BACKGROUND LEVELS OF PRIORITY POLLUTANT METALS IN RHODE ISLAND SOILS

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INTRODUCTION

The goal of this study was to investigate the occurrence, geochemical abundance and scatter of the metals regulated by hazardous materials programs in Rhode Island soil.

Due to the natural occurrence of metals, it is necessary for environmental site investigations to attempt to determine the levels of metals in soil beyond the influence of the site being investigated. These levels are referred to as background. These results are then used as control samples and compared to other site samples and available literature to determine the degree and extent of environmental contamination at the site.

The problem with this situation is that available literature is very limited, and the cost of analyzing samples discourages many project managers from taking what they perceive to be unnecessary samples. Also, one or two attempts at taking representative background samples can be insufficient and can lead to over or under stating the extent of contamination. Therefore it is often difficult for regulators, consultants or responsible parties to address the detection of priority pollutant metals at a site. This project's goal is to attempt to solve this problem by utilizing existing site data from both the Federal and State hazardous waste and hazardous materials regulatory programs.

This study relies entirely upon data which was generated under one of two regulatory authorities. The first program is under the Comprehensive Environmental Response Compensation and Liability Act, commonly referred to as Superfund. Superfund is a Federal program which is run by the United States Environmental Protection Agency (USEPA). The purpose of this program is to investigate and clean up the nation's worst hazardous waste disposal sites.

The second regulatory program which generated samples used in this study was the Rhode Island Department of Environmental Management's Division of Site Remediation, which regulates the investigation and cleanup of sites similar to those in the Federal Superfund program. This State program follows the general framework of the Federal program but is much smaller in size. Although these samples are generated by another organization, they are included in this study because the goals of both the State and Federal programs are very similar and the same USEPA laboratory procedures were required for both programs.

This study compiles a comprehensive database of background levels of priority pollutant metals throughout the State of Rhode Island utilizing 106 sample points. Figure 1 shows an outline of Rhode Island and the approximate locations of the sampling points. In addition to the gathering of analytical results, the average land usage in the vicinity of the site was also recorded. The data was then statistically evaluated with the goal of establishing statewide background levels as well as investigating to what degree man's activities influence these levels.

PARAMETERS AND METHODOLOGIES

The analytical results presented in this study included only total recoverable levels of the metals. Samples were taken from approximately the top two feet of surficial soil in the vicinity of the site investigated.

It is standard operating procedure for environmental investigators to remove approximately the top 2 inches of soil prior to collecting a background sample. This procedure is an attempt to limit the effects of potential pollutant sources such as automobile emissions, road runoff or other very common sources of soil contamination.

The data used throughout this study were obtained from analytical results from USEPA laboratory methods. These methods are described in great detail in the EPA document entitled: *EPA Methods for the Chemical Analysis of Water and Wastes, and Test Methods for Evaluating Solid Waste (SW-846)*. The EPA laboratory method numbers are: antimony (6010), arsenic (7060), beryllium (6010), cadmium (6010), chromium (6010), copper (6010), lead (6010 and 7421), mercury (7470 and 7471), nickel (6010), selenium (7740), silver (6010), thallium (7840, 7841 and 6010) and zinc (6010).

Although all of this data was generated using consistent EPA methodologies, the individual quality assurance and quality control procedures followed by the laboratories did vary. This variance is due to the overlapping jurisdiction of the State and Federal hazardous materials programs. The federally investigated sites utilized the USEPA's Contract Laboratory Program (CLP). This program was initiated at the same time as the Superfund program. Its purpose is to provide consistent, high quality, legally defensible analytical results to support the Superfund program on a nationwide basis. These program laboratories utilize the same USEPA laboratory analytical methodologies as standard laboratories, but the CLP also mandates strict procedures for documentation of quality assurance and quality control.

CLP data are accepted nationwide as the highest quality data available[1]. This program is not available, however, for use by State personnel or private contractors. Thus data generated by a second quality assurance and quality control program is incorporated into this study. This second program is one which meets the requirements of the State but which does not include as heavy an emphasis on validation procedures and legal defensibility as the CLP.

The land usage type was primarily determined by reviewing the report which contained the analytical results and was supplemented by interviews with State personnel familiar with the site. In order to make this study more useful, land usage was broken down into two general categories. These were:

A. High Density: used to indicate industrial parks, urban areas, areas of heavy, historic development (such as the former Naval Base, Quonset Point) and densely populated residential areas. Fifty nine sampling points (56%) were considered to be in a high density land usage area.

