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EFFECTS OF UPLAND DISPOSAL OF DREDGED MATERIAL ON GROUNDWATER QUALITY

by

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The objective of this study was to evaluate the impact of upland disposal of dredged material on groundwater quality. To this end, a baseline field study and sampling program was instituted at four case study sites: Grand Haven, Michigan; Sayreville, New Jersey; Houston, Texas; and Mobile, Alabama. Analyses of soil, disposed sediments, interstitial water, and groundwater were to provide information and data by which this impact could be quantified.		

(Continued)

20. ABSTRACT (Continued).

The initial phase of the study included a literature review. Preliminary field testing was performed to characterize the hydrogeological system to define leachate pathways and possible controlling mechanisms from each site.

Collection of groundwater samples consisted of two distinct sampling efforts. The initial study, U. S. Army Engineer Waterways Experiment Station Technical Report D-78-43, utilized 26 water samplers installed in or adjacent to each site, including 12 located within the dredged material, 10 offsite, and 4 directly below the site. Four field samplings were performed at approximately 3-month intervals.

The second sampling effort relied upon six groundwater wells; three wells were situated below each site, two samplers were downgradient from the fill, and the remaining well was designated as a background well. The total number of samplings consisted of two at Pinto Island, four at Grand Haven, and five at Sayreville and Houston.

(Analyses of leachates from this sampling effort showed data comparable to the initial study.) These data revealed that potential adverse water quality impact could exist. Degradation of groundwater resources within the proximity of the site would most probably be due to chloride, potassium, sodium, calcium, total organic carbon, alkalinity, iron, and manganese. Cadmium, copper, lead, mercury, nickel, zinc, and phosphorus concentrations were found to exist at levels that do not seem to pose water quality problems.

PREFACE

This report is the result of a continued field study designed to quantitatively describe the effect of the disposal of dredged material upon groundwater quality in confined upland disposal areas. The dredged material disposal areas of this investigation included the following four sites: Grand Haven, Michigan; Sayreville, New Jersey; Houston, Texas; and Mobile, Alabama.

This investigation was performed under an extension of Contract No. DACW39-76-C-0171 entitled, "Physical and Chemical Characterization of Dredged Material Sediments and Leachates in Confined Land Disposal Areas." The original contract between the U. S. Army Engineer Waterways Experiment Station (WES), Vicksburg, Mississippi, and the University of Southern California (USC), Los Angeles, California, was funded by the Dredged Material Research Program (DMRP), Work Unit 2D05, which was part of DMRP Task 2D, "Confined Disposal Area Effluent and Leachate Control," of the Environmental Impacts and Criteria Development Project (EICDP). The continuation of the contract was funded jointly by the Dredging Operations Technical Support Program and the following U. S. Army Engineer Districts: New York, Galveston, Mobile, and Detroit.

The research was conducted under the supervision of Dr. Kenneth Y. Chen, Professor and Director, Environmental Engineering Program University of Southern California. Laboratory and data analyses were coordinated by Robert D. Morrison. Individuals contributing to the laboratory analyses at USC were: R. Stearns, M. Lu, A. Anderson, G. Sawtelle, R. Santa Maria, A. Hsu, C. K. Tau, T. Tsai, and M. Cassidy. Ms. C. McMahon performed the editing and typing.

Field sampling at Grand Haven, Houston, and Mobile was conducted by

Mark Bulot of SCS Engineers of Long Beach, California, acting as subcontractor for USC in this study. Sampling at the Sayreville site was supervised by Chris Zeppe of the New York District.

The contract was monitored by Mr. R. E. Hoeppel, Environmental Laboratory (EL), WES, under the supervision of Dr. R. M. Engler, Manager of EICDP. The study was under the general supervision of Dr. John Harrison, Chief, EL.

Commanders and Directors of WES during the period of this study and preparation of this report were COL J. L. Cannon, CE, and COL N. P. Conover, CE. Technical Director was Mr. F. R. Brown.

CONTENTS

	<u>Page</u>
P R E F A C E	1
LIST OF FIGURES	4
CONVERSION FACTORS, U. S. CUSTOMARY TO METRIC (SI) UNITS OF MEASUREMENT	6
PART I: INTRODUCTION	7
PART II: SAMPLING PROGRAM	9
PART III: RESULTS AND DISCUSSION	15
Characteristics of Leachates	17
pH	17
Total Dissolved Solids (TDS)	33
Major Ions	36
Chlorinated Hydrocarbons'	59
Trace Metals	59
PART IV: PREDICTION OF WATER QUALITY	87
Introduction	87
Water Quality Models	87
Conclusions	112
PART V: CONCLUSIONS	115
APPENDIX A. GROUNDWATER ANALYSIS FOR SELECTED PARAMETERS AT THE FOUR CASE STUDY SITES	
APPENDIX B. SOLUBILITY EQUILIBRIUM GRAPHS FOR Cd, Cu, Fe, Mn, Ni, Pb, and Zn	
APPENDIX C. RESULTS OF SOLUBILITY EQUILIBRIUM CONCENTRATIONS	

LIST OF FIGURES

Number	<u>Page</u>
1. Houston site	10
2. Grand Haven site	11
3. Sayreville site	12
4. Pinto Island site	13
5. Relationship between cations and anions and total ionic concentration	35
6. Comparison of chloride values for groundwater samples	37
7. Comparison of alkalinity values for groundwater samples	39
8. Comparison of total carbon values for groundwater samples	41
9. Comparison of total organic carbon values for groundwater samples.	42
10. Comparison of total inorganic carbon values for groundwater samples	43
11. Comparison of organic nitrogen for groundwater samples	45
12. Comparison of ammonia nitrogen values for groundwater samples	46
13. Comparison of nitrate values for groundwater samples	47
14. Comparison of total phosphorus values for groundwater samples	49
15. Comparison of orthophosphate values for groundwater samples	50
16. Comparison of sulfate values for groundwater samples	52
17. Comparison of sodium values for groundwater samples	54
18. Comparison of potassium values for groundwater samples	55
19. Comparison of calcium values for groundwater samples	56
20. Comparison of magnesium values for groundwater samples	58
21. Comparison of cadmium values for groundwater samples	68
22. Comparison of copper values for groundwater samples	71
23. Comparison of iron values for groundwater samples	75
24. Comparison of lead values for groundwater samples	77

LIST OF FIGURES (Continued)

<u>Number</u>	<u>Page</u>
25. Comparison of manganese values for groundwater samples	79
26. Comparison of mercury values for groundwater samples	81
27. Comparison of nickel values for groundwater samples	83
28. Comparison of zinc values for groundwater samples	85
29. Na-Cl diagram for Sayreville	91
30. Na-Cl diagram for Pinto Island	92
31. Na-Cl diagram for Grand Haven	93
32. K-Cl diagram for Sayreville	94
33. K-Cl diagram for Pinto Island	95
34. K-Cl diagram for Grand Haven	96
35. Mg-Cl diagram for Sayreville	97
36. Mg-Cl diagram for Pinto Island	98
37. Mg-Cl diagram for Grand Haven	99
38. Ca-Cl diagram for Sayreville	100
39. Ca-Cl diagram for Grand Haven	101

CONVERSION FACTORS, U. S. CUSTOMARY TO METRIC (SI)

UNITS OF MEASUREMENT

U. S. customary units of measurement used in this report can be converted to metric (SI) units as follows:

<u> Multiply </u>	<u> By </u>	<u> To Obtain </u>
Feet	0.3048	Metres
Miles (U. S. statute)	1.609344	Kilometres

EFFECTS OF UPLAND DISPOSAL OF DREDGED MATERIAL
ON GROUNDWATER QUALITY

PART I: INTRODUCTION

1. The purpose of this study was to understand the fate of contaminants within sediments placed in upland disposal sites. The scope of work was defined and performed to achieve the following twofold objectives:

a. To perform a detailed physical and chemical characterization of dredged sediment and subsoil core samples at all sampling sites. These data were to be used to define:

- (1) Contaminant levels in the dredged sediments and adjacent soils.
- (2) Correlation between total contaminant levels and contaminant mobility.
- (3) Transport mechanisms responsible for contaminant migration.

b. To monitor leachate and groundwater quality at different dredged material land disposal sites. This information was to be used to determine:

- (1) Time-dependent changes in leachate quality at different depths.
- (2) Effects of soil attenuation of mobile constituents.
- (3) Changes in soil moisture.
- (4) Groundwater dilution of leachates.

2. Some of these original goals were modified so that areas of particular interest could be studied in detail during the project continuation. Of special interest were the following:

- a. **Verification of postulated transport mechanisms developed in the initial phase of the study.***
- b. **Impact of water quality parameters omitted in the initial phase of the study.***
- c. **Correlation of data trends between the initial phase and the subsequent analysis.**
- d. **Development of predictive methodology of groundwater quality resulting from upland disposal of dredged material.**

3. **Due to budgetary constraints, only leachate and groundwater samples were collected and analyzed in this phase. The background data collected for the first phase study was also included to ascertain the temporal impact of upland dredged material disposal on groundwater quality.**

* Yu, K.Y. et al. 1978. "Physical and Chemical Characterization of Dredged Material Sediments and Leachates in Confined Land Disposal Areas," Technical Report D-78-43, U. S. Army Engineer Waterways Experiment Station, CE, Vicksburg, Miss.

PART II: SAMPLING PROGRAM

4. The four upland dredged material disposal sites chosen for the original study were again sampled in this study phase. The four sites were as follows:

- a. Houston, Texas (Clinton site) (Figure 1).
- b. Grand Haven, Michigan (Verplanks' Coal and Dock Co. site) (Figure 2).
- c. Sayreville, New Jersey (National Lead Industries, #4 site) (Figure 3).
- d. Mobile, Alabama (Pinto Island site) (Figure 4).

Detailed physiographical and hydrogeological descriptions of each facility are described in the original report.*

5. Six groundwater monitoring wells from the original study were chosen for sampling. Well selections for the present study were based on the following rationale: availability and importance of the data from the original study, proximity of wells to one another for modeling purposes, ease of access throughout the sampling program ability to collect the requisite sample volume, and location within the hydrogeological system. These criteria and others were considered in selecting wells illustrated in Figures 1-4. Of the designated wells, three were situated directly beneath the disposal site while two were located off-site along observed groundwater flow directions. One well was designated as a background well. Well logs describing lithology for each site can be reviewed in Appendices B, D, F, and H of the original report.*

* Yu, K. Y. et al. 1978. "Physical and Chemical Characterization of Dredged Material Sediments and Leachates in Confined Land Disposal Areas," Technical Report D-78-43, U. S. Army Engineer Waterways Experiment Station, CE, Vicksburg, Miss.

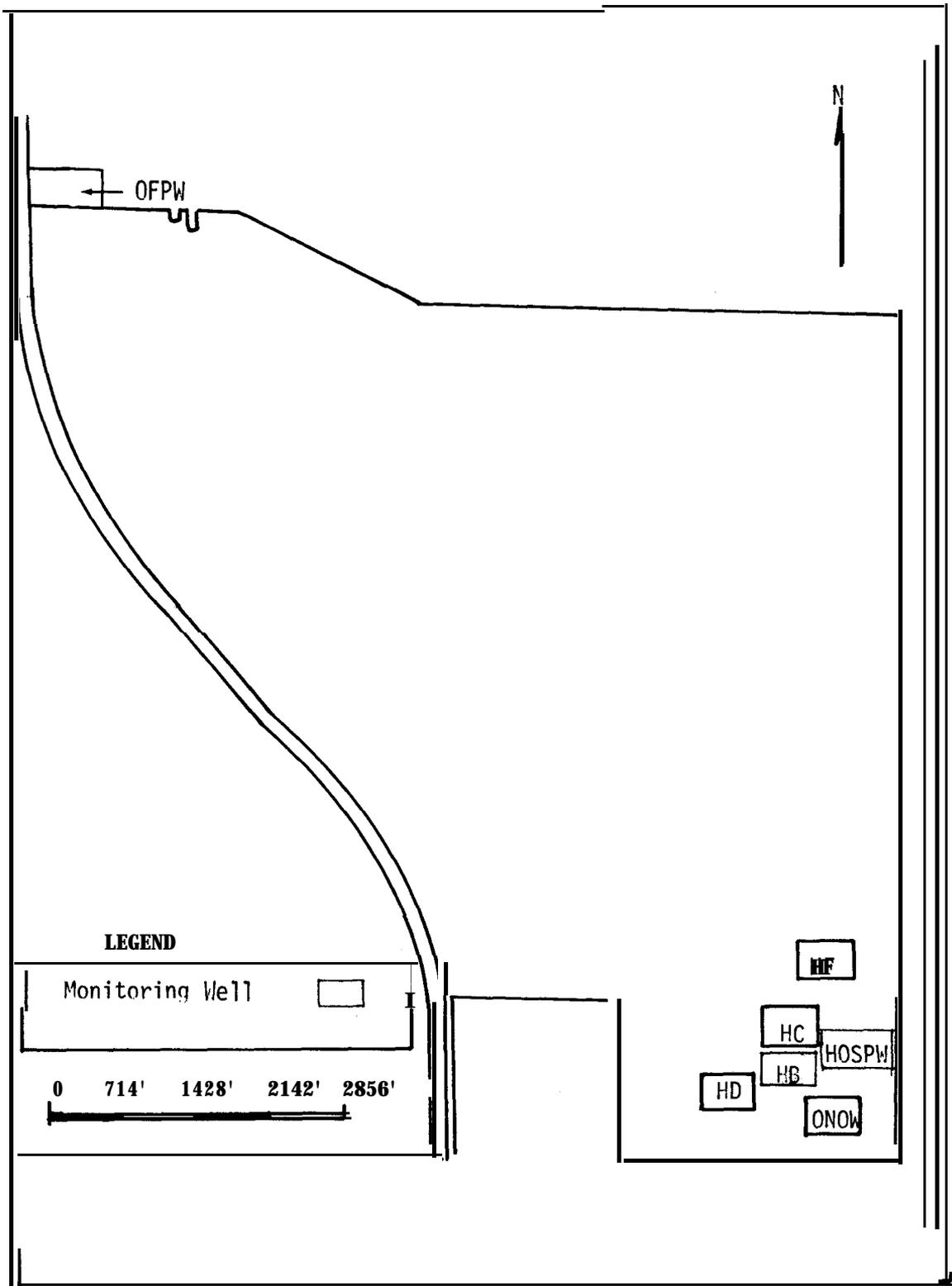


Figure 1. Houston site

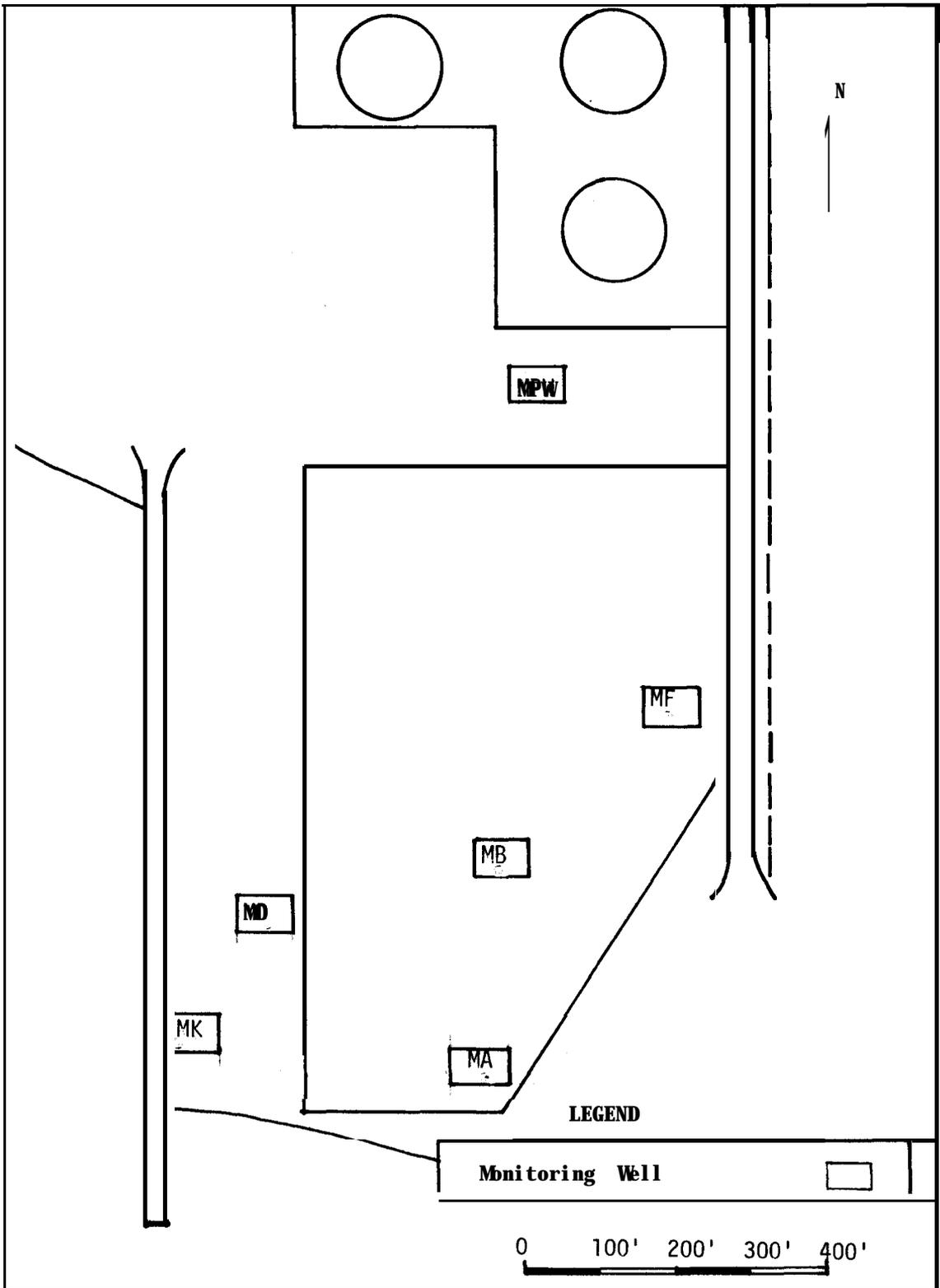


Figure 2. Grand Haven site

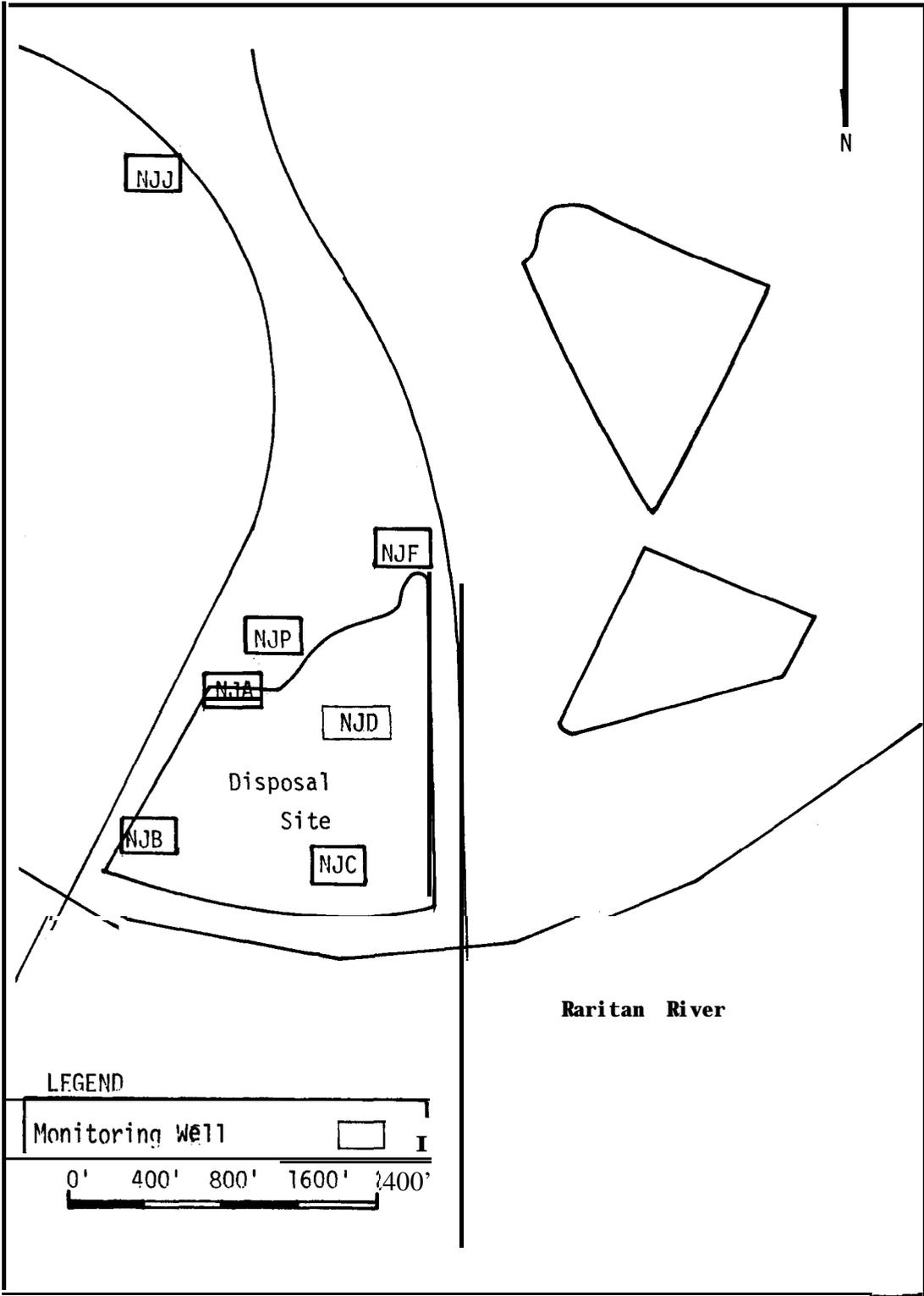


Figure 3. Sayreville site

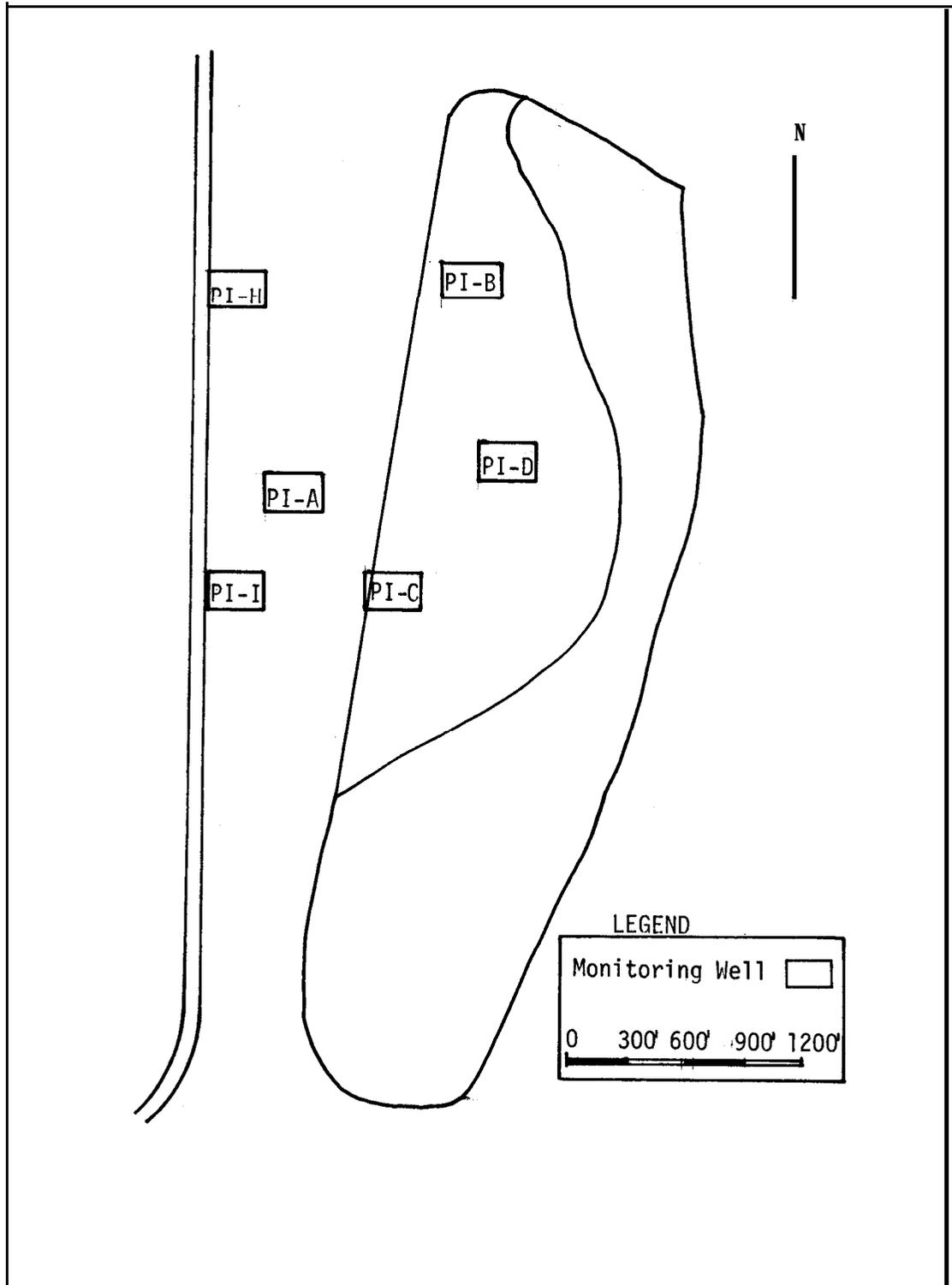


Figure 4. Pinto Island site

6. In several instances, sampling wells from the first phase study were unavailable. Because of vandalism a new offsite well (MK) was installed downgradient from the Grand Haven site. At the Michigan and Houston sites, wells situated offsite (MPW and OFPW) which were previously utilized for pumping tests were used for sampling purposes. The original wells at Pinto Island were utilized for sampling.

7. Existing wells at Sayreville were used for the initial four sampling visits. Prior to the fifth sampling, however, all offsite wells were destroyed. Therefore, the fifth and final sampling visit to Sayreville resulted in sampling only four onsite locations (NJA, NJB, NJC, NJD) . While well NJD was not sampled during the first four visits of the study, the data were available from the previous study.

8. Sampling procedures and methodologies developed during the course of the original project were followed in an effort to provide correlatable results between two series of data. Frequency of sampling varied among the four sites. The Pinto Island site was sampled only twice due to budgetary constraints. The number of sampling periods and dates are as follows:

Site	Sampling Period				
	1	2	3	4	5
Grand Haven, Michigan	9/7/78	12/11/78	1/22/79	3/31/79	
Sayreville, New Jersey	11/27/78	12/29/78	1/28/79	3/25/79	7/16/79
Houston, Texas	9/5/78	12/3/78	1/20/79	3/25/79	6/10/79
Pinto Island, Alabama	5/26/79	7/5/79			

PART III: RESULTS AND DISCUSSION

9. Analysis of groundwater during the second sampling program was designed to complement data from the initial effort. Analytical emphasis of these water samples deviated from the original study so that unnecessary repetition of data would be avoided.

10. Due to inadequate sample volume in some cases, the priority for analysis was needed. Evaluation of the results or lack of data from the original study determined analysis priorities in this phase. The order of priority was determined as follows:

- a. Chlorinated hydrocarbons.
- b. Trace metals.
- c. Nitrogen and phosphorus species.

Due to the low level of chlorinated hydrocarbons, especially polychlorinated biphenyls (PCB's) in water samples, extraction of large volumes of water is required in order to detect PCB's presence; therefore, in some cases, analysis of other parameters was eliminated.

11. For purposes of statistical comparison, a well grouping scheme was devised which roughly paralleled that developed in the initial study. The well grouping for each site was as follows:

<u>Site</u>	<u>Background (BG)</u>	<u>Undersite (US)</u>	<u>Monitoring (Mw)</u>
Grand Haven, Michigan	MPW	MA, MB, MG	MD, MK
Sayreville, New Jersey	NJJ	NJA, NJB, NJC, NJD	NJF, NJP
Houston, Texas	OPFW	HB, HC, HD, HE, HDSPW ONOW	None
Pinto [S]and, Alabama	PI-I	PI-B, PI-C, PI-D	PI-H, PI-A

12. The well designations (i.e., BG, US, and Mw) correspond to

the following categories:

- a. BG (background) represents a well whose water samples were deemed representative of indigenous groundwater quality.
- b. US (undersite) refers to a well situated in the zone directly underlying the disposal site.
- c. MW (monitoring well) consists of wells located downgradient hydrologically from the site and US wells.

13. This scheme was maintained throughout the project except at the Houston site where continuity of site water with the groundwater was highly suspect due to the presence of a thick, continuous clay subsoil. Therefore, only one well (OPW) was designated as a background well while no offsite monitoring wells were sampled.

