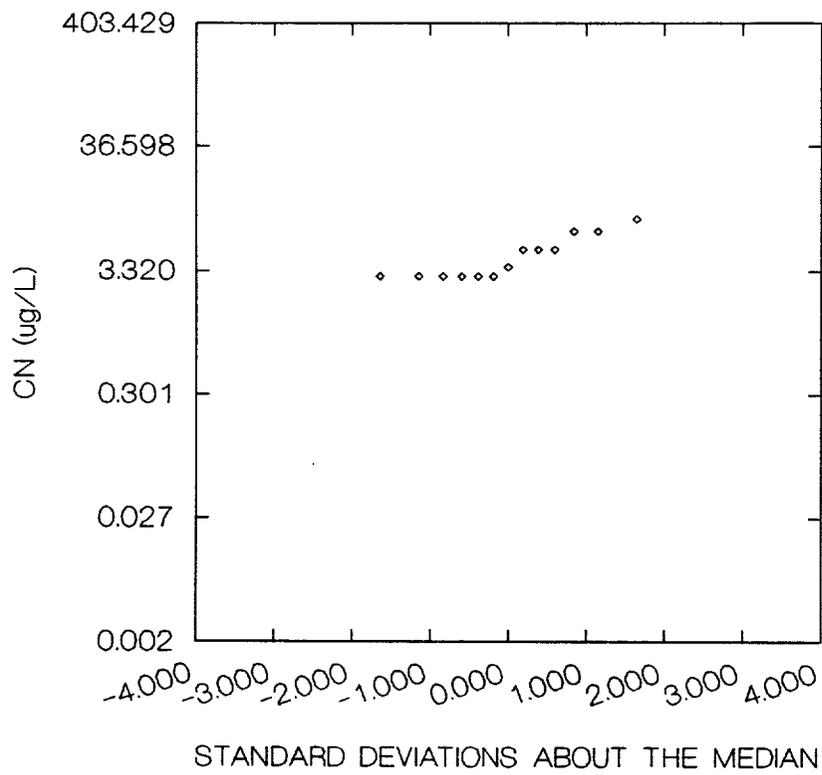
McNairy Groundwater: Cumulative Probability Graph. Cobalt



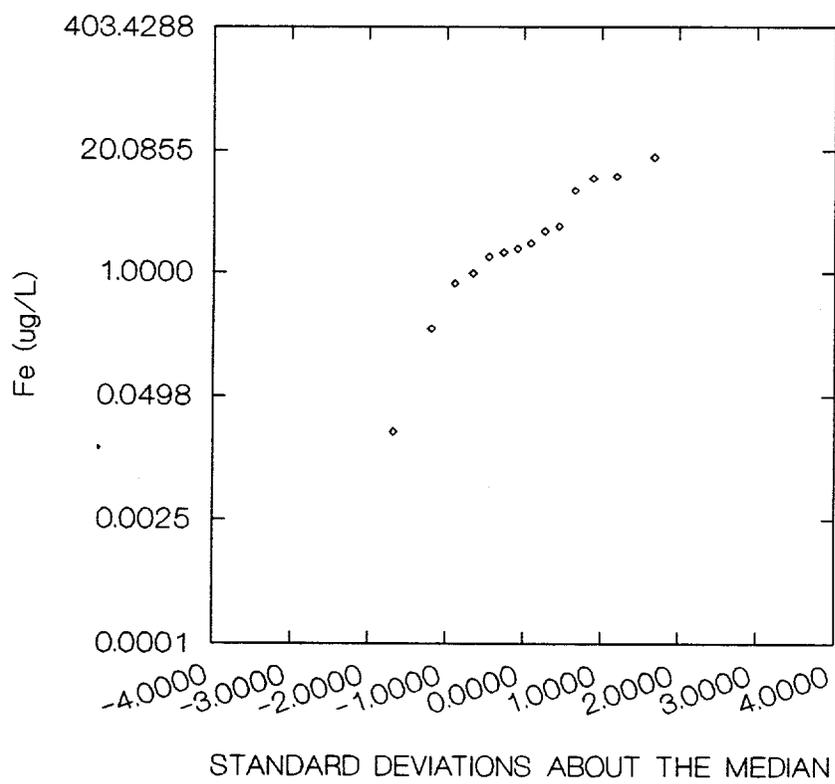
McNairy Groundwater: Cumulative Probability Graph, Copper



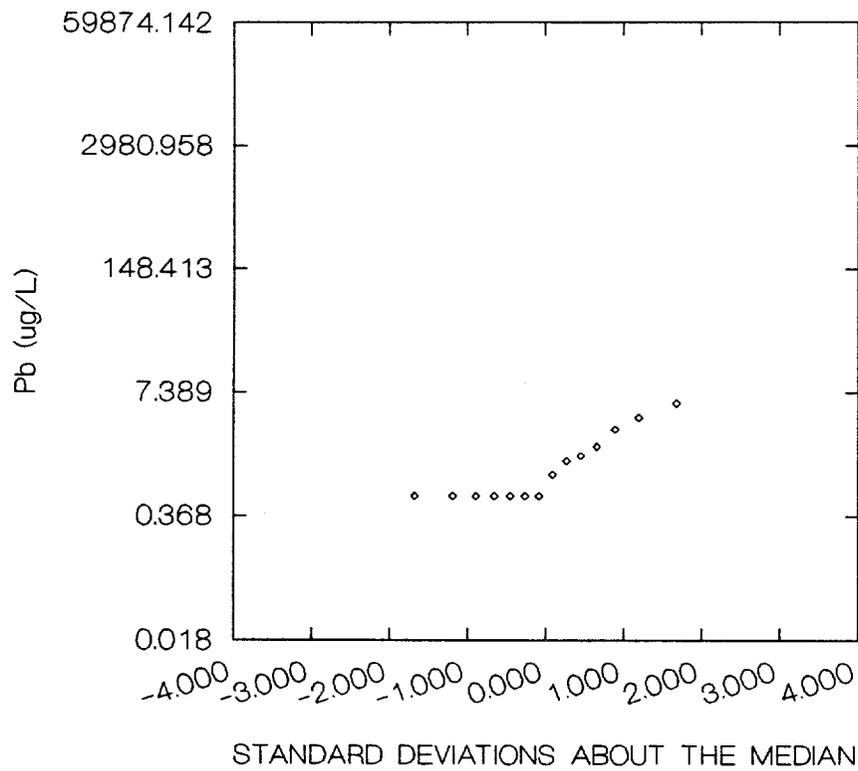
McNairy Groundwater: Cumulative Probability Graph, Cyanide



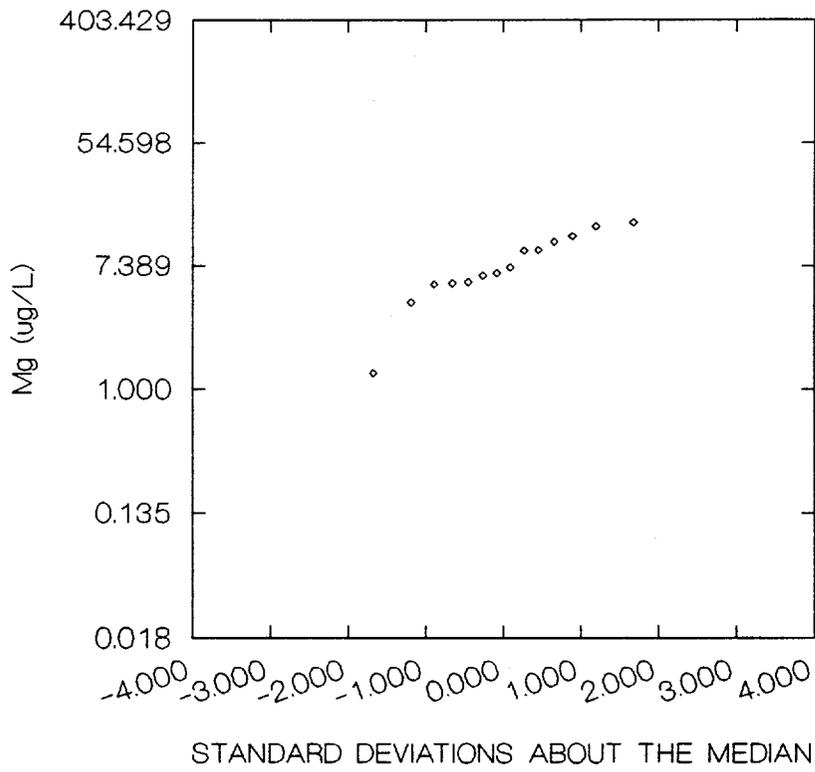
McNairy Groundwater: Cumulative Probability Graph, Iron



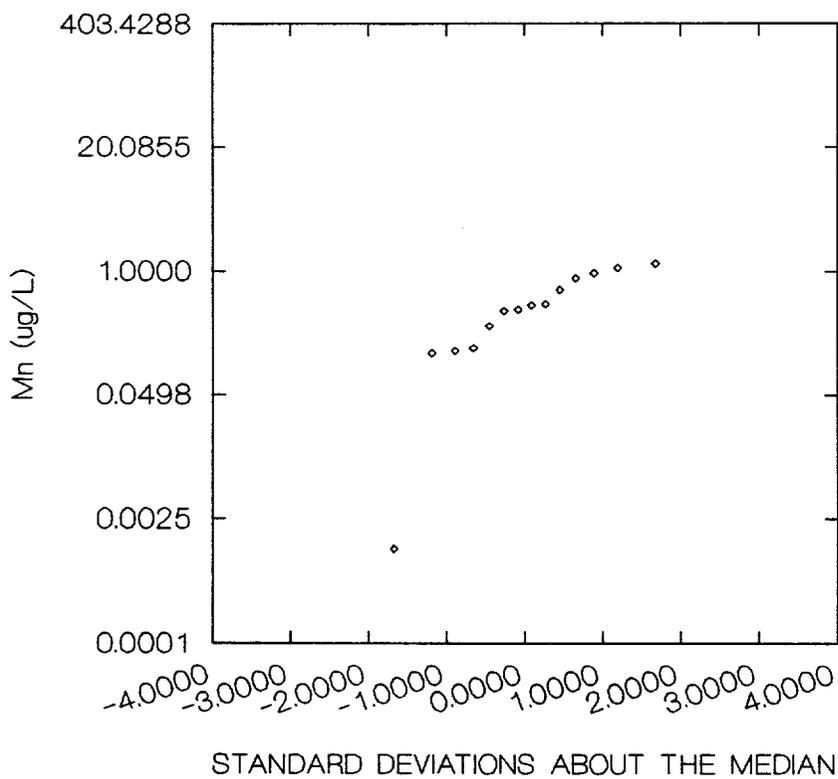
McNairy Groundwater: Cumulative Probability Graph, Lead



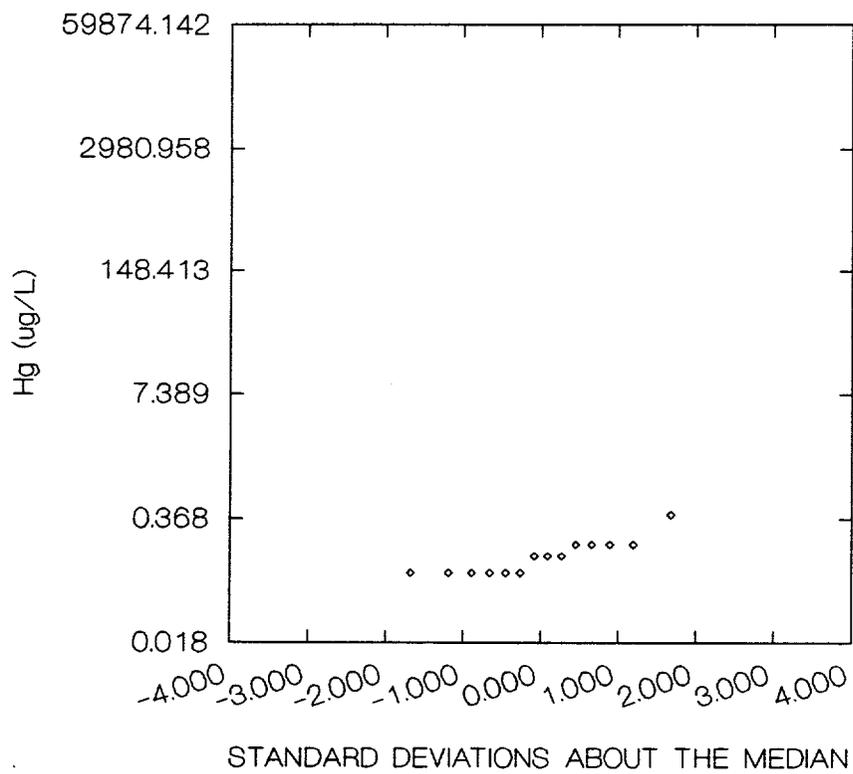
McNairy Groundwater: Cumulative Probability Graph, Magnesium



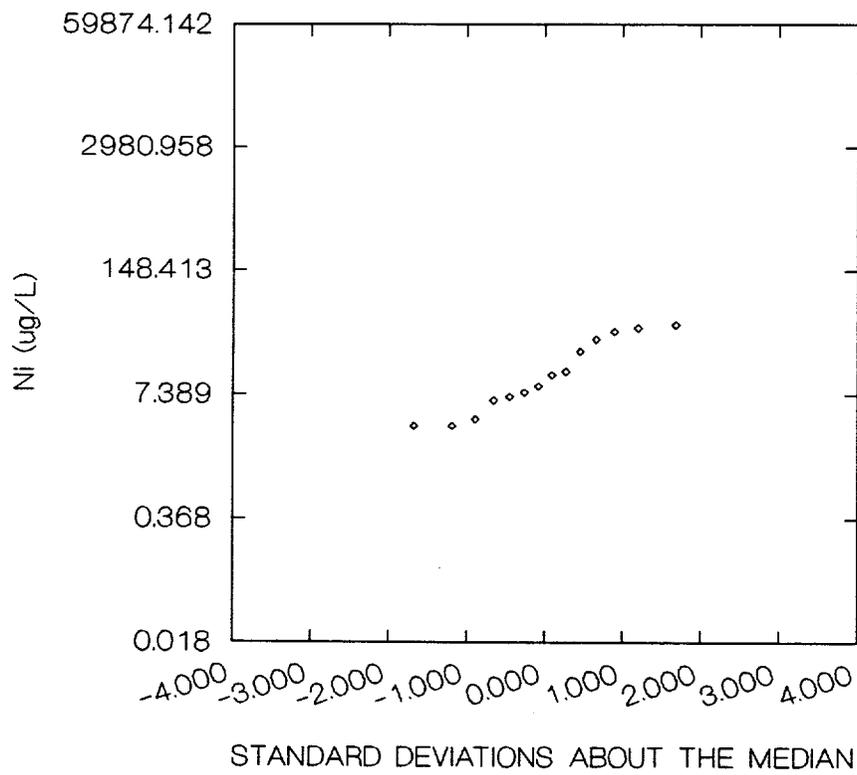
McNairy Groundwater: Cumulative Probability Graph, Manganese



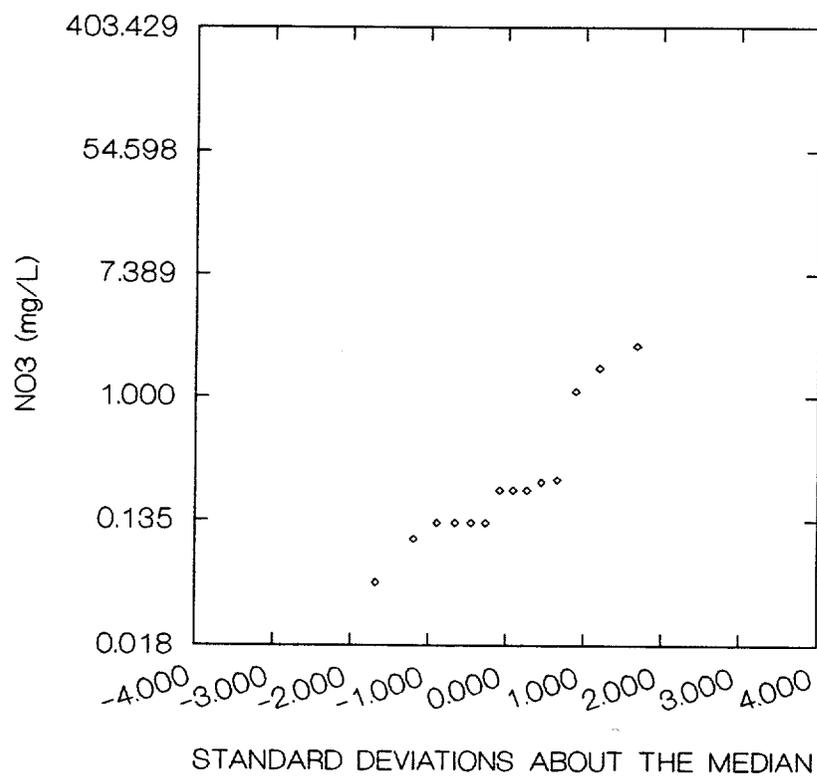
McNairy Groundwater: Cumulative Probability Graph, Mercury