B. Low Density: used to indicate areas with low density residential development and very limited commercial or industrial usage. Forty seven sampling points (44%) were considered to be in a low density land usage area.

FREQUENCY OF OCCURRENCE

A total of 106 samples were included in this study. However, due to the variety of site characteristics and the organization taking the samples, not all samples were analyzed for all parameters. Each metal was analyzed in at least 84 of the 106 samples.

On a statewide and land usage basis Table 1 indicates a metal's frequency of occurrence in samples for which it was analyzed. Very few trends are apparent in this analysis, but several points are noteworthy. Arsenic, cadmium, copper and mercury occur at significantly higher rates in high density areas than low density, suggesting that their occurrence is likely influenced by land usage. Barium, beryllium and nickel, however, occur at significantly lower rates in high density areas than in low density areas, suggesting that their occurrence is not impacted by man's usage and is likely a soil property.

On a statewide basis, six metals occurred in less than 20 percent of the samples analyzed for that parameter. These were antimony, cadmium, mercury, selenium, silver and thallium. Review of the occurrence data suggested that the presence of these metals could be more the result of man's impact than natural occurrence.

STATISTICAL ANALYSIS

The goal of this study was to investigate the occurrence, geochemical abundance and scatter of the metals regulated by hazardous materials programs. Prior to proceeding, two decisions were necessary. The first regarded how to handle a non-detect sampling result, and the second regarded the validity of statistically analyzing sampling results for metals which occurred infrequently.

For the purposes of calculating averages and deviations, this study assumed a level of half of the method detection limit (as reported in the certificate of analysis for sample results) was present for results reported as non-detectable. Based on this assumption, all metals which did not occur in at least 20 percent of the samples were not statistically analyzed, as the sample detection limits would have disproportionately weighted the results. These metals (antimony, cadmium, mercury, selenium, silver and thallium) are reported in Table 2 along with their respective ratio of occurrence and range of detected levels. Using the 20% cutoff criterion left beryllium, which occurred at 47.7%, as the lowest occurring metal carried forward in the study.

The analytical results for the remaining eight, more commonly occurring, metals in the study (arsenic, barium, beryllium, chromium, copper, lead, nickel and zinc) were studied in greater detail. These data were compiled into a series of frequency bar graphs which compare ranges of analytical results to their frequency. These graphs, as shown on Figures 1 through 8, indicate that the analytical results for all of the metals are positively skewed and lognormal.

Due to the lognormal distribution, the geometric data were selected as the most representative of geochemical abundance[2]. The bar graphs also indicate that several of the results may fall outside of the expected range of variation and are thus suspect. Utilizing the geometric data, a 95% confidence interval was determined, and results falling outside of the interval were eliminated. As the data were positively skewed, only the upper bound of the confidence intervals was necessary. This value was calculated as the product of the geometric average and the geometric deviation to the second power.

For comparative purposes, arithmetic average and deviation, geometric average and deviation and the geometric data with 95% confidence were calculated on a statewide and land usage basis for each of the commonly occurring metals. These results are depicted in Table 3 and 4.

The results of the categorical analysis of this data by land usage were somewhat surprising. Comparing the results of the land usage data with the statewide data, one expects a comparison of potential pollutant levels (in this case metals) would be the largest for high density areas and lowest for low density areas. This was not consistently the case.

Geometric average levels detected in high density areas were greater than the low density average for arsenic, copper and lead and significantly less than the low density average for barium, chromium and nickel.

The results for beryllium and zinc did not fit into either of the above categories. The results for beryllium showed no variance when comparing land usages to the statewide average using the geometric data and a slight variance in the arithmetic data. The zinc arithmetic average indicated a level for high density usage above the low density average, while the geometric data indicated a level lower than the statewide average for the same category.

This inconsistency of the results with regard to land usage is likely the result of most samples containing very little if any actual surficial soil. It is standard operating procedure for environmental investigators when taking background samples to remove the top two inches of soil in an effort to avoid ubiquitous contamination such as automobile emissions or road runoff. This procedure appears to have impacted the results of this investigation with regard to investigating the relationship between land usage and the geochemical abundance of a metal.