14. A statistical approach ("P" values) based upon sample variation (i.e., mean and range) was used for data evaluation.

15. The students t-test was used to analyze the significance of the differences between the three previously described well groups. Probability values developed from the t-test data were calculated to reflect the probability of having value differences larger than chance. Table 1 lists the results of this analysis. Low "p" values listed in Table 1 indicate that statistical similarity is high for the two well groups considered.

16. In order to compare the results of the "p" values in Table 1 with the probability data obtained in the original study, a comparison between the corresponding well groups was conducted. This comparison between the two data sets, listed in Table 2, was developed utilizing the more extensive data collected in the original study as a base for comparison. (The resulting difference is listed as either plus or

minus by which the groundwater "p" values differed from the earlier "p" amounts).

17. While comparisons presented in Table 2 provide a generalized view of these differences, individual sampling stations comprising the well groupings selected in the initial study were not identical to those used in these analyses. Another major difference is that, in the original effort, data were collected from samplers located in the zone of aeration and within the fill material while this analysis included only leachate and groundwater samples. These differences account for some of the observed discrepancies in the "p" values.

Characteristics of Leachates

18. Presentation of the groundwater data includes statistical comparison of the three well groups. Similarities and differences between the "p" values obtained for this study as compared to the results from the first phase study are discussed. Individual sample analyses are presented in Appendix A. Graphic presentation of the data is illustrated in Figures 6-28 in which the range and mean concentration values for the three well groups (BG, US, MW) are listed.

pH

19. For leachate migration, pH is a major factor in regulating the rates and extent of the reactions occurring at the soil/water interface. pH measurements were made in the field at the time of sample collection, as well as an analysis in the laboratory upon receipt of the samples.

20. Samples from the Sayreville site exhibited unusually low pH values with a range of 3.4 to 6.7 for the various well groups.

Table 1

Statistical Characteristics of Groundwaters

Parameter	Site	Location	# of Samples	Range	Mean	S. D.	BG vs MW	BG vs US	US vs MW
pH	Grand Haven	BG	1	6.9 - 7.3	7.1	0.17			
		US	8	6.8 - 8.0	7.1	0.31	0.42	0.7	0.7
		MW	4	6.9 - 7.3	7.0	0.14			
Houston	BG	4	6.7 - 7.6	7.0	0.24				
	US	20	6.6 - 7.6	7.0	0.24		0.79		
Sayreville	Sayreville	BG	4	3.1 - 3.7	3.40	0.29			
		US	16	6.1 - 7.2	6.53	0.29	0.01	0.01	0.48
		MW	7	6.2 - 7.3	6.74	0.49			
Pinto Island	Pinto Island	BG	2	7.0 - 7.5	7.25	0.35			
		US	6	6.9 - 7.5	7.22	0.26	0.65	0.9	0.58
		MW	4	6.8 - 7.4	7.10	0.35			
Grand Haven	Grand Haven	BG	20						
		US	88	249 - 4810	109	98.9			
		MW	a	10	994	1930	2050	0.54	0.01
Houston	Houston	BG	2	307 - 731	498	300			
		US	1100	-9160	5574	2350		0.001	
		MW	4	469 - 7040	764	223			
Sayreville	Sayreville	BG	16	6750 - 9950	8660	1040	0.01	0.001	0.001
		US	7	1570 - 5030	3150	1620			
		MW	4		67	17			
Pinto Island	Pinto Island	BG	4	59 - 280	181	64	0.09	0.03	0.38
		US	4	72 - 509	290	200			
		MW	2						

(Continued)

NA = not available; ND = not detectable.

Table 1 (Continued)

Parameter	Site	Location	# of Samples	Range	Mean	S. D.	BG vs MW	BG vs US	us vs MW
Alkalinity, ppm	Grand Haven	BG	12	-	27.7	15.1			
		US	17	331 - 47.5	89.5	88.6	0.1	0.035	0.88
		MW	20	260	84.7	87.0			
	Houston	BG	18	80	46.1	23.2	--	0.01	--
		US	40	257	137	82.3			
	Sayreville	BG	N0		ND	0			
		US	16		69	49.7	--	--	0.01
		MW	7	17.9	21.1	14.5			
	Pinto Island	BG	56	187	121	92.6			
		US	6	5.6 - 30	20.6	9.2	0.22	0.18	0.37
		MW	4	19 - 28	25	4.2			
	Grand Haven	BG	50	105	77.5	30.6			
US		50	452	242	137	0.99	0.01	0.01	
MW		42	407	77	38.5				
Houston	BG	52	177	118	48.6	--	0.01	--	
	us	44	490	364	105				
Sayreville	BG	4	40	15.8	16.4				
	US	16	430	202	112	0.01	0.01	0.013	
	MW	7	200	113	45.3				
Pinto Island	BG	75	85	80	7.07				
	US	28	100	68.8	23.5	0.4	0.38	0.9	
	MW	4	90	66.2	28				

(Continued)

Table 1 (Continued)

Parameter	Site	Location	# of Samples	Range	Mean	S. D.	BG vs MW	BG vs US	us vs MW
Total Organic Carbon, ppm	Grand Haven	BG	4	21 - 64	35.5	19.5			
		us	12	25 - 282	136	93	0.38	0.01	0.01
		MW	8	22 - 122	50.5	30.9			
	Houston	BG	5		41.3				
		US	25	11 - 117	66	105		0.01	--
	Sayreville	BG	4	1.5 - 33	9.63	15.6			
		US	16	13.5 - 220	90.7	66.2	0.025	0.01	0.51
		MW	7	12 - 176	72.4	57.4			
	Pinto Island	BG	2	50 - 63	56.5	9.19			
		US	6	16 - 55	40.7	14.3	0.7	0.7	0.94
		MW	4	20 - 55	40.0	14.7			
	Grand Haven	BG	4	20 - 80	42	26.5			
US		12	25 - 180	105	82.7	0.34	0.035	0.01	
MW		8	20 - 45	26.5	8.2				
Houston	BG	5	34 - 63	52.4	11.4				
	us	25	36 - 450	194	125		0.01	--	
Total Inorganic Carbon, ppm	Sayreville	BG	4	0.2 - 10	6.15	3.28			
		US	16	10 - 200	97.6	97.6	0.01	0.01	0.038
	Pinto Island	BG	2	24 - 68	41.0	18.3			
		us	6	22 - 25	23.5	2.12			
MW	us	10	10 - 65	28.1	20.1	0.79	0.6	0.86	
	MW	4	10 - 45	26.2	16.5				

(Continued)

Table 1 (Continued)

Parameter	Site	Location	# of Samples	Range	Mean	S. D.	B	G	v	BG ss US		us vs MW
										MW	MW	
TKN, ppm	Grand Haven	BG	4	11.1 - 24.5	17.6	6.17						
		US	12	24.7 - 76.3	44.7	16.9	0.01				0.01	0.01
	Houston	MW	8	0 - 13.7	4.25	5.5						
		BG	5	9.9 - 30	21.0	9.07					0.01	
	Sayreville	US	25	0 - 435	7.13	121						
		BG	4	4.2 - 117 21.7	12.9	7.2						
	Pinto Island	US	16	41.0 -	71.0	21.3	0.03				0.01	0.15
		MW	7	1.4 - 73.5	38.4	29.4						
	Grand Haven	BG	2	11.7 - 97	24.6	18.2						
		US	6	0 - 13.3	4.02	4.68	0.01				0.01	0.91
	Houston	Mw	4	0 - 11.2	4.10	5.1						
		BG	4	0 - 7.0	3.72	3.46						
Sayreville	US	12	0 - 18	7.20	6.26	0.85				0.7	0.01	
	MW	8	0 - 11.9	4.01	5.04							
Pinto Island	BG	2	0 - 313 16.7	6.45	6.49							
	US	4	0 - 20.8	20.5	62.0					0.01		
Organic Nitrogen, ppm	Sayreville	BG	4	4.2 - 20.8	10.7	8.2						
		US	16	0 - 45	18.7	13.2	0.01				0.01	0.3
Pinto Island	Mw	BG	7	1.4 - 10.5	5.80	3.1						
		US	2	2.5 - 0.7	2.0	0.71						
Grand Haven	Mw	BG	6	1.5 - 0.7	0.12	0.29					0.01	
		US	4	0 - 0	0	0						--

(Continued)

Table 1 (Continued)

Parameter	Site	Location	# of Samples	Range	Mean	S. D.	BG vs MW	BG vs US	US vs MW
Ammonia Nitrogen, ppm	Grand Haven	BG	4	ND - 1.4	0.77	0.59			
		US	11	ND - 7.2	2.7	2.5	1.42	-3.15	4.87
		MW	6	ND - .72	0.14	0.29			
	Houston	BG	2	0.7 - 2.8	4.7				
		US	420	ND - 420	11.2	2.1		-3.97	
	Sayreville	BG	3	ND - 5.7	0.19	0.32			
		US	9	3 - 13.1	5.6	3.19	-4.31	-7.97	1.21
		MW	6	ND - 13.1	4.3	4.8			
	Pinto Island	BG	2	ND 0.2 - 3.5	22.6	17.5			
US		6	ND - 11.2	3.8	4.4	5.84	6.10	-0.21	
MW		4	ND - 11.2	4.1	5.06				
Nitrate, ppm	Grand Haven	BG	4	0.46 - 6	3.5	2.3			
		US	12	0.52 - 57	22.1	21.7	0.60	0.011	0.06
		MW	8	0.5 - 38	6.1	13.0			
	Houston	BG	5	0.38 - 47.5	15.9	18.6			
		US	25	0.3 - 97.8	20.5	26.4		-0.63	
	Sayreville	BG	3	0.67 - 2.2	1.62	0.83			
MW		6	2.1 - 66.4	45.4	13.9	0.03	-0.001	0.01	
Pinto Island	BG	2	ND, 44 - 7.56	0.50	0.08				
	US	6	ND - 67.6	1.38	3.0	0.50	0.50	0.90	
	MW	4	ND - 67.6	1.59	2.9				

(Continued)

Table 1 (Continued)

Parameter	Site	Location	# of Samples	Range		Mean	S. D.	BG VS MW	BG VS US	us vs MW
Nitrite, ppm	Grand Haven	BG		0.006	0.1	0.03	0.05			
		US	1:	0.008	0.46	0.05	1.3	-0.413	-1.55	1.18
		MW	8	0.003	0.3	0.12	0.28			
	Houston	BG	5	0.12	0.5	0.214	0.16			
		US	25	ND	1.1	0.27	0.28		-0.269	**
	Sayreville	BG	3	0.01	0.15	0.063	0.076			
		US	9	0.07	2.1	0.551	0.74	-1.43	-1.48	1.32
		MW	6	0.008	0.4	0.098	0.17			
	Pinto Island	BG	2	0.008	0.04	0.025	0.024			
		US	6	0.005	0.16	0.059	0.069	-0.343	-0.221	-0.196
		MW	4	0.004	0.35	0.104	0.164			
	Grand Haven	BG		ND	0.28	0.08	0.012			
US		1:	ND	0.35	0.07	0.12	0.51	0.92	0.37	
MW		8	ND	0.53	0.14	0.17				
Houston	BG	2:	ND	5	3.11	3.4				
	US		ND	5	2.13	3.5		0.58	**	
Sayreville	BG	4	ND	406	0.124	0.19				
	US	16	ND	1.40	0.125	0.34	0.70	0.99	0.60	
	MW	7	ND	0.388	0.081	0.14				
Pinto Island	BG	2	ND	0.031	0.016	0.2				
	US	6	ND	1.73	0.722	0.88	0.31	0.10	0.28	
	MW	4	ND	0.781	0.218	0.33				

(Continued)

Table 1 (Continued)

Parameter	Site	Location	# of Samples	Range		Mean	S.	D.	BG vs MW	BG vs US	us vs Mw
				BG	Mw						
Sulfate, ppm	Grand Haven	BG	4	58							
		US	12	100	255	167	99				
		MW	8	47	1480 658	585 316	536 212		0.13	0.02	0.15
	Houston	BG	2	19	5000	779	1298				
		US	4				1358			0.05	--
		MW	16	376	810	553	186				
	Sayreville	BG	7	259	2680	1190	758		0.015	0.01	0.01
		US	4	154	382	243	101				
		MW	2	26		55					
	Pinto Island	BG	2	73	3::	179	7.4				
		US	6				9.5			0.47	0.01
		MW	4	27	57	42	15				
Grand Haven	BG	4	0								
	US	12	0.1	1.2	0.38	0.56					
	MW	8	0.06	1.8	2.56	3.13		0.38	0.04	0.075	
	BG	5	0.4	7.2	3.09	3.40					
	US	25	0.1	54	6.89	13.0		--	0.22	--	
	MW	7	ND								
Houston Sayreville	BG	4	ND	0.2	0.063	0.095					
	US	16	ND	0.8	0.303	0.237		0.60	0.01	0.01	
	MW	7	ND	0.2	0.097	0.100					
	BG	2	0.1	0.3	0.2	0.14					
	US	6	0.06	1.4	0.61	0.63		0.28	0.20	0.08	
	MW	4	0.05	0.126	0.072	0.037					

(Continued)

Table 1 (Continued)

Parameter	Site	Location	# of Samples	Range		Mean	S. D.	BG vs MW	BG vs US	us vs MW
				min	max					
Sodium ppm	Grand Haven	BG	4	9	13	11.0	1.93			
		US	12	36	1930	726	800	0.38	0.01	0.03
		MW	8	8.8	832	119	288			
	Houston	BG	3	74	204	146	66.1		0.001	--
		US	15	452	3590	2010	1090			
	Sayreville	BG	4	308	1710	389	693			
		US	9	1640	5020	2070	1390	0.025	0.001	0.01
		MW	6	279	2910	1170	1030			
	Pinto Island	BG	2	50	53	51.4	1.9			
		us	6	8	199	83.9	87.5	0.07	0.42	0.29
		MW	4	70	253	148	77.8			
	Grand Haven	BG	US	4	2.5	10.6	4.8	3.8		
US			12	1.4	70	16.9	12.2	0.85	0.01	0.01
MW			8	0.67	17	5.3	5.8			
Houston		BG	3	5	208	16.5	12.7		0.01	--
		US	15	7	208	173	99.8			
Sayreville	BG	3	5	17	10	6.2				
	us	9	85	101	91.3	4.8	0.01	0.01	0.01	
	MW	6	25	82	46.1	21.5				
Pinto Island	BG	2	10	13.5	11.7	2.4				
	US	6		31	21.0	7.5	0.3	0.04	0.08	
	MW	4	12.3	18	14	2.4				

(Continued)

Table 1 (Continued)

Parameter	Site	Location	# of Samples	Range	Mean	S. D.	BG vs MW	BG vs US	us vs MW
Calcium ppm	Grand Haven	BG	4	2.5 - 10.6	4.8	3.8			
		US	12	1.4 - 70	16.9	12.2	0.85	0.01	0.01
		MW	8	0.67 - 17	5.3	5.8			
	Houston	BG	3	90 - 126	102	20.5	**	0.01	--
		US	15	95 - 613	309	107			
	Sayreville	BG	3	19 - 48	33.4	14.4	0.04	0.01	0.01
		US	9	79 - 464	303	144			
		MW	6	28 - 96	67.3	22.4			
	Pinto Island	BG	2	30 - 36	33.6	3.96	0.25	0.22	0.99
		US	6	22 - 94	21.0	0.41			
		MW	4	29 - 86	14	25.6			
	Magnesium ppm	Grand Haven	BG	4	6 - 21.2	12.6	6.85		
US			12	10 - 170	63.0	46.5	0.15	0.01	0.01
MW			8	5 - 32	19.7	8.05			
Houston		BG	3	10 - 130	73.0	51.7	--	0.01	--
		US	15	40 - 675					
Sayreville		BG	3	95 - 160	128	32.5	0.46	0.01	0.01
	MW	6	186 - 770	492	190.0				
Pinto Island	BG	2	74 - 250	155	65.2				
	US	1	13.5 - 16.8	15.1	2.33	0.12	0.04	0.15	
	MW	1	13.3 - 16.7	31.4	14.6				

(Continued)

Table 1 (Continued)

Parameter	Site	Location	# of Samples	Range	Mean	S. D.	BG vs MW	BG vs US	us vs MW
Cadmium ppb	Grand Haven	BG	3	ND - 1	0.83	1.04	0.37	0.46	0.49
		US	6	ND - 0.5	0.22	0.23			
		MW							
	Houston	BG	3	ND - 4	1.50	2.18		0.1	--
		US	15	0.3 - 7	1.1	20.5			
		MW	6	2 - 118	100.645	14.84	0.2	0.88	0.3
	Pinto Island	BG	NA		NA	NA	NA	NA	NA
		US	NA		NA	NA	NA	NA	NA
		MW	NA		NA	NA	NA	NA	NA
Grand Haven	BG	US	3	7 - 40	25.6	16.9			
		US	9	5 - 50	30.5	16.3	0.63	0.68	0.24
		MW	6	10 - 50	20.0	15.5			
	Houston	BG	3	ND - 20	15.0	2.18		0.1	
		US	15	10 - 130	10.9	20.5			
		MW	3						
Sayreville	US	9	41 - 1300	548	663				
	MW	6	2.5 - 270	101.388	81.184	0.2	0.3	0.08	
Pinto Island	BG	NA		NA	NA	NA	NA	NA	
	US	NA		NA	NA	NA	NA	NA	
	MW	NA		NA	NA	NA	NA	NA	

(Continued)

Table 1 (Continued)

Parameter	Site	Location	# of Samples	Range	Mean	S. D.	BG vs MW	BG vs US	US vs MW
Iron, ppm	Grand Haven	BG	3	0.02 - 0.50	0.40	c.173			
		US	9	0.20 - 7.20	1.5	2.24	0.07	0.15	0.55
		MW	6	1.0 - 1.70	1.4	0.63			
	Houston	BG	3	0.02 - 0.8	0.47	0.405	--	0.1	--
		US	15	0.51 - 17	2.55	4.69			
	Sayreville	BG	3	0.5 - 2.84	1.4	1.0	0.18	0.01	0.12
		US	9	0.002 - 4	0.60	0.67			
		MW	6	N0 - 7.8	1.94	3.0			
	Pinto Island	BG	NA	NA	NA	NA	NA	NA	NA
		US	NA	NA	NA	NA	NA	NA	NA
		MW	NA	NA	NA	NA	NA	NA	NA
	Lead, ppb	Grand Haven	BG	3	0.1 - 10	0.7	0.5		
US			9	0.1 - 40	11.2	13.5	0.3	0.05	0.09
MW			6	0.2 - 10	2.5	3.7			
Houston		BG	3	2 - 20	9.6	9.2	--	0.01	--
		US	15	9 - 100	45.9	24.2			
Sayreville		BG	3	3.0 - 0.2	9.3	7.7	0.71	0.78	0.9
	us	9		11.4	18				
	Mw	6	4.0 - 17	12.5	16.9				
Pinto Island	BG	NA	NA	NA	NA	NA	NA	NA	
	us	NA	NA	NA	NA	NA	NA	NA	
	Mw	NA	NA	NA	NA	NA	NA	NA	

(Continued)

Table 1 (Continued)

Parameter	Site	Location	# of Samples	Range	Mean	S. D.	BG vs MW	BG vs US	US vs MW
Manganese, ppm	Grand Haven	BG	3	0.05 - 0.5	0.32	0.24			
		us	9	0.2 - 17	4.1	5.5	0.68	0.08	0.06
		MW	5	0.02 - 1	0.4	0.46			
	Houston	BG	3	ND - 4	1.7	0.20		0.038	
		us	15	ND - 20	6.5	6.5			
	Sayreville	BG	3	2 - 28.9	11.6	14.9			
		US	9	0.86 - 18	7.1	6.0	0.28	0.63	0.01
		MW	6	0.22 - 1	0.64	0.33			
	Pinto Island	BG	NA	NA	NA	NA	NA	NA	NA
US		NA	NA	NA	NA	NA	NA	NA	
MW		NA	NA	NA	NA	NA	NA	NA	
Mercury, ppb	Grand Haven	BG	3	0.3 - 1.9	1.2	0.8			
		US	9	0.1 - 2.6	1.5	0.9	0.99	0.63	0.5
		MW	6	0.2 - 2.2	1.2	0.7			
	Houston	BG	3	0.02 - 0.06	0.037	0.02		0.04	
		us	15	0.01 - 0.31	0.13	0.102			
	Sayreville	BG	3	ND	1.4	1.2			
US		9	ND	1.8	0.4	0.9	0.65	0.55	
MW		6	ND	1.3	1.5				
Pinto Island	BG	NA	NA	NA	NA	NA	NA	NA	
	US	NA	NA	NA	NA	NA	NA	NA	
	MW	NA	NA	NA	NA	NA	NA	NA	

(Continued)

Table 1. (Concluded)

Parameter	Site	Location	# of p I e s	Range		Mean	S. D.	BG vs. MW	BG vs US	US vs MW	
				Min	Max						
Nickel, ppb	Grand Haven	BG	3	8		11					
		US	9	10 - 15		86.9	119 3.6	0.4	0.09	0.1	
		MW	6	6 - 40		15.8	12.8				
	Houston	BG	3	ND	40	2.3	20.7		0.9		
		US	15								
	Sayreville	BG	3		13 - 500	656	65.9				
US		9		1.8 - 420	37.0	174 21.3	0.43	0.27	0.2		
MW		6									
Pinto Island	BG	NA			NA	NA					
	us	NA			NA	NA		NA	NA	NA	
	MW	NA			NA	NA					
Grand Haven	BG	3		0.2 - 0.26	0.23	0.03					
	us	9		0.05 - 0.5	0.22	0.16	0.25	0.38	0.45		
	MW	6		0.06 - 0.6	0.16	0.12					
Houston	BG	3		0.05 - 0.06	0.04	0.03		0.06			
	US	15		0.02 - 0.8	0.15	0.21					
Sayreville	BG	9		1.8 - 2.6	2.16	0.40					
	us	6		0.09 - 3.1	0.78	1.08	0.01	0.01	0.1		
	MW			0.003 - 0.52	0.16	0.21					
Pinto Island	BG	NA			NA	NA					
	US	NA			NA	NA		NA	NA	NA	
	MW	NA			NA	NA					

NA = Not available.
 ND = Not detectable.

T a b l e 2**Percentage Difference Between Data Sets**

Parameter	Site	Comparison*		
		BG vs MW	BG vs US	US vs MW
Potassium	Grand Haven	-0.35	-0.14	0.01
	Sayreville	0.89	0.06	0.005
	Pinto Island	-0.03	-0.03	0.07
Sodium	Grand Haven	-0.27	0.19	0.15
	Sayreville	0.08	0.009	0.0
	Pinto Island	0.18	-0.41	-0.28
Calcium	Grand Haven	0.03	0.0	0.0
	Sayreville	0.11	0.0	0.0
	Pinto Island	0.20	-0.21	-0.98
Magnesium	Grand Haven	0.20	0.01	0.0
	Sayreville	-0.18	0.0	0.0
	Pinto Island	0.08	0.0	-0.14
Sulfate	Grand Haven	0.09	0.66	-0.03
	Sayreville	0.10	0.0	0.0
	Pinto Island	-0.17	-0.32	-0.24
Alkalinity	Grand Haven	0.21	-0.025	-0.87
	Sayreville			0.03
	Pinto Island	-0.15	-0.16	-0.36
TOC	Grand Haven	0.37	0.11	0.0
	Sayreville	0.21	0.0	-0.49
	Pinto Island	-0.63	-0.69	-0.64
Cadmium	Grand Haven	-0.02	-0.26	0.0
	Sayreville	0.6	-0.65	0.02
	Pinto Island	NA	NA	NA
Nickel	Grand Haven	-0.39	-0.02	-0.07
	Sayreville	-0.33	0.03	0.18
	Pinto Island	NA	NA	NA

(Continued)

*BG = background well; MW = monitoring well; US = undersite well;
 NA = not analyzed.

Table 2 (Concluded)

Parameter	Site	Comparison*		
		BG vs MW	BG vs US	US vs MW
Manganese	Grand Haven	0.07	0.11	0.34
	Sayreville	0.07	-0.51	0.39
	Pinto Island	NA	NA	NA
Iron	Grand Haven	-0.06	0.60	-0.40
	Sayreville	0.17	0.11	0.28
	Pinto Island	-0.17	0.37	-0.47
Copper	Grand Haven	-0.54	0.02	-0.14
	Sayreville	0.03	-0.25	0.23
	Pinto Island	NA	NA	NA
Zinc	Grand Haven	-0.20	-0.35	-0.13
	Sayreville	0.58	0.0	0.14
	Pinto Island	NA	NA	NA
Mercury	Grand Haven	-0.09	0.27	0.37
	Sayreville	00.54	-0.37	0.35
	Pinto Island	NA	NA	NA
Lead	Grand Haven	-0.25	0.81	0.01
	Sayreville	-0.64	-0.53	-0.89
	Pinto Island	NA	NA	NA
Chloride	Grand Haven	48	14	24
	Sayreville	-11	0.01	0.01
	Pinto Island	14	0.02	0.0

Grand Haven and Pinto Island groundwater samples ranged from 7.0 to 7.2; Houston undersite samples had a mean pH value of 6.1.

Total Dissolved Solids (TDS)

21. Groundwater analyses at each of the sites revealed that the dissolved solids consisted primarily of inorganic salts, with small amounts of organic matter. Table 3 summarizes the concentration of total dissolved solids (TDS) for each site location. Among the sites, the undersite (US) samples closely reflected the salinity of the dredged material. The average undersite concentrations of TDS ranged from 22.4 g/l at the Sayreville site; 15.4 g/l at the Houston site; 8.27 g/l at the Grand Haven site; to 0.825 g/l at the Pinto Island site.

22. With the exception of Pinto Island, TDS concentrations of US samples were clearly higher than MW samples which in turn were higher than BG well locations. This trend suggests an increase in TDS caused by leaching from the disposal area. This will be explored further in the evaluation of each individual parameter. Individual ion concentrations are contained in Table 1.

23. The major cations analyzed include sodium, potassium, calcium and magnesium. Anionic species tested were chloride, sulfate, and bicarbonate. Theoretically, because every solution exists in an electrically neutral state, the sum of the cations should be balanced by the sum of the anions in solution. Figure 5 shows the relationship between ionic imbalance (Σ cations - C anions) and the total ionic concentration for each of the samples. Concentrations of total cations plus anions ranged from 5 meq/l to several hundred meq/l. Deviations from the center line indicate that error may be involved in the analysis of major ions.