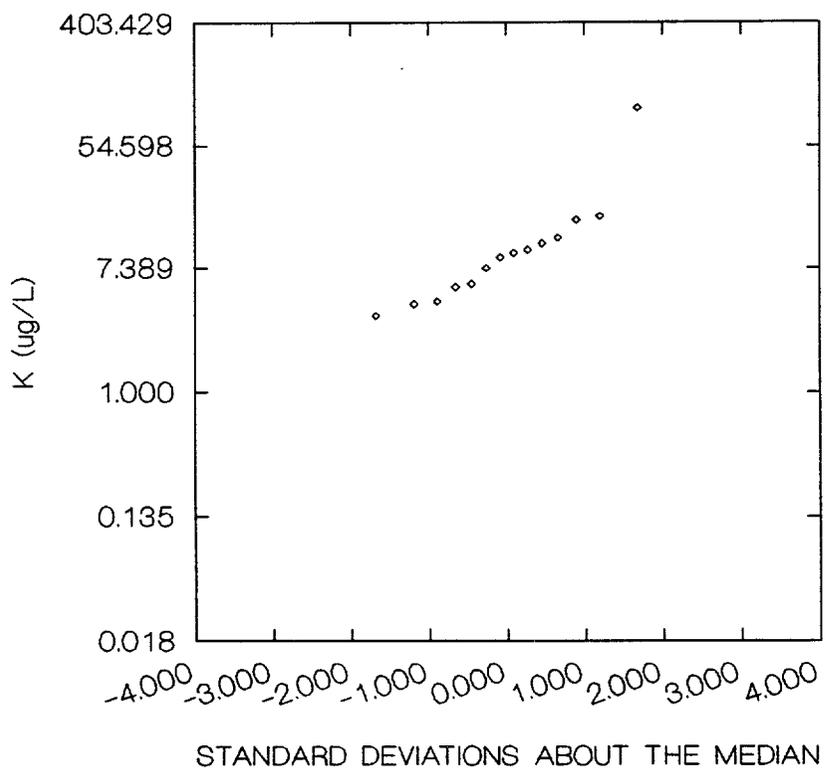
McNairy Groundwater: Cumulative Probability Graph, Nickel



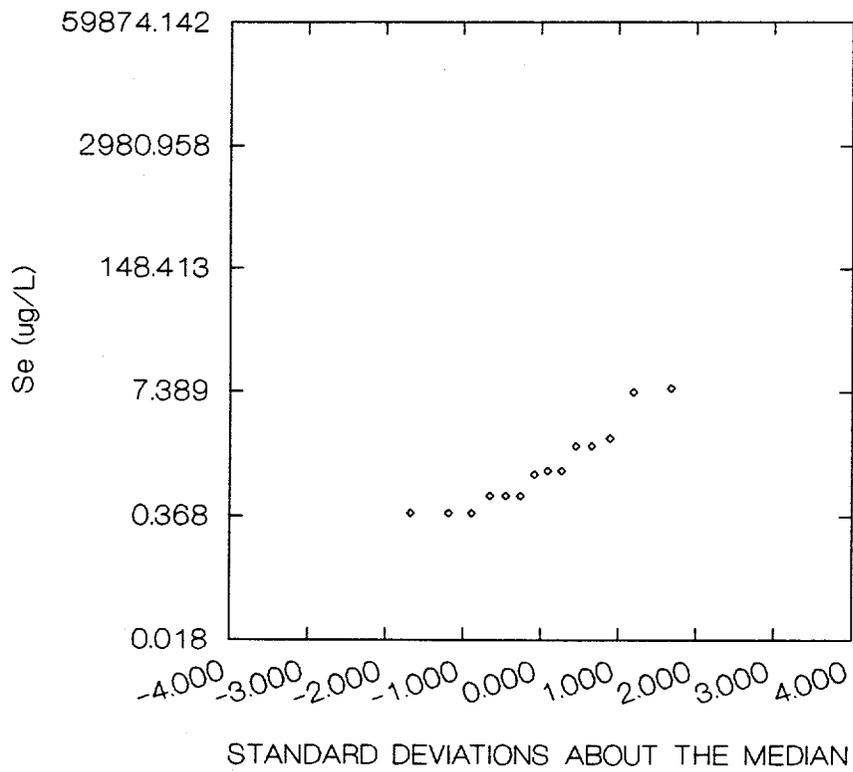
McNairy Groundwater: Cumulative Probability Graph, Nitrate



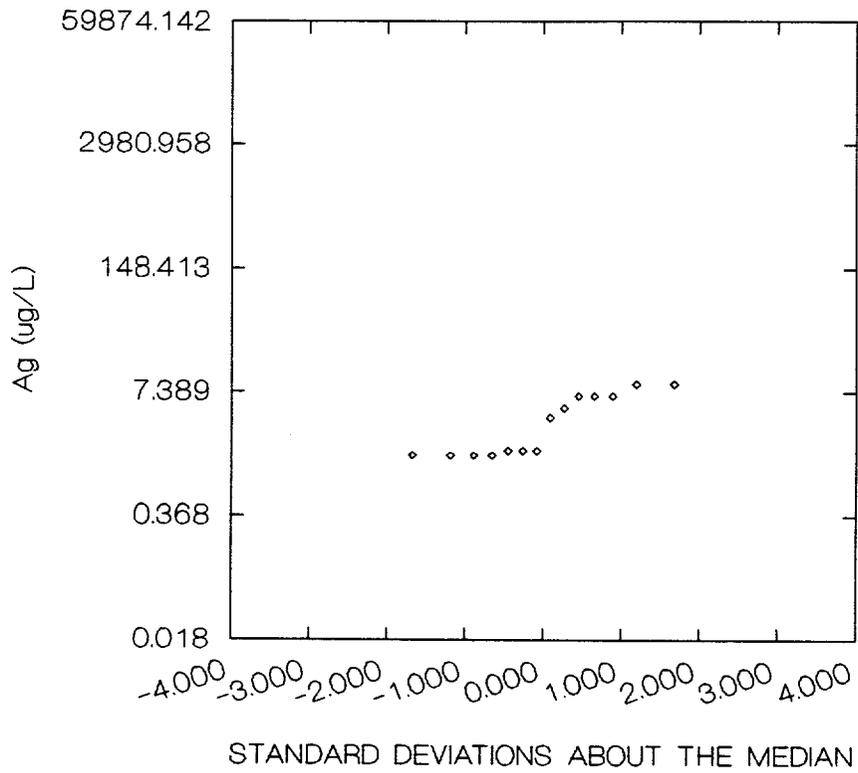
McNairy Groundwater: Cumulative Probability Graph, Potassium



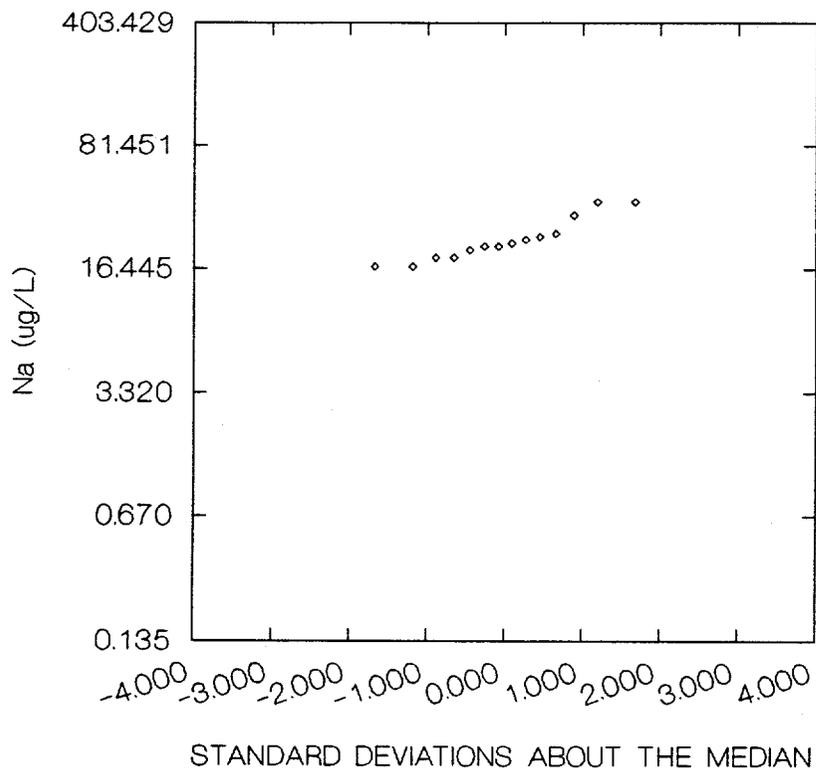
McNairy Groundwater: Cumulative Probability Graph, Selenium



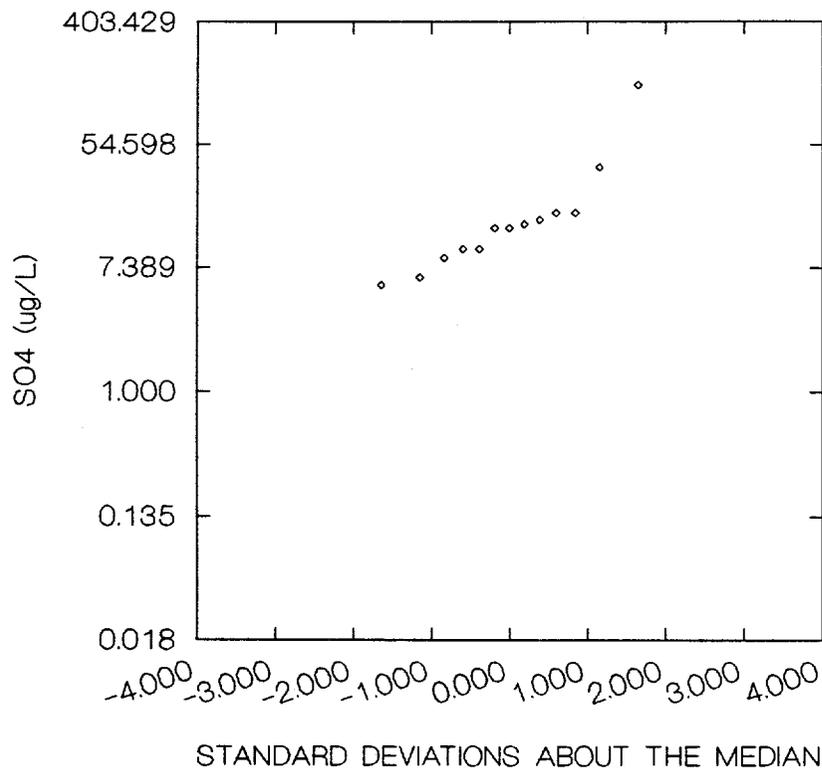
McNairy Groundwater: Cumulative Probability Graph, Silver



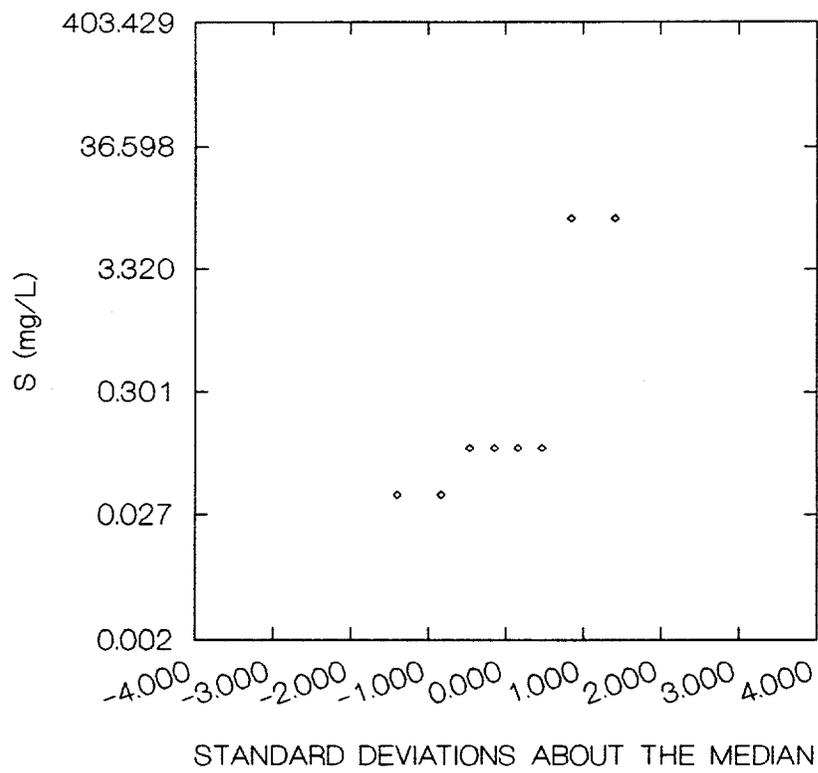
McNairy Groundwater: Cumulative Probability Graph, Sodium



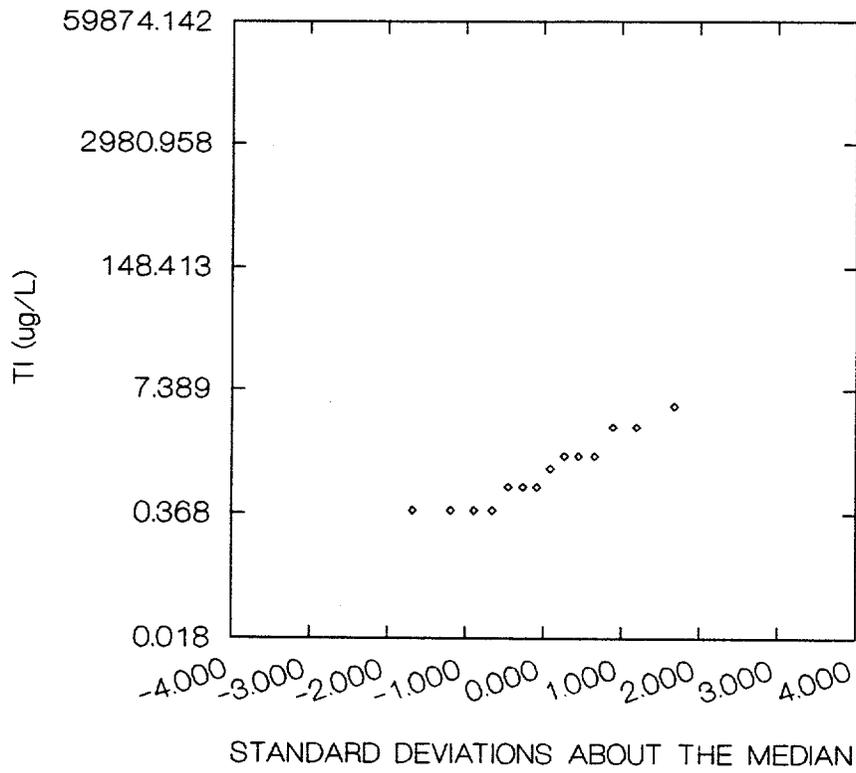
McNairy Groundwater: Cumulative Probability Graph, Sulfate