OTHER INVESTIGATIONS

Only one investigation of similar scope could be located. This was by the United States Geological Survey and entitled: *Elemental Concentrations in Soils and Other Surficial Materials of the Conterminous United States (USGS Professional Paper 1270)*[3]. This investigation began in 1961 and continued in several phases until 1981. Samples were collected by USGS scientists when traveling to project sites and during field work for other studies. A total of 1,318 samples were taken as part of this investigation and analyzed for either 35 or 46 elements depending upon the time period the sample was taken. All 14 metals which were part of this study were included in the USGS study. The USGS study included 28 samples in New England, one of which was near the Rhode Island/Connecticut border.

The results of the USGS study are presented in Table 5. The data from this study also indicated that the metals concentrations were positively skewed and lognormal. For this reason it was concluded that the geometric average and deviation were more representative of the geochemical abundance than the arithmetic data. Arithmetic averages were also calculated for comparative purposes.

The USGS found that three metals (cadmium, silver and thallium) were not detected at sufficient frequency to allow averages and deviations to be calculated. This finding is consistent with this study, as all three of these metals were detected at frequencies too low to evaluate the levels on a statewide basis (cadmium 14.4%, silver 4.2%, thallium 4.8%).

Comparison of the remaining three low occurrence metals in the Rhode Island study with the USGS findings was noteworthy. Antimony was detected at 5.9% in Rhode Island, which is relatively consistent with the USGS finding of 23.7%. However the results of this comparison for mercury (17.3% (RI) vs. 100% (USGS)) and selenium (14.1% (RI) vs. 84.1% (USGS)) show that these two metals occur at significantly higher rates in the eastern United States as a whole than they do in Rhode Island.

In general, geometric averages for the eight common Rhode Island metals were all substantially lower than the USGS results. The exception was lead, with 13.91 mg/kg (RI) versus 14 mg/kg (USGS). Barium had the greatest differential, 19.56 mg/kg (RI) to 420 mg/kg (USGS). A review of the entire data set indicates that almost all of the Rhode Island results did fall within the range of the USGS results.

SUMMARY AND CONCLUSION

The findings of this investigation indicate that of the fourteen metals most commonly regulated by hazardous materials programs in Rhode Island (antimony, arsenic, barium, beryllium, cadmium, chromium, copper, lead, mercury, nickel selenium, silver, thallium, zinc), six occur only infrequently in Rhode Island soil (antimony, cadmium, mercury, selenium, silver, thallium). Their occurrence is likely the result of anthropogenic effects. Occurrence of the more common metals in Rhode Island soils (arsenic, barium, beryllium, chromium, copper, lead, nickel, zinc) is more likely the result of nature.

For the common metals, distribution of the geochemical abundance levels is lognormal and positively skewed. For all metals in this investigation, results were consistently lower than the results found for the eastern United States in a comparable study by the United States Geological Survey.

The results of the categorical analysis of this data by land usage indicate that arsenic, copper and lead occur at greater levels in high density areas than low density. This result suggests that their concentration is slightly influenced by land usage. Barium, chromium and nickel, however, occur at significantly lesser levels in high density areas than in low density areas, suggesting that their concentration is not impacted by man and is likely entirely a soil property. The results for beryllium and zinc showed little variance by land usage.

During this investigation there was a large amount of thought given to the idea of applying a confidence interval to the data and eliminating the data points which did not fall within this interval. As an original premise of this study was that the samples in it were representative of background conditions at a given site, it would seem arbitrary to then eliminate values which did not fall within an expected range. In reviewing the data set, however, it was obvious the certain values were very suspicious. Therefore, a 95% confidence interval was established using the geometric data. Applying the confidence interval to the statistical results for the common metals allowed data to be eliminated for four of the metals. The results of this application were most notable for arsenic, which had its Statewide geometric average drop almost 30%.

In conclusion, eight metals regulated by hazardous material programs are common in Rhode Island soil. These are arsenic, barium, beryllium, chromium, copper, lead, nickel and zinc. Six metals regulated by the hazardous material programs are not common in Rhode Island soil. These are antimony, cadmium, mercury, selenium, silver and thallium. The geometric average with the application of the 95% confidence interval is the best estimate of the geochemical abundance of priority pollutant metals in Rhode Island soil.