Table 3
Concentration of Total Dissolved Solids

<u>Site</u>	<u>Location</u>	<u>TDS, mg/l</u>
Sayreville, N. J.	BG	4242
	US	22400
	MW	8426
Pinto Island, Ala.	BG	530
	US	825
	MW	1010
Grand Haven, Mich.	BG	745
	us	8270
	MW	2120
Houston, Tex.	MW	1170
	us	15400

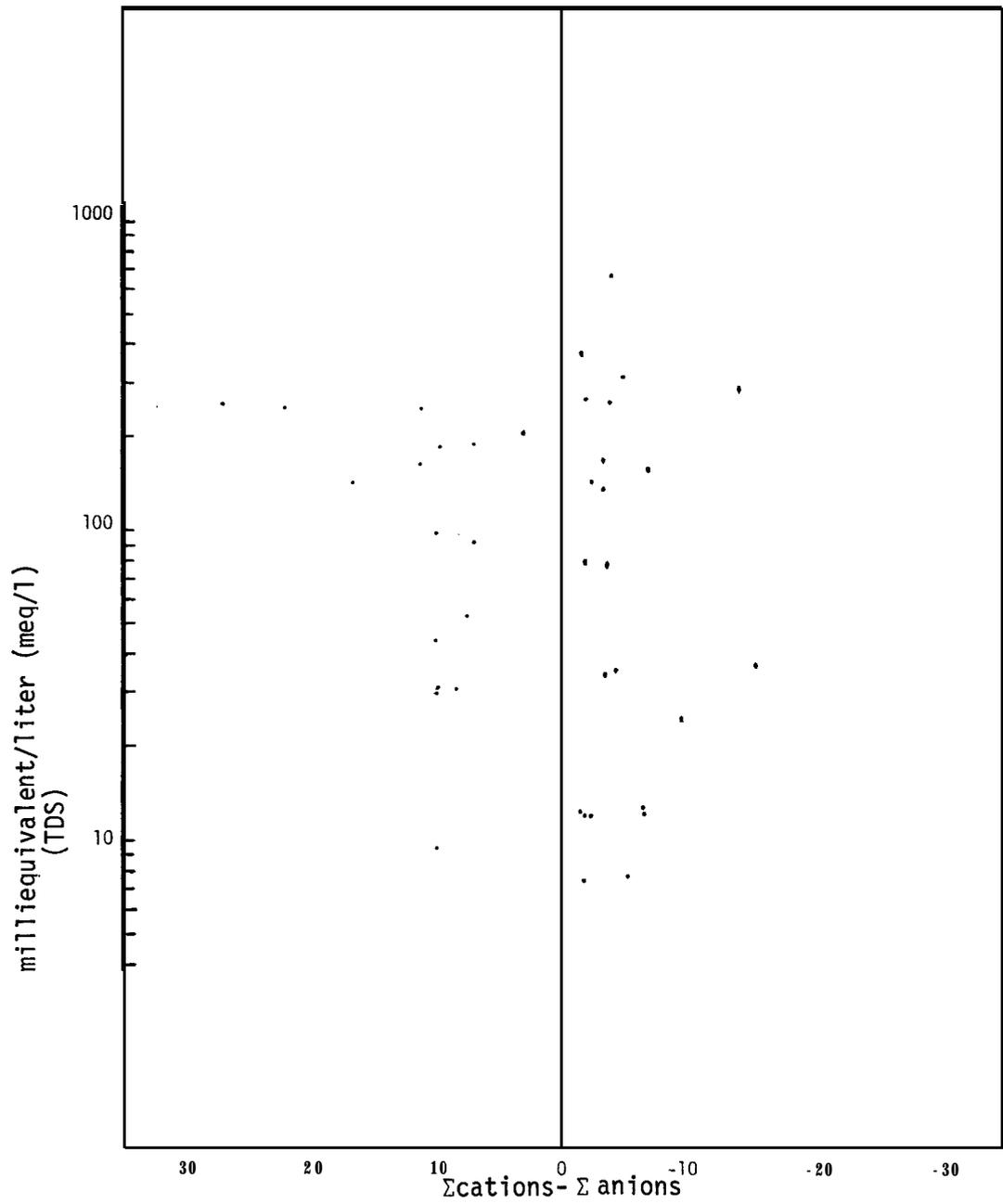


Figure 5. Relationship between cations and anions and total ionic concentration

Major Ions

Chloride

24. Chloride concentrations of the four case study sites ranged from a low of 10 mg/l to a high of almost 10,000 mg/l as shown in Figure 6. Values obtained from the four sites correspond to the salinity of the dredging sites from which the dredged material was obtained. The Sayreville site exhibited the highest overall concentrations among all three well groups (i.e., MW BG, and US), which is expected, considering the saline setting. Sayreville also displays a high degree of chloride migration. Low "P" values reinforce this conclusion for the three well groups.

25. Grand Haven exhibited a similar trend as was observed at Sayreville. This relationship suggests that chloride leached from the dredged material into the zone underlying the disposal area where it was greatly diluted by less saline indigenous waters. The slight difference between the background and monitoring wells suggests that the chloride observed in the monitoring wells was well mixed with background groundwaters prior to reaching the offsite monitoring wells.

26. Pinto Island represented a deviation in the pattern observed at the three other sites. This phenomenon could be explained in part by the higher Cl concentrations obtained at one offsite well which averaged 455 mg/l at a 20-ft depth.* The Grand Haven MPW well probably intersects a deeper saline water body than the shallower monitoring well (PI-H). Using PI-H as a representative of monitoring well values, a mean concentration of 90 mg/l is obtained, which supports the

* A table of factors for converting U.S. customary units of measurement to metric (SI) units is presented on page 6.

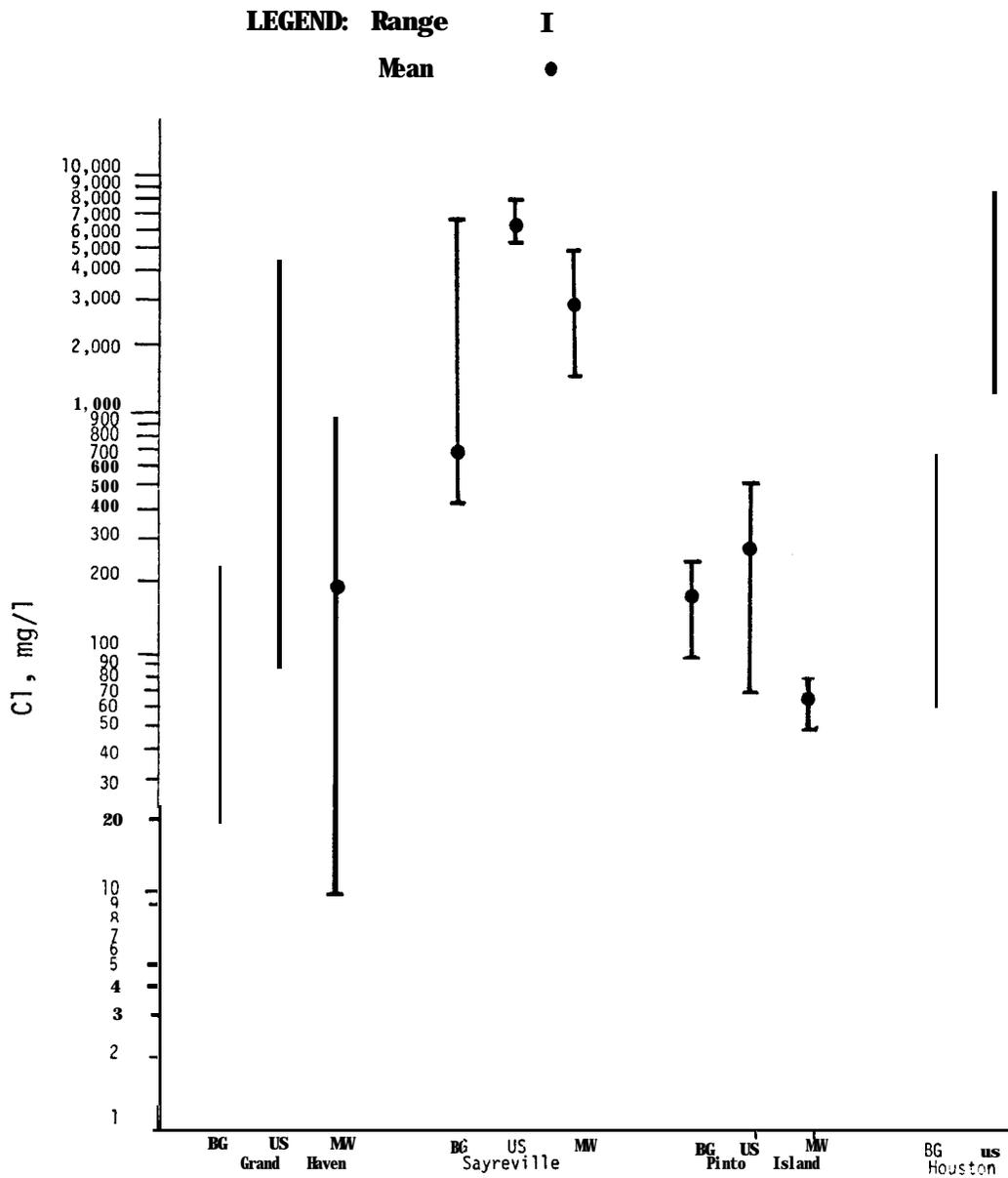


Figure 6. Comparison of chloride values for groundwater samples

previously described dilution effect of the undersite samples by native groundwater.

27. Samples from Houston sites exhibited an undersite mean of 5.56 mg/l and an offsite average of 0.603 mg/l. Correlation of the two data sets is difficult due to the discontinuity of groundwater conditions created by the clay subsoil. The higher onsite salinity reflects the saline environment in which the dredged slurry was obtained,

28. Chloride values for all sites reported in the first phase were generally lower than in the second phase. This difference could be attributed to the additional disposal of dredged sediments between the two sampling phases.

29. Due to the fact that chloride from dredged material can be readily leached into the undersite samples, increments of chloride concentration in groundwater resulting from the disposal of dredged material should be an important consideration in selecting a disposal site.

Alkalinity

30. Mean alkalinity values for undersite samples ranged from a high value of 137 mg/l at Houston, to a low of 20.6 mg/l for Pinto Island wells. Undersite mean sample values ranged from 89 mg/l at Grand Haven sites, 69 mg/l at Sayreville sites, to about 18 mg/l at the Pinto Island sites. The concentration range is shown in Figure 7.

31. Sayreville samples exhibited a range of alkalinity values from barely detectable to a high of 197 mg/l. Low alkalinity values are usually associated with low pH values of the surrounding medium, with water samples from well NJJ being a case in point: average pH values

LEGEND: Range \bar{I}
Mean •
ND = not detectable

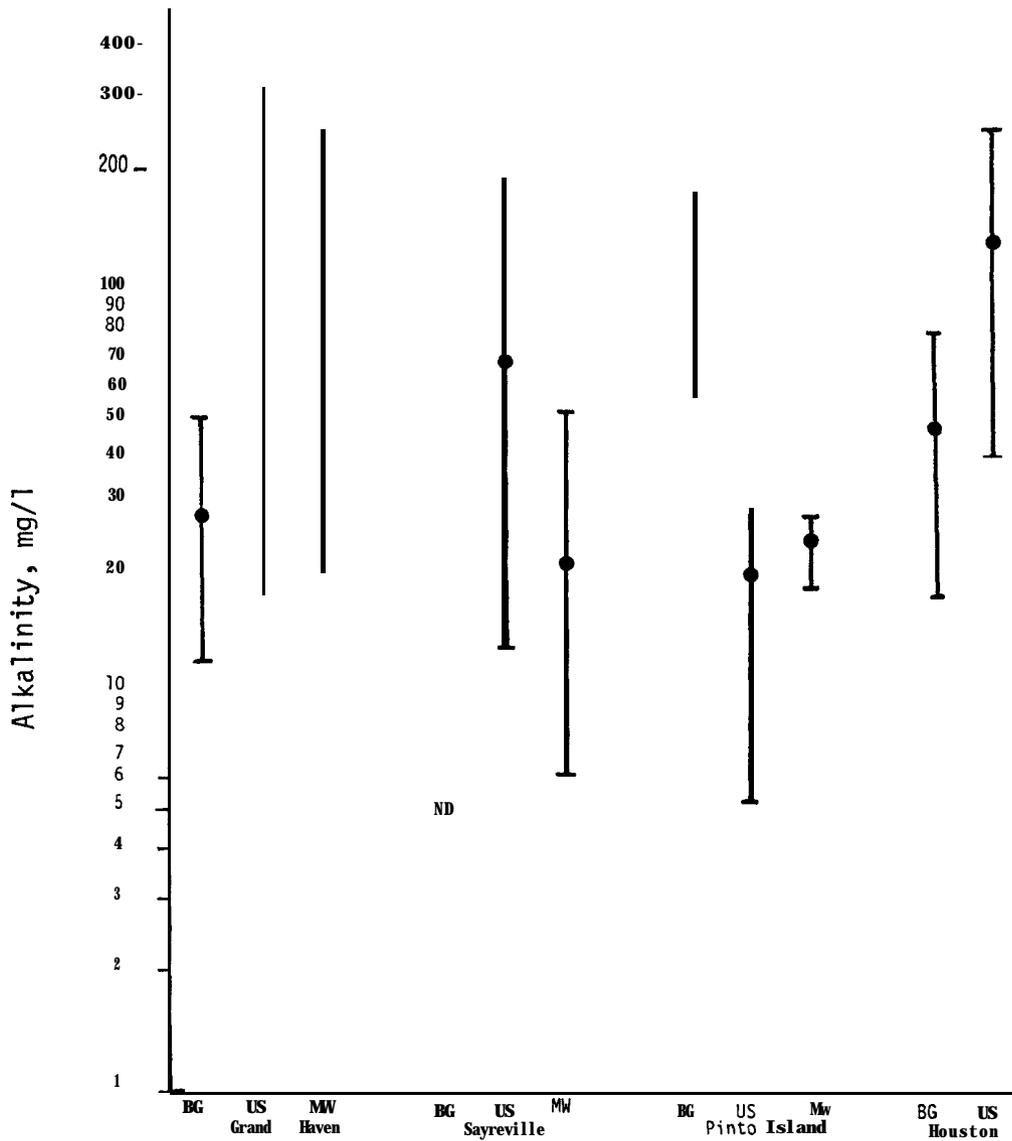


Figure 7. Comparison of alkalinity values for groundwater samples

were 3.4 with alkalinity values close to zero. At three out of four well sites, undersite well samples were found to contain the highest alkalinity values followed by groundwater and background values. Alkalinity generated from the dredged material seems to be neutralized by the acidic soil upon leaching. The remaining alkalinity might be further diluted in the groundwater system

TC, TOC, and TIC

32. Total carbon (TC) and total organic carbon (TOC) were determined. Total inorganic carbon (TIC) was obtained from the difference of the two. Concentration ranges of these parameters are presented in Figures 8, 9, and 10.

33. Mean total organic carbon (TOC) values in undersite waters ranged from a high of 170 mg/l at Houston sites to a low of 40 mg/l at the Pinto Island sites. The TOC ranges encountered in this study were similar to data in the previous study. Concentrations of TOC in Grand Haven, Sayreville, and Houston samples exhibited a decrease in the order of undersite, monitoring well, and background groundwater, respectively. The trend observed in TOC was identical to that for alkalinity except at the Pinto Island site, where background values were found to be higher than either undersite or monitoring well groups. This observation is similar to the results from the first phase study.

34. Both TOC and TIC appear to have increased in the monitoring wells resulting from the disposal of dredged material. Changes in concentration of total inorganic carbon, which is mostly alkalinity, appear to be affected in part by both biological oxidation, as well as dissolution/precipitation of calcite. Alkalinity and TOC observed in

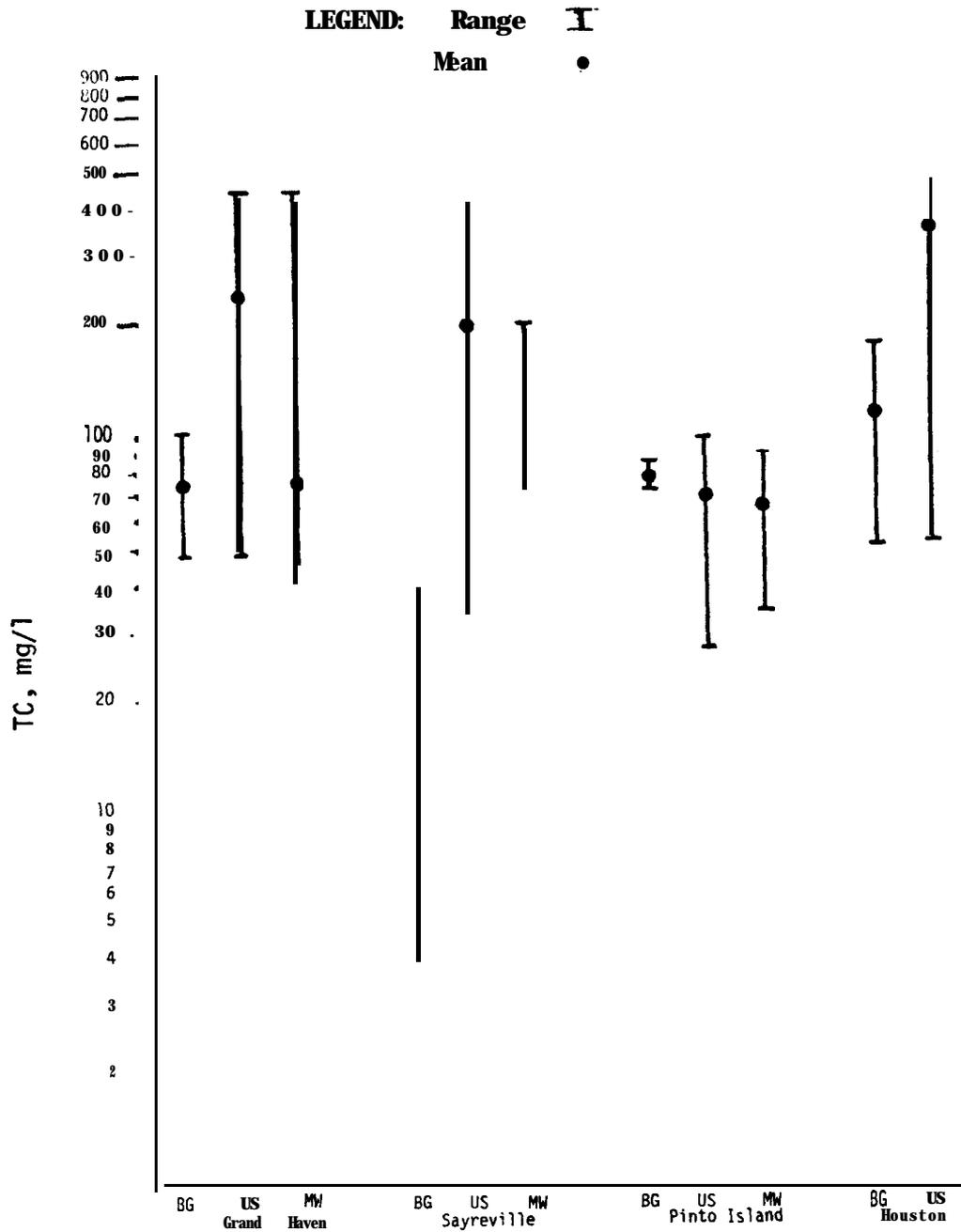


Figure 8. Comparison of total carbon values for groundwater samples

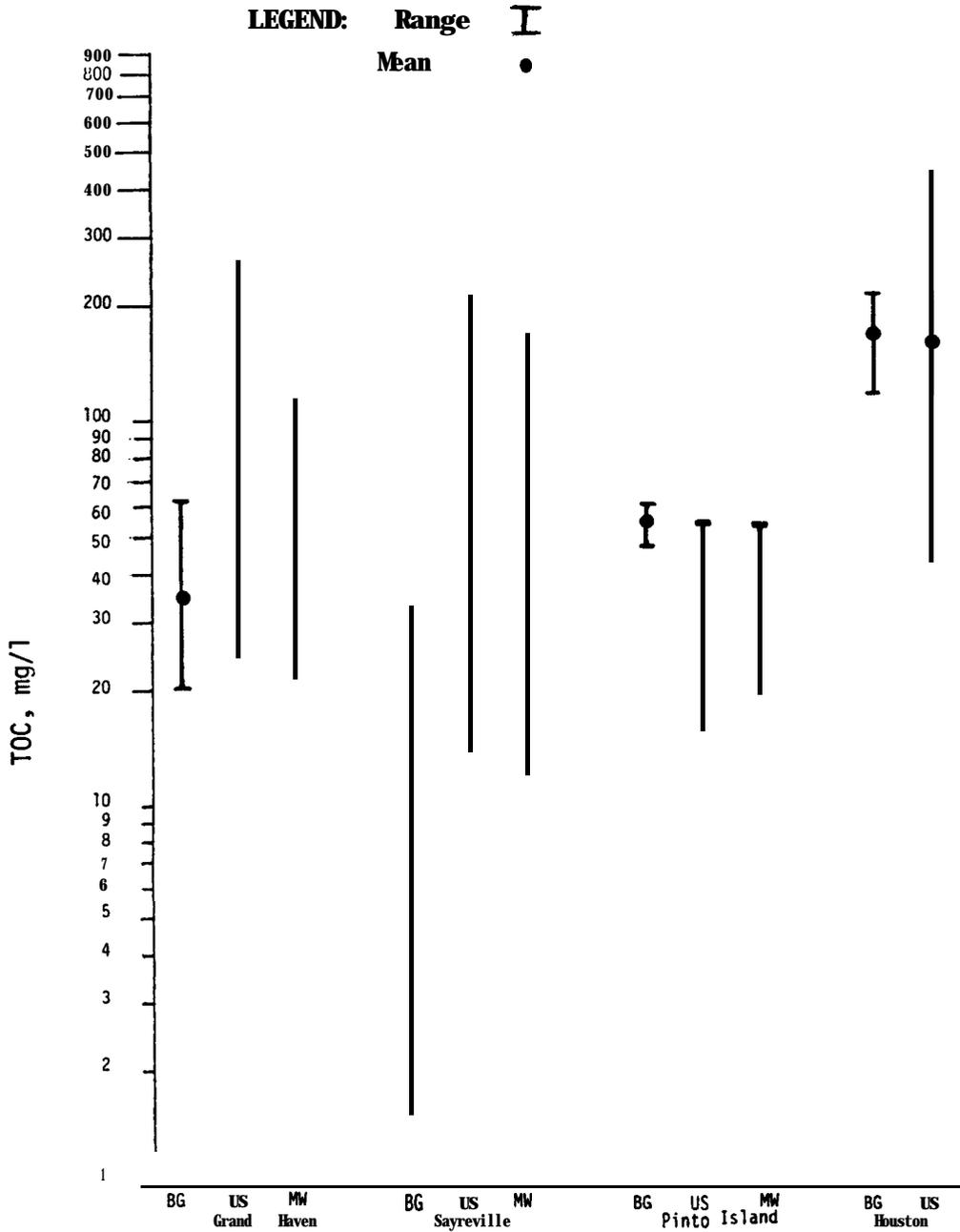


Figure 9. Comparison of total organic carbon values for groundwater samples

LEGEND: Range I
Mean •

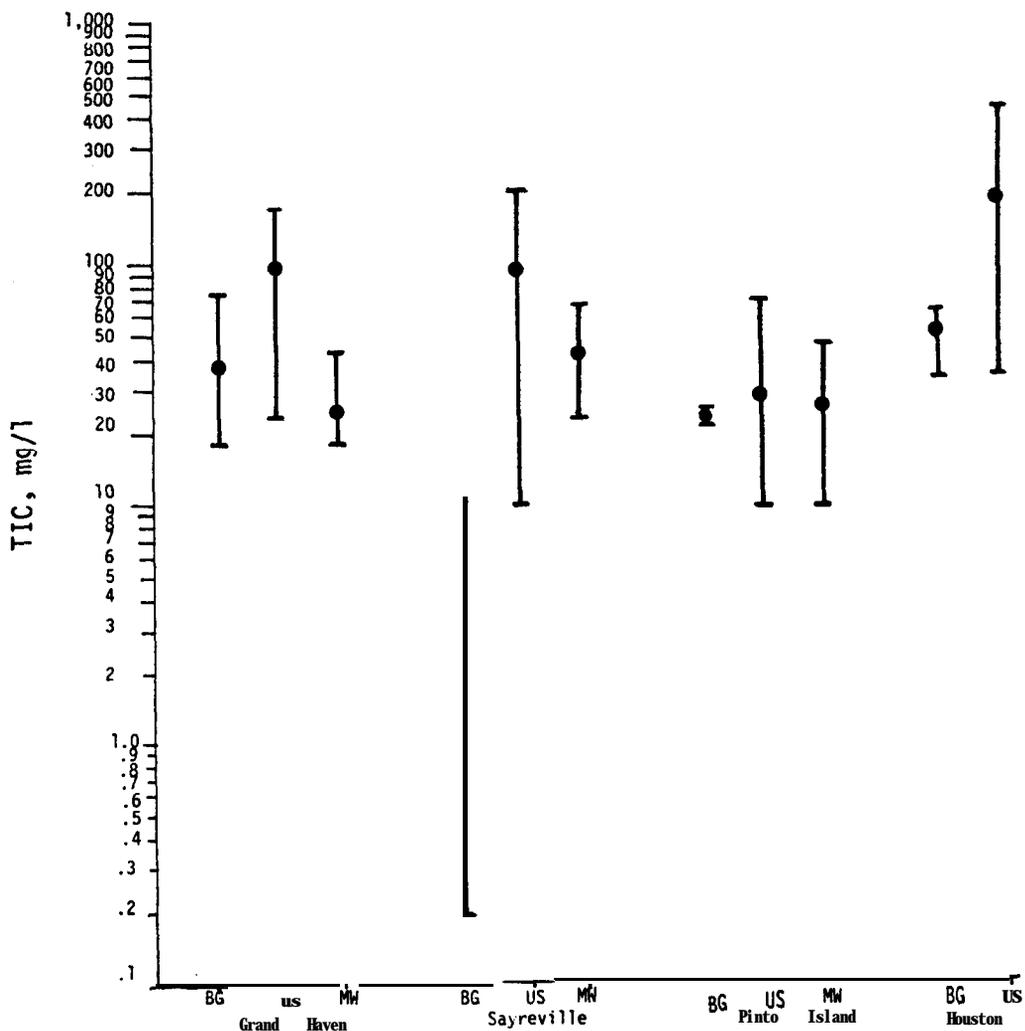


Figure 10. Comparison of total inorganic carbon values for groundwater samples

the groundwater wells were similar to data from the original study except at Sayreville, where onsite values were higher for the second sampling phase. The increase noted at Sayreville sites could be due to the disposal of large volumes of dredged sediments between the two sampling periods.

Nitrogen Species

35. Nitrogen species analyzed in the groundwater samples included ammonia, organic nitrogen, nitrite, and nitrate. Due to the rapidly changing nature of nitrogen species, precautions were taken to minimize the transformations prior to analysis. The results are shown in Figures 11, 12, and 13.

36. Organic nitrogen values ranged from a high of about 300 mg/l at Houston to below detection limits at other locations. Samples from the Sayreville site exhibited higher overall concentrations than the other sites with undersite, background, and monitoring well concentrations of 18.7, 10.8, and 5.8 mg/l, respectively. Data in Figure 11 indicate that organic nitrogen from undersite samples was mostly converted to other forms before reaching the monitoring wells.

37. As shown in Figure 12, there is no clear trend on the transformation and migration of ammonia from the disposal sites, with the exception of the Pinto Island site. The undersite samples usually contained the highest ammonia concentration.