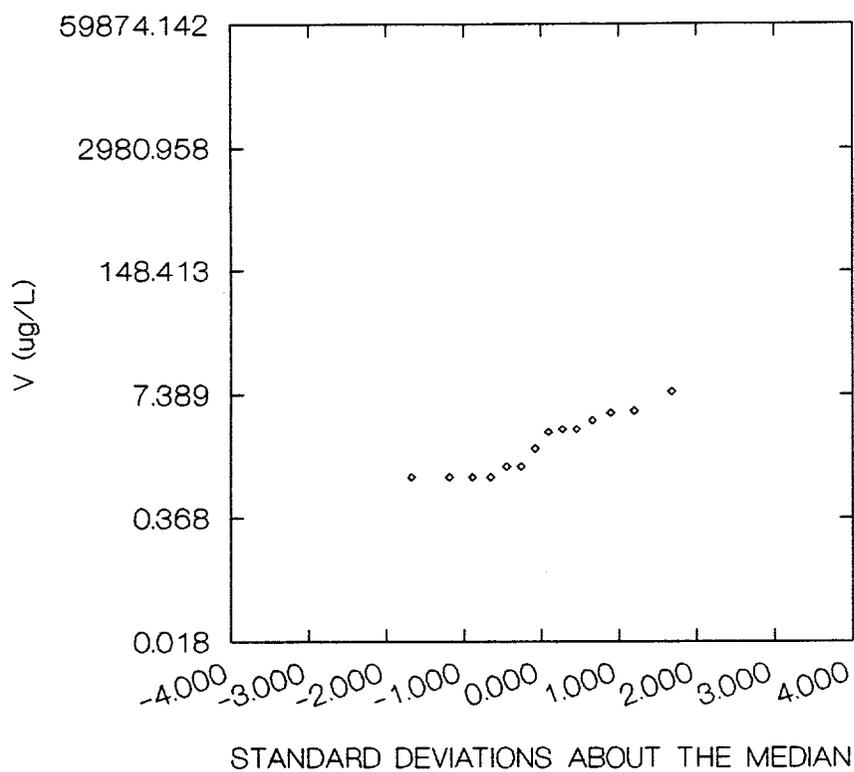
McNairy Groundwater: Cumulative Probability Graph, S



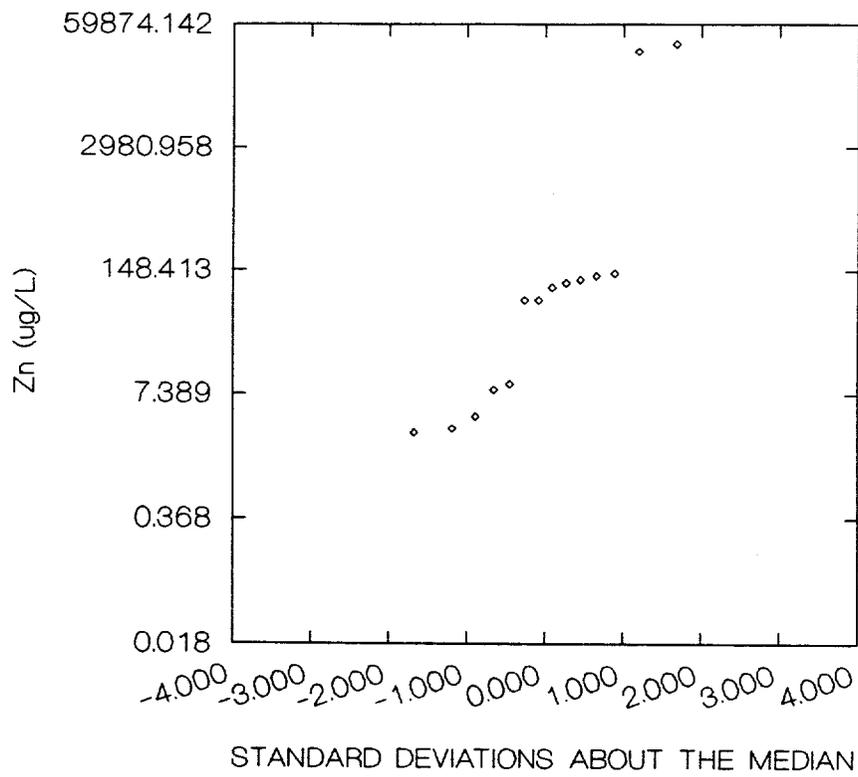
McNairy Groundwater: Cumulative Probability Graph, Thallium



McNairy Groundwater: Cumulative Probability Graph, Vanadium



McNairy Groundwater: Cumulative Probability Graph, Zinc



APPENDIX B

**EVALUATION OF PHASE I AND II DATA FOR
ADEQUACY FOR DETERMINATION OF BACKGROUND CONCENTRATIONS OF
PESTICIDES AND POLYNUCLEAR AROMATIC HYDROCARBONS**

This page left intentionally blank.

Evaluation of Phases I and II Data for Adequacy for Determination of Background Concentrations of Pesticides and Polynuclear Aromatic Hydrocarbons

Richard R. Bonczek and Fred G. Dolislager
Risk Analysis Section, Oak Ridge National Laboratory

Introduction

Soil sampling data from *Results of the Site Investigation, Phase I at the Paducah Gaseous Diffusion Plant Paducah, Kentucky (KY/ER-4)* and *Results of the Site Investigation, Phase II at the Paducah Gaseous Diffusion Plant Paducah, Kentucky (KY/SUB/138-97777C P-03/1991/1)* were evaluated to determine if background concentrations of selected pesticides and polynuclear aromatic hydrocarbons could be established using the method presented in *Inorganic Soil and Groundwater Chemistry Near Paducah Gaseous Diffusion Plant, Paducah, Kentucky (ORNL/GWPO/TM-XX)*. This evaluation was performed because CERCLA guidance (RAGS; EPA, 1989) allows for the removal of anthropogenic (i.e., man-made) chemicals during risk assessment if these chemicals can be identified as not being site related. The pesticides and polynuclear aromatic hydrocarbons selected for evaluation were those considered as potentially from non-site sources in *Final Report on the Background Soil Characterization Project at the Oak Ridge Reservation, Oak Ridge, TN (ES/ER/TM-84)*. The primary objective of this evaluation was to determine if soil sampling data were of sufficient quality and quantity to use with the aforementioned analytical method. A secondary objective was to apply the method if data were deemed of sufficient quality and quantity.

Data Summary

A total of 824 samples were analyzed for one or more of the selected pesticides or polynuclear aromatic hydrocarbons during the Phases I and II Site Investigations. Sampling and analyses for these data were performed in the manner that was previously described in *Data Quality Objectives for Remedial Response Activities Development Process (EPA, 1987)* as Level IV DQO. The analytes selected for evaluation and their frequency and range of detection are contained in Table 1.

Table 1. Selected pesticides and polynuclear aromatic hydrocarbons and frequency of detection in samples collected during the Phases I and II Site Investigations.

Analyte	Number of Observations	Number of Detects	Frequency of Detects (%)	Range of Detected Concentrations (mg/kg)
Pesticides and Polychlorinated Biphenyls				
4,4'-DDD	346	0	0.0	---
4,4'-DDE	676	3	0.4	0.0012 - 67
4,4'-DDT	676	7	1.0	0.22 - 64
Aldrin	346	0	0.0	---
Alpha-Chlordane	676	0	0.0	---

Table 1. Selected pesticides and polynuclear aromatic hydrocarbons and frequency of detection in samples collected during the Phases I and II Site Investigations.

Analyte	Number of Observations	Number of Detects	Frequency of Detects (%)	Range of Detected Concentrations (mg/kg)
Pesticides and Polychlorinated Biphenyls				
Alpha-BHC	346	2	0.6	0.0024 - 0.23
Aroclor 1016	440	0	0.0	---
Aroclor 1221	440	0	0.0	---
Aroclor 1248	824	14	1.7	0.1 - 55
Aroclor 1254	824	26	3.2	0.19 - 19000
Aroclor 1260	824	76	9.2	0.039 - 150000
Beta-BHC	676	0	0.0	---
Delta-BHC	676	0	0.0	---
Dieldrin	676	1	0.1	0.0008
Endosulfan I	346	0	0.0	---
Endosulfan II	346	0	0.0	---
Endosulfan Sulfate	346	0	0.0	---
Endrin	676	1	0.1	24
Endrin Ketone	676	0	0.0	---
Gamma-Chlordane	346	0	0.0	---
Heptachlor	676	0	0.0	---
Heptachlor Epoxide	676	0	0.0	---
Lindane (Gamma-BHC)	676	0	0.0	---
Methoxychlor	346	0	0.0	---
Toxaphene	346	0	0.0	---
Polynuclear Aromatic Hydrocarbons				
Acenaphthene	782	6	0.8	0.046 - 3.2
Acenaphthylene	449	3	0.7	0.16 - 3.6

Table 1. Selected pesticides and polynuclear aromatic hydrocarbons and frequency of detection in samples collected during the Phases I and II Site Investigations.

Analyte	Number of Observations	Number of Detects	Frequency of Detects (%)	Range of Detected Concentrations (mg/kg)
Polynuclear Aromatic Hydrocarbons				
Anthracene	450	12	2.7	0.047 - 23
Benzo(a)anthracene	781	32	4.1	0.058 - 120
Benzo(a)pyrene	781	26	3.3	0.064 - 1200
Benzo(b)fluoranthene	781	34	4.4	0.056 - 830
Benzo(g,h,i)perylene	781	17	2.2	0.054 - 3700
Benzo(k)fluoranthene	781	26	3.3	0.048 - 1100
Chrysene	781	32	4.1	0.065 - 1100
Dibenzo(a,h)anthracene	450	5	1.1	0.056 - 4.3
Fluoranthene	781	59	7.6	0.046 - 2400
Fluorene	450	9	2.0	0.14 - 17
Ideno(1,2,3-c,d)pyrene	781	17	2.2	0.051 - 73
Naphthalene	781	8	1.0	0.063 - 130
Phenanthrene	781	48	6.1	0.036 - 1000
Pyrene	781	56	7.2	0.083 - 1800

As indicated in Table 1, the number of samples per analyte ranged from 346 to 824. Therefore, in terms of total samples analyzed, data quantity appears to be sufficient to apply the method used for the inorganic chemicals. However, the frequency of detection for each analyte is low. For several analytes, the frequency of detection is zero; the frequency of detection never exceeds 10% for any analyte.

Discussion

The analytical method contained in *Inorganic Soil and Groundwater Chemistry Near Paducah Gaseous Diffusion Plant, Paducah, Kentucky* does not specify the number of samples nor the frequency of detection required to determine background concentrations. However, it would seem reasonable that the data set evaluated using this method should be of sufficient size, in terms of both total number of samples analyzed and frequency of detection, to allow for a reasonable estimate of analyte concentration distribution over samples. Because the frequency of detection is so low for each of the selected pesticides and polynuclear aromatic hydrocarbons, it does not appear that the statistical method can be applied to the current data set.

The forthcoming background soils field investigation should consider pesticides and polynuclear aromatic hydrocarbons in its sampling and analysis plan.

Conclusions

From this data summary, it is apparent that data for all selected pesticides and polynuclear aromatic hydrocarbons are too sparse to apply the method described in *Inorganic Soil and Groundwater Chemistry Near Paducah Gaseous Diffusion Plant, Paducah, Kentucky*. Background concentrations for the selected pesticides and polynuclear aromatic hydrocarbons cannot be determined from the available data using this analytical method. Additional samples for analysis for pesticides and polynuclear aromatic hydrocarbons are required if background concentrations of these analytes are to be established.

Bibliography

Moore, G.K. 1994. *Inorganic Soil and Groundwater Chemistry Near Paducah Gaseous Diffusion Plant, Paducah, Kentucky*. ORNL/GWPO/TM-XX.

United States Department of Energy. 1991. *Results of the Site Investigation, Phase I at the Paducah Gaseous Diffusion Plant, Paducah, Kentucky*. KY/ER-4.

United States Department of Energy. 1992. *Results of the Site Investigation, Phase II at the Paducah Gaseous Diffusion Plant, Paducah, Kentucky*. KY/SUB/138-97777C P-03/1991/1.

United States Environmental Protection Agency. 1987. *Data Quality Objectives for Remedial Activities Development Process*. OSWER Directive 9355.0-7B.

United States Environmental Protection Agency. 1989. *Risk Assessment Guidance for Superfund. Part A. Human Health Evaluation Manual*. OSWER Directive 9285.7-01a.

APPENDIX C

**RADIONUCLIDE DATA OF BACKGROUND
AND CONTAMINATED SOILS AT
PADUCAH GASEOUS DIFFUSION PLANT**

This page left intentionally blank.

Radionuclide Data of Background and Contaminated Soils at Paducah Gaseous Diffusion Plant (PGDP)

The Environmental Restoration Program at PGDP needs background concentrations of radionuclides in soils and sediments to determine the risk assessment and cleanup level for the contaminated sites. Radionuclide data sets of both background and known contaminated sites were produced during Phase I and II Site Investigations. Statistical analyses and data evaluation were performed to establish a reasonable and acceptable background concentration (activity) of naturally occurring radionuclides in the soil for risk assessment and cleanup level establishment. The objective of the data analysis was to provide recommendations to ER decision makers and regulators for future actions on the background soil characterization.

Status of the Data Set

An electronic form of the data set for radionuclides was prepared by Gerry Moore (ORHSP) and transferred to Rick Bonczek (Risk Assessment Group of HSR). The number of detects and undetects for individual analytes was given in Table R-1. The total number of samples was not constant among the analytes. The analytes that were frequently determined were gross alpha, gross beta, neptunium-237, plutonium-239, technetium-99, thorium-230, uranium-234, uranium-235, and uranium-238. Fission and activation products in the above list could come from one or two sources, global fallout and/or PGDP activity. The uranium series radionuclides could come from natural soils and PGDP activity. Source-term separation and interpretation is a difficult, but not an impossible, task if the data set is complete. Unfortunately, the data set is incomplete and does not include other important radionuclides contributing to the background risk.

Statistical Analyses

Statistical analyses were conducted by HSR using SAS package. A cumulative probability graph was prepared for the individual analytes. The data points in the graphs included detection limits for the undetects. Summary statistics of each individual analyte data set were presented with the cumulative probability graphs. Interpretation of the results was based on the observation and judgement concerning whether the log-transformed radionuclide data plots have a single straight line or two or more intersecting lines when plotted on cumulative probability paper. The background information of this particular statistical approach was discussed in the method section for the inorganic results.

Evaluation

The radionuclide data were evaluated using the plot results and the interrelationships among the radionuclides present in these soils. The major problem of the radionuclide data set is a lack of completeness. For example, many other naturally occurring radionuclides, such as potassium-40, radium-226 and thorium series isotopes (Th-232, Th-228) in the soils, should be analyzed with the radionuclides in the data set for the background risk assessment. The gross alpha and beta data are useful for locating a rad-contaminated site but less meaningful for risk calculation of a specific radionuclide.

Gross alpha: The probability plot of gross alpha showed two intersecting lines at the LN 2 although data are normally distributed as a single line (Plots R-1 and 2). The major contributors of gross alpha activity in the background soils are the uranium and thorium series isotopes. However, the relationship between alpha activity and uranium activity should be maintained since the data set included uranium-contaminated soil as indicated by the uranium data. Unfortunately, the mean activity of the uranium series alone was higher than the mean alpha activity.

Gross beta: The probability plot of gross beta showed three intersecting lines with two intersecting points at LN 1 and LN 3 (Plots R-3 and 4). The first intersection point may be caused by noise or represent a problem with analytical data at the lower activity level. The major activity contributor for gross beta is potassium-40. One other potential contributor is technetium-99, provided the soils became contaminated by technetium during the enrichment process. Potassium-40 values for the PGDP site soil are not available in this data set, but the beta activity contributed by potassium-40 would be more than 15 pCi/g. The result showed that the mean activity value of gross beta was 27 pCi/g although the mean activity value of technetium-99 was 20 pCi/g.

Neptunium-237: Neptunium-237 is a global fallout and/or activation product of other actinides. Forty samples out of 220 soil samples have a detectable amount of this isotope. The mean activity level of 2 pCi/g was considerably higher than found in the Oak Ridge Soil data. Eleven samples of the forty detect samples have levels above 0.5 pCi/g. The cumulative probability plot of the radionuclide did not show an intersection point that would be used to estimate a background activity value (Plots R-5 and 6). Data evaluation at this point is very difficult because of a lack of information related to sample description and site history. The activity level of neptunium in the soils, however, may not pose a problem for the overall background risk assessment.