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TABLE 1
FREQUENCY OF OCCURRENCE
STATEWIDE AND LAND USAGE COMPARISON

	STATEWIDE	HIGH DENSITY	LOW DENSITY
ANTIMONY	5.9% (5)	7.0% (3)	4.8% (2)
ARSENIC	76.4% (81)	81.4% (48)	70.2% (33)
BARIUM	82.4% (75)	74.5% (38)	92.5% (37)
BERYLLIUM	47.7% (42)	35.6% (16)	60.5% (26)
CADMIUM	14.4% (14)	20.0% (10)	8.5% (4)
CHROMIUM	90.6% (96)	93.2% (55)	87.2% (41)
COPPER	75.3% (73)	80.0% (44)	69.0% (29)
LEAD	94.2% (98)	94.9% (56)	93.3% (42)
MERCURY	17.4% (17)	19.6% (10)	14.9% (7)
NICKEL	59.2% (58)	41.8% (23)	81.4% (35)
SELENIUM	14.1% (13)	15.2% (7)	13.0% (6)
SILVER	4.2% (4)	5.9% (3)	2.3% (1)
THALLIUM	4.8% (4)	2.3% (1)	7.3% (3)
ZINC	92.6% (88)	96.3% (52)	87.8% (36)

Note: (n) indicates the actual number of positive detections
References: 4 - 80

TABLE 2
RANGE OF CONCENTRATIONS FOR LOW OCCURRENCE METALS

METAL	RATIO OF OCCURRENCE	RANGE DETECTED (mg/kg)
ANTIMONY	5: 85	2.00 - 5.90
CADMIUM	14: 97	0.22 - 3.50
MERCURY	17: 98	0.02 - 0.50
SELENIUM	13: 92	0.05 - 1.10
SILVER	4: 95	0.20 - 1.30
THALLIUM	4: 84	0.43 - 0.94

References:4 - 80

TABLE 3
STATISTICAL SUMMARY TABLE
ARITHMETIC DATA
(all results in mg/kg)

LAND USAGE	STATEWIDE		HIGH DENSITY		LOW DENSITY	
METAL	AVE.	DEV.	AVE.	DEV.	AVE.	DEV.
ARSENIC	2.71	2.93	2.74	2.86	2.66	3.01
BARIUM	25.80	21.61	24.15	24.34	27.91	17.31
BERYLLIUM	0.55	0.43	0.54	0.42	0.57	0.44
CHROMIUM	9.20	9.73	8.08	6.99	10.61	12.19
COPPER	13.56	28.22	15.28	35.24	11.30	14.28
LEAD	33.50	55.54	39.55	66.00	25.58	36.14
NICKEL	6.81	9.33	6.03	10.63	7.80	7.21
ZINC	41.94	73.44	48.44	94.84	33.37	22.85

References: 4 - 80

TABLE 4
STATISTICAL SUMMARY TABLE
GEOMETRIC DATA
(all results in mg/kg)

LAND USAGE	STATEWIDE		HIGH DENSITY		LOW DENSITY	
METAL	AVE.	DEV.	AVE.	DEV.	AVE.	DEV.
ARSENIC	1.67	1.53	1.80	1.41	1.52	1.68
95 % CI	1.19	1.29	1.25	1.15	1.12	1.44
BARIUM	19.57	16.61	17.01	16.76	23.40	16.43
95 % CI	NA	NA	NA	NA	NA	NA
BERYLLIUM	0.43	1.47	0.43	1.44	0.43	1.51
95 % CI	0.38	1.50	0.38	1.46	0.38	1.54
CHROMIUM	6.53	4.72	6.08	4.78	7.14	4.65
95 % CI	NA	NA	NA	NA	NA	NA
COPPER	6.41	4.69	6.59	4.66	6.19	4.72
95 % CI	5.98	4.31	5.81	4.31	NA	NA
LEAD	13.91	11.36	15.66	11.25	11.92	11.50
95 % CI	NA	NA	NA	NA	NA	NA
NICKEL	4.37	3.02	3.73	3.15	9.33	2.84
95 % CI	4.24	2.92	3.53	3.06	NA	NA
ZINC	25.27	22.06	24.38	22.10	26.49	22.01
95 % CI	NA	NA	NA	NA	NA	NA

95 % CI = statistical recalculated data after application of 95 % confidence interval