38. Mean nitrate values ranged from a high of 400 mg/l for the undersite samples at Sayreville, to about 1 mg/l at Pinto Island. The mean nitrate concentrations correlated closely with ammonia nitrogen data for the wells at the Sayreville, Grand Haven, and Houston sites. This

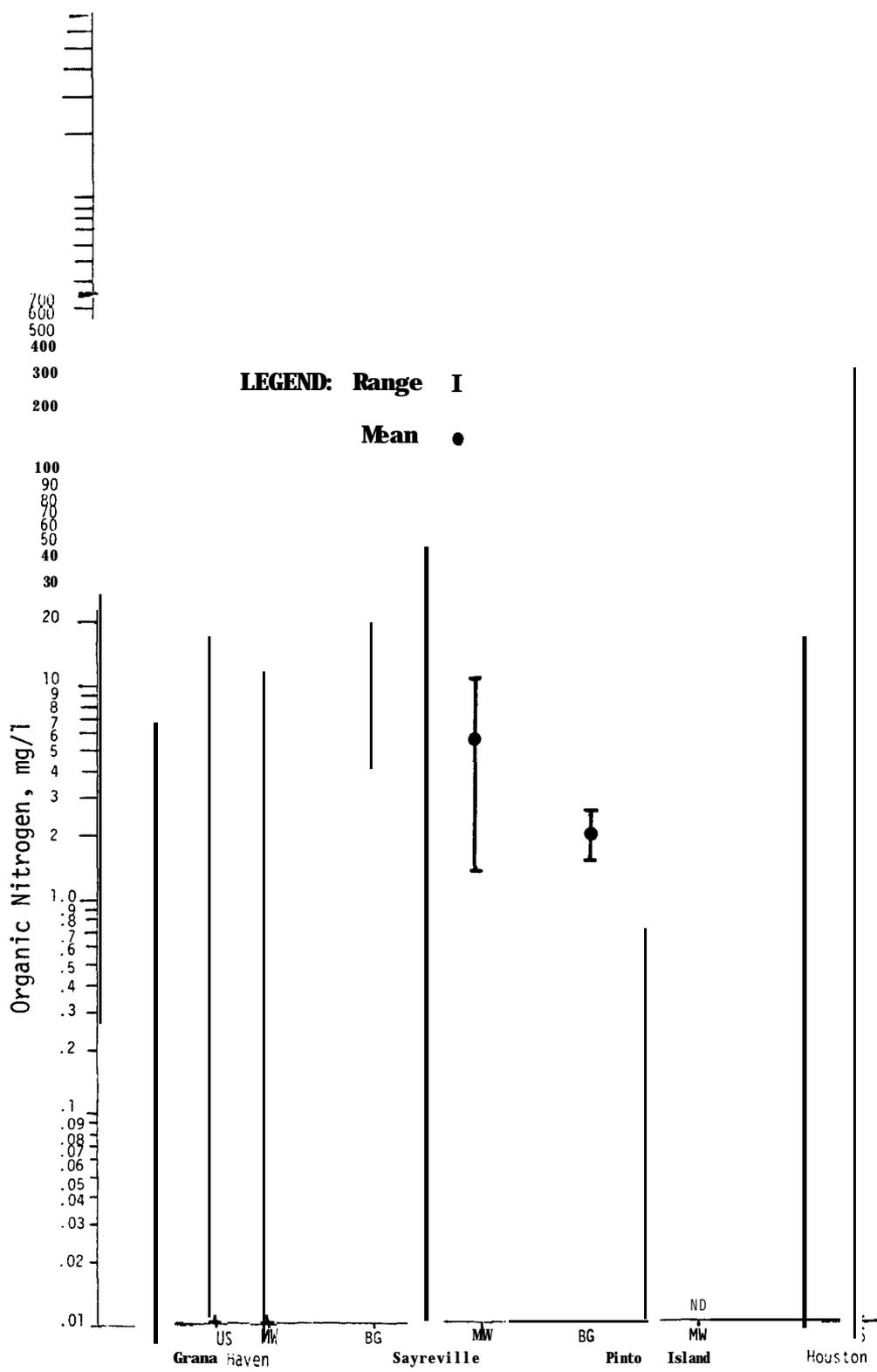


Figure 11. Comparison of organic nitrogen for groundwater samples

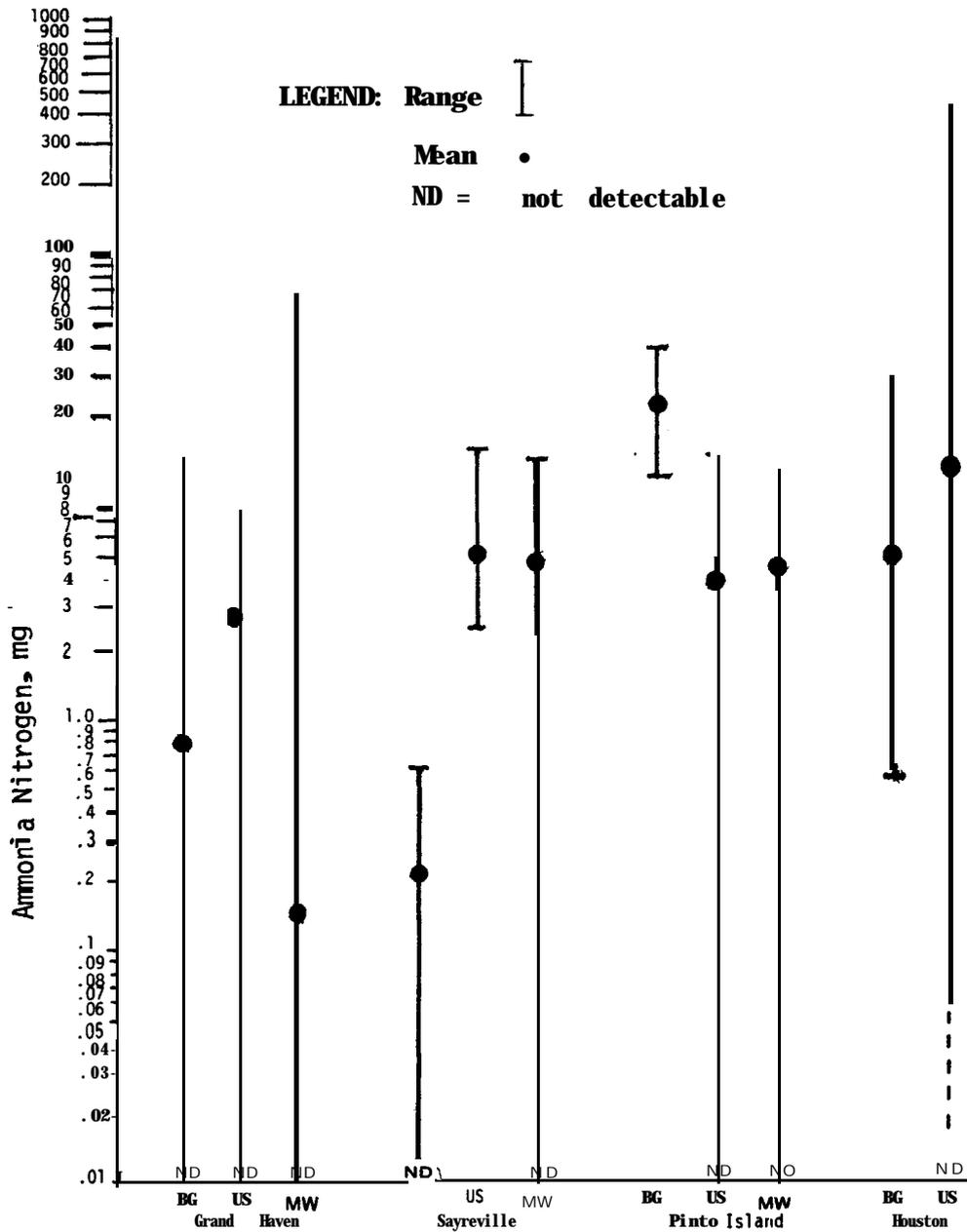


Figure 12. Comparison of ammonia nitrogen values for groundwater samples

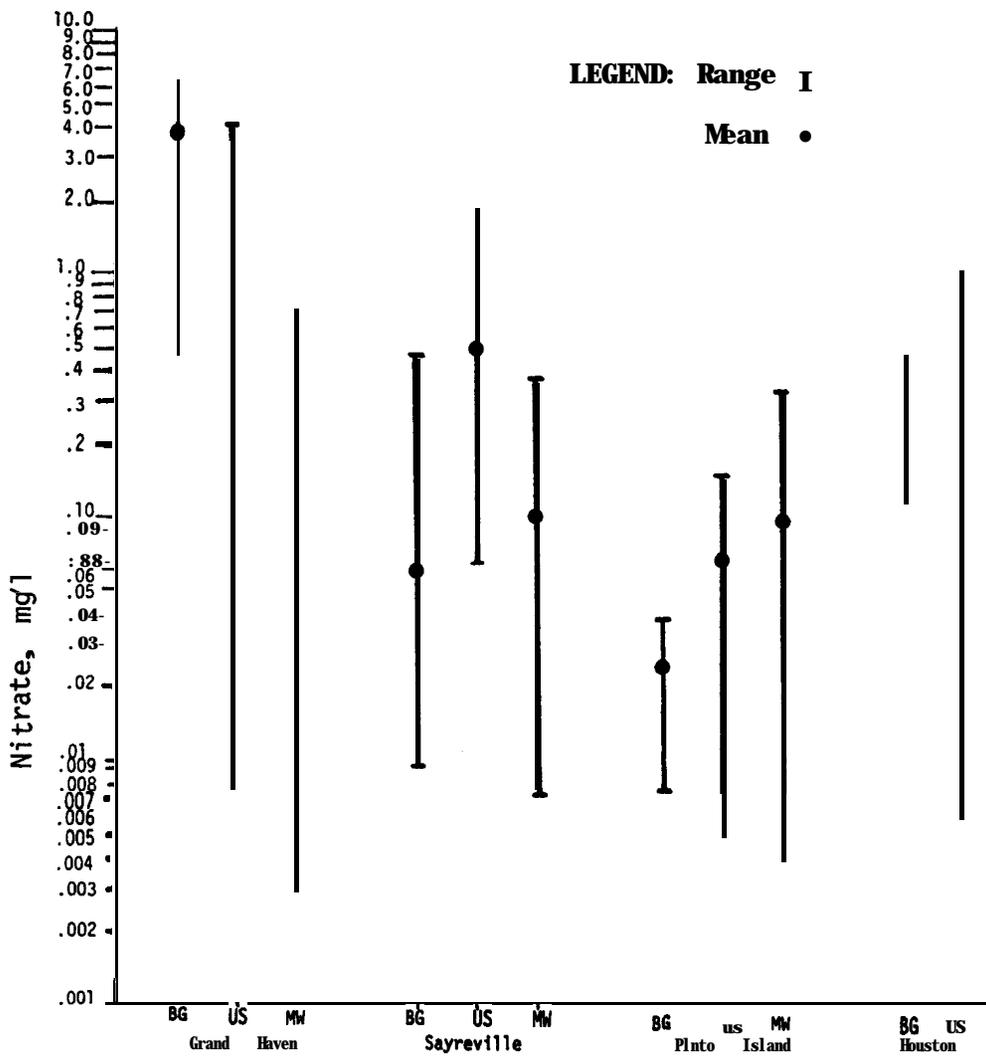


Figure 13. Comparison of nitrate values for groundwater samples

relationship indicates that some degree of nitrification is occurring in the aerobic surface soils and interstitial waters in the unsaturated zone. Nitrate concentrations show increases downgradient from each of the Grand Haven, Sayreville, and Pinto Island sites. Concentration of nitrate above 10 mg/l (as N) is generally considered to be unsuitable for domestic consumption.

39. Nitrite concentrations show mean values in all samples of less than 0.1 mg/l. The average total Kjeldahl nitrogen (TKN) values (organic plus ammonia nitrogen) range from a high of 713 mg/l to a low of 4.0 mg/l for the four sites. With the exception of Pinto Island, TKN comprised the bulk of the nitrogen species at each site. As indicated previously, Sayreville was the only site with an increase in TKN in monitoring wells.

Total Phosphorus and Phosphate

40. Concentrations of total phosphorus and orthophosphate are shown in Figures 14 and 15. Mean total phosphorus ranged from an onsite high of 6.9 mg/l at Houston sites to less than 0.1 mg/l at the background well at Sayreville. All four sites revealed a low "p" value in the undersite versus background correlations with the exception of Houston, where mean values of 3.11 and 2.13 mg/l were recorded for background water samples and undersite water samples.

41. Orthophosphate phosphorus levels recorded for the groundwater samples were fairly low, ranging from below the detection limit to an average high of 3.0 mg/l. Statistical analyses revealed that Pinto Island exhibited a dissolution potential for phosphate throughout both sampling phases. Soluble phosphate concentrations appeared to correlate

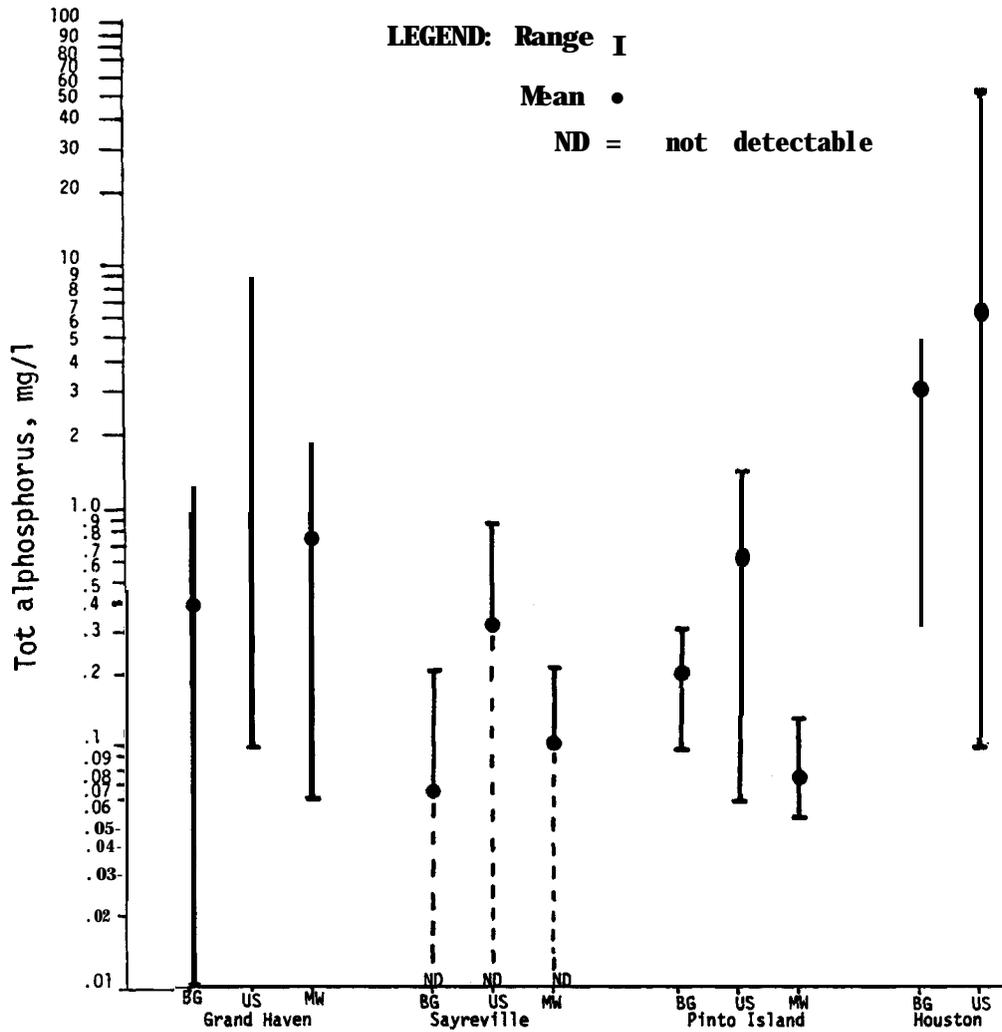


Figure 14. Comparison of total phosphorus values for groundwater samples

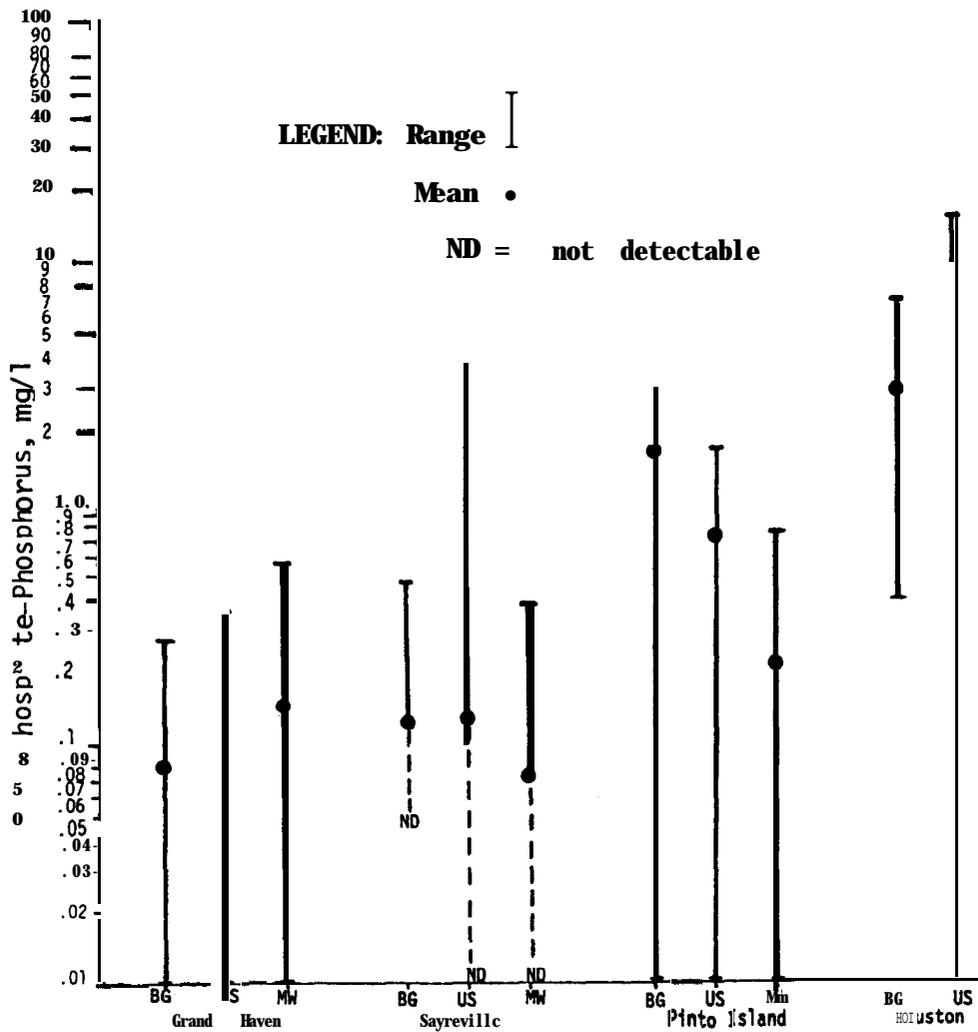


Figure 15. Comparison of orthophosphate values for groundwater samples

fairly well with pH values. Solutions with high pH values tended to contain higher phosphate than solutions with low pH values. This observation could be due to greater phosphate adsorption by clay minerals at low pH. Concentrations of orthophosphate appear to be regulated in part by ferric phosphate and calcium phosphate solubility. This relationship, which was postulated in the original study, correlates well with the compiled groundwater data.

Sulfate

42. Sulfate concentrations range from a low of 10 mg/l to a high value of 6000 mg/l. This extreme variation represented the concentration range in the undersite samples from Houston sites. The variation of sulfate concentrations among all four sites is quite similar to that of chloride concentrations. The less saline environment of the Pinto Island site contained the lowest concentration of sulfate as well as chloride. In general, the undersite samples contained the highest concentration of sulfate. The levels in the background groundwater and monitoring wells did not follow any fixed pattern. Sulfate concentrations in all sites are shown in Figure 16.

Sodium and Potassium

43. The highest overall sodium concentration was observed at Sayreville, followed by Houston, Grand Haven, and Pinto Island, respectively. This order is similar to that of chloride concentrations. Undersite sodium values were significantly higher than either background or monitoring well concentrations except for Grand Haven. Background values obtained were the lowest among the three well groups analyzed. Observed "p" values were found to be similar between the two data sets

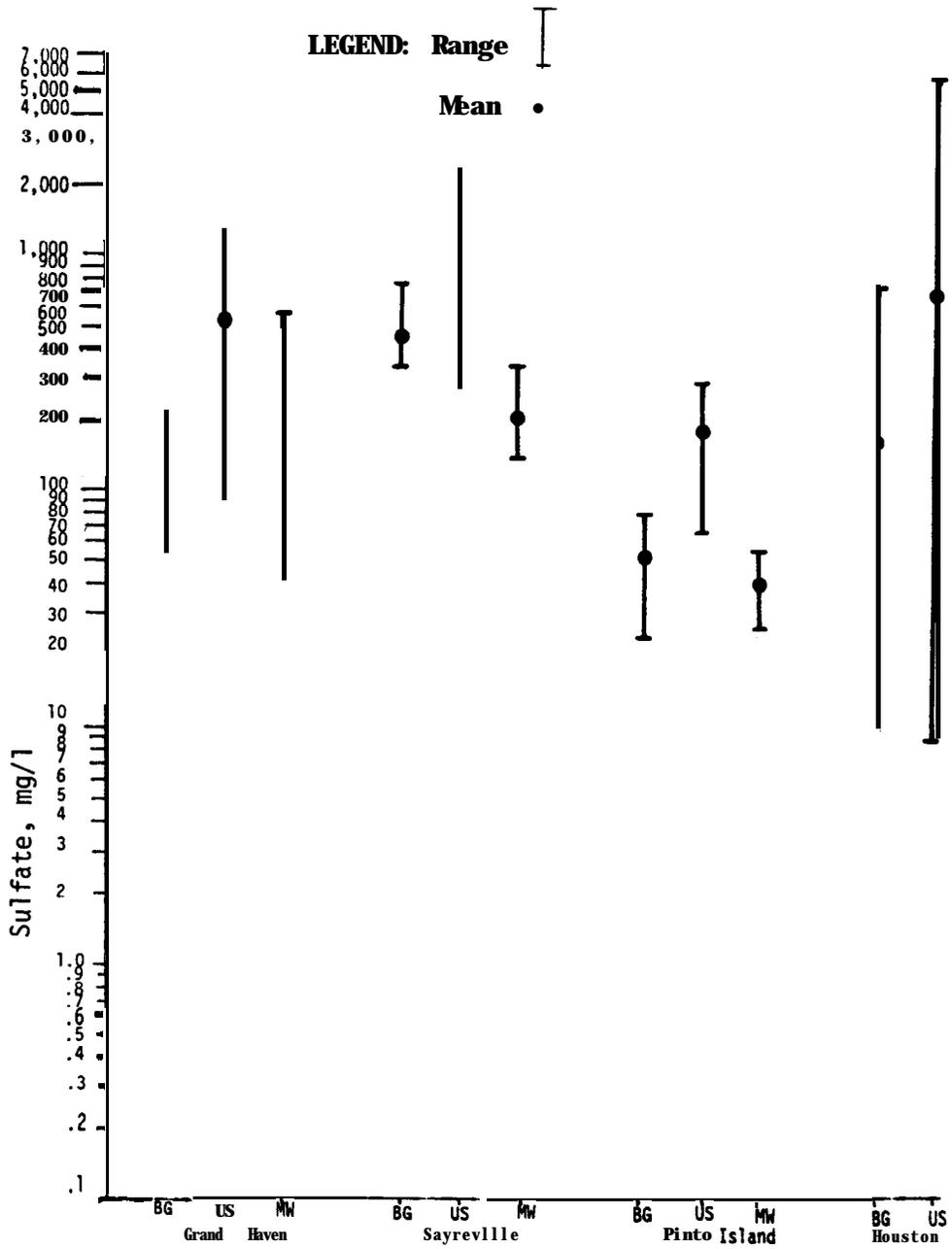


Figure 16. Comparison of sulfate values for groundwater samples

(see Table 1). The concentration range is shown in Figure 17.

44. Potassium trends were similar to those observed for sodium. Undersite values were the highest with background values the lowest. Values ranged from a mean of 170 mg/l for undersite wells at the Houston site to a mean low value of 5.0 mg/l for offsite monitoring wells at the Grand Haven site as shown in Figure 18.

45. Based on the initial analyses of dredged sediments and groundwater samples obtained from both sampling efforts, a potential increase for sodium and potassium appears to exist downgradient from the sites.

Calcium and Magnesium

46. Calcium values at the four case study sites range from an average high of 476 mg/l for undersite wells at Grand Haven to a low of 33.4 mg/l for the background wells at Sayreville, New Jersey, as shown in Figure 19.

47. Calcium values obtained from groundwater wells at the four sites generally showed higher undersite values than both the background and monitoring wells. Background values were the lowest in all cases. This statistical difference between background and undersite wells indicates that a concentration gradient exists for the migration of Ca from the sites.

48. Trends observed in the previous study indicated similar relationships between sampling points within the dredged material and the underlying soil. Comparison between these sampling points suggests a potential for leaching from the dredged material to the underlying soil and groundwater.