Plutonium-239: Plutonium-239 is also a global fallout product unless PGDP used the isotope for a special purpose. Plutonium-239 was detected in 63 of 220 total soil samples. Its mean activity in the soils (4 pCi/g) is higher than the known global fallout value (< 0.1 pCi/g). Seven samples of the 63 detect samples had activity levels greater than 2.5 pCi/g. A cumulative probability graph of detects alone showed either a single or more than two statistical population (Plots R-7 and 8). The results indicated that a number of soil samples appeared to be contaminated with this radionuclide. The population was not normally

distributed but showed two separate population groups when the activities of the detects and undetects were plotted together. This result showed that a considerable number of detect samples had lower activity values than the detection limit. More information is required for detailed evaluation; however, the data did not show a clear cut background activity level for plutonium.

Technetium-99: The cumulative probability graph for the detects and undetects of technetium-99 showed two statistical populations with one intersection point and the activity value at the intersection point was not too much different from the fallout technetium activity. Technetium was detected in 186 out of 292 total samples. The plot of detects alone did not show such clear separation (Plots R-9 and 10). Technetium-99 is a spontaneous fission product of uranium-235 and a byproduct of enrichment processes. The technetium contamination in the soil, groundwater, and waste is well known. However, establishment of background technetium-99 level in soils is difficult because of analytical problems involved with this radionuclide. Technetium has very long half-life but is not considered a likely driver for health and environmental risk at off-site locations.

Thorium-230: Thorium-230 is a decay product of uranium-234 which in turn is a decay product of uranium-238. Therefore, the thorium distribution should be related to uranium distribution if they represent actual background levels in the soils. Thorium-230 was detected in 132 out of 220 total samples. However, there were too many undetects! All of the soils should have a detectable amount of thorium-230. The probability plot of detects showed a distinguishable intersection point having a reasonable background activity level (about 1 pCi/g). However, the intersection point is not clearly observable when the undetects were included in the plot (Plots R-11 and 12).

Uranium-234: Uranium-234 is a decay product of uranium-238. Uranium-234 was detected in 184 out of 220 total soil samples. Both plots, with and without undetects, showed an intersection point at $\text{Ln } C = -1$ (0.37 pCi/g) (Plots R-13 and 14). The intersection point for thorium-230 was $\text{Ln } C = 0$ (1 pCi /g). If the thorium-230 and uranium-234/238 are natural, then their activity ratios should be close to theoretical values. During enrichment processes, however, the activity ratios among these radionuclides could be changed. Therefore, the activity of an individual isotope alone may not be sufficient to establish the background activity level.

Uranium-235: Uranium-235 was detected in 86 out of 116 total soil samples. This is a much smaller data set in comparison to the uranium-234 and uranium-238 data sets. The reason is unknown, but this is one of the major mistakes made by this investigation. The uranium-235 to uranium-238 ratio can provide us both the nature and the extent of the contamination. If the soil samples have only natural background levels of uranium, the uranium activity ratio should be 0.046. This ratio could be changed in either direction depending on whether the soil was contaminated with enriched or depleted uranium. Both plots, with and without detects, showed an intersection point at $\text{Ln } C = -4$ (0.018 pCi/g) (Plots R-15 and 16).

Uranium-238: The number of detects and undetects of uranium-238 was very similar to

uranium-234. This demonstrated some consistency of the data set but the quality of the data set is still questionable because of the large number of undetects in the data set. The probability distribution plots with and without undetects showed two populations and an intersection point at $\text{Ln } C = -1$ (0.37 pCi/g) (Plots R-17 and 18). The uranium-238 activities at the intersection point were the same as uranium-234. Furthermore, the activity ratio of uranium-235 to uranium-238 at the intersection points was 0.049 which is reasonably close to the calculated ideal value. However, thorium-230, a decay product of uranium-234, had a considerably higher activity at the intersection point than the expected value from the uranium-234 results. These internal inconsistencies among the uranium decay series isotopes should be carefully reevaluated before the use of this data set for possible background level estimation.

Recommendations

Careful planning, sampling, and appropriate methods of analyses of the background soils from different formations and depth is the best, simplest, and most cost-effective way to acquire data for background risk assessment. Resampling and analysis for background level radionuclide determinations are recommended based on the following assessment:

- (1) Exclusion of commonly occurring radionuclides in these soils (e.g., potassium-40, cesium-137, radium-226, and thorium series) is not justifiable to regulators.
- (2) Measurements are not reliable (i.e., there are too many undetects and too wide a range of activity ratios among the decay-chain radionuclides).
- (3) No obvious separation of background and contaminated soil activity populations was observed in the probability plots for some radionuclides. If there is separation, the activity of the intersection point is either too low or too high in comparison to expected or known background values for these radionuclides.
- (4) A better background database for uranium isotopes should be acquired for two reasons: (a) many soils at the Paducah facility are contaminated by either enriched or depleted uranium and (b) uranium was the main process product at the Paducah facility.
- (5) The statistical method employed in this investigation may not be sensitive enough to separate background levels of the radionuclides from different soil series or geologic units. These methods should be reevaluated.

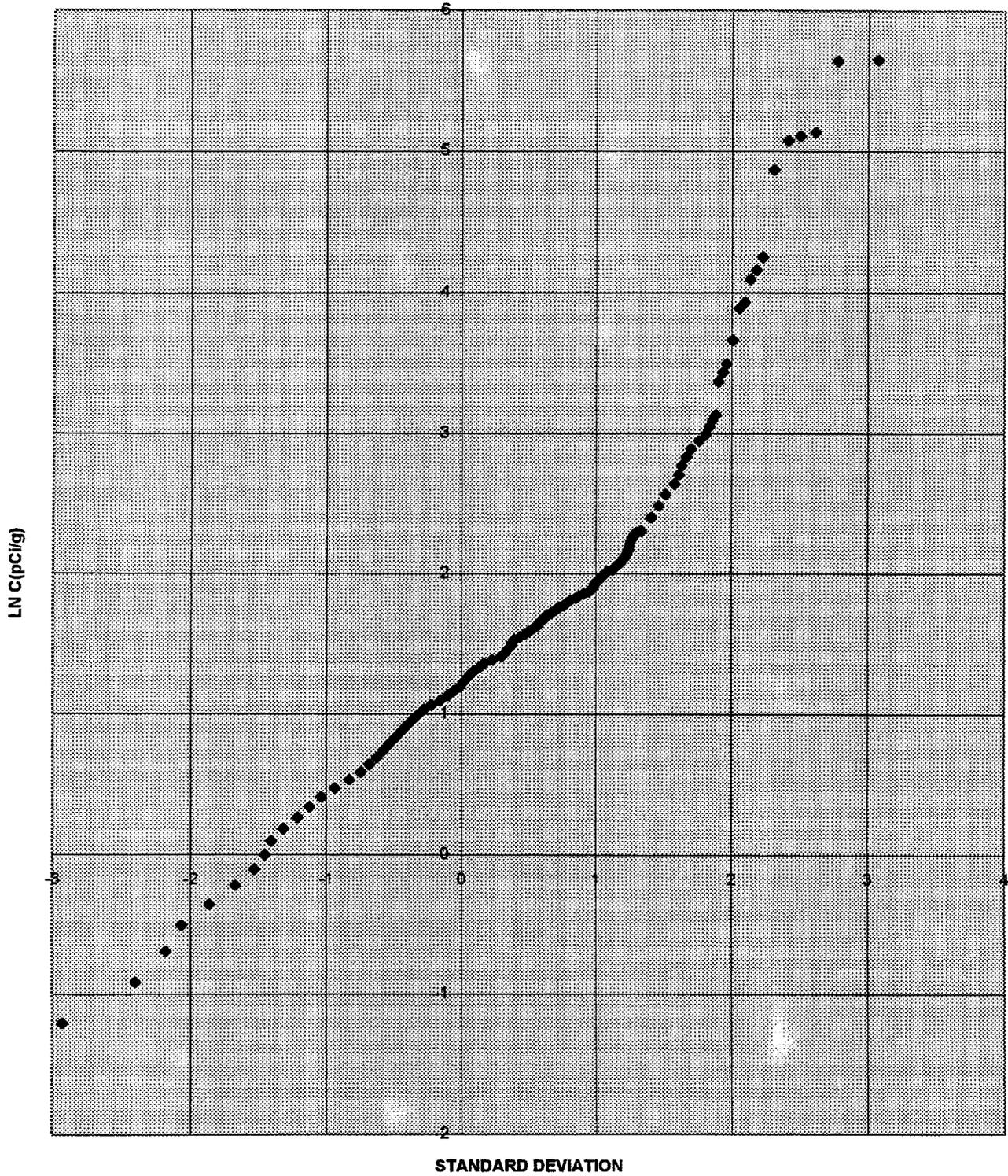
Table R-1. Frequency of detects and undetects of radionuclides.

Qualifier	Frequency	Percent
ALPHA QUALIFIER FIELD 1		
D	550	93.4
U	39	6.6
BETA QUALIFIER FIELD 1		
D	587	99.7
U	2	0.3
NEPTUNIUM-237 QUALIFIER FIELD 1		
D	40	18.2
U	180	81.8
PLUTONIUM-239 QUALIFIER FIELD 1		
D	63	28.6
U	157	71.4
TECHNETIUM-99 QUALIFIER FIELD 1		
D	186	63.7
U	106	36.3
THORIUM-230 QUALIFIER FIELD 1		
D	132	60.0
U	88	40.0
URANIUM-234 QUALIFIER FIELD 1		
D	184	83.6
U	36	16.4
URANIUM-235 QUALIFIER FIELD 1		
D	86	74.1
U	30	25.9
URANIUM-238 QUALIFIER FIELD 1		
D	186	84.5
U	34	15.5

D = Detected

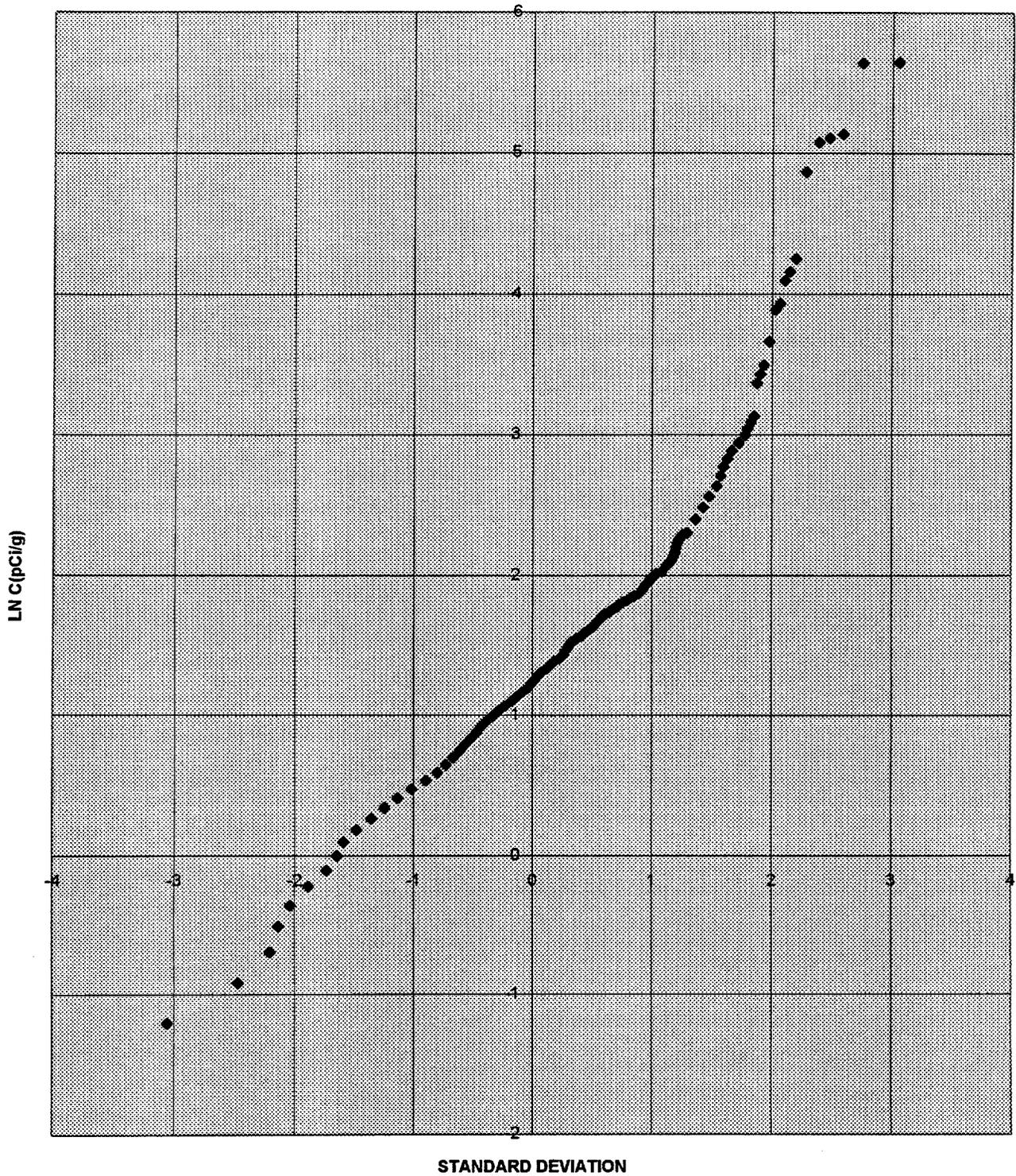
U = Not detected

ALPHA DETECTS AND UNDETECTS



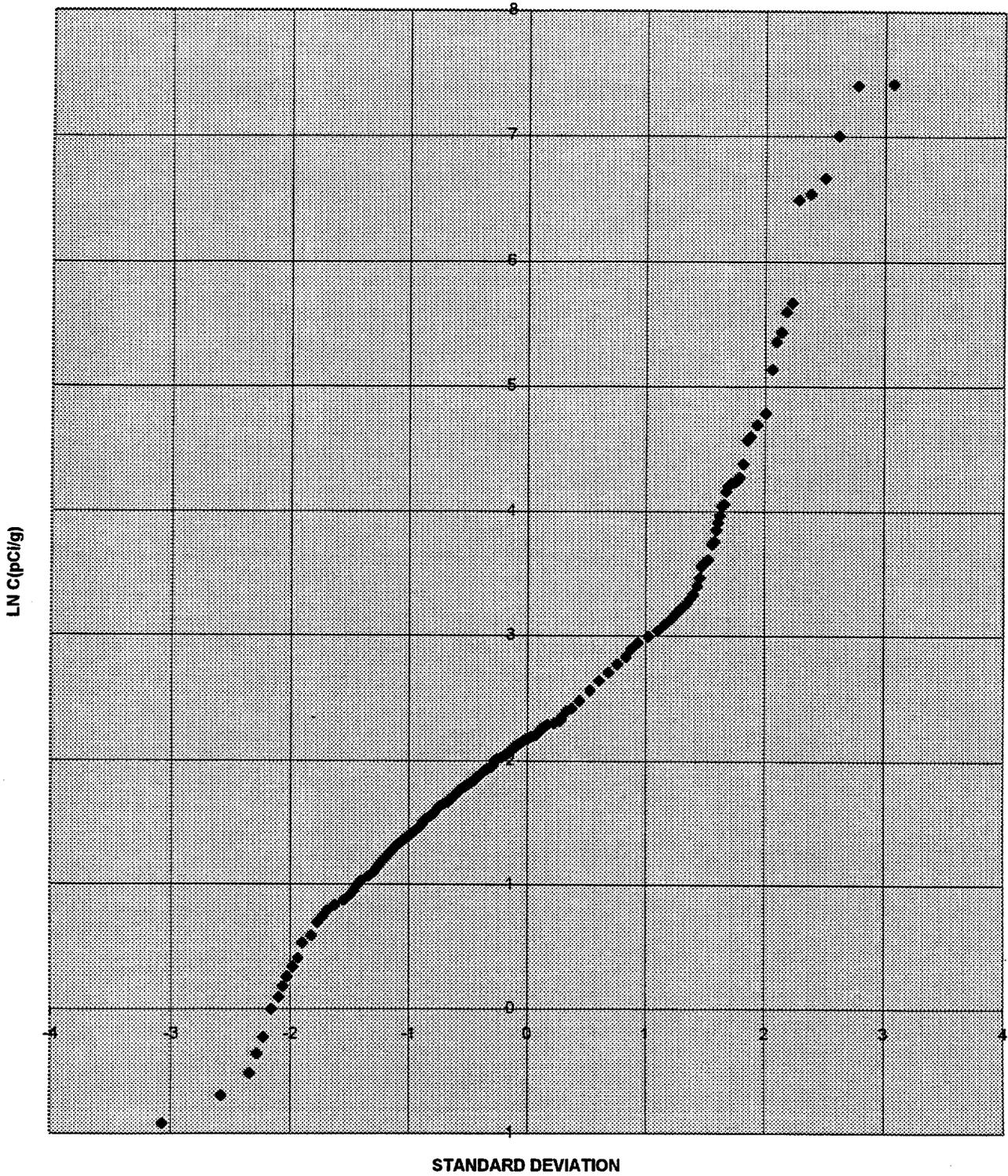
Plot R-1. Standard deviation of detects and undetects for gross alpha activity in soils.