NA = all values in data set fell within 95 % confidence interval

References: 4 - 80

TABLE 5
SUMMARY OF USGS RESULTS
FOR THE EASTERN UNITED STATES
ALL RESULTS IN mg/kg

METAL	FREQ.	AVERAGE ARITH.	GEOM.	GEOMETRIC DEVIATION	RANGE
ANTIMONY	23.7%	0.76	0.52	2.38	<1 - 8.8
ARSENIC	98.9%	7.40	4.80	2.56	<0.1 - 73
BARIUM	100%	420	290	2.35	10 - 1,500
BERYLLIUM	32.2%	0.85	0.55	2.53	<1 - 7
CHROMIUM	100%	52	33	2.60	1 - 1,000
COPPER	98.1%	22	13	2.80	<1 - 700
LEAD	78.0%	17	14	1.95	<10 - 300
MERCURY	100%	0.12	0.81	2.52	0.01 - 3.4
NICKEL	82.0%	18	11	2.64	<5 - 700
SELENIUM	84.1%	0.45	0.30	2.44	<0.1 - 3.9
ZINC	98.1%	52	40	2.11	<5 - 2,900

References:4 - 80

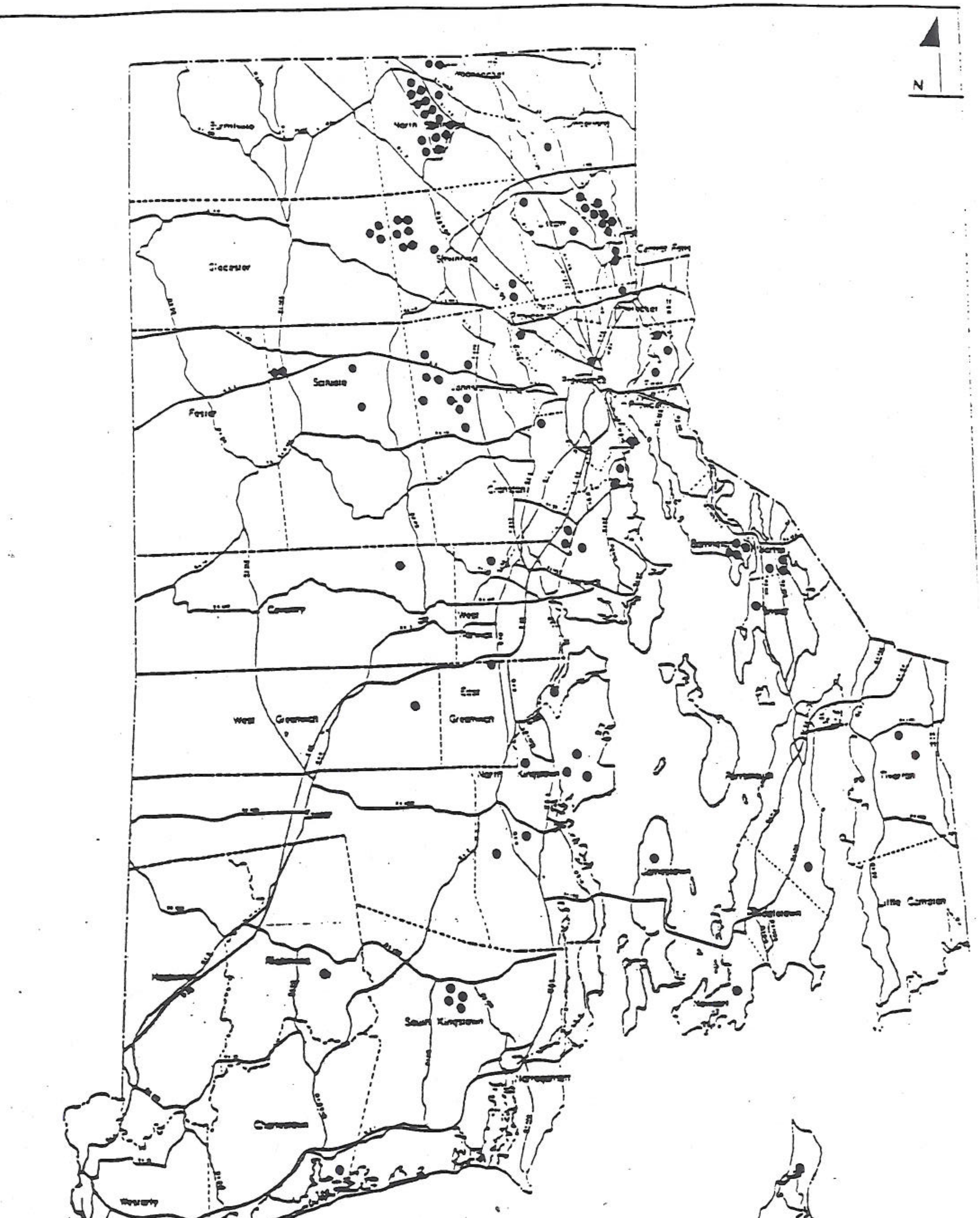

FIGURE 1
SAMPLE LOCATIO

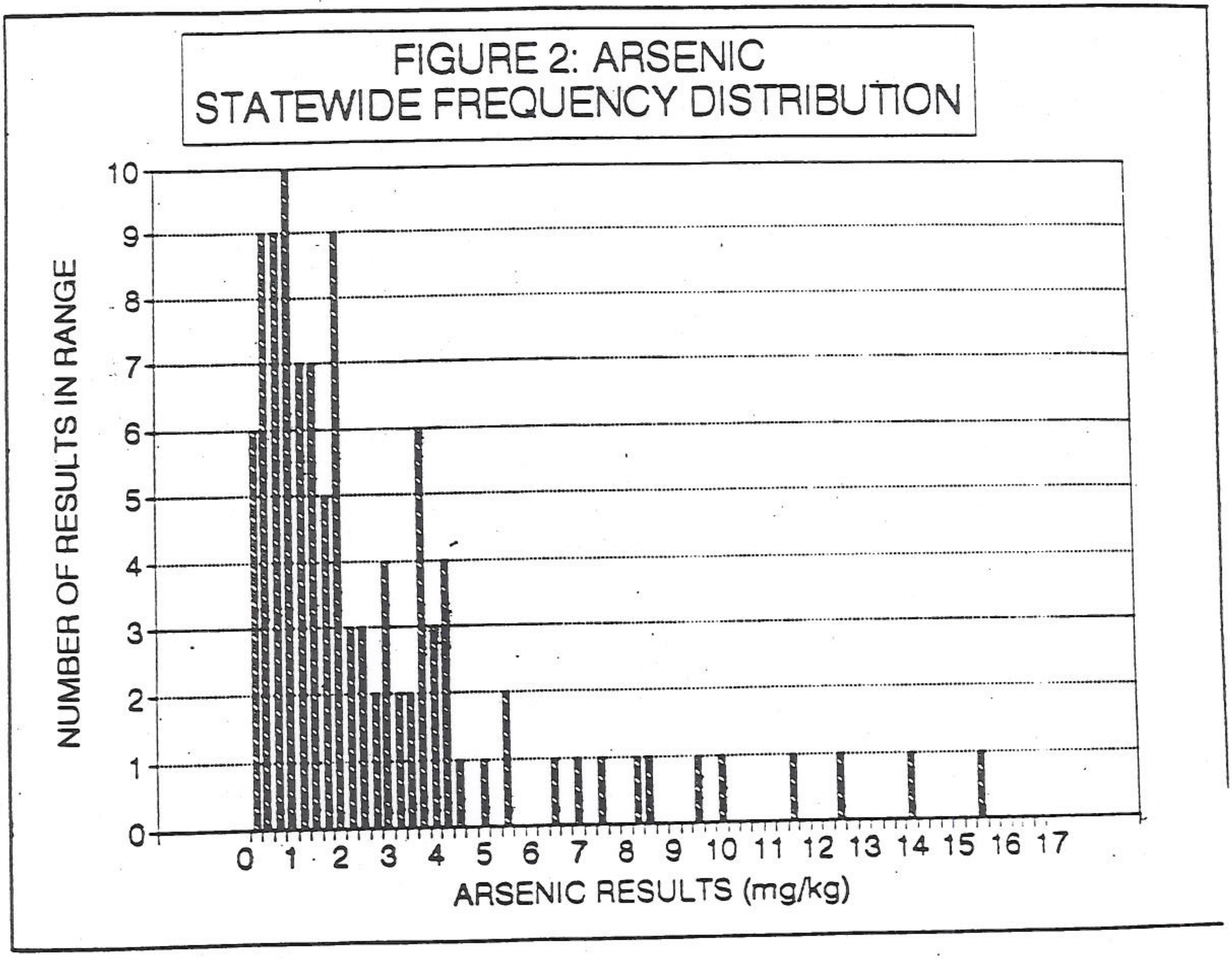
FIGURE 2: ARSENIC
STATEWIDE FREQUENCY DISTRIBUTION
NUMBER OF RESULTS IN RANGE
0
1
2
3
4
5
6
7
8
9
10
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
ARSENIC RESULTS (mg/kg)