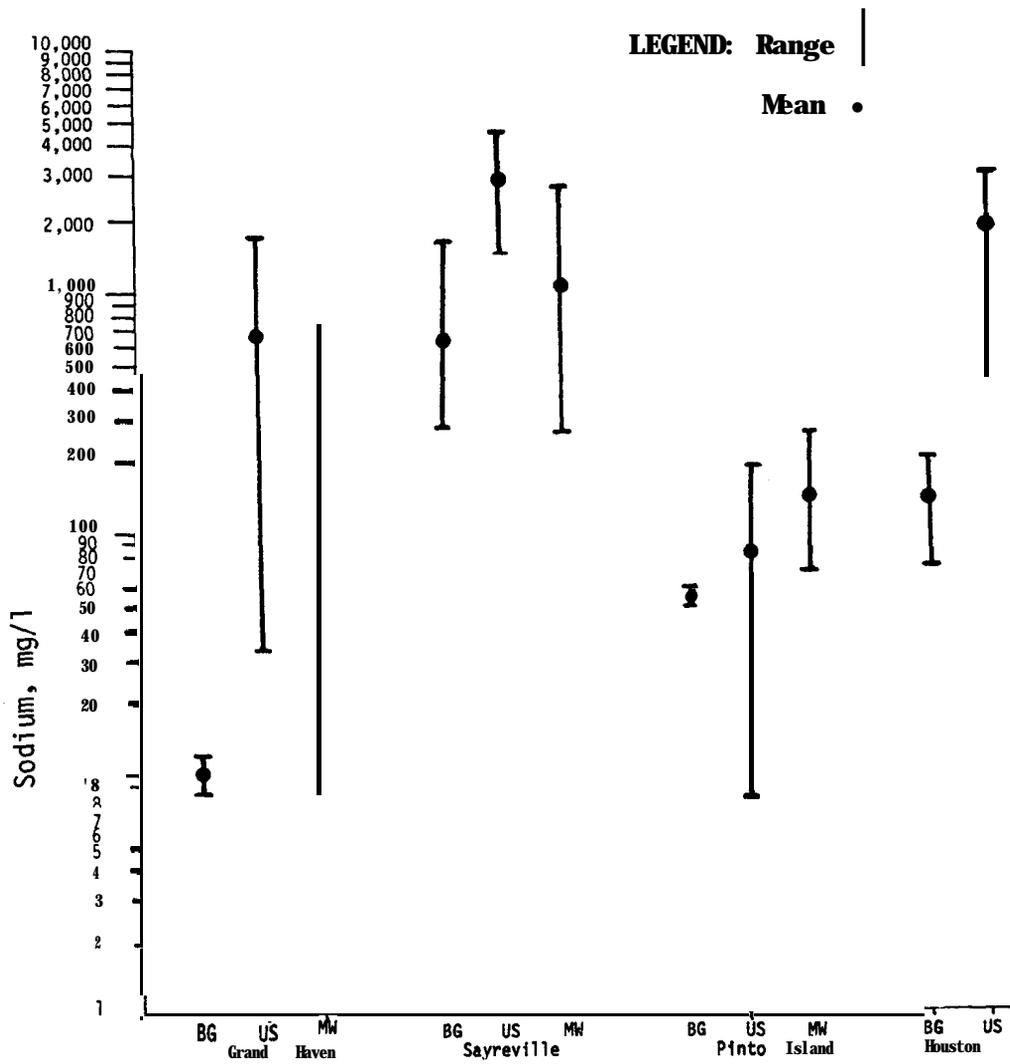


Figure 17. Comparison of sodium values for groundwater samples

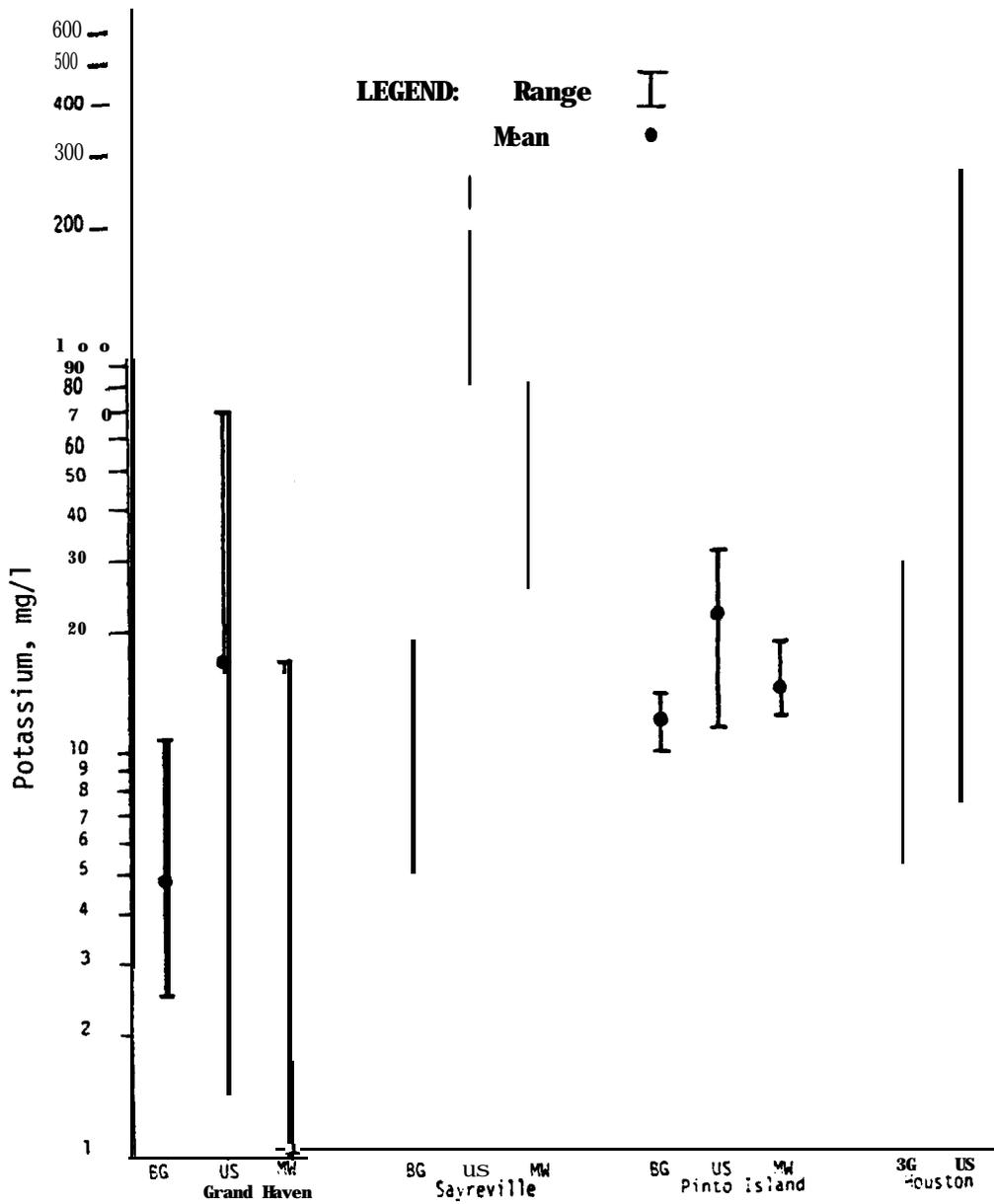


Figure 18. Comparison of potassium values for groundwater samples

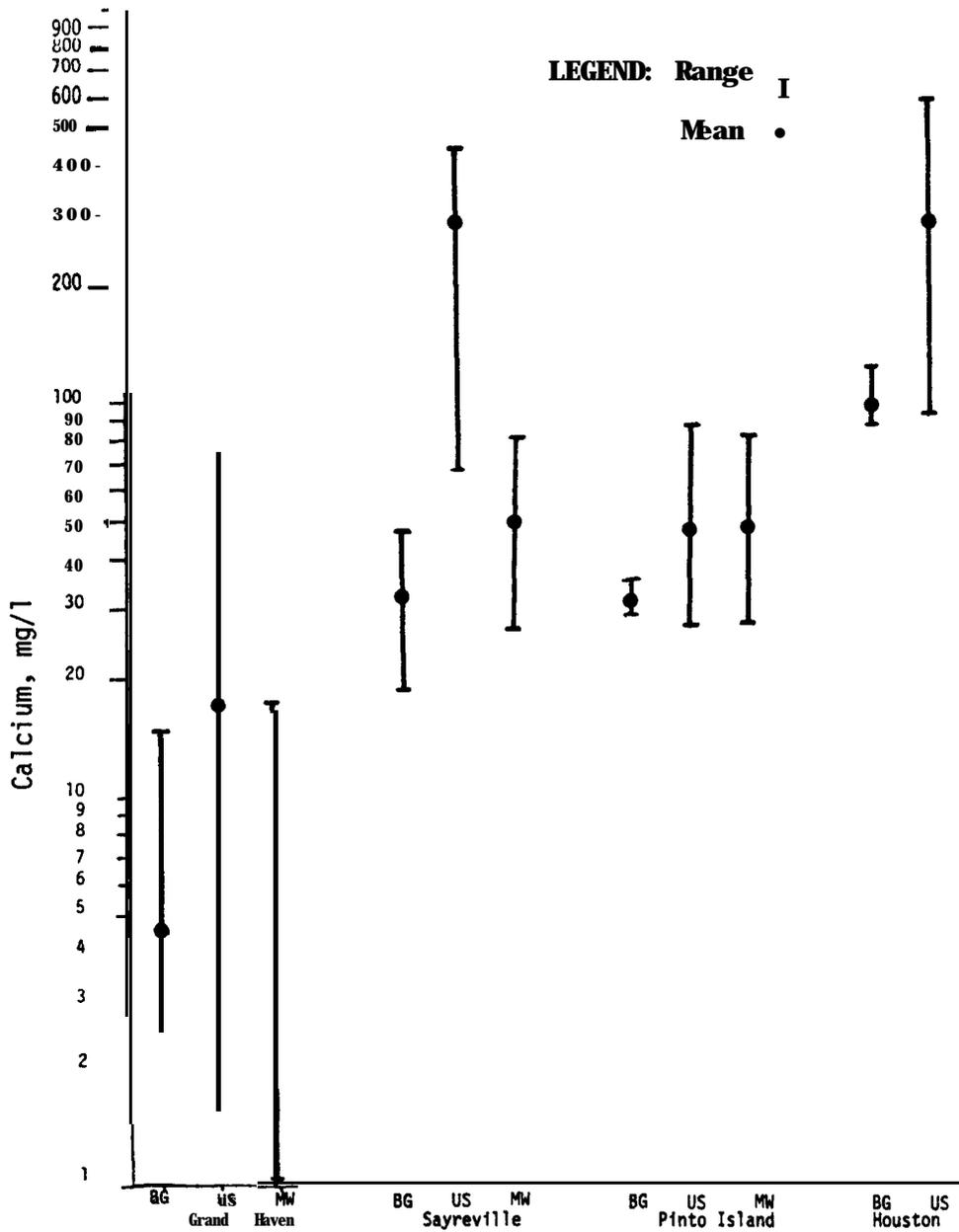


Figure 19. Comparison of calcium values for groundwater samples

49. The general statistical trend observed at the four sites in both the original study and in the present study reveal a maximum calcium concentration within the dredged material with a decreasing vertical and horizontal gradient. Background values were lower than those at the other well groupings.

50. Concentration trends for magnesium were similar to those observed for calcium as shown in Figure 20. All four sites exhibited higher undersite values than the corresponding monitoring well groups. Background mean values were the lowest among the three groups. This relationship indicates a high probability that an increase in magnesium concentrations in groundwater could result from the upland disposal of dredged material.

51. Dredged material obtained from saline environments exhibited higher magnesium levels than those taken from freshwater environments. The mean undersite concentrations of magnesium varied from 490 mg/l at the Sayreville site, 290 mg/l at the Houston site, 60 mg/l at the Grand Haven site, to 30 mg/l at the Pinto Island site. These values are approximately equal to the levels of magnesium in the interstitial water of the sediments obtained from the dredging sites.

52. Concentrations of calcium leaching from the disposal sites are in part controlled by the formation of calcium carbonate and calcium sulfate. At Sayreville, where samples exhibited low pH values (3.1-3.7), alkalinity was generally very low and sulfate concentration was high. The background well selected at Sayreville (NJ) exemplified this phenomenon with average $\text{SO}_4^{=}$ and Ca^{+2} concentrations of 546 mg/l and 33.4 mg/l, respectively, at a pH of 3.4. Calculations indicate the Ca and SO_4 concentrations to be close to the solubility product limit for CaSO_4

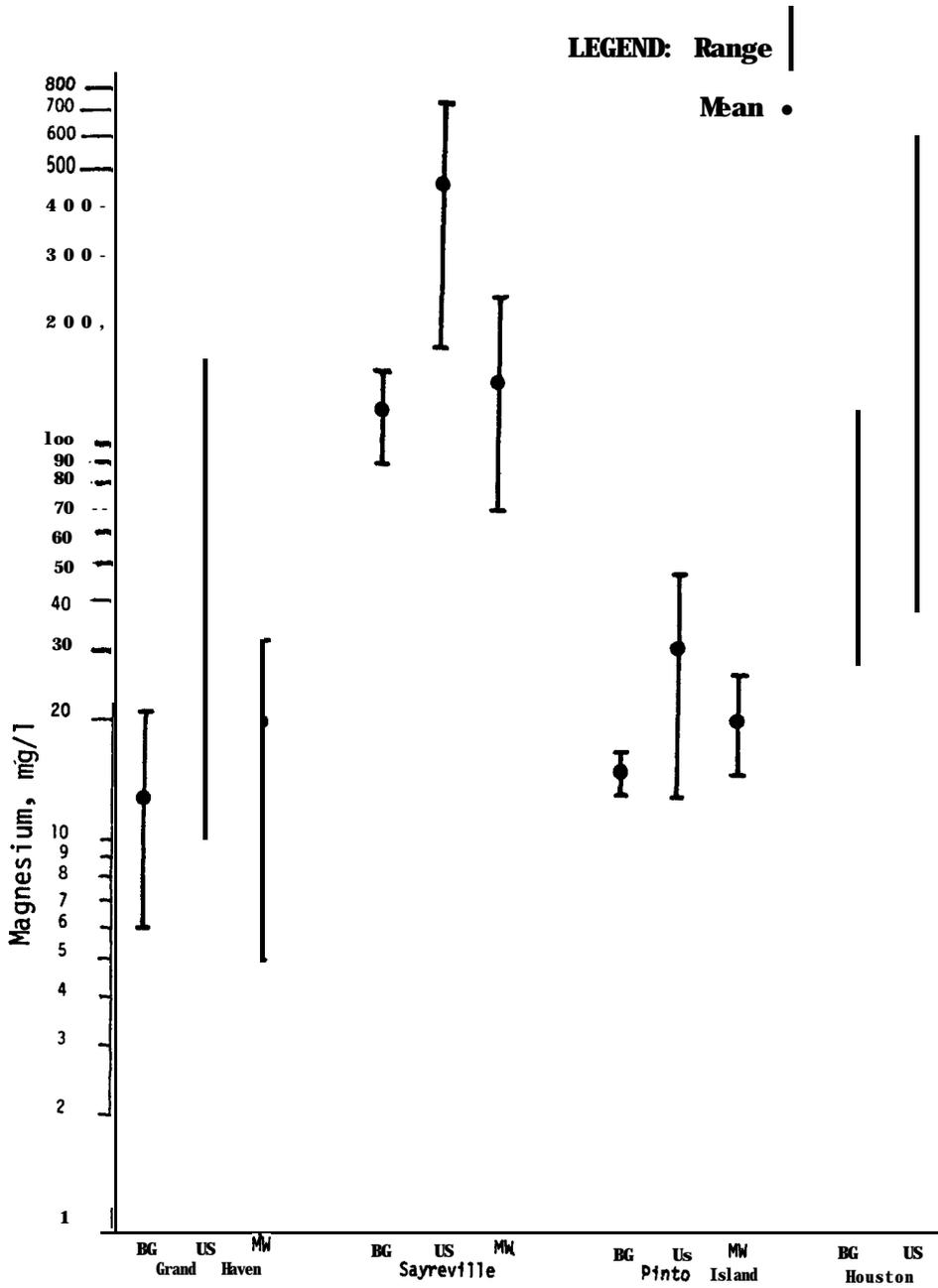


Figure 20. Comparison of magnesium values for groundwater samples

($K_{sp} = 2.5 \times 10^{-6}$). Other wells at Sayreville also followed this pattern, especially for the low pH groundwaters. Calculations performed for calcium carbonate solubility indicate that calcite is the solubility controlling solid for sites with high pH values.

Chlorinated Hydrocarbons

53. Chlorinated hydrocarbons were analyzed for all the collected groundwater samples. Included in the tests were three widely used forms of PCB's (Aroclor, 1242, 1254, and 1260) and chlorinated pesticides such as op' and pp' isomers of ODT and its analogs DDE and DDD. Analyses of 96 water samples indicated that levels of both PCB's and chlorinated pesticides were at nondetectable levels.* Detection limits for total PCB's and chlorinated pesticides were 0.1 and 0.01 $\mu\text{g}/\text{l}$, respectively. Forty groundwater samples analyzed in the first phase study exhibited no detectable soluble species.

54. Adsorption of the chlorinated hydrocarbons onto clay and organic matter is known to remove chlorinated hydrocarbons from solution. Clays observed at Houston, Grand Haven, and Pinto Island, and loams encountered at Sayreville and Pinto Island, together with the organic laden dredged material and surface soils, would provide a conducive setting for this phenomenon.

Trace Metals

55. Trace metals analyzed in this study include the same elements included in the original study. Most of these elements were found to be in the micrograms per litre or submicrograms per litre range and correlated fairly well with the earlier trace metal data.

56. In the original study, several assumptions concerning the

* Two water samples showed detectable PCB's: an undersite well from Houston (HD, 1.45 $\mu\text{g}/\text{l}$) and a monitoring well from Pinto Island (PI-H, 2.2 $\mu\text{g}/\text{l}$). Since continued monitoring of these wells failed to show additional contamination, an interference problem was suspected.

controlling solids under various conditions were presented. Under aerobic conditions, the stable solids that control the metal solubilities are usually oxides, hydroxides, or carbonates. In a reducing environment, trace metals are believed to precipitate as metal sulfides. From these two assumptions, a number of relationships were postulated that are described in detail in the original work.

57. By assuming carbonate and sulfide to be the controlling solids in the majority of cases, theoretical diagrams can be constructed to illustrate the suspected metal concentrations with pH as a master variable. Tables 4, 5, and 6 may be used for this purpose.

58. The total carbonate (CT) values of $10^{-1.5}$ to $10^{-3.5}$ moles were selected for calculating soluble concentrations of metal species. Calculated values were based on the levels of alkalinity determined from water samples. Reference to these soluble metals species concentrations will be made throughout the trace metals discussions.

Cadmium

59. Cadmium values were found to range from a high of 50 $\mu\text{g}/\text{l}$ in samples collected under the Sayreville site to nondetectable levels at Grand Haven (Figure 21). Sayreville generally exhibited higher background, underside, and monitoring well values. Grand Haven cadmium analyses revealed values in the submicrogram per litre range. Houston samples varied from an average background concentration of 1.5 to 10.9 $\mu\text{g}/\text{l}$ for the underside well groups. Observed values were similar to those reported in the first sampling program with the exception of samples from Sayreville sites, which showed lower levels in the current study.

60. The high cadmium concentration found in the Sayreville samples

Table 4
Ionic Strength and Activity Coefficient

<u>Sample</u>	<u>Ionic Strength</u>	<u>Neutral Species</u>	<u>Activity Coefficient</u>		
			<u>Mnovalent Ion</u>	<u>Divalent Ion</u>	<u>Trivalent Ion</u>
Houston	MW 0.18	1	0.71	0.25	0.05
	UW 0.028	1	0.85	0.52	0.23
Grand Haven	US 0.083	1	0.78	0.35	0.09
	MW 0.023	1	0.86	0.54	0.25
	BG 0.008		0.91	0.69	0.43
Sayreville	US 0.26		0.68	0.21	0.03
	MW 0.093		0.76	0.34	0.09
	BG 0.046		0.82	0.44	0.16

* MW = monitoring well; US = undersite well; BG = background well.

Table 5

Important Solubility Products (K_s) of Metal Species*

<u>Metal</u>	<u>Oxide</u>	<u>Hydroxide</u>	<u>Carbonate</u>	<u>Sulfide</u>	<u>Chloride</u>	<u>Phosphate</u>	<u>Silicate</u>
Cd(II)	20.4	13.6	13.6	26.1		6.25 (CaHOP ₄)	3.7 (CaSiO ₃)
Ca(II)		5.26	8.32 (calcite), 8.22 (aragonite), 16.7 ** (dolomite)	2.94		26 (Ca ₃ (PO ₄) ₂) 1.14 (CaH ₂ (PO ₄) ₂)	52.3 ** (anorthite), 585 (Ca-mont- morillonite)
Cu(II)	20.4	18.6	9.63 (CuCO ₃), 33.2 (CuCO ₃ (OH) ₂)	35.2		6.4 (CaHOP ₄ (H ₂ O) ₂) 40.6 (Ca ₅ OH(PO ₄) ₃) 44.6 (Ca ₅ OH(PO ₄) ₃) 120.8 (Ca ₁₀ (PO ₄) ₆ ·F ₂)	
Fe(II)		15.3	10.2	16.9(FeS)		33.3	18.9 **
Fe(III) 8	0 ** (Fe ₂ O ₃)	39.3		18.2		25.8	
(Continued)							

Table 5 (Continued)

Metal	Oxide	Hydroxide	Carbonate	Sulfide	Chloride	Phosphate	Silicate
Pb(II)	15.4 (PbO)	16.1 18.8 (Pb ₃ (OH) ₂ (CO ₃) ₂)	13.1	26.6	4.79	43.5, 12.6 ** (PbHPO ₄)	
Mn(II)		9.2 (active) 11.6 (brucite)	4.9 (magnesite), 5.4 (nesquehonite), 16.7 ** (MgCa(CO ₃) ₂)		4.44 ** (MgCl ₂ (H ₂ O) ₆), 4 ** (KMgCl ₃ (H ₂ O) ₃)	28.4 (Mg ₃ (PO ₄) ₂) 12.6 ** (MgNH ₄ (PO ₄)) 13.2 ** (MgNH ₄ PO ₄ (H ₂ O) ₆) 5.0 ** (MgHPO ₄ (H ₂ O) ₃)	
Mn(II)	0.92 **	12.7	9.3	12.9 (crystalline), 15.7 (precipitated)		22	13.2 **
Hg(II)	25.7 **	25.4		52.2 (metacinnabar) 53.6 (cinnabar)			

(Continued)

Table 5 (Continued)

Metal	Oxide	Hydroxide	Carbonate	Sulfide	Chloride	Phosphate	Silicate
K(I)			-4.11				76** (orthoclase) 124** (muscovite)
Na(I)							40.6** (albite) 294** (Na-montmorillonite)
Ni(II)	14.81 (fresh) 17.31 (aged)		18.5 25.7				
Zn(II)	15.7 (amorphous) 16 (amorphous, aged) 16.9 (cryst. aged)		25.2 (sphaerite) 22.8 (wurzite) 22.1 (precipitated)		36.7	21.03**	

(Continued)

Table 5 (Concluded)

* Values in $p_{K_{sp}}$ (log K_{sp}) when I (ionic temperature) = 0, T (temperature) = 25°C.

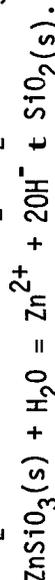
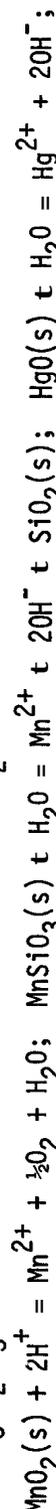
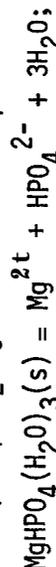
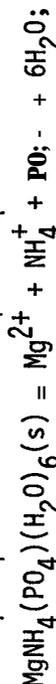
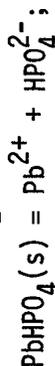
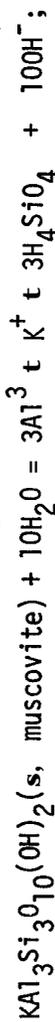


Table 6

Metal-Ligand Formation Constants

<u>Metal</u>	<u>Ligand</u>	<u>log K₁</u>	<u>log K₂</u>	<u>log K₃</u>	<u>log K₄</u>	<u>log K₅</u>	<u>log K₆</u>
Cd(II)	Cl ⁻	2.69	2.69	2.78	2.91	1.00	2.25
	OH ⁻	6.08	8.70	8.38	8.42	7.78	6.90
	CO ₃ ⁼			6.24			
	HS ⁼	7.94	15.21	17.09	19.29		
Cu(II)	SO ₄ ⁼	- 0.96	- 0.06	1.69			
	Cl ⁻	1.58	1.47	1.39	1.29		
	OH ⁻	6.0	13.18	14.42	14.56		
	CO ₃ ⁼	6.77	10.01				
	SO ₄ ⁼	1.8	1.9	2.3			
Fe(II)	Cl ⁻	0.38	0.81				
	OH ⁻	6.10	9.07	8.23			
	SO ₄ ⁼	2.3					
Fe(III)	Cl ⁻	1.22	1.72	0.52	- 3.21		
	OH ⁻	10.16	20.37		35.29		
	SO ₄ ⁼	4.0	5.4				

(Continued)

Table 6 (Concluded)

<u>Metal</u>	<u>Ligand</u>	<u>log K₁</u>	<u>log K₂</u>	<u>log K₃</u>	<u>log K₄</u>	<u>log K₅</u>	<u>log K₆</u>
Mn(II)	Cl^-	1.08	1.52	1.11			
	OH^-	3.82		7.8			
	$\text{SO}_4^{=}$	2.11					
Ni(II)	Cl^-	0.72	0.70				
	OH^-	4.70	10.96				
	$\text{SO}_4^{=}$	2.18					
Pb(II)	Cl^-	1.60	1.78	0.78	1.04	1.52	3.02
	OH^-	6.73	11.11	14.11	16.20		
	$\text{CO}_3^{=}$	7.4	9.89				
	$\text{SO}_4^{=}$	2.62	0.85				
Zn(II)	Cl^-	0.43	0.61	0.53	0.20		
	OH^-	4.4	12.89	14.4	15.5		
	$\text{SO}_4^{=}$	2.37					

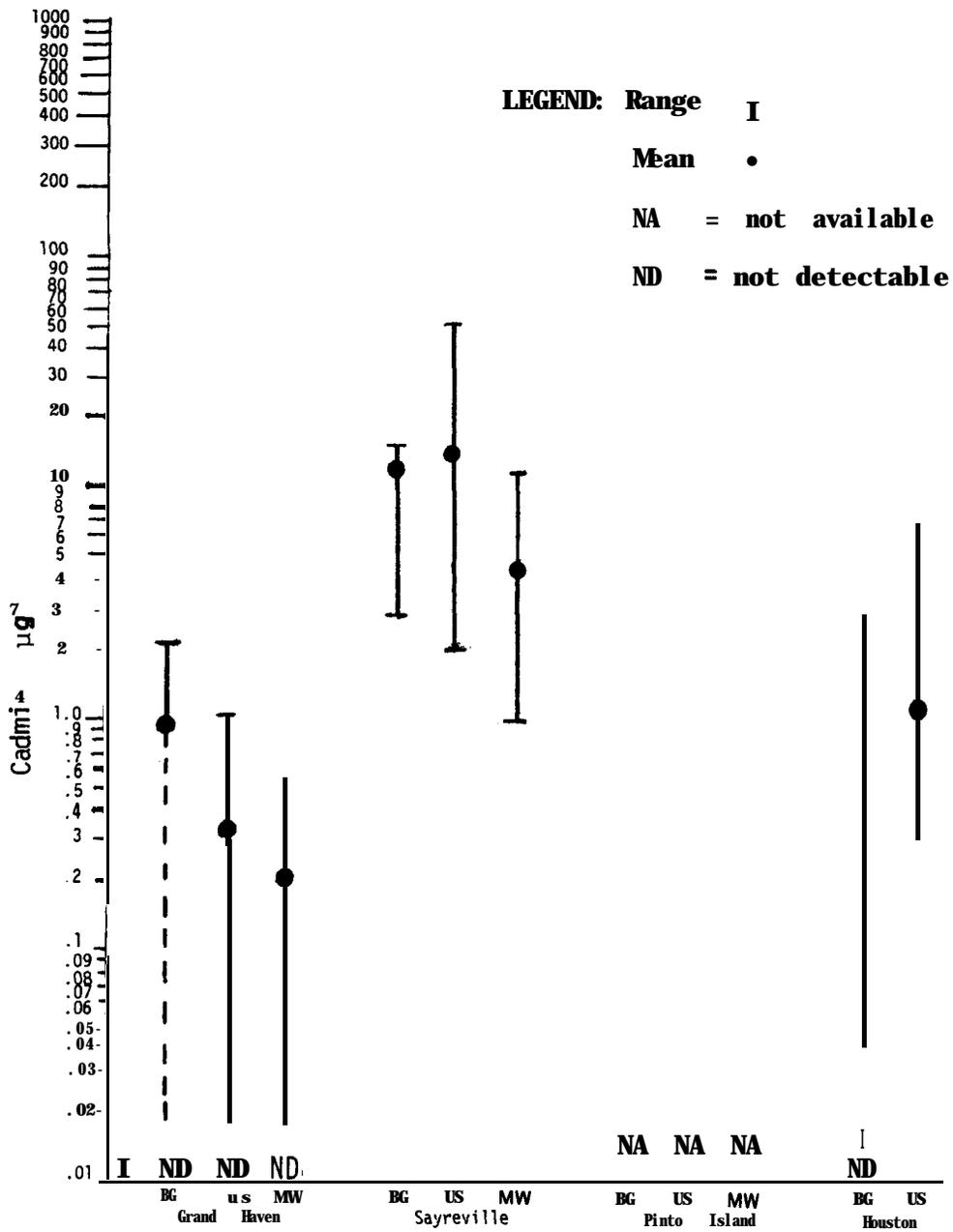


Figure 21. Comparison of cadmium values for groundwater samples

appears to be, greatly influenced by surrounding industrial activity. Background values obtained in the initial study and during the project extension revealed greater values than the undersite concentration. A probability value depicting a strong statistical relationship suggests the correlation of indigenous cadmium values with industrial sources.

61. The potential for cadmium leaching from Grand Haven and Sayreville appears to occur. As presented later in Part XV of this report, the major controlling mechanisms appear to be regulated by either cadmium sulfide or cadmium carbonate solids and by adsorption.

62. Total free sulfide (S_T) in solution include H_2S , HS^- , and $S^{=}$. The distribution of these species is pH dependent. The concentration of the sulfide ion can be calculated as follows:

$$S^{=} = \frac{S_T}{1 + \frac{K}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}} \quad (1)$$

63. Through the use of data in Tables 4, 5, and 6, theoretical solubility values can be calculated. These values are based upon the assumptions that in an oxidizing condition cadmium carbonate is the controlling solid where:

$$Cd^{+2} = \frac{K_{sp}}{[CO_3]} = \frac{10^{-13.69}}{[CO_3]} \quad (2)$$

In a reducing setting where cadmium sulfide is the stable solid, cadmium concentrations are given by:

$$Cd^{+2} = \frac{K_{sp}}{[S^{=}]} = \frac{10^{-26.96}}{[S^{=}]} \quad (3)$$

Based upon the sulfide concentration, the soluble cadmium can range from

submicrogram per litre to micrograms per litre.

64. Free cadmium concentrations calculated from these equations for both sulfide and carbonate solids for the three sites are tabulated as follows:

<u>Site</u>	<u>pH Range</u>	<u>CdS Control, $\mu\text{g/l}$</u>	<u>CdCO₃ Control, mg/l</u>
Sayreville	3.1-7.3	$2.1 - 4.2 \times 10^{-4}$	$2.2 \times 10^{-4} - 7.2$
Grand Haven	6.8-8	$1.3 \times 10^{-7} - 2 \times 10^{-3}$	2.2 - 24
Houston	6.6-7.8	$1.3 \times 10^{-16} - 2.1 \times 10^{-3}$	1.4 - 11

65. Values for the oxidizing environment were similar to those observed for high pH values. At the other end of the pH scale, the observed values were lower than the theoretical concentrations.

Copper

66. Samples from Sayreville sites exhibited the highest copper concentrations. Average background values of 548 $\mu\text{g/l}$ were significantly higher than the undersite level of 101 $\mu\text{g/l}$ and offsite monitoring groundwater wells of 39 $\mu\text{g/l}$. The highest recorded copper concentrations in the groundwater samples were found in the background well NJJ of 13 mg/l which was similar to the relationship reported in the initial report. Concentration ranges of copper are shown in Figure 22.

67. Low pH values in the Sayreville samples (range of 3.1 - 7.3) may partially account for the observed copper levels. The background well, NJJ, with an average pH of 3.4, exhibited the highest concentrations of soluble copper. Previously reported high Eh values at Sayreville, which, in conjunction with the low pH, suggest an effective acidic and oxidizing environment conducive to the support of solubilization of copper. However, the simple solubility

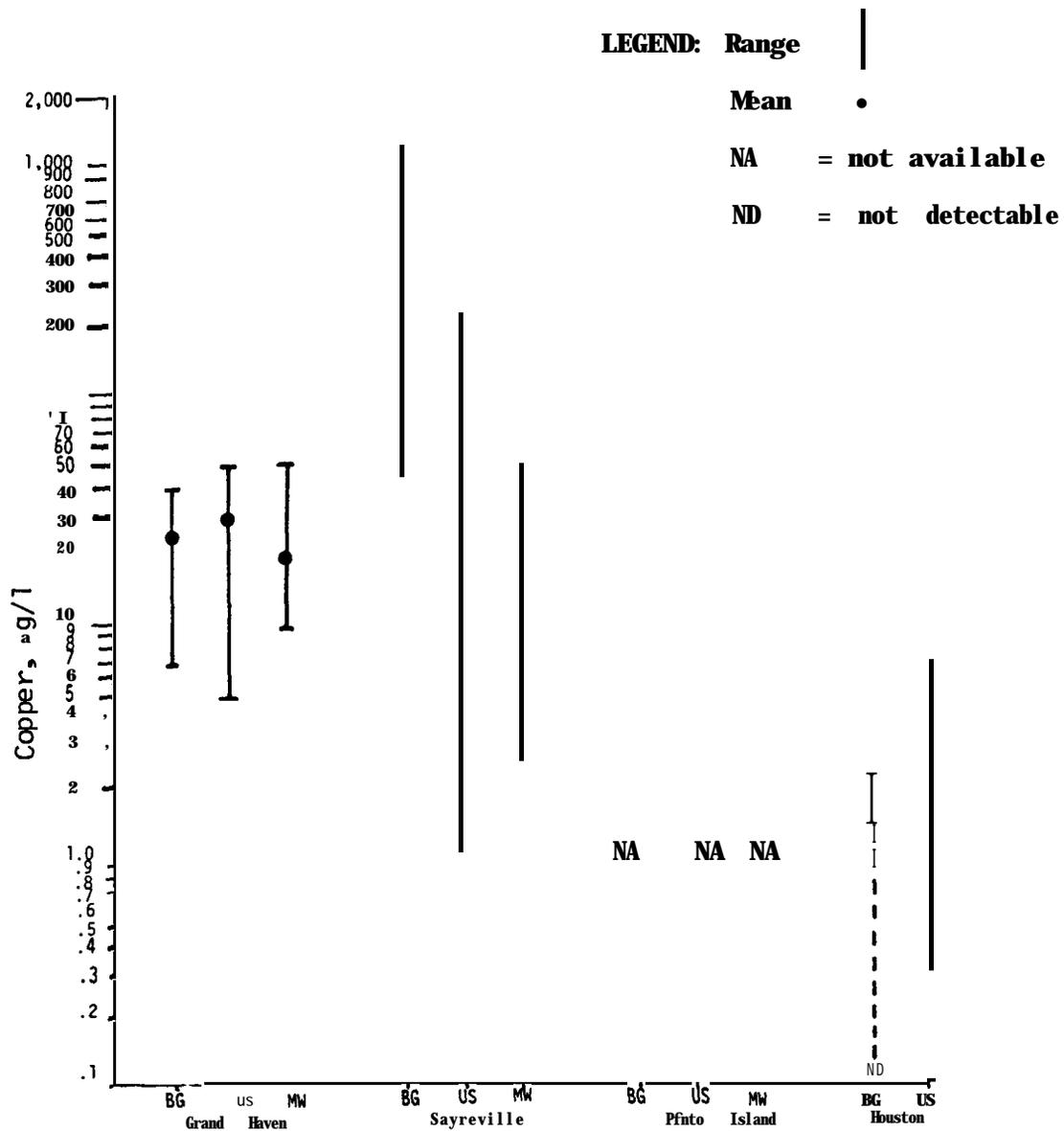


Figure 22. Comparison of copper values for groundwater samples

concentrations for Cu^{+2} result in levels several orders of magnitude higher than those observed. This observation suggests that several attenuation mechanisms exist which may be responsible for the measured values. Several proposed phenomena may include sorption of copper by iron and manganese oxides, interactions with clay and organic particulates, and copper chelation with humic substances. The situation of the Sayreville site in a marsh area may support the general assumption that copper is strongly complexed with organic matter. In some ways, all of the mechanisms mentioned probably govern the transport and observed copper levels in the disposal sites. Probability values calculated for copper for the three well groups provided poor correlation between groups. Reported values were within \pm 25 percent of results obtained in the first sampling program

68. Grand Haven background and undersite average copper values were similar (25 versus 30 $\mu\text{g}/\text{l}$) and student t-tests suggested a significant probability in this relationship. It is difficult to speculate as to the leaching potential at the site due to this relationship.