ALPHA DETECTS



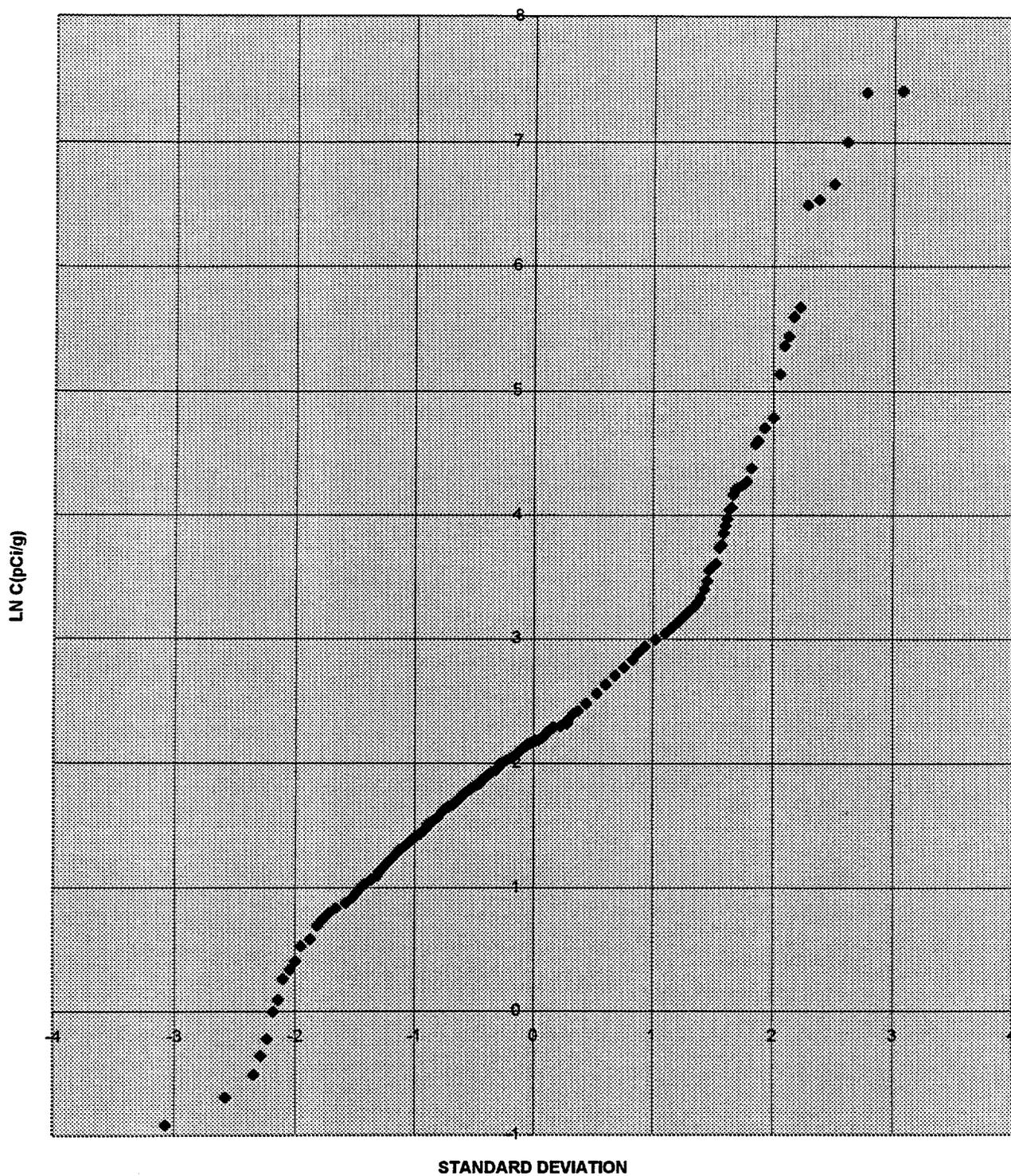
Plot R-2. Standard deviation of detects for gross alpha activity in soils.

BETA DETECTS AND UNDETECTS



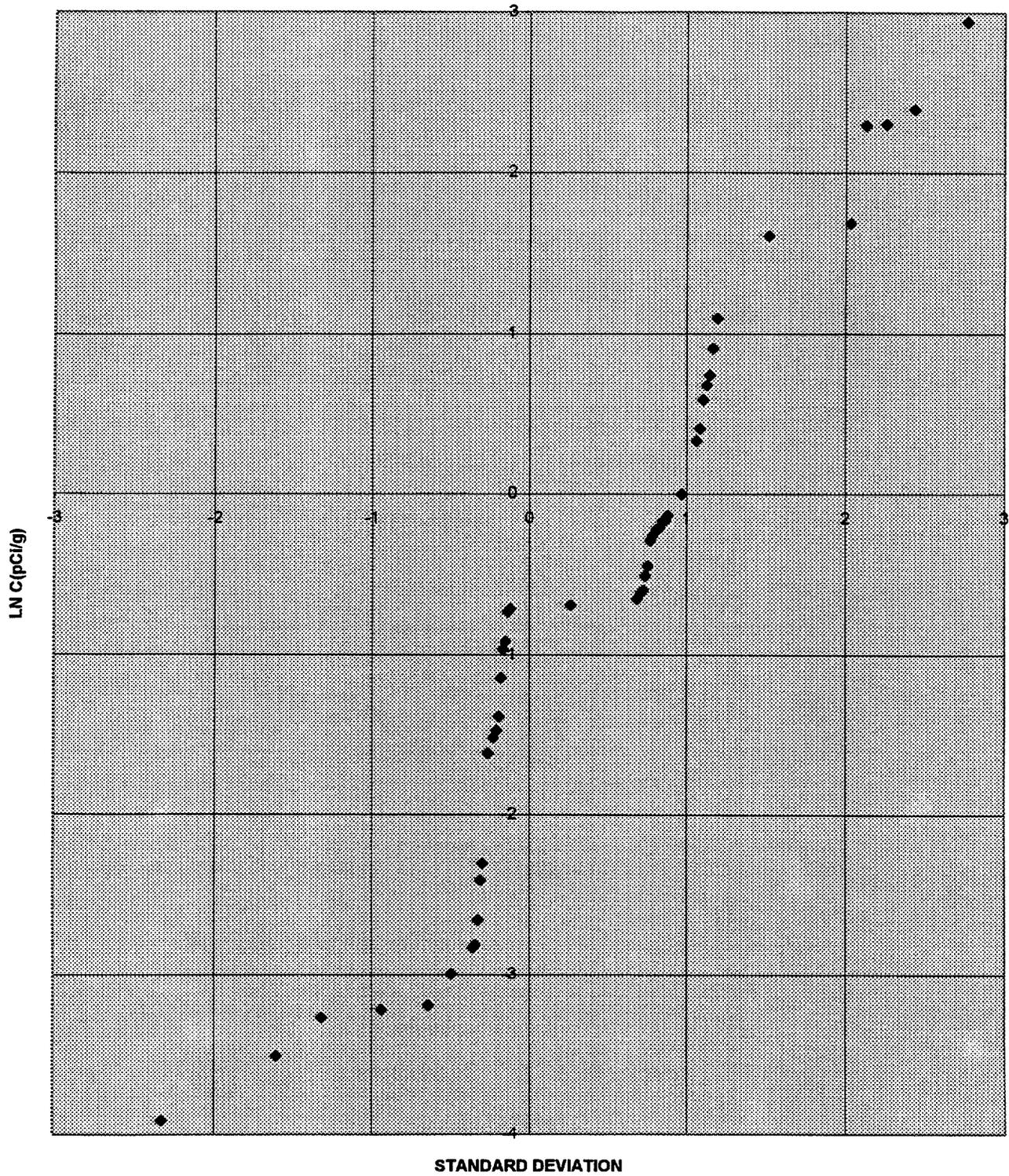
Plot R-3. Standard deviation of detects and undetects for gross beta activity in soils.

BETA DETECTS



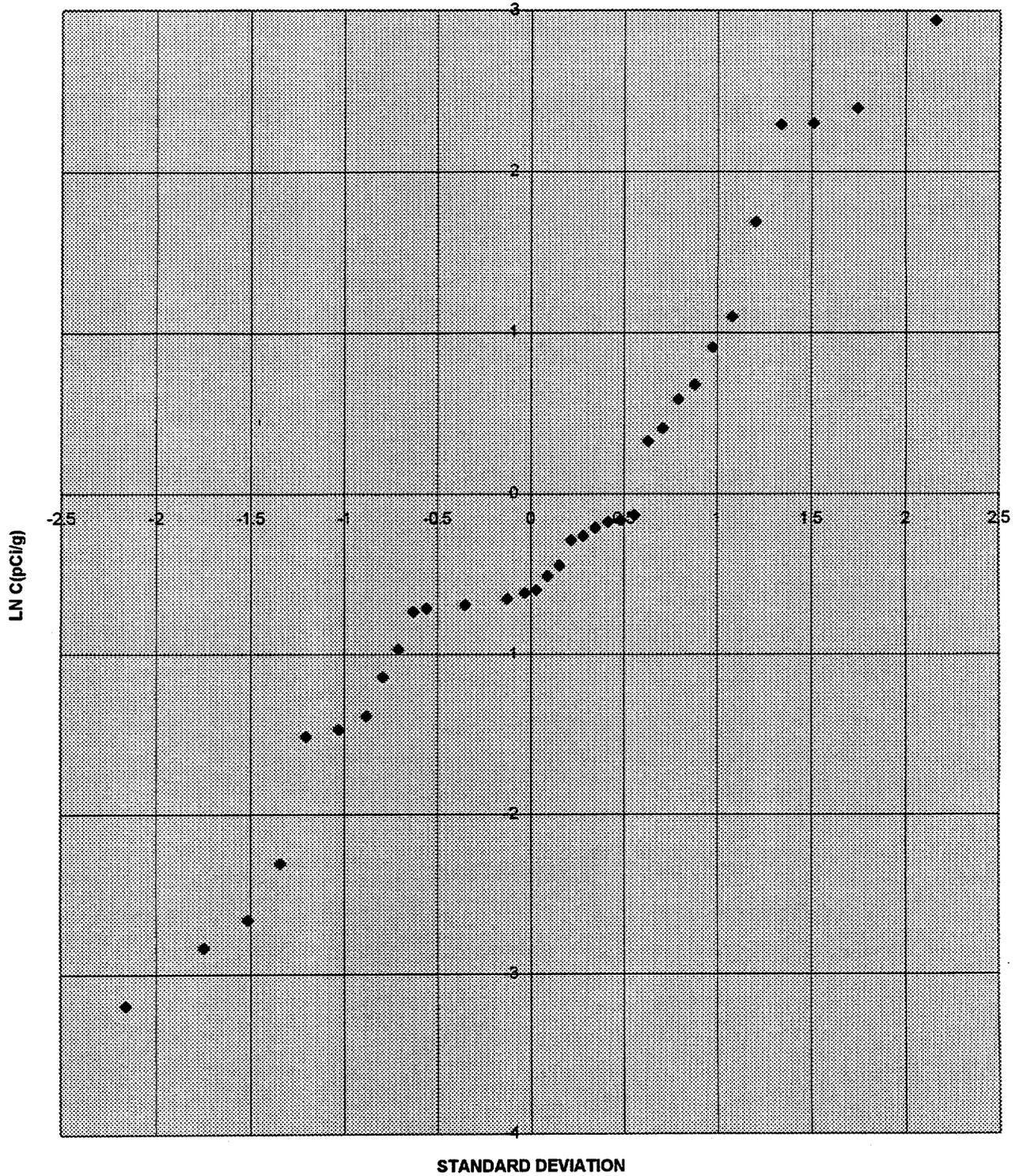
Plot R-4. Standard deviation of detects for gross beta activity in soils.

NEPTUNIUM-237 DETECTS AND UNDETECTS



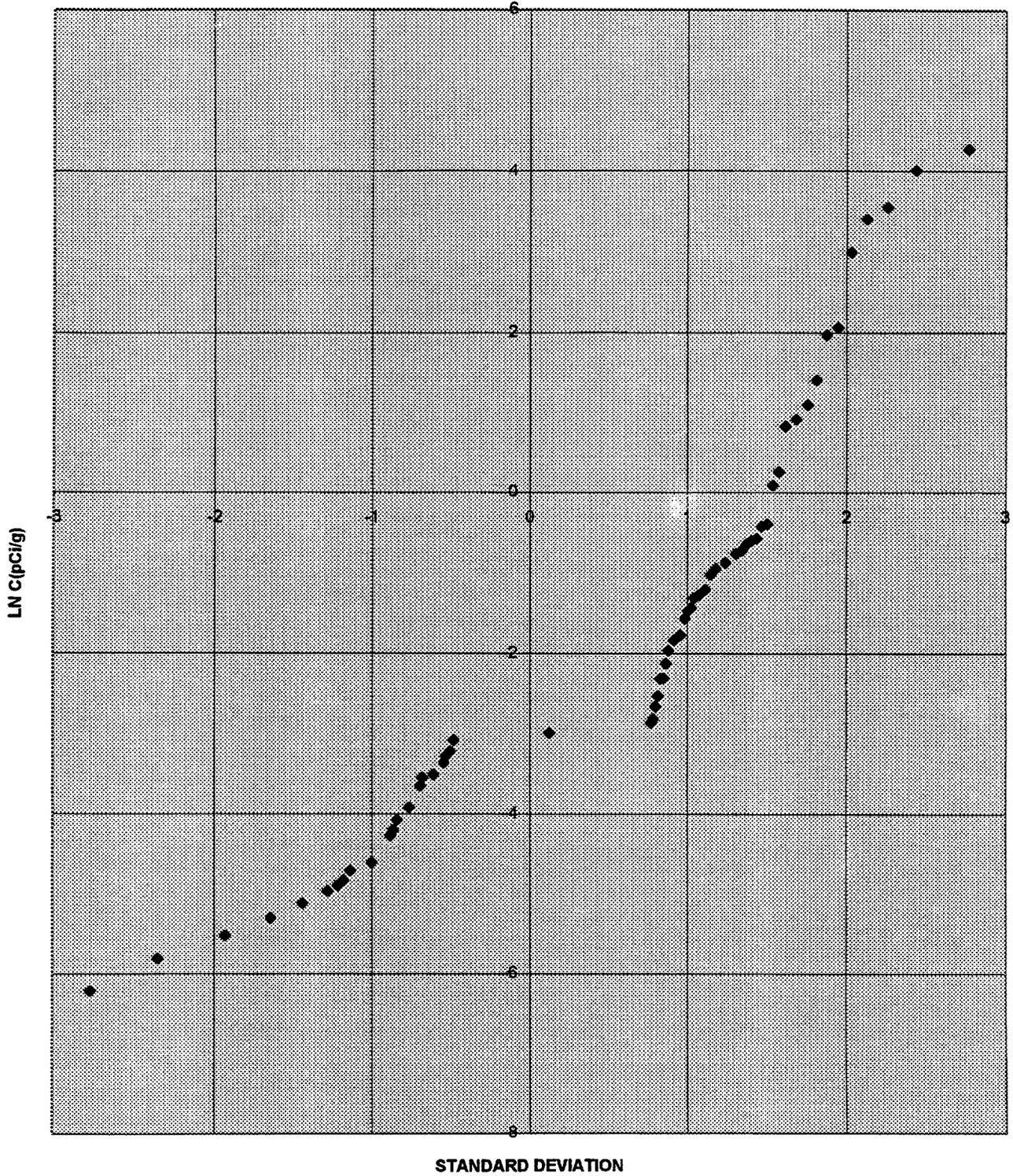
Plot R-5. Standard deviation of detects and undetects for neptunium-237 activity in soils.