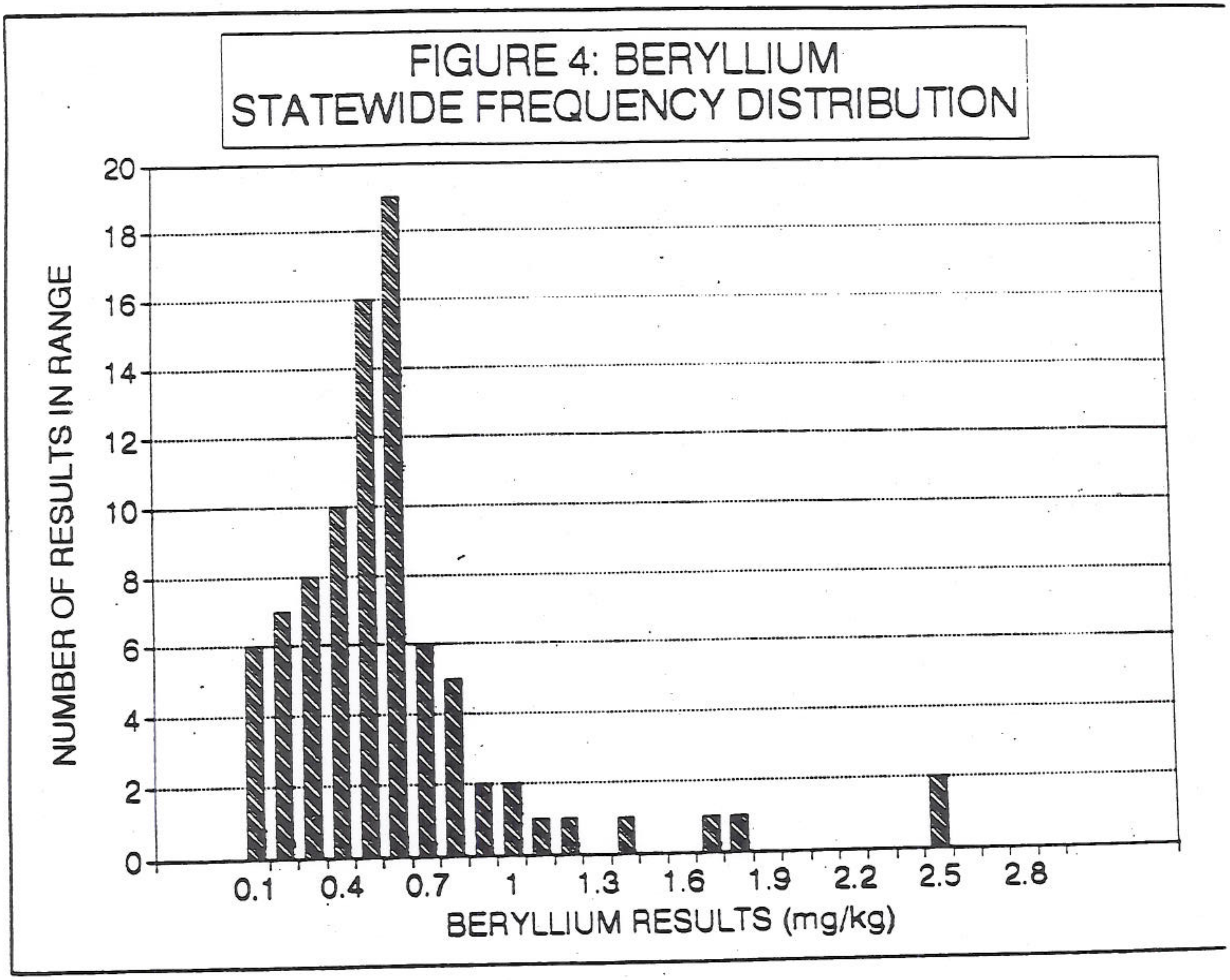

FIGURE 4: BERYLLIUM
STATEWIDE FREQUENCY DISTRIBUTION
NUMBER OF RESULTS IN RANGE
20
18
16
14
12
10
8
6
4
2
0
0.1
0.4
0.7
1
1.3
1.6
1.9
2.2
2.5
2.8
BERYLLIUM RESULTS (mg/kg)