69. Copper levels at Houston were found to be higher in the under-site samples (44.6 $\mu\text{g}/\text{l}$) than in the sole background well (7.2 $\mu\text{g}/\text{l}$). The existence of a dense clay underlying the site could provide an excellent medium for the adsorption of the majority of the positively charged copper species. This setting could partially account for the lower offsite values.

70. Theoretical copper calculations can be obtained from simple solubility concentrations. In an oxidizing environment the copper concentrations can be determined using the following equation:

$$\text{Cu}^{+2} = \frac{K_s^{\frac{1}{2}}}{\text{OH}^- \text{CO}_3^{= \frac{1}{2}}} = \frac{10^{-16.6}}{\text{OH}^- \text{CO}_3^{= \frac{1}{2}}} \quad (4)$$

In a reducing environment copper sulfide is expected to be the controlling solid due to its low solubility product. In this case, the copper concentration is as follows:

$$\text{Cu}^{+2} = \frac{K_{sp}}{S} = \frac{10^{-36.4}}{s} \quad (5)$$

By using these solubility equations, the following values can be calculated:

<u>Site</u>	<u>pH Range</u>	<u>Oxidizing CuCO₃ Control (µg/l)</u>	<u>Reducing CuS Control (µg/l)</u>
Sayreville	3.1-7.3	1.3 - 2.0 x 10 ³	4.0 x 10 ⁻⁸ - 1.6 x 10 ⁻¹⁴
Houston	6.6-7.8	0.178 - 1.99	4.01 x 10 ⁻¹⁴ - 2.53 x 10 ⁻¹⁵
Grand Haven	6.8-8.0	0.505 - 2.5	2.53 x 10 ⁻¹⁴ - 2.01 x 10 ⁻¹⁵

71. Observed values of soluble copper are generally in agreement with the predicted values from calculations based on Cu₂CO₃(OH)₂ as the controlling solid. Deviation from calculations may result from adsorption, precipitation, or complexation. Complexation with other ligands, for example, may result in higher copper concentrations through solubilization. Copper complexation with organic matter, chloride, hydroxide, and sulfate is quite common.

72. Existing high levels of copper in the background groundwater at Sayreville complicate the establishment of leaching effects of copper from the site. Both undersite and background values were higher than

monitoring well values, which were situated in a marsh area relatively free from intrusion of background sources and from tidal influences. Lower values in the three monitoring wells could be due to the complexing with organics to form insoluble complexes in the marsh areas or through precipitation or adsorption mechanisms. The hydrogeological setting at Houston precludes any valid correlation between the under-site and background samples.

Iron

73. Soluble iron concentrations measured in the groundwater samples varied greatly. A difference of up to four orders of magnitude was observed as shown in Figure 23. The wide variations are probably a combined effect of pH, redox, and complexation.

74. Low pH and Eh waters are known to favor the mobilization of iron. However, in nature, low pH is generally the result of oxidation. At the Sayreville site, where the lowest pH values were encountered (3.4-6.7), iron values were generally lower than Grand Haven or Houston sites with more alkaline environments. Obviously, within the pH and Eh values encountered in this study, the effect of redox conditions is much more profound than variation in pH values. A potential for mobilization appears to exist at Grand Haven, Houston, and, possibly, Sayreville. Grand Haven and Houston both exhibit higher undersite values with decreasing levels in surrounding groundwater samples. While the Sayreville site exhibited a potential for mobilization from the dredged material to groundwater, the high background values (1.4 mg/l) tend to negate such speculation.

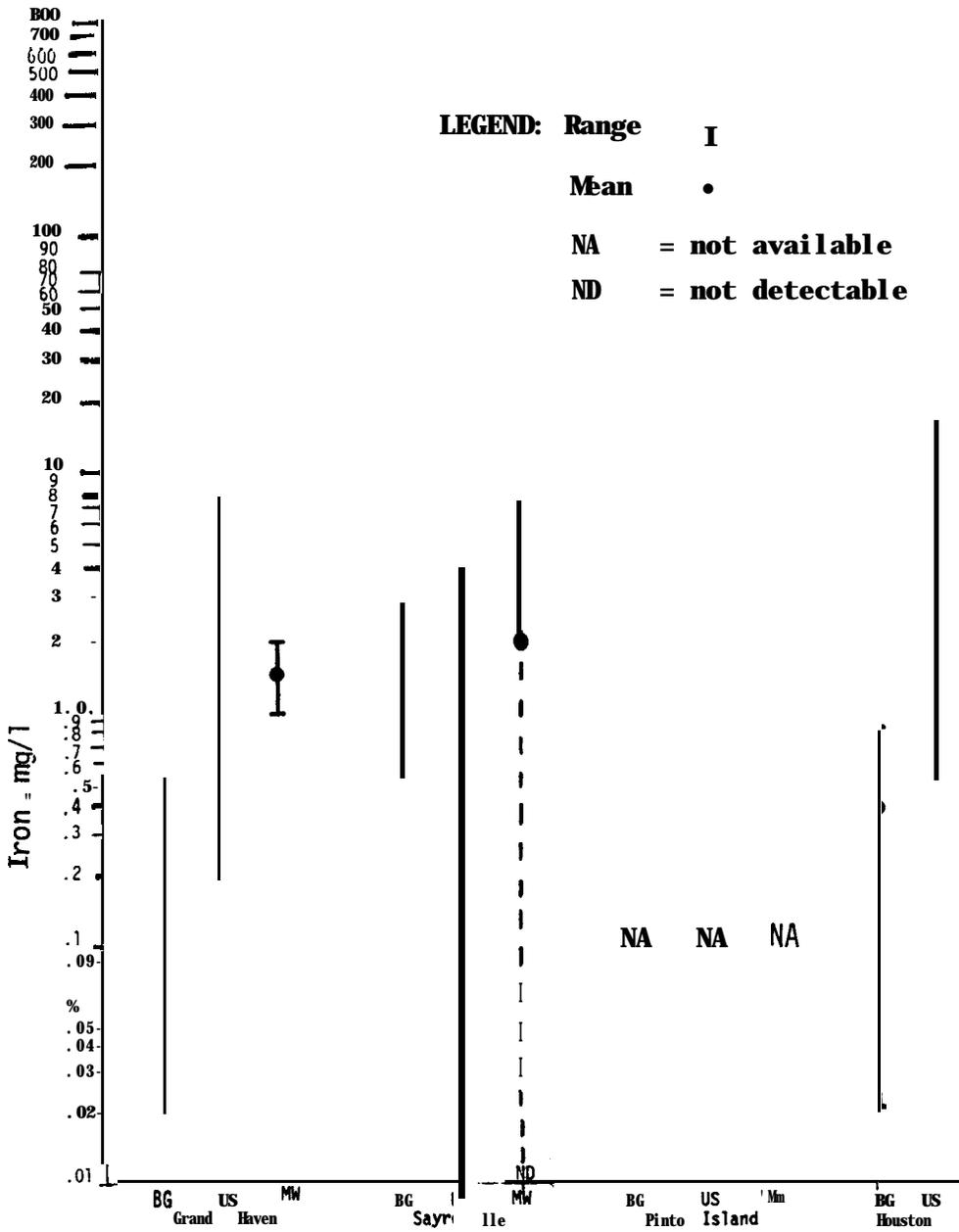


Figure 23. Comparison of iron values for groundwater samples

Lead

75. Lead was present at low concentrations in leachates and groundwaters at the three monitoring sites. Houston samples exhibited the highest concentrations with an average of 45.9 $\mu\text{g/l}$ for onsite wells and 9.6 $\mu\text{g/l}$ for the background wells. Of the three sites, onsite values were found to be highest with background wells containing the lowest soluble lead concentrations. This is shown in Figure 24.

76. Lead sulfate is believed to be the controlling solid in low pH and high sulfate groundwater samples. Calculations performed in the original study, assuming a sulfate value of $10^{-2.5}$ M and a total carbon value of $10^{-3.3}$ M reveal that lead sulfate is the controlling solid at pH values of less than 6. Lead carbonate becomes the controlling solid in the 6 to 11.5 pH range. By using these data, the following theoretical values can be developed:

<u>Site</u>	<u>pH Range</u>	<u>Actual Range Lead, $\mu\text{g/l}$</u>	<u>Theoretical Calculation PbCO_3 as Control Solid $K_{\text{sp}} = 10^{-13.30}$ $\mu\text{g/l}$</u>
Sayreville	3.1-7.3	0.2-60	$1.04 \times 10^{-4} - 3.28 \times 10^3$
Houston	6.6-7.8	2-100	$2.07 \times 10^2 - 10.4 \times 10^4$
Grand Haven	6.8-8.0	0.4-40	$1.04 \times 10^3 - 2.07 \times 10^4$

77. As revealed from the theoretical versus observed groundwater values, the analytical concentrations are close to the theoretical range. The lower actual values are most probably due to adsorption by clay minerals which were found in the majority of the site soils.

78. Of the three sites for which lead was analyzed, the Grand Haven site appeared to represent the greatest leaching potential with background, undersite, and monitoring well levels of 0.7, 11.2, and

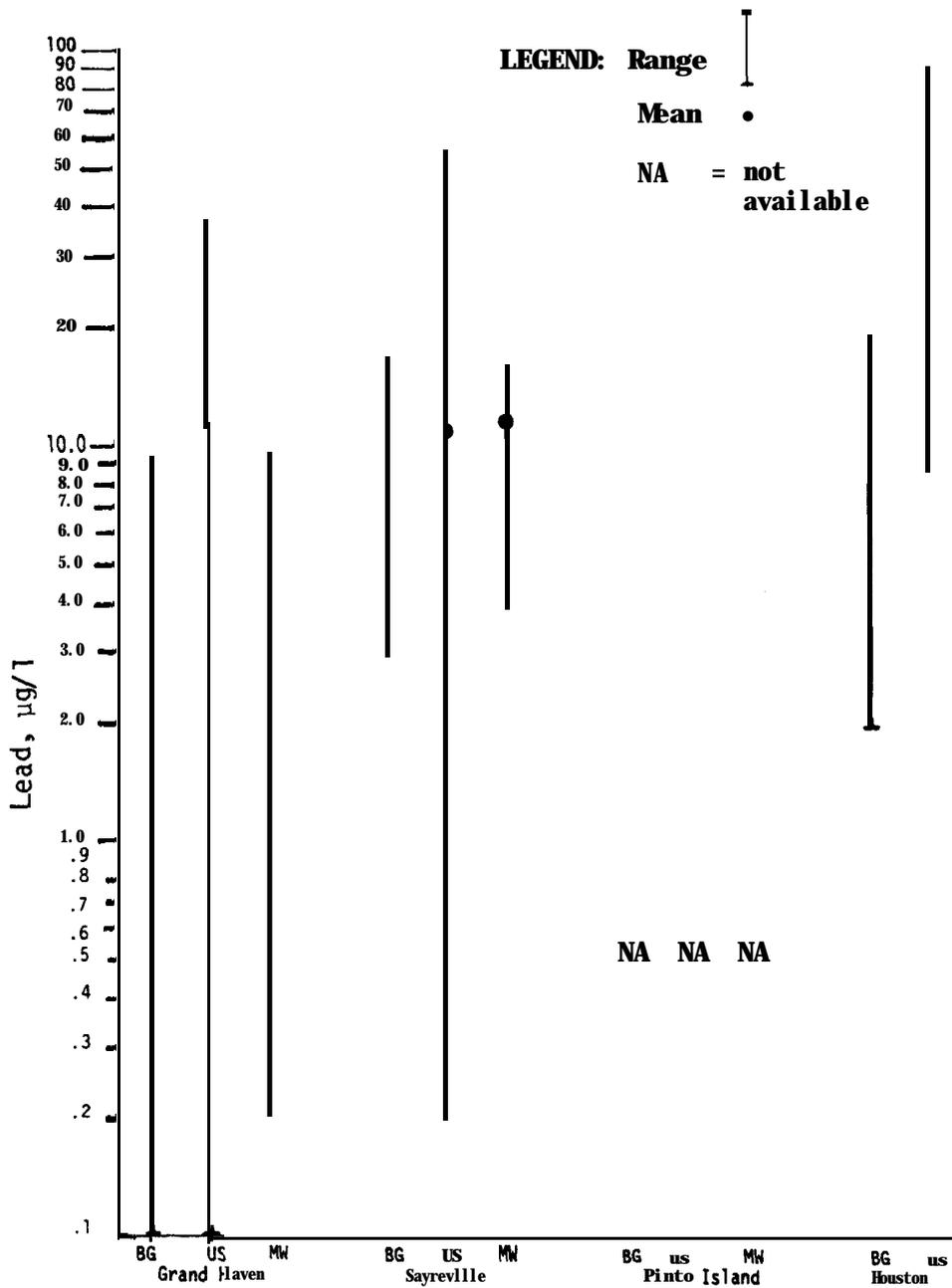


Figure 24. Comparison of lead values for groundwater samples

2.5 µg/l, respectively.

79. The other two monitored sites indicated little or no leaching potential.

Manganese

80. The majority of groundwater samples tested for soluble manganese were found to be greater than the recommended Environmental Protection Agency drinking water standard of 0.05 mg/l. Sayreville generally exhibited the highest values (Figure 25).

81. Manganese data suggest a leaching potential at Grand Haven and possibly Sayreville. A low value of "P" for undersite versus surrounding groundwater supports this conclusion. A similar situation exists at the Sayreville site where the average undersite value for manganese was 7.1 mg/l and the average value for monitoring wells was 0.64 mg/l. The high manganese value for the background well, NJJ, of 11.6 mg/l may indicate a favorable pH and redox combination for the solubilization of manganous species.

82. Houston's undersite high manganese value of 6.5 mg/l is difficult to correlate with the background well due to the hydrogeological system. Comparison of these two values and the potential impact is therefore difficult. However, substantial leaching of manganese is possible.

83. Manganese appears to represent a potential threat to indigenous groundwater sources. The contribution of manganese to monitoring wells seems to be negligible at the Sayreville site; Houston could pose a potential hazard, although the clay aquifer under the site may preclude significant manganese movement. Leachate samples from the undersite wells

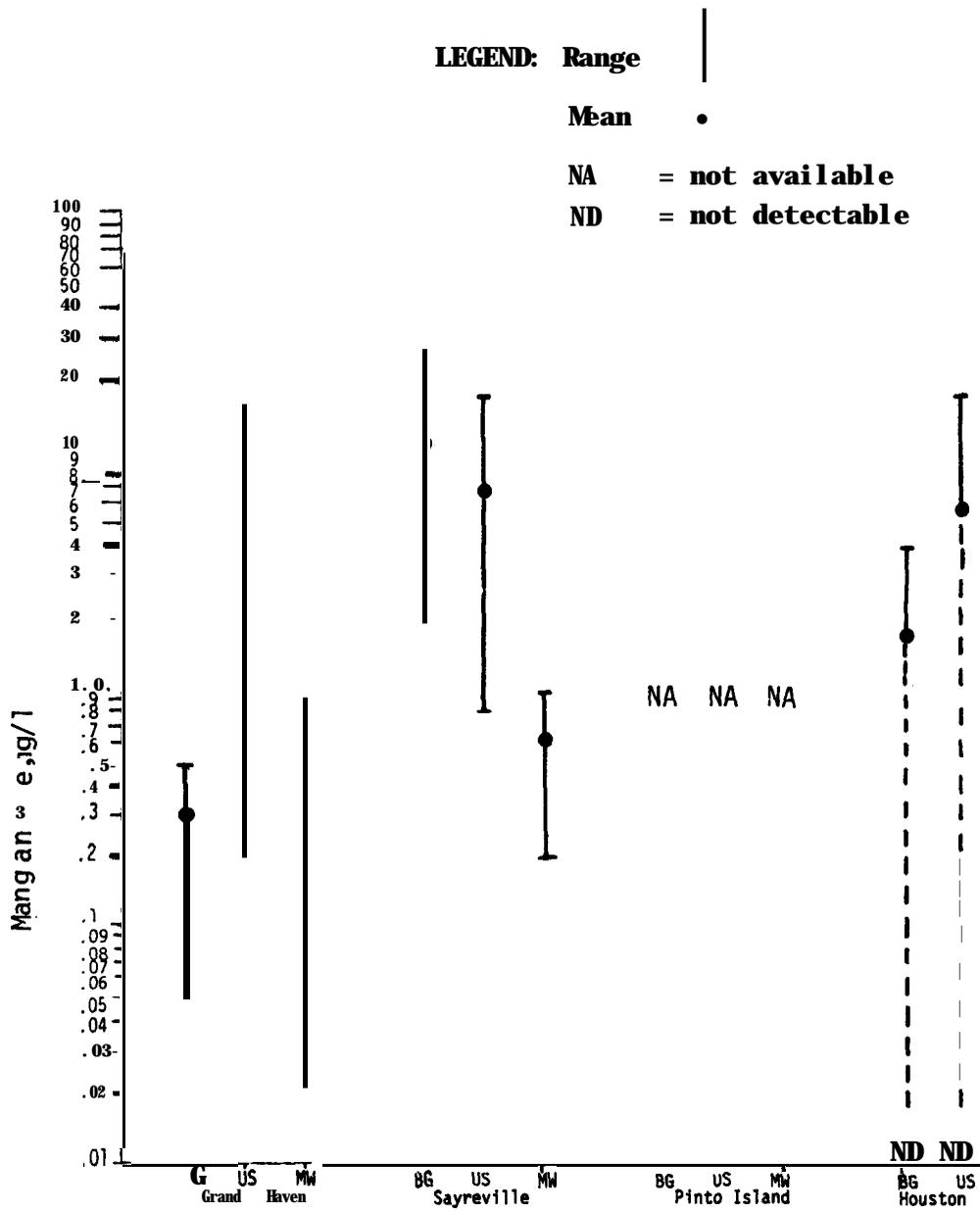


Figure 25. Comparison of manganese values for groundwater samples

at Grand Haven appear to represent the greatest potential for contaminating groundwater since the undersite concentrations were greater than the groundwater levels.

Mercury

84. Mercury values, as determined by the cold vapor method, produced a range of values from below detection ($<0.01\mu\text{g/l}$) to a high of $33\ \mu\text{g/l}$ for one sample. Most samples were near $1\ \mu\text{g/l}$ as shown in Figure 26.

85. Sayreville generally exhibited the highest mercury concentrations with an undersite average value of $1.8\ \mu\text{g/l}$, a monitoring well value of $1.3\ \mu\text{g/l}$, and a background groundwater value of $1.4\ \mu\text{g/l}$. Statistically, these values have high "P" values and are therefore not highly correlatable. Because mercury can be removed through complexations with soil organic matter and adsorbed into inorganic sediment, potential for mercury mobilization appears to be minimal. The difference among well groups also suggests such a trend.

86. Mercury concentrations are controlled by mercury sulfide (HgS , $K_{sp} = 10^{-5.39}$) in a reduced environment and mercury hydroxide ($\text{Hg}(\text{OH})_2$, $K_{sp} = 10^{-25.4}$) in an oxidizing environment. The free mercury values (Hg_f) are established for either of these controlling solids by the following equation:

$$\text{Hg}_f = \frac{10^{-53.9}}{[\text{S}]} \quad \text{or} \quad \frac{10^{-25.4}}{[\text{OH}^{-2}]} \quad (6)$$

Considering each of these two controlling solids, soluble mercury concentrations can be calculated for the ranges of observed pH values.

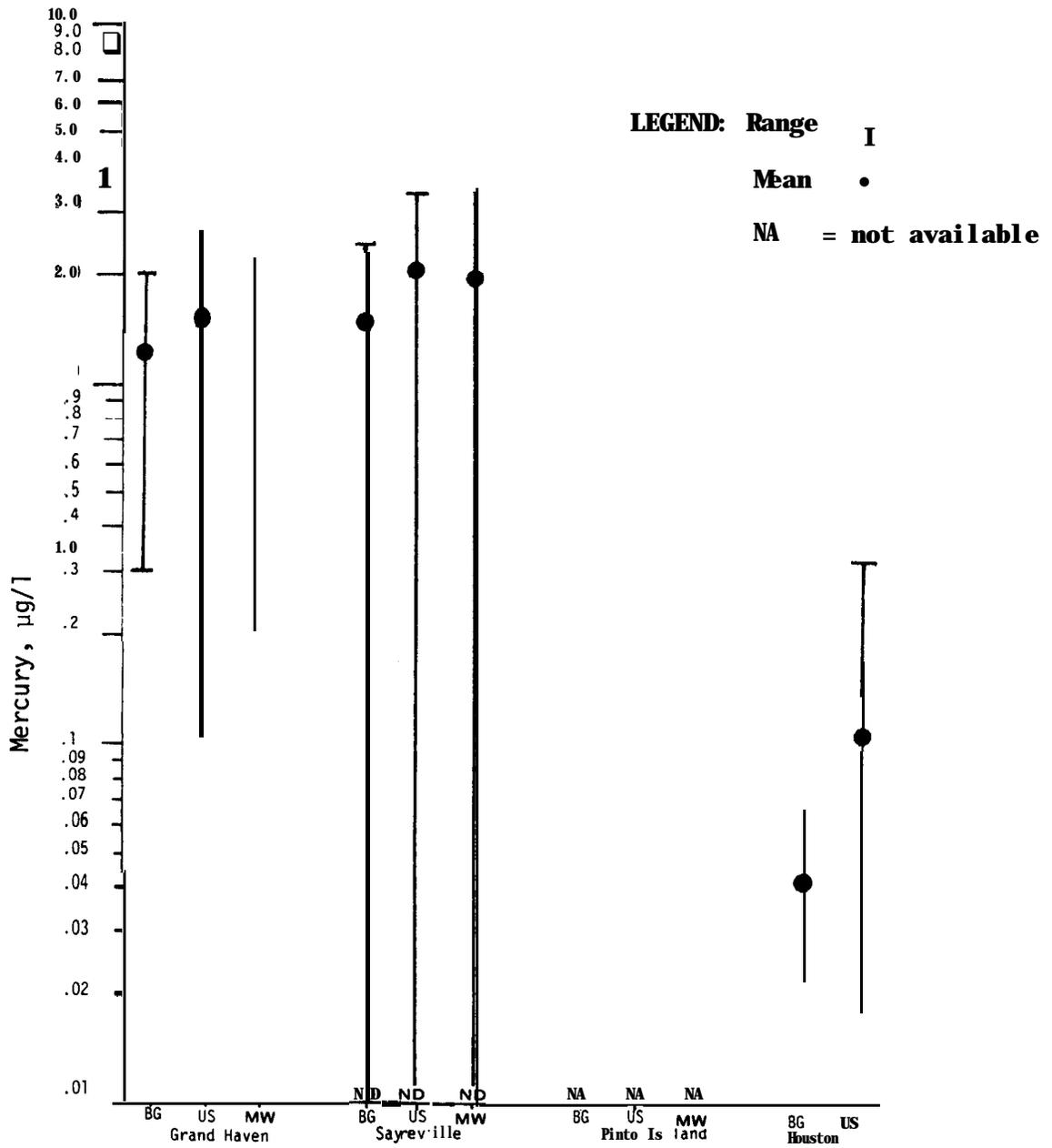


Figure 26. Comparison of mercury values for groundwater samples

<u>pH</u>	<u>Hg(OH)₂ Control, µg/l</u>	<u>HgS Control, µg/l</u>
3.1	1.05 x 10 ⁴	4.0 x 10 ⁻²⁵
6.6	5.04 x 10 ⁻³	4.0 x 10 ⁻³¹
6.8	2.01 x 10 ⁻³	2.53 x 10 ⁻³¹
7.3	2.01 x 10 ⁻⁴	1.59 x 10 ⁻³¹
7.8	2.01 x 10 ⁻⁵	2.53 x 10 ⁻³²
8.0	7.98 x 10 ⁻⁶	2.01 x 10 ⁻³²

87. Observed mercury levels were found to be much higher than those theoretical calculations. This phenomenon can be explained by the contribution of mercury ligands (i.e., hydroxide, chloride, sulfide, and organic ligands) to the total concentration. This input could be expected to increase the mercury concentrations by several orders of magnitude above the theoretical solubility values.

88. Examination of groundwater data from this study in conjunction with earlier information indicates that a leaching potential does not exist for mercury species.

Nickel

89. Nickel concentrations in the study site are shown in Figure 27. Concentrations in groundwater wells ranged from 900 µg/l at Sayreville to nondetectable at Houston. A possible leaching potential between Sayreville's undersite and groundwater wells exists.

90. Grand Haven nickel concentrations exhibited a potential for leaching. Undersite mean values were 87 µg/l followed by offsite concentrations at the monitoring and background well groups of 15.8 and 11 µg/l, respectively. The "P" values between the well groups at Grand Haven reinforce this supposition. Average nickel concentrations of 128 µg/l

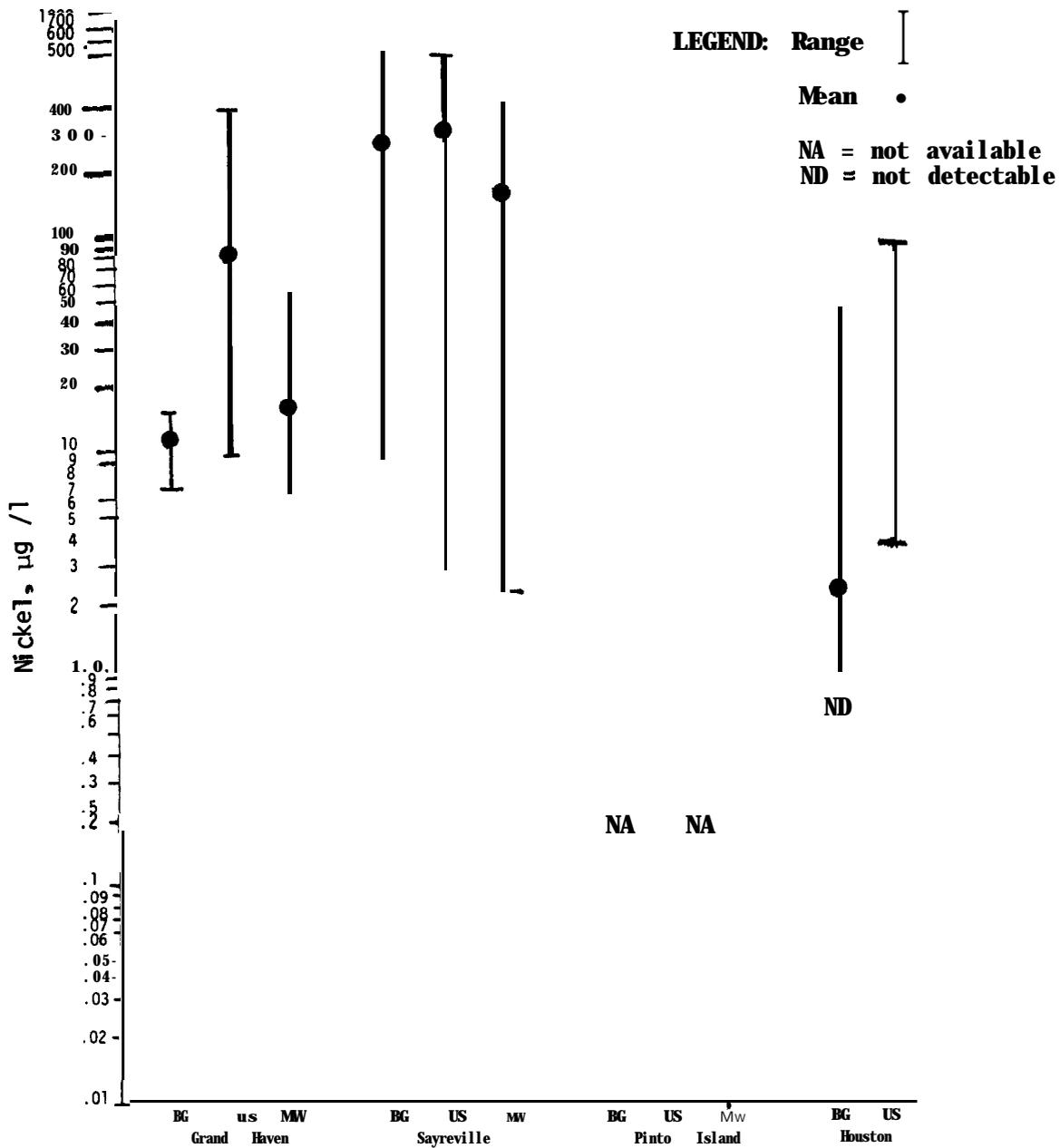


Figure 27. Comparison of nickel values for groundwater samples

from the first sampling at Grand Haven within the fill correlate well with the decreases observed in the present study. This concentration corresponds to an 18 percent nickel decrease between onsite data and the undersite wells. An attenuation of 67 percent occurred between undersite and the monitoring well groups.