NEPTUNIUM-237 DETECTS



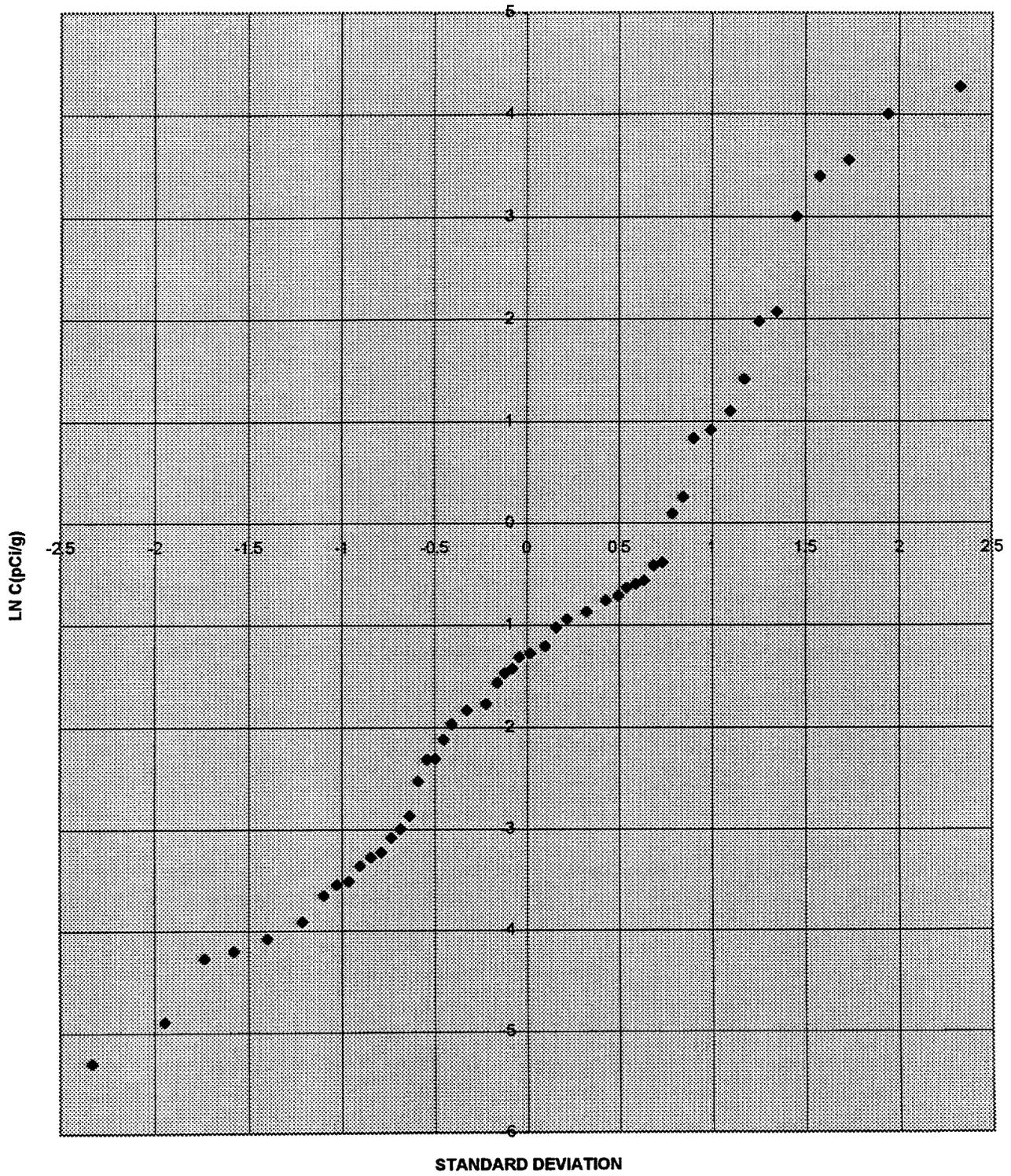
Plot R-6. Standard deviation of detects for neptunium-237 activity in soils.

PLUTONIUM-239 DETECTS AND UNDETECTS



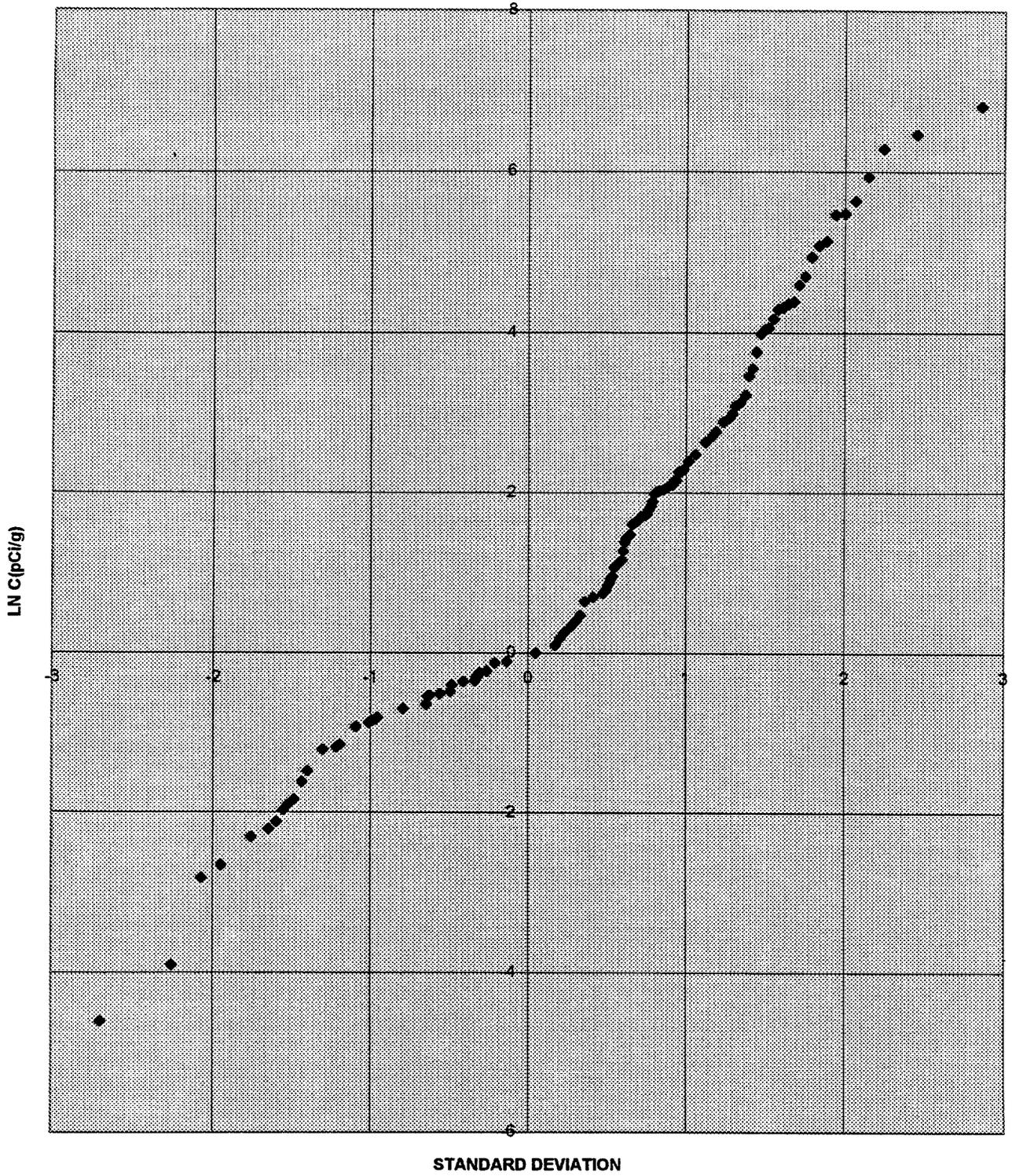
Plot R-7. Standard deviation of detects and undetects for plutonium-239 activity in soils.

PLUTONIUM-239 DETECTS



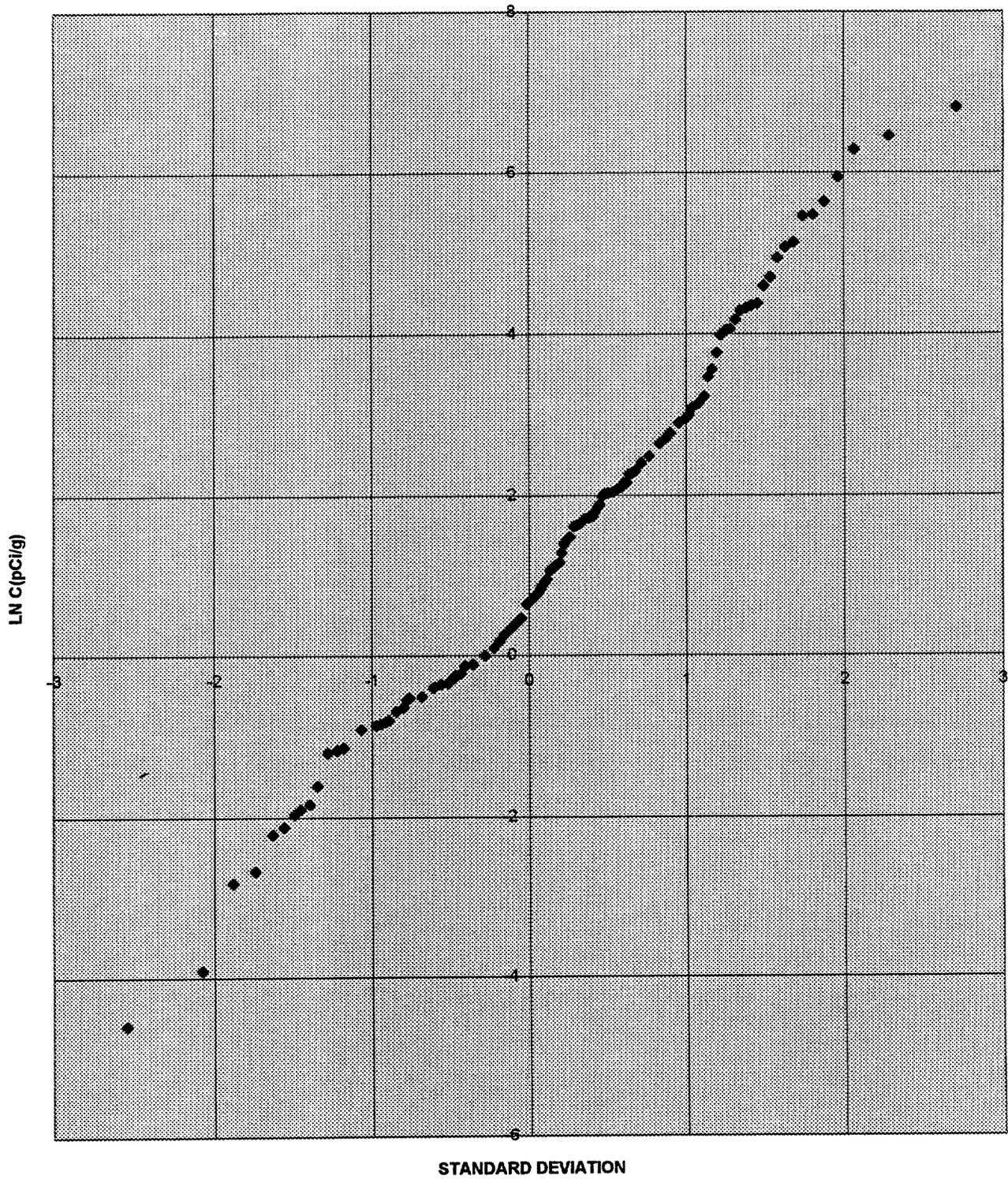
Plot R-8. Standard deviation of detects for plutonium-239 activity in soils.

TECHNETIUM-99 DETECTS AND NONDETECTS



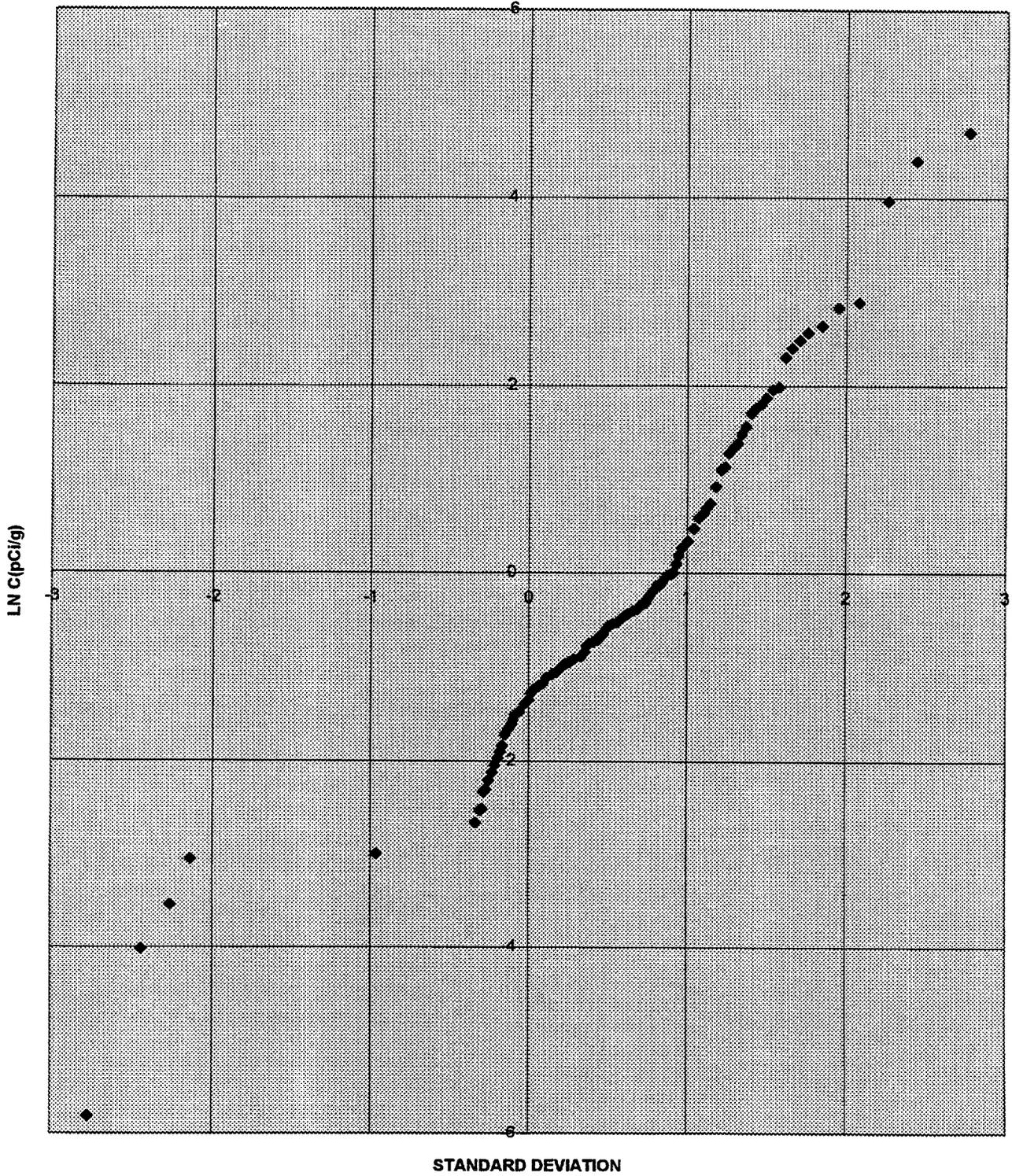
Plot R-9. Standard deviation of detects and undetects for technetium-99 activity in soils.