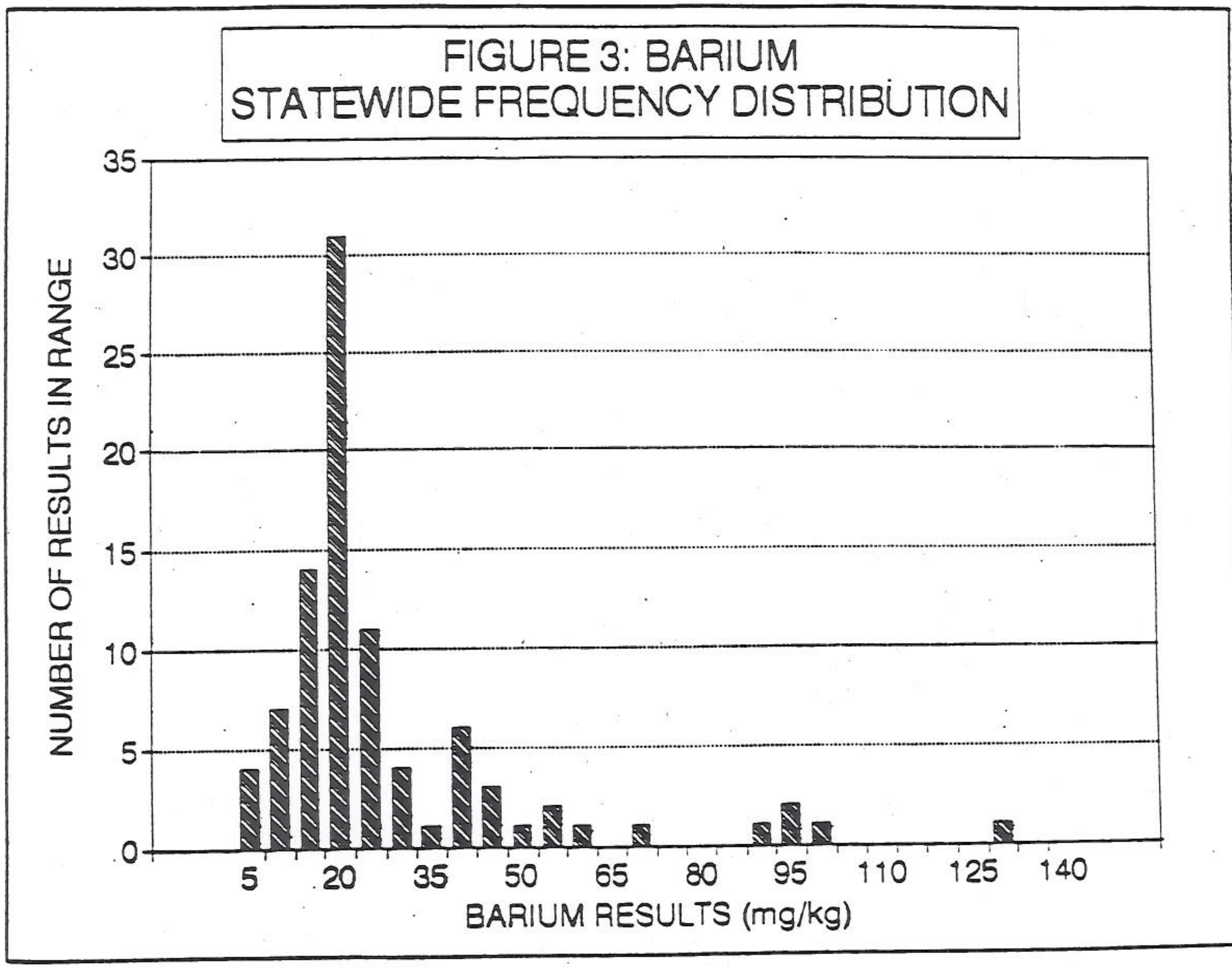
FIGURE 3: BARIUM
STATEWIDE FREQUENCY DISTRIBUTION
NUMBER OF RESULTS IN RANGE
0
5
10
15
20
25
30
35
5
20
35
50
65
80
95
110
125
140
BARIUM RESULTS (mg/kg)