91. Average nickel concentration for undersite well groups at Houston was 2 $\mu\text{g}/\text{l}$ with a background value of 20 $\mu\text{g}/\text{l}$. This situation, considering the isolated hydrogeological condition of the Houston site, precludes a plausible explanation.

92. Soluble nickel represented a leaching potential at the Grand Haven site. This conclusion, based solely on the groundwater samples, corresponds well with data generated in the first sampling program. Sayreville exhibited a high probability that leaching of nickel occurred based on onsite information from the original study and groundwater data from the undersite and monitoring well groups in the present study.

Zinc

93. As shown in Figure 28, concentrations of zinc in all sites studied were generally below 1 mg/l with the exception of the Sayreville site. Sayreville groundwater samples were found to contain the highest soluble zinc concentrations. The mean value at the background well was 2.2 mg/l with undersite averaging values of 0.78 mg/l and downstream wells exhibiting a mean of 0.16 mg/l . These high values are understandable in view of the proximity of National Lead Industry's titanium oxide plant situated approximately 1 mile from the site. Grand Haven contained similar average values for the three well groups, while Houston displayed greater undersite values than background values.

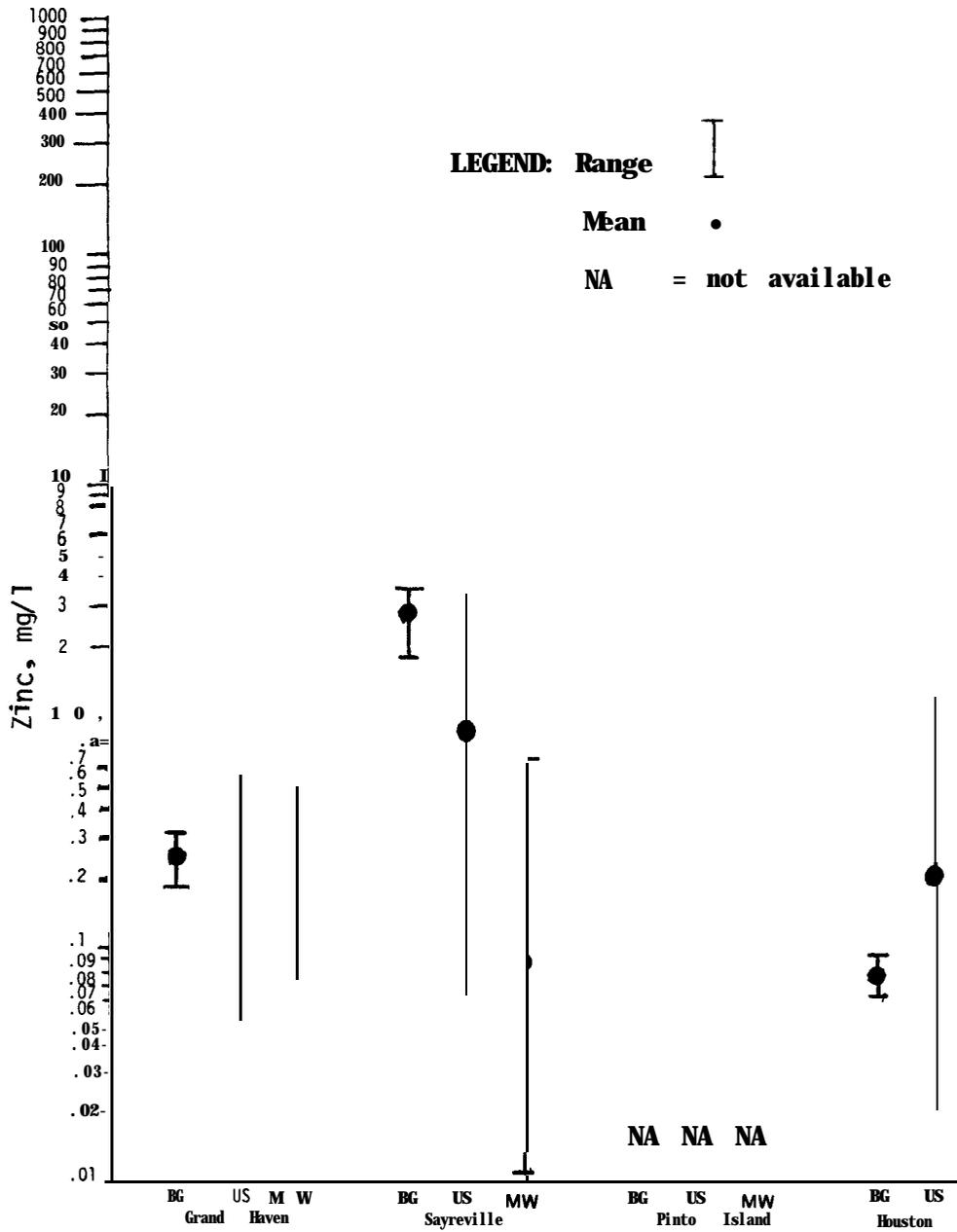


Figure 28. Comparison of zinc values for groundwater samples

94. Houston exhibited background zinc levels (0.04 mg/l) below the onsite concentrations (0.15 µg/l). Isolation of the fill material from indigenous groundwater by the impervious clay soils makes correlations between onsite and background values highly speculative.

95. Grand Haven exhibited average background values nearly identical to the onsite concentrations. Average downstream monitoring well values were found to be slightly lower.

96. Of the three sites, Sayreville reflected higher background zinc levels than either the onsite or downstream groundwater values. Soluble phase zinc concentrations at Grand Haven were nearly identical for all three well categories and Houston's hydrogeological peculiarities preclude definite relationships between the higher onsite values and the lower background values.

PART IV: PREDICTION OF WATER QUALITY

Introduction

97. Statistical analyses of the data generated from this study as well as the previously generated data indicate that there is a potential for groundwater contamination. While the degree to which these potential pollutants affect groundwater quality is a factor of many variables, theoretical models may be useful in defining the extent of the problem. Several available models, including adsorption, equilibrium and dilution, were reviewed for possible use. Two of these, the dilution and solubility equilibrium models, are presented as possible explanations for the observed results.

98. The dilution model was selected for use in determining whether dilution is a controlling mechanism for observed concentrations. Ions conducive to this model include sodium and potassium which do not readily form solid compounds or complexes under ordinary conditions.

99. The selected solubility calculation was chosen for its applicability for metals involved in dissolution-precipitation reactions. Applicable ions include calcium, magnesium, cadmium, copper, iron, lead, manganese, and nickel. Descriptions of the dilution and solubility equilibrium models are presented in the following pages.

Water Quality Models

Dilution Model

100. The dilution approach is designed to provide an indication of those metals which are largely controlled by dilution. By selecting a conservative element such as chloride, an example of an ideal dilution

situation can be presented. In this example, two waters with different chloride concentrations (Cl_1 and Cl_2) are mixed with the resulting water containing a chloride concentration between Cl_1 and Cl_2 . The chloride concentration of the mixed water would depend upon the concentration of Cl_1 and Cl_2 as well as the degree of mixing as expressed by:

$$Cl_1 \text{ (mixed)} = \frac{V_1 \times Cl_1 + V_2 \times Cl_2}{V_1 + V_2} \quad (7)$$

where V = volume of water

Cl = chloride concentration

Utilizing this approach with a conservative parameter along with another water quality criterion (Y), additional information may be developed.

Two water samples A and B are provided as an example:

<u>Water Body</u>	<u>Chloride Concentration</u>	<u>Y Concentration</u>
A	200	Y_1
B	50	Y_2

By mixing varying amounts of A and B, new water bodies containing different Y and Cl combinations may be created. If both chloride and Y are assumed to be conservative properties, a $Y-Cl$ plot should result in a straight line. Also, simple calculations can be performed. As an example, assume:

$$\begin{aligned} Y_1 &= 80 \text{ mg/l}, & Cl_1 &= 400 \text{ mg/l}, & V_1 &= 3 \text{ l} \\ Y_2 &= 20 \text{ mg/l}, & Cl_2 &= 100 \text{ mg/l}, & V_2 &= 1 \text{ l} \end{aligned}$$

With this information, the following calculations may be made:

$$Y = \frac{3 \times 80 \text{ mg/l} + 1 \times 20 \text{ mg/l}}{3 + 1} = 65 \text{ mg/l} \quad (8)$$

$$Cl = \frac{3 \times 400 \text{ mg/l} \times 1 \times 100 \text{ mg/l}}{3 + 1} = 325 \text{ mg/l} \quad (9)$$

If Y is a nonconservative property, other controlling mechanisms would be assumed to exert a partial or major influence. If other controlling mechanisms reduce the concentration of Y from solution, the points corresponding to the diluted water would be expected to lie below the line. Utilizing the example in which A (leachate) and B (background) are used, the following combinations would be expected:

- a. The Y-Cl plot is a straight line indicating that Y is a conservative property. Depending upon the proximity of the data to either A or B, the degree of mixing and volume of water involved could be postulated.
- b. All data points are above the V_1-V_2 line indicating that a minimum of one additional controlling mechanism releasing Y into solution exists.
- c. All data points are below the V_1-V_2 line indicating that at least one additional controlling mechanism exists for removal of Y from the solution.
- d. Data points provide no discernable pattern. In this case, a number of controlling mechanisms and interference sources may exist.

101. An attempt to explain the observed values of some parameters according to this model necessitates that carefully chosen wells be considered. The wells should be free of apparent sources of interference (i.e., tidal, groundwater flow reversal, and anomalies) and be situated in a groundwater flow path so that interception of the same water between wells may be compared. For this purpose, three wells were chosen at a given site which met these criteria, namely, background, under-site, and downstream wells. The following wells were chosen at three of the four field sites:

<u>Site</u>	<u>Background</u>	<u>Undersite</u>	<u>Offsite Monitoring Well</u>
Sayreville	NJJ	NJA	NJF
Grand Haven	MPW	MB	MD
Pinto Island	PI-I	PI-D	PI-H

The locations of these wells are illustrated in Figures 1-4. Pinto Island, which was sampled only twice, does not provide sufficient data points for a rigorous examination. Houston was not examined due to the hydrogeological situation which precluded such an examination.

102. The dilution approach was utilized for all heavy metals (Y) analyzed in the groundwater samples. Of the elements plotted against Cl, sodium appeared to result in the straightest line (see Figures 29-31). Discrepancies in the Na-Cl plots for Grand Haven could be a result of numerous exchange mechanisms (Figure 31). These factors were also apparent by the close correlation of the monitoring well values to background levels.

103. Plots for K-Cl provide relatively straight lines for Pinto Island and Sayreville. Plots of the K-Cl data for Grand Haven do not appear to result in a discernable pattern, suggesting that a number of other mechanisms exist (Figures 32-34).

104. The Mg-Cl and Ca-Cl plots are illustrated in Figures 35-39. The Mg-Cl plots for the three sites corresponded roughly to a straight line. This observation suggests that magnesium is diluted into the groundwater at a fairly constant rate. The deviations from a straight line suggest that other mechanisms (e.g., ion exchange) exist. The Ca-Cl plots showed a similar trend with the majority of plot deviations

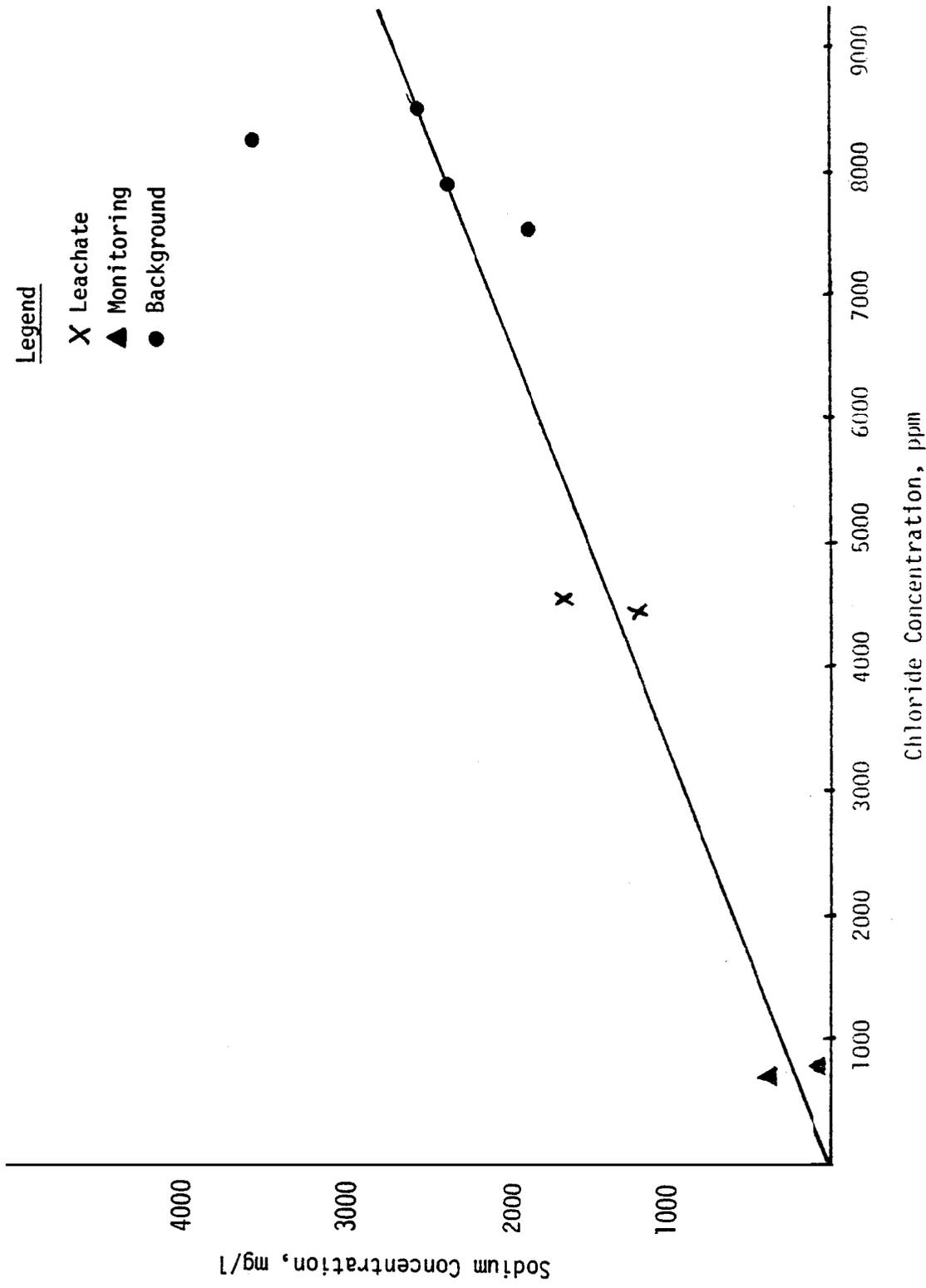


Figure 29. Na-Cl diagram for Sayreville

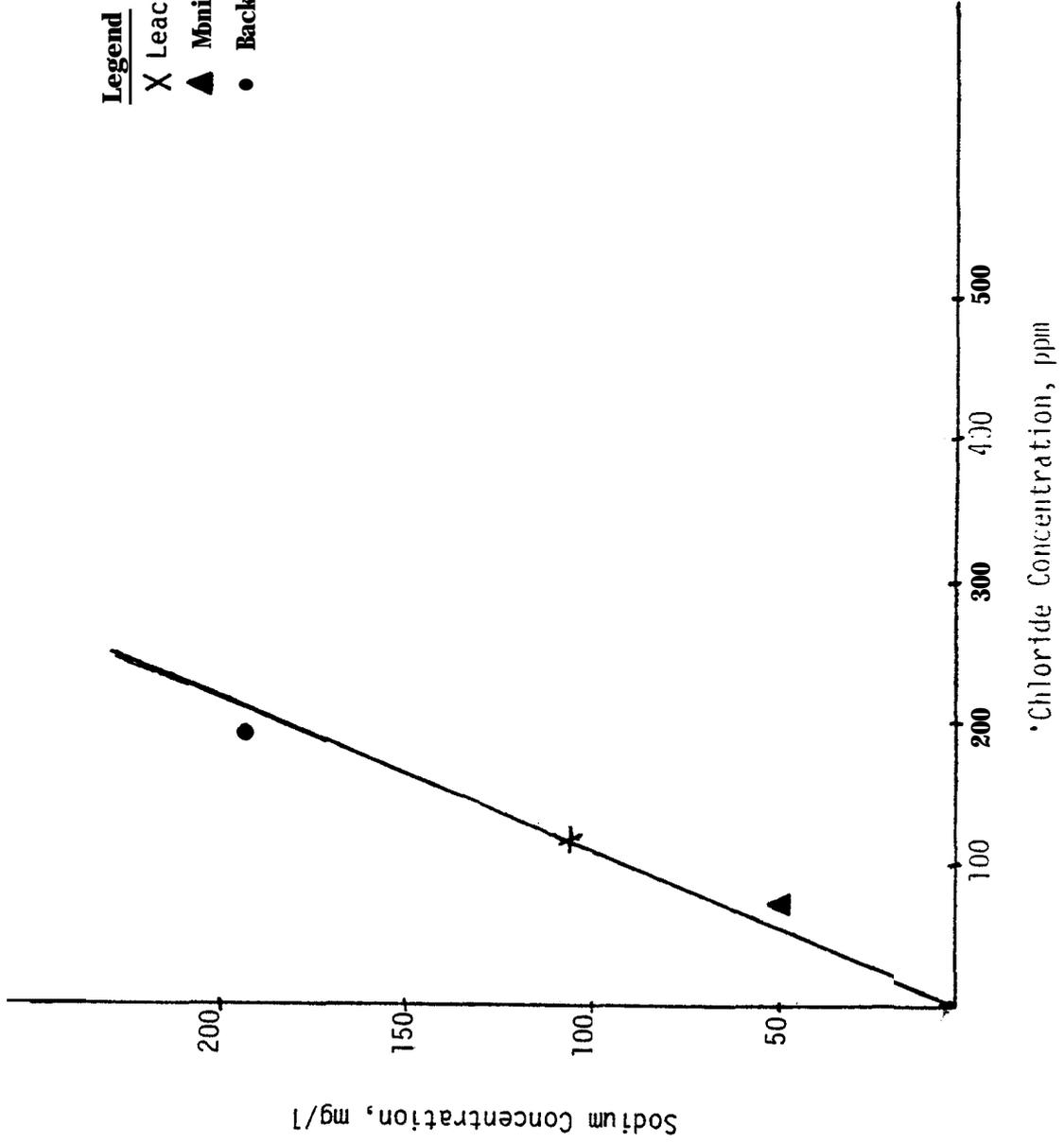
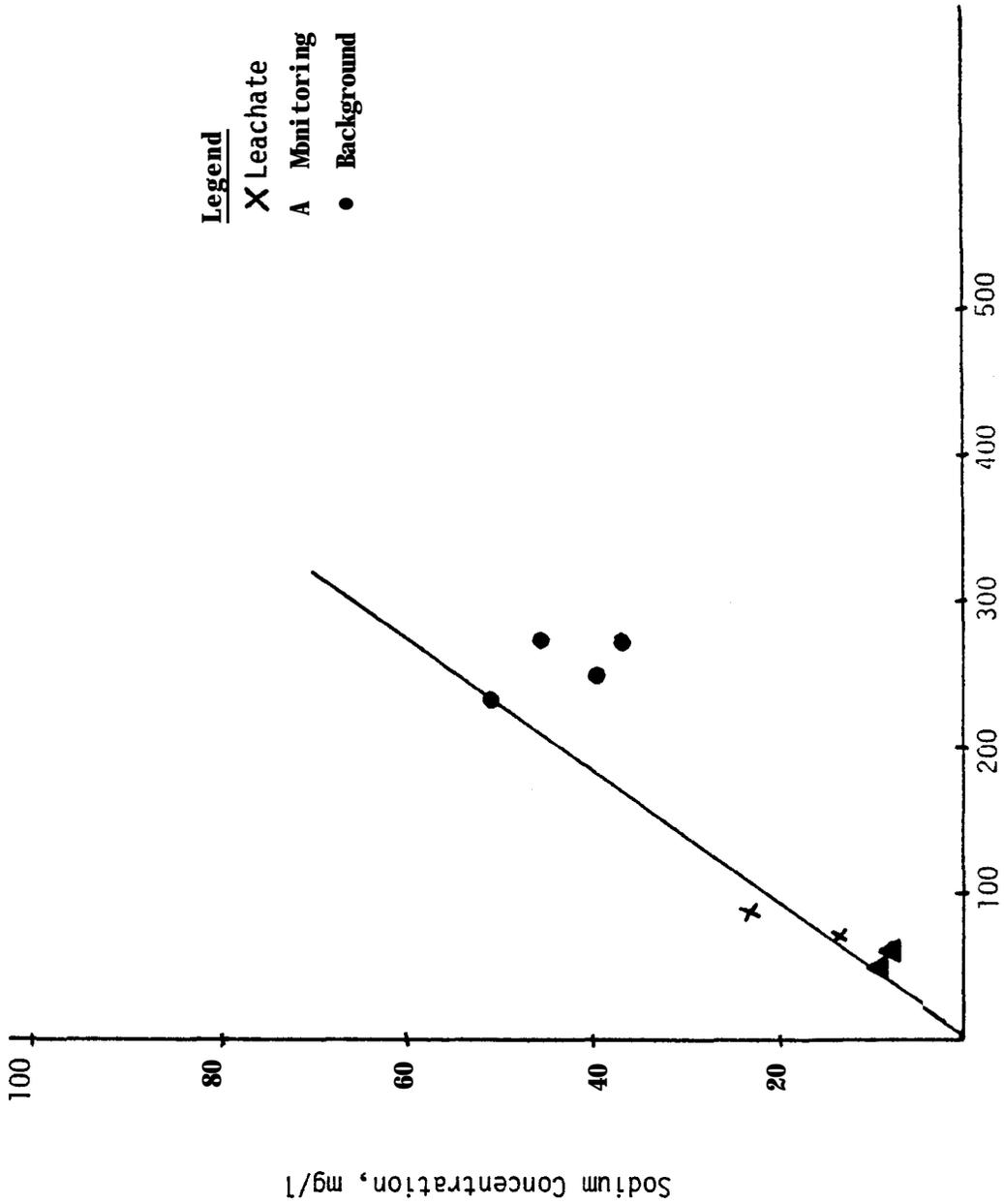
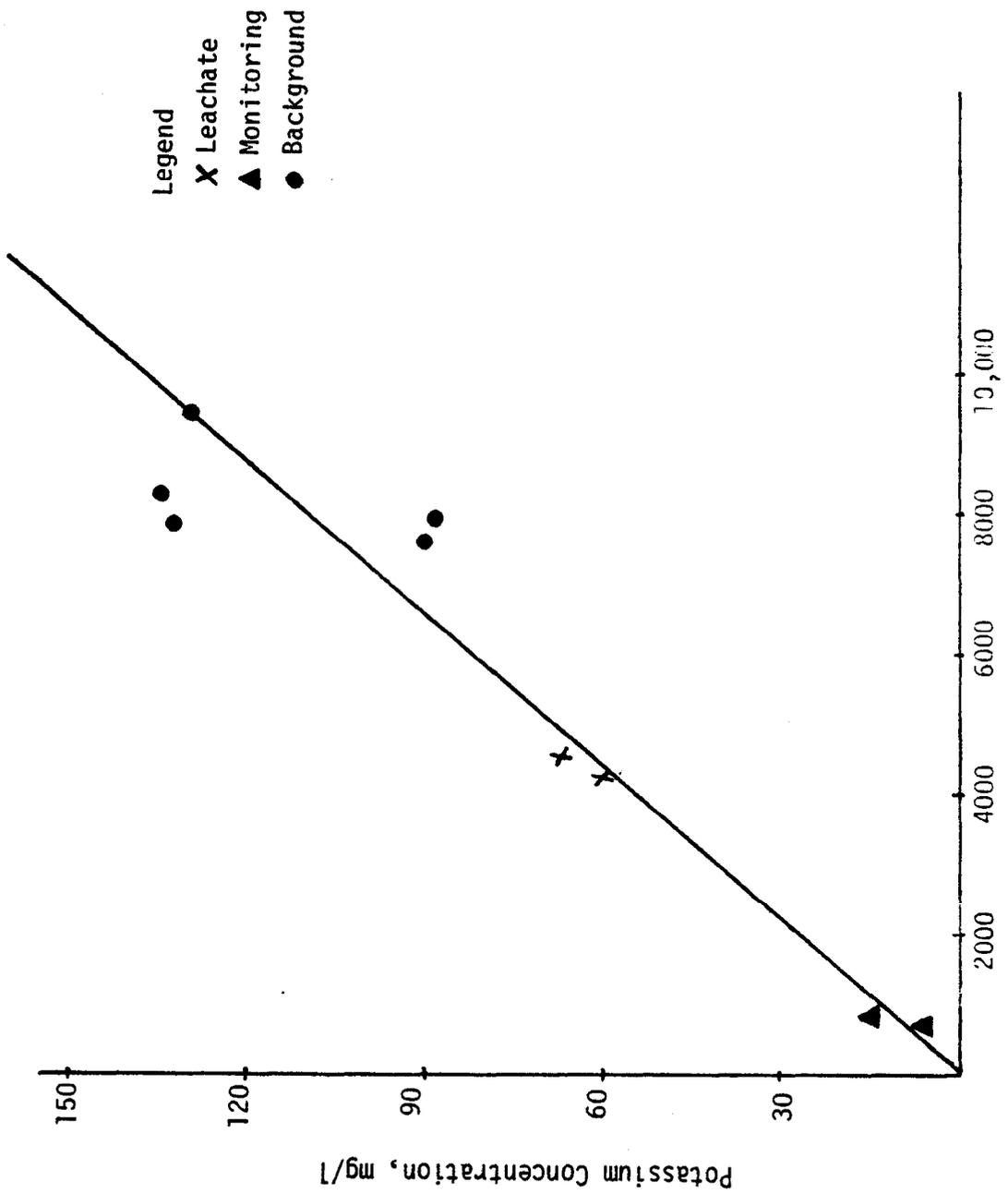


Figure 30. Na-Cl diagram for Pinto Island



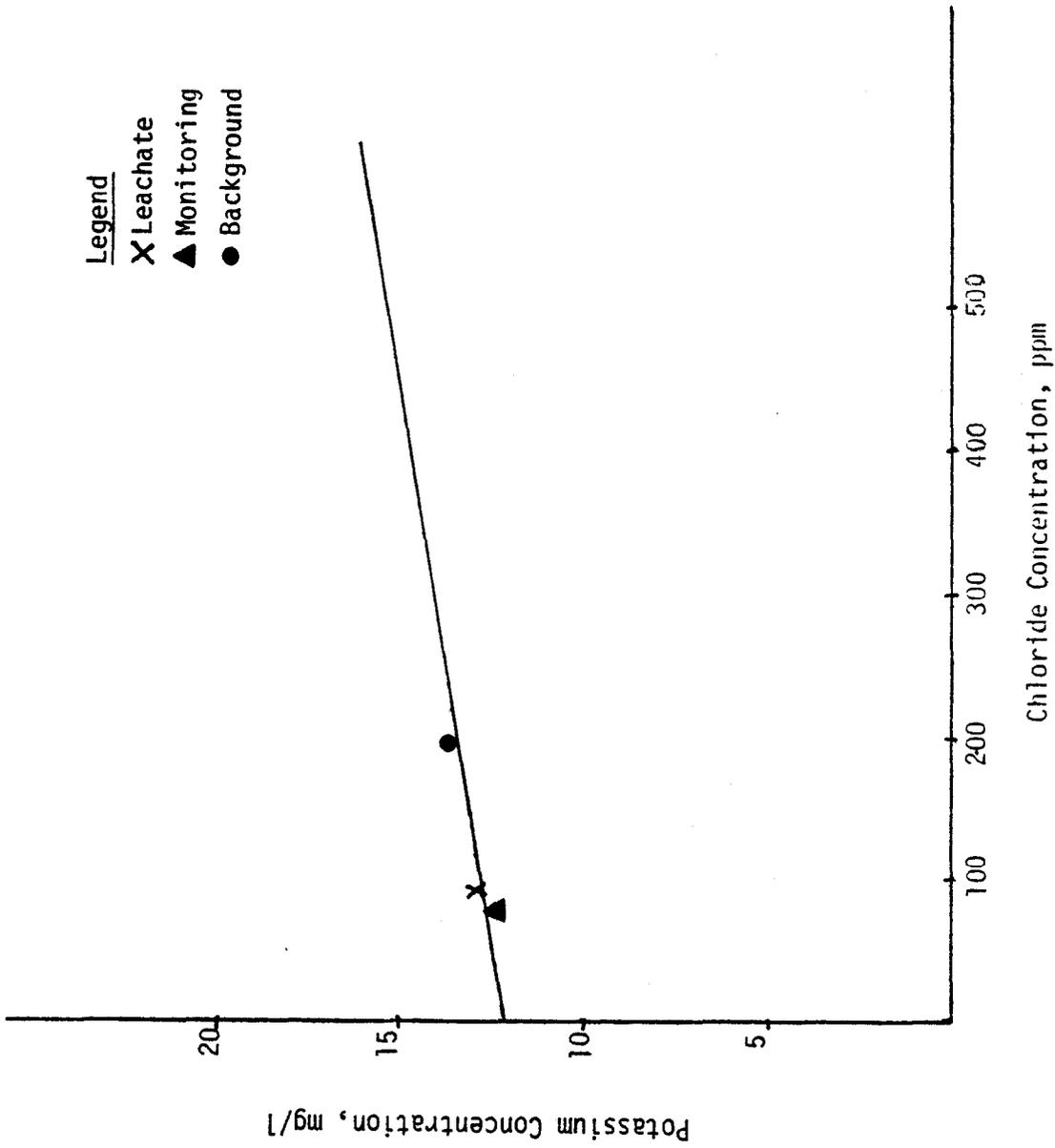
' Chloride Concentration, ppm

Figure 31. Na-Cl diagram for Grand Haven



Chloride Concentration, ppm

Figure 32. K-Cl diagram for Sayreville



Legend
 X Leachate
 ▲ Monitoring
 ● Background

Figure 33. K-Cl diagram for Pinto Island

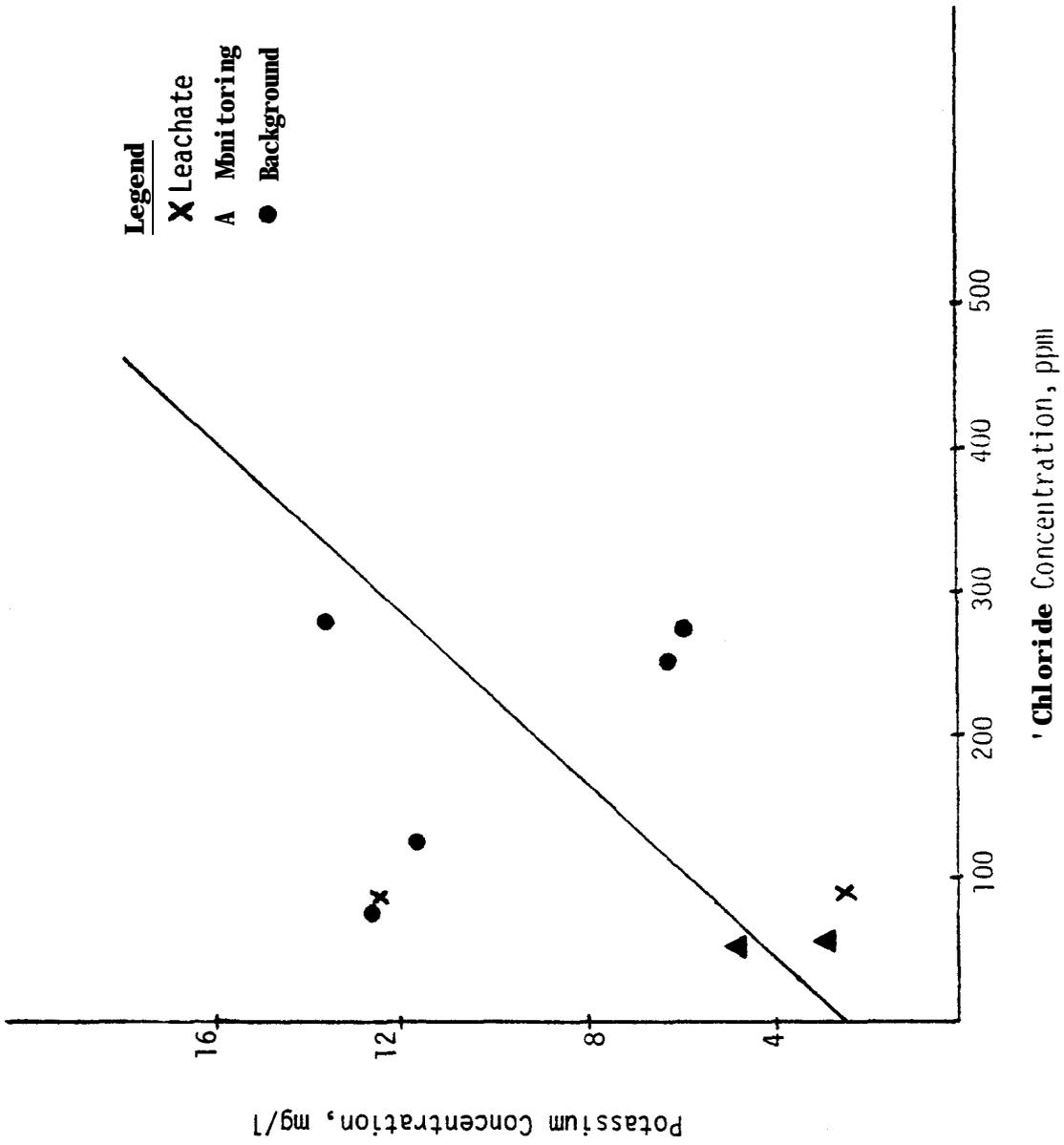


Figure 34. K-Cl diagram for Grand Haven

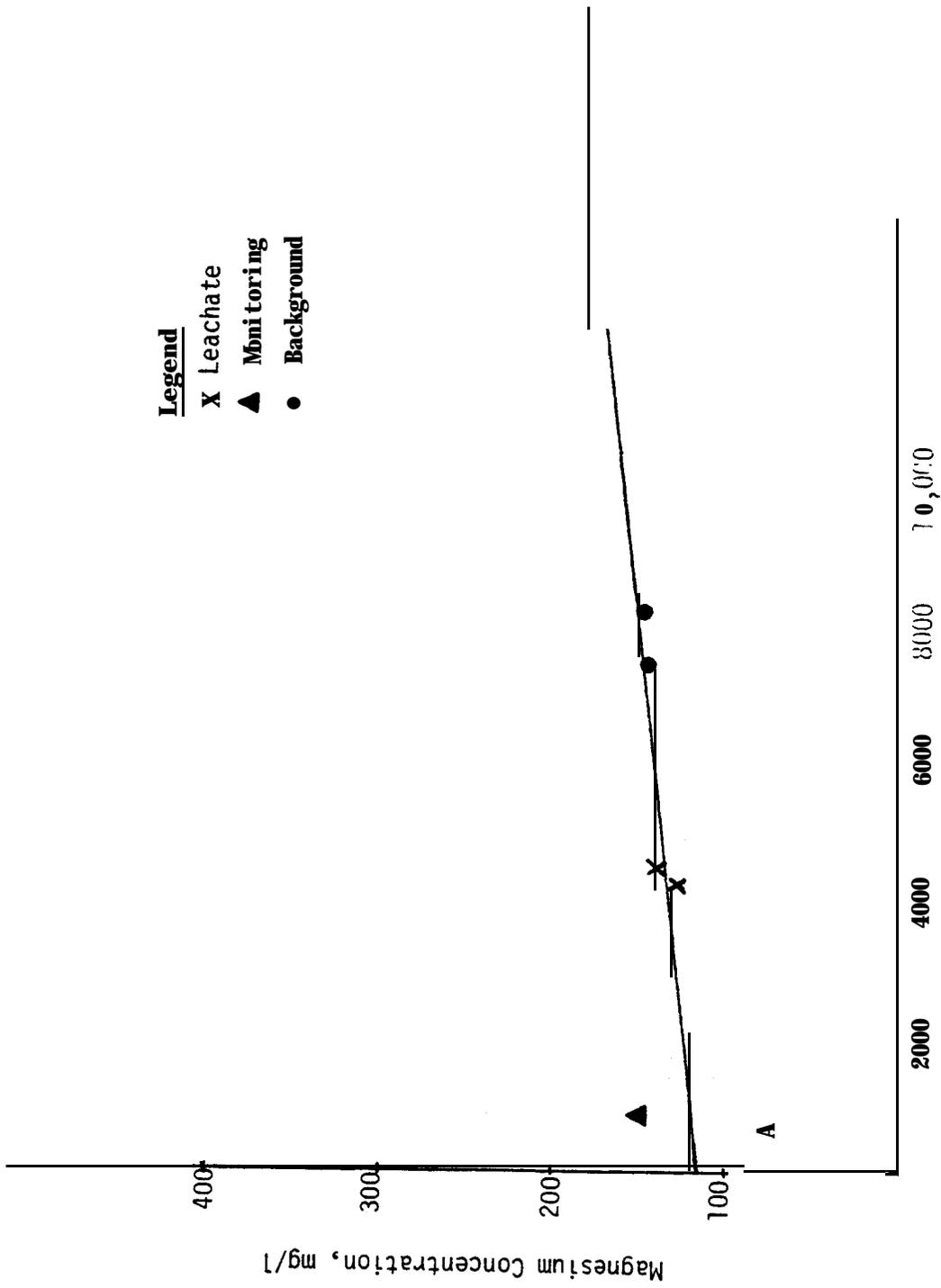


Figure 35. Mg-Cl diagram for Sayreville

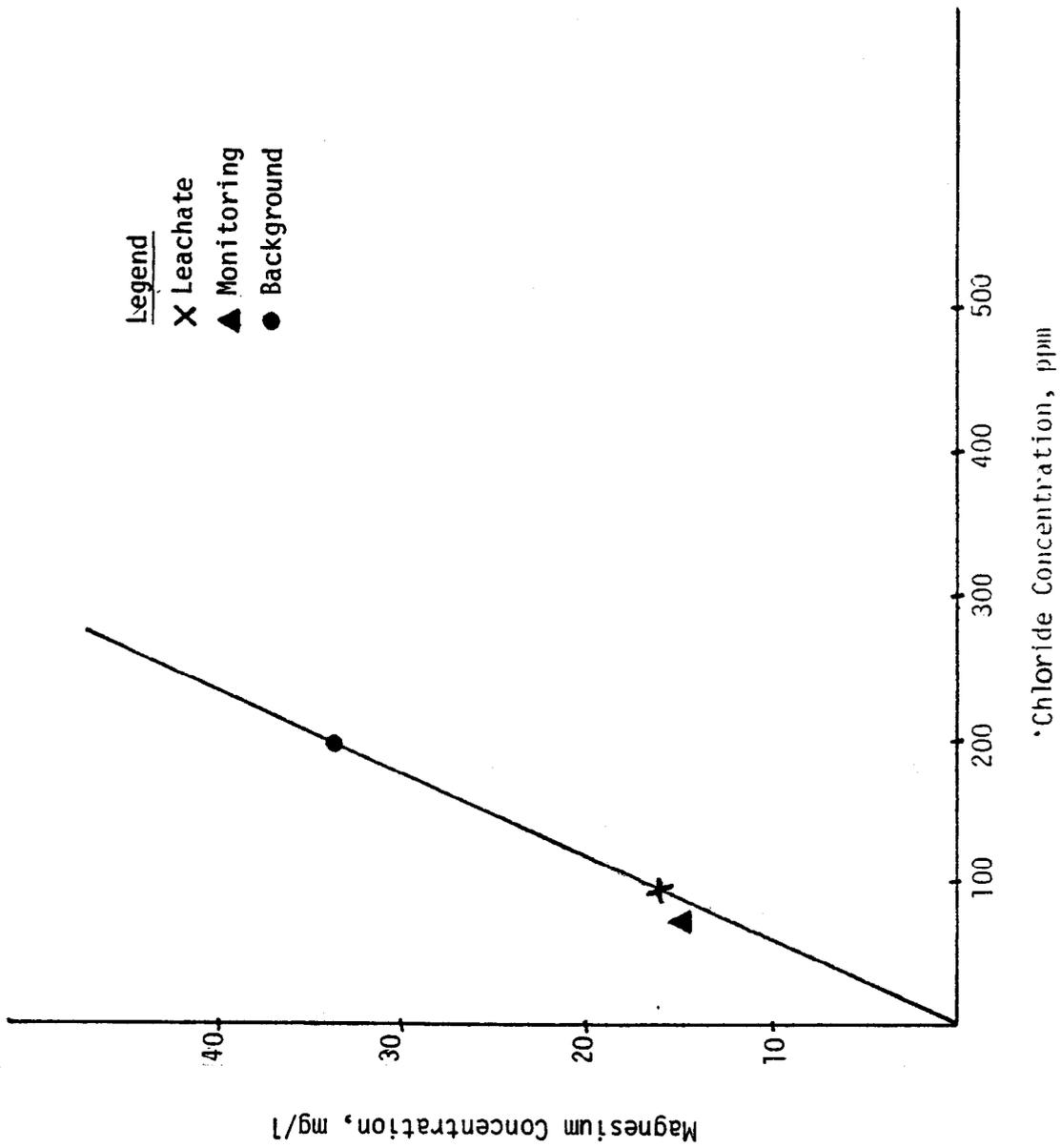


Figure 36. Mg-Cl diagram for Pinto Island

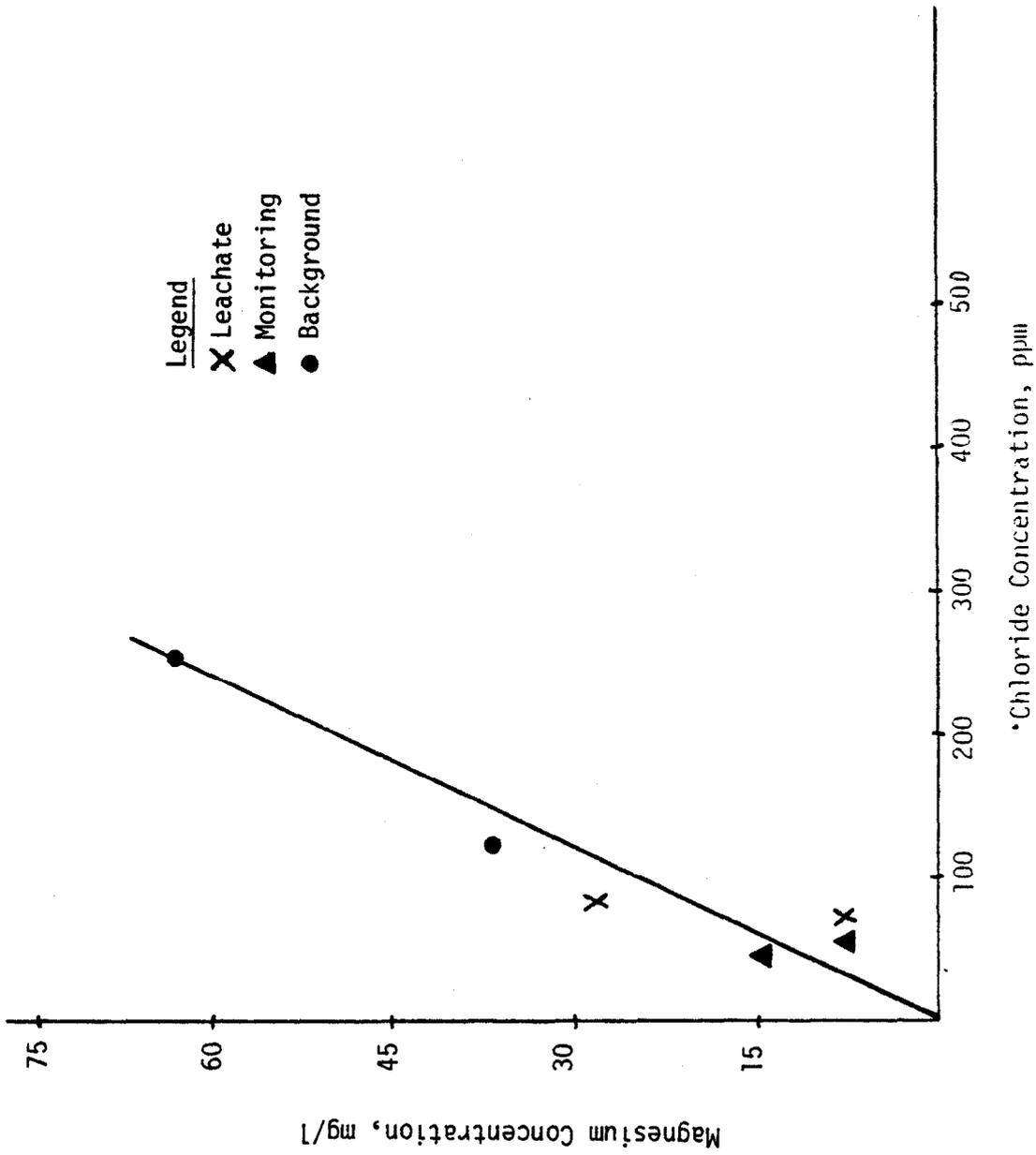


Figure 37. Mg-Cl diagram for Grand Haven

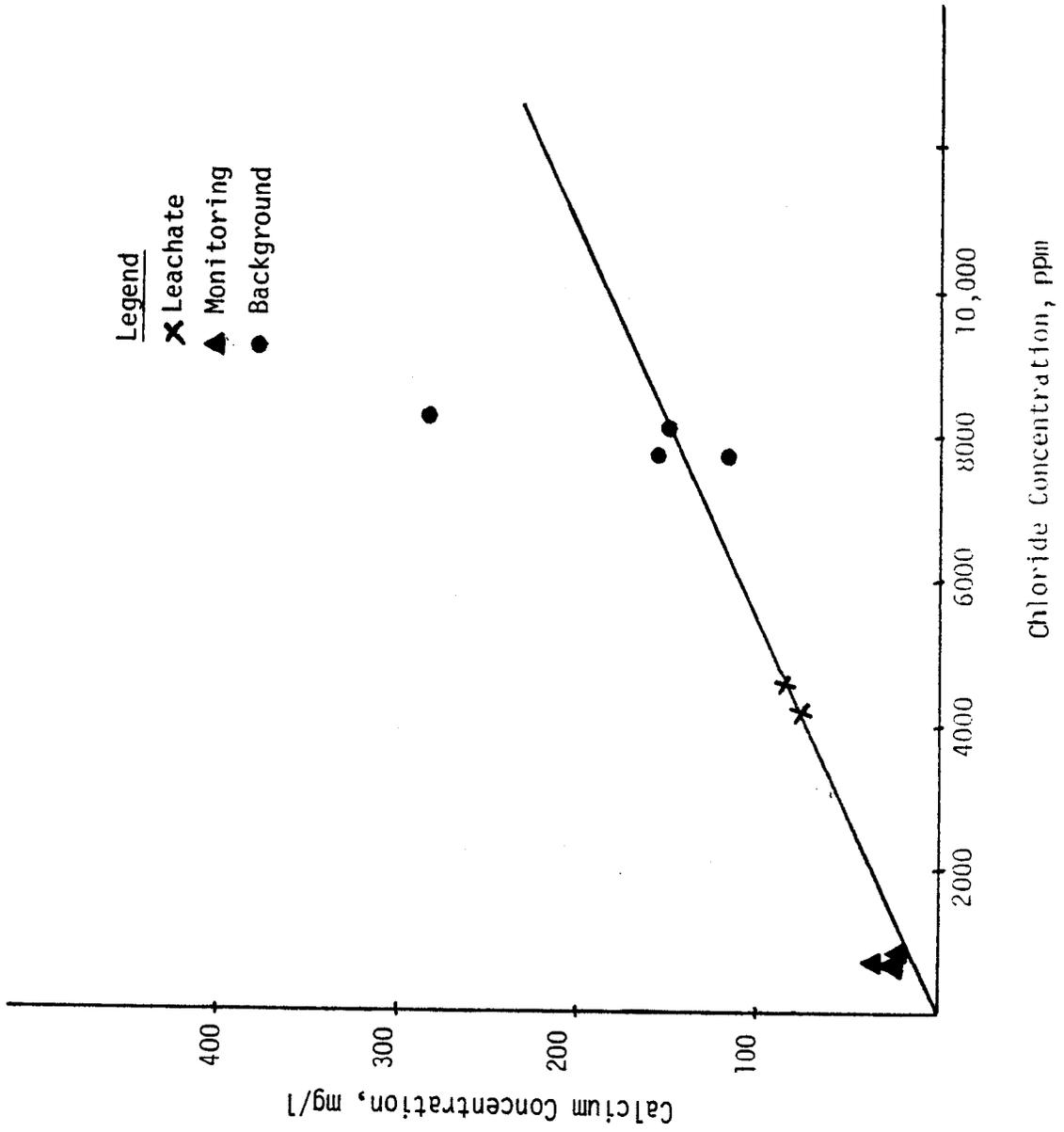


Figure 38. Ca-Cl diagram for Sayreville

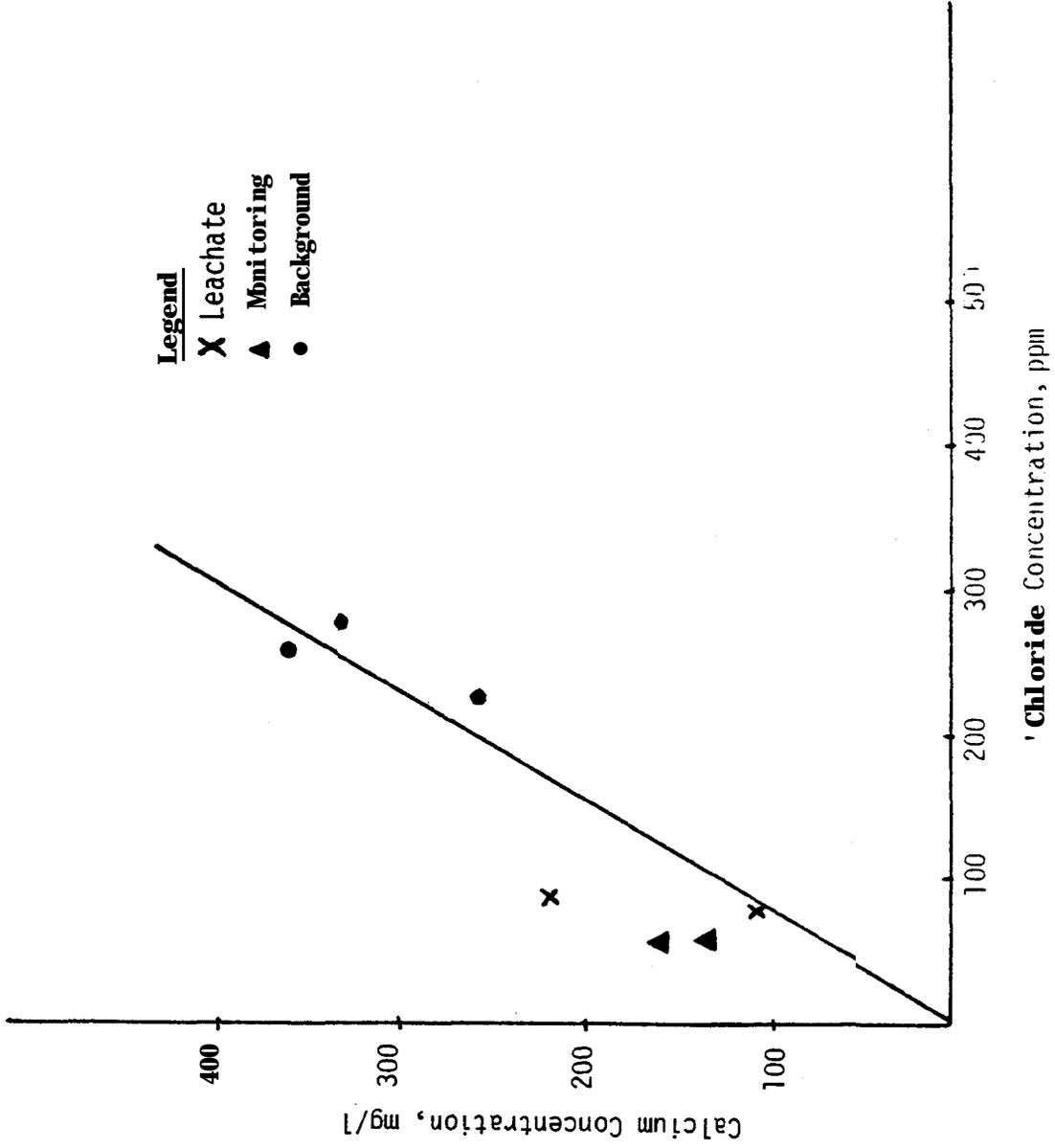


Figure 39. Ca-Cl diagram for Grand Haven

situated above the line. Release of calcium through a number of possible reactions within the groundwater systems could account for the plots.

105. Trace metals were plotted in a similar fashion. No discernable pattern was observed with a wide scattering of data points. This result is expected considering the highly complex mechanisms affecting the trace metal concentrations. These metals are addressed in the solubility equilibrium model.

106. In summary, dilution appears to be a dominant factor for regulating the concentrations of sodium and chloride in groundwater. Dilution also appears to represent a controlling factor in regulating calcium and magnesium concentrations and to a lesser degree potassium. Plots of trace metals resulted in no observable trends.

Solubility Equilibrium Model

107. Controlling mechanisms which account for trace metal levels in groundwaters include a number of complex interacting reactions. Mechanisms such as precipitation/dissolution, complexation, and adsorption may react in concert or singularly to determine the concentration of a trace metal in a given situation. A method by which the dissolution/precipitation phenomena may be used to predict these values is the solubility equilibrium approach. Application of this model for the observed groundwater trace metal concentrations is presented in the following section.

108. Solubilities of metal ions can change as redox conditions fluctuate. Solubility of a metal ion is usually governed by a controlling solid, via a solid species of high stability. In an aerobic

environment, stable solids that control the solubilities of the metal ions include oxides, hydroxides, carbonates, and silicates. Under moderate to extreme reducing conditions, most metals readily precipitate as sulfides.

109. In addition to the solubilities of the controlling solids in regulating concentrations of migrating trace metals, complexation can account for some unusually high levels of metals in solution. Major ligands responsible for forming soluble complexes include chloride, organic species, hydroxide, carbonate, and sulfate. The complexation effect of trace metals is an important feature of the solubility equilibrium model.

110. The adsorption mechanisms, though not considered in the solubility equilibrium model, could be responsible for reducing certain trace metal concentrations below the theoretical solubility equilibrium value. A model characterizing the effects of adsorption upon trace metal transport necessitates consideration of the highly heterogeneous chemical and physical nature of the soil/groundwater system

111. The solubility equilibrium model is based upon the solubility of controlling solids and the complex-forming ligands. Model calculations result in free metal ion concentrations at each sampling location, as well as values for potential complexed metal ions in solution. Calculated values from equilibrium model would appear high with respect to the measured values if adsorption is a major immobilizing factor. Values appear low if any soluble complexes are excluded in the model calculation.

112. Controlling solids. For the purposes of equilibrium

calculations, some controlling solids are assumed for each redox condition. Based upon previous discussion