TECHNETIUM-99 DETECTS



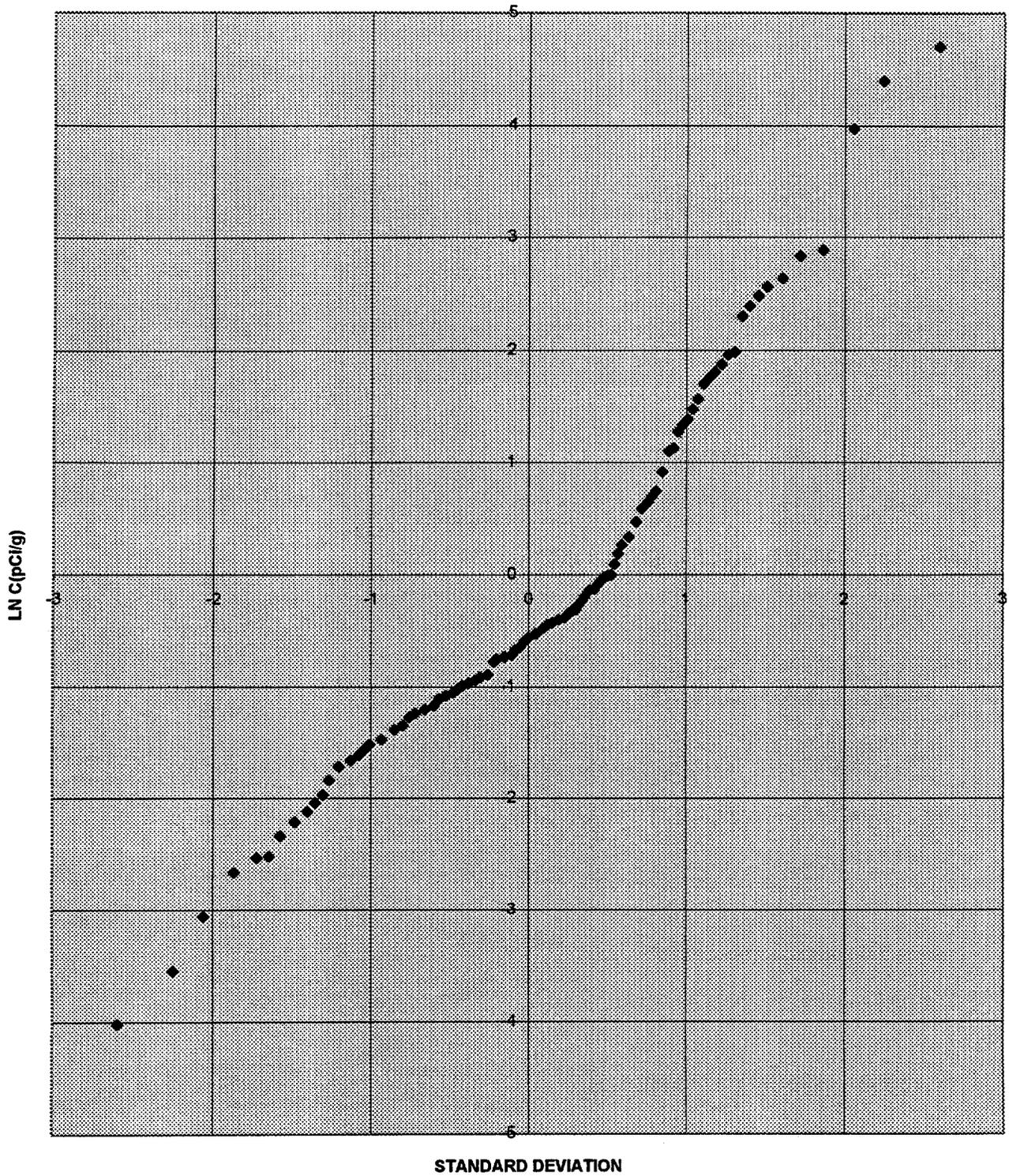
Plot R-10. Standard deviation of detects for technetium-99 activity in soils.

THORIUM-230 DETECTS AND UNDETECTS



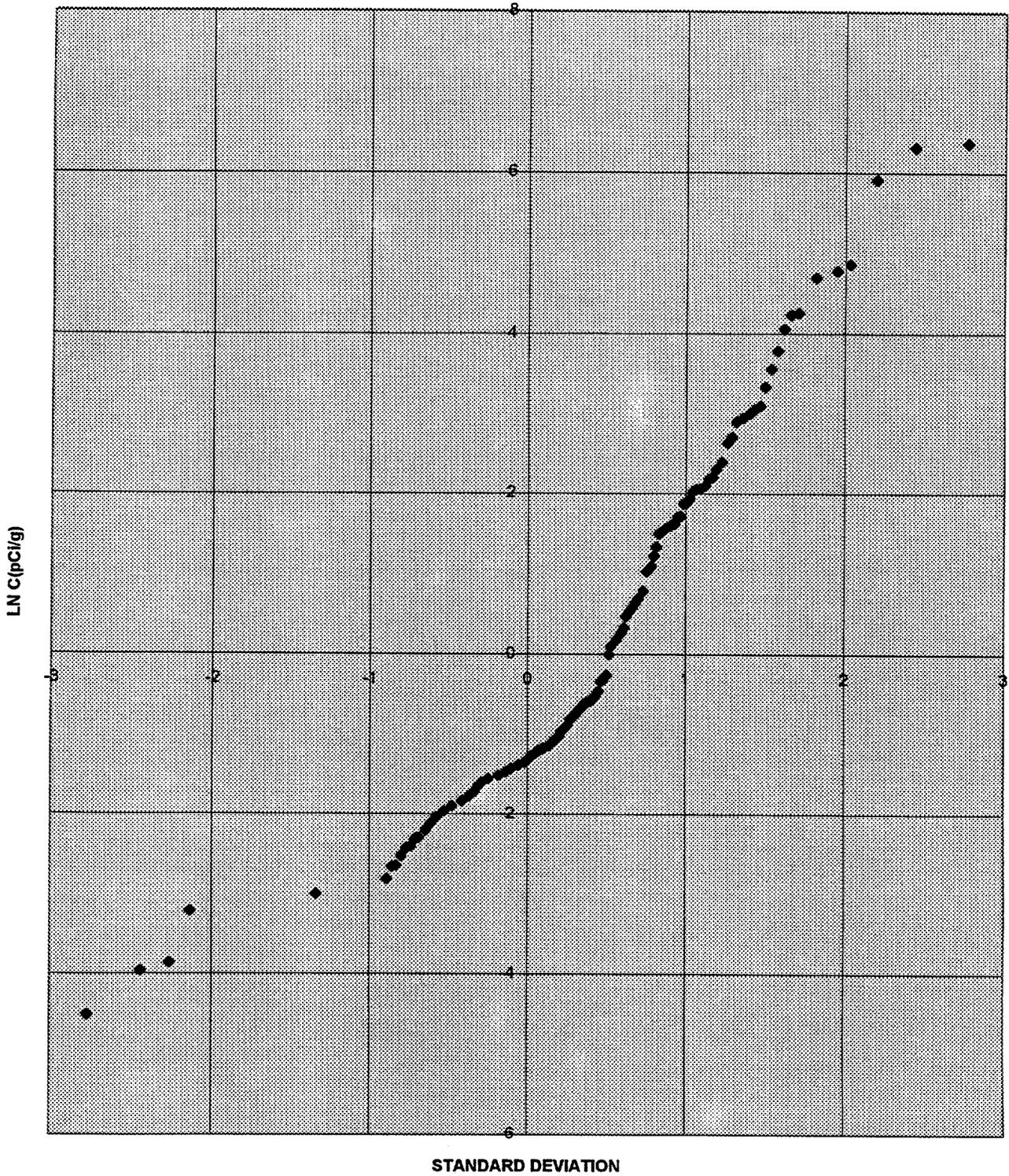
Plot R-11. Standard deviation of detects and undetects for thorium-230 activity in soils.

THORIUM-230 DETECTS



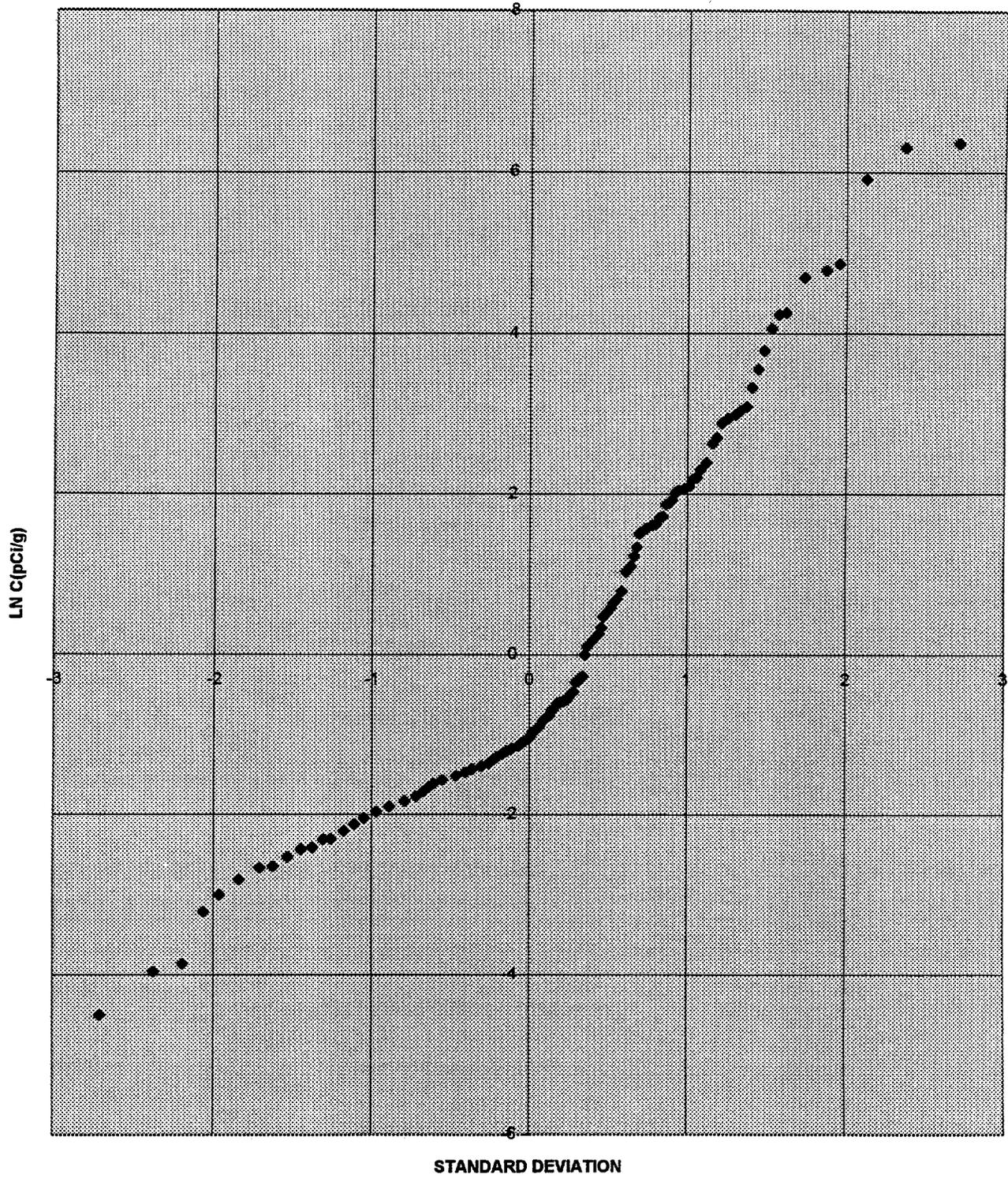
Plot R-12. Standard deviation of detects for thorium-230 activity in soils.

URANIUM-234 DETECTS AND UNDETECTS



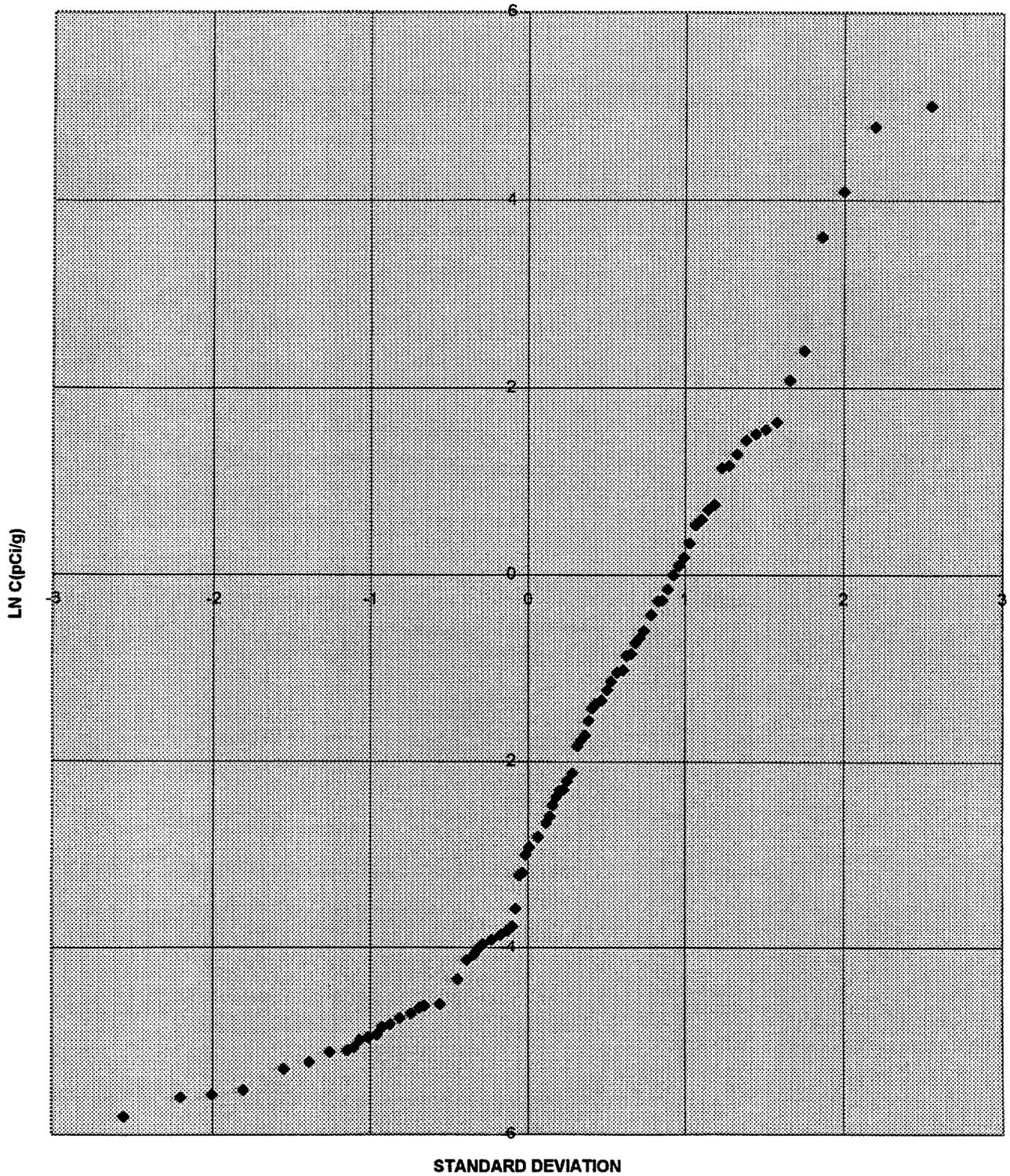
Plot R-13. Standard deviation of detects and undetects for uranium-234 activity in soils.

URANIUM-234 DETECTS



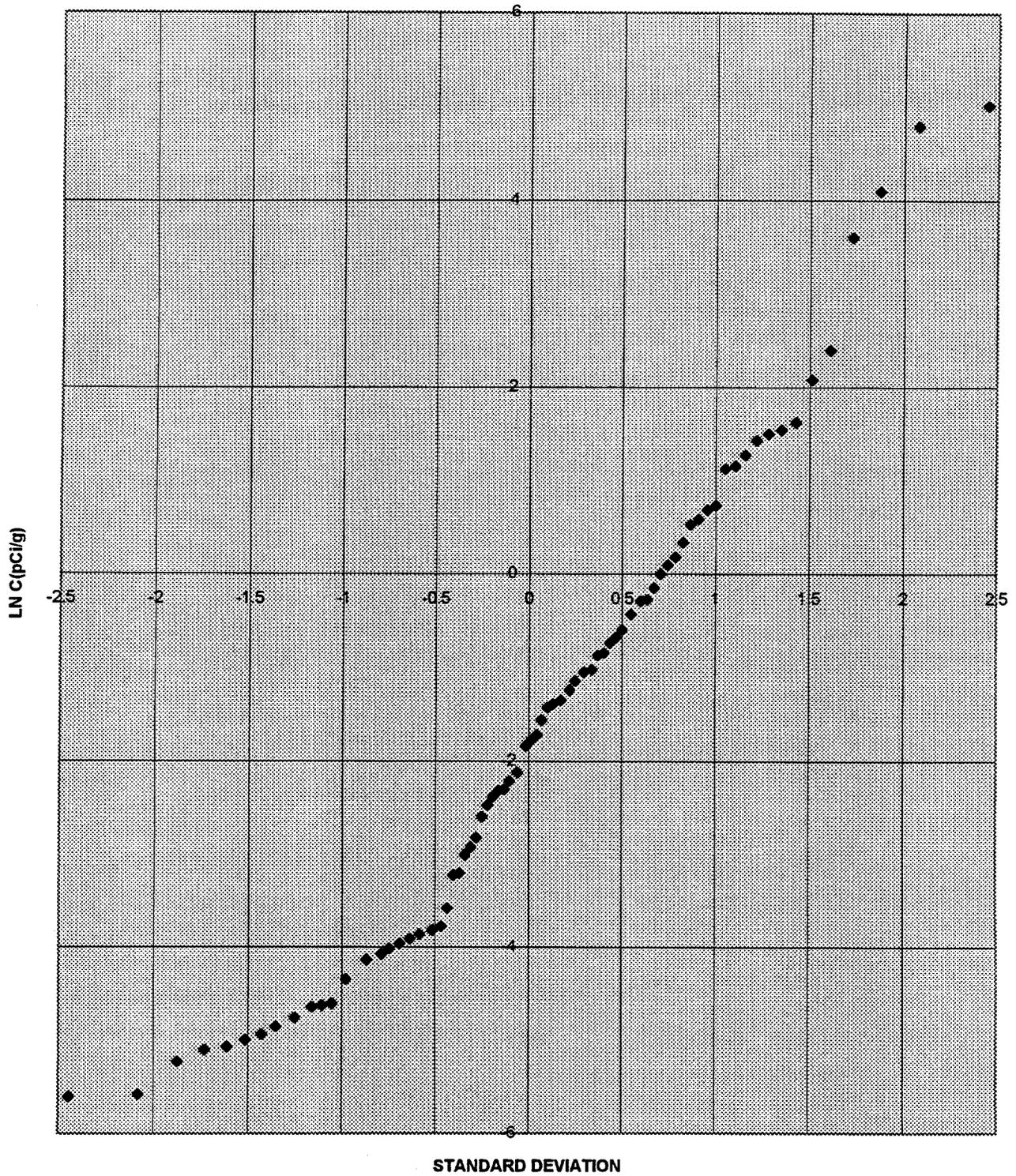
Plot R-14. Standard deviation of detects for uranium-234 activity in soils.

URANIUM-235 DETECTS AND UNDETECTS



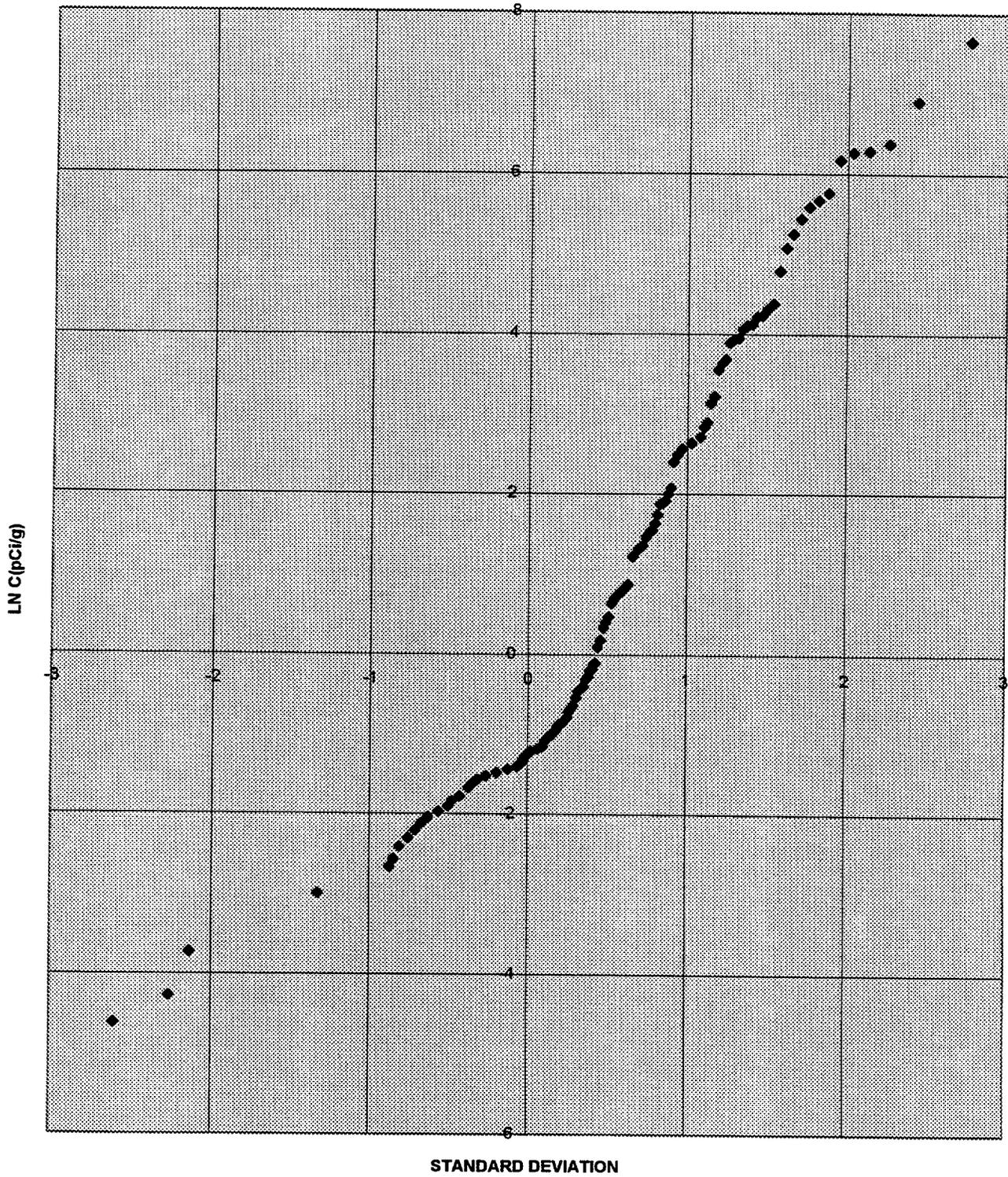
Plot R-15. Standard deviation of detects and undetects for uranium-235 activity in soils.

URANIUM-235 DETECTS



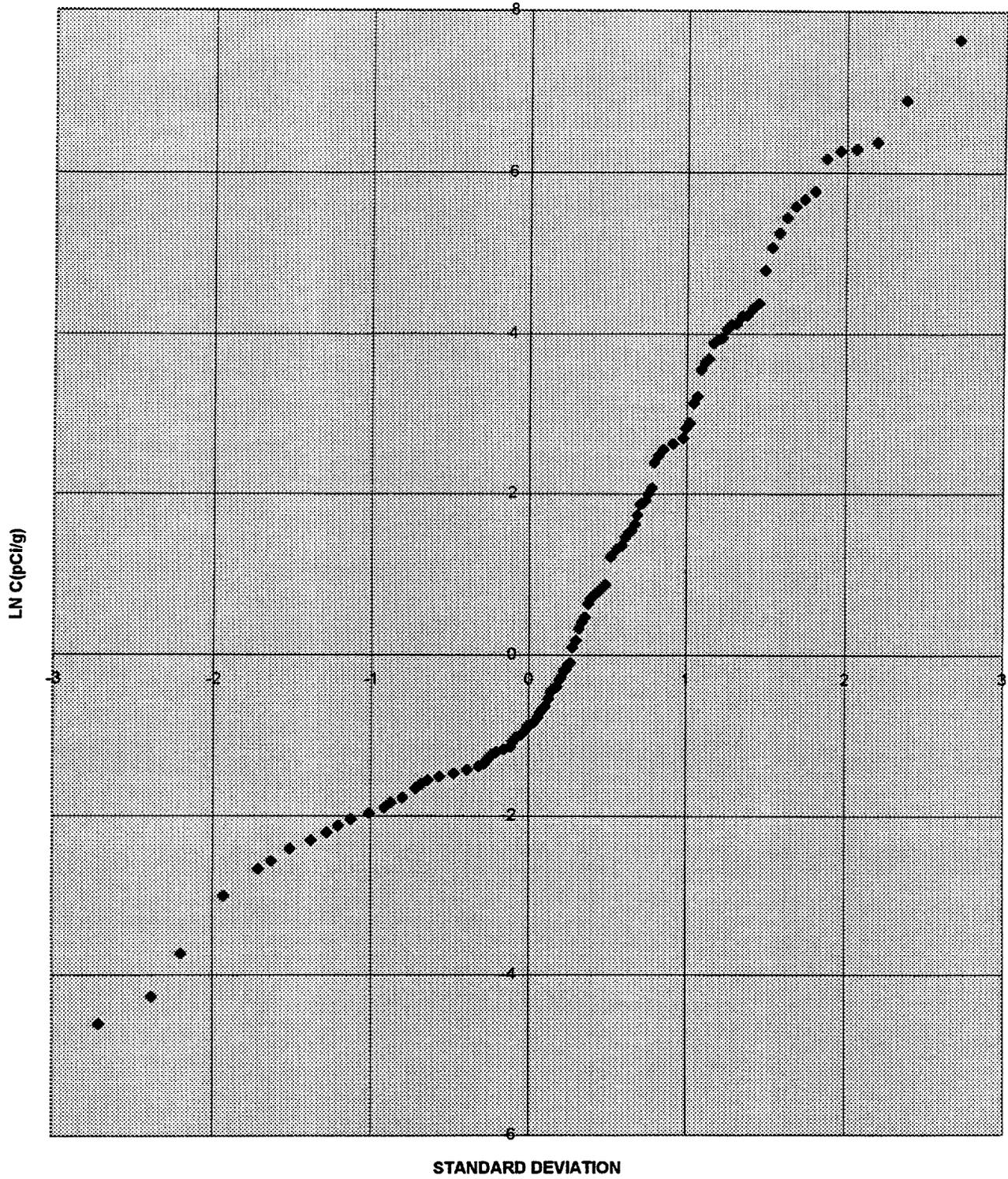
Plot R-16. Standard deviation of detects for uranium-235 activity in soils.

URANIUM-238 DETECTS AND UNDETECTS



Plot R-17. Standard deviation of detects and undetects for uranium-238 activity in soils.

URANIUM-238 DETECTS



Plot R-18. Standard deviation of detects for uranium-238 activity in soils.

INTERNAL DISTRIBUTION

- | | | | |
|-----|------------------|---------|-----------------------------|
| 1. | F. A. Anderson | 35. | A. J. Kuhaida |
| 2. | L. V. Asplund | 36. | P. J. Lemiszki |
| 3. | R. O. Barnett | 37. | J. M. Loar |
| 4. | L. D. Bates | 38. | C. J. Marshall |
| 5. | F. P. Baxter | 39. | G. R. Miller |
| 6. | D. T. Bell | 40. | G. R. Moline |
| 7. | B. A. Berven | 41. | G. K. Moore |
| 8. | H. L. Boston | 42. | C. A. Motley |
| 9. | R. B. Clapp | 43. | J. B. Murphy |
| 10. | K. W. Cook | 44. | M. J. Norris |
| 11. | R. B. Cook | 45. | R. S. Poling |
| 12. | T. K. Cothron | 46. | D. E. Reichle |
| 13. | J. H. Cushman | 47. | W. L. Richards |
| 14. | V. H. Dale | 48. | C. T. Rightmire |
| 15. | F. P. Delozier | 49. | T. H. Row |
| 16. | A. F. Diefendorf | 50. | W. E. Sanford |
| 17. | R. B. Dreier | 51. | F. E. Sharples |
| 18. | T. O. Early | 52. | D. S. Shriner |
| 19. | N. T. Edwards | 53. | E. D. Smith |
| 20. | J. M. Forstrom | 54. | S. H. Stow |
| 21. | D. E. Fowler | 55. | L. E. Toran |
| 22. | C. W. Gehrs | 56. | L. O. Vaughan |
| 23. | P. A. Gourieux | 57. | D. B. Watson |
| 24. | J. T. Grumski | 58. | S. H. Welch |
| 25. | C. S. Haase | 59. | R. K. White |
| 26. | S. G. Hildebrand | 60. | S. L. Winters |
| 27. | R. K. Holmes | 61. | T. F. Zondlo |
| 28. | D. D. Huff | 62. | Central Research Library |
| 29. | L. P. Hull | 63-77. | ESD Library |
| 30. | G. K. Jacobs | 78-79. | Laboratory Records Dept. |
| 31. | W. K. Jago | 80. | Laboratory Records, ORNL-RC |
| 32. | P. Kanciruk | 81. | ORNL Patent Section |
| 33. | R. H. Ketelle | 82. | ORNL Y-12 Technical Library |
| 34. | H. L. King | 83-107. | PGDP/KEVIL Library |

EXTERNAL DISTRIBUTION

108. D. W. Dollins, U.S. Department of Energy, Paducah Site Office, P.O. Box 1410, Paducah, KY 42002-1410
109. R. C. Edwards, U.S. Department of Energy, Paducah Site Office, P.O. Box 1410, Paducah, KY 42002-1410
110. R. N. Farvolden, Professor, Department of Earth Sciences, University of Waterloo, Waterloo, Ontario N2L 3G1 Canada

111. D. W. Freckman, Director, College of Natural Resources, 101 Natural Resources Building, Colorado State University, Fort Collins, CO 80523
112. G. Y. Jordy, Director, Office of Program Analysis, Office of Energy Research, ER-30, G-226, U.S. Department of Energy, Washington, DC 20545
113. S. L. Lankford, U.S. Department of Energy, Oak Ridge Operations Office, IRC Building, P.O. Box 2001, Oak Ridge, TN 37838-8541
114. E. R. Meehan, U.S. Department of Energy, Portsmouth Site Office, P.O. Box 628, Piketon, OH 45661-7550
115. A. Patrinos, Director, Environmental Sciences Division, Office of Health and Environmental Research, ER-74, U.S. Department of Energy, Washington, DC 20585
116. M. E. Redfield, U.S. Department of Energy, Paducah Site Office, P.O. Box 1410, Paducah, KY 42002-1410
117. G. S. Sayler, Professor, 10515 Research Drive, Suite 100, The University of Tennessee, Knoxville, TN 37932-2567
118. J. T. Sweeney, U.S. Department of Energy, Oak Ridge Operations Office, IRC Building, P.O. Box 2001, Oak Ridge, TN 37838-8541
119. F. J. Wobber, Environmental Sciences Division, Office of Health and Environmental Research, ER-74, U.S. Department of Energy, Washington, DC 20585
120. Office of Assistant Manager for Energy Research and Development, U.S. Department of Energy Oak Ridge Operations, P. O. Box 2001, Oak Ridge, TN 37831-8600
- 121-122. Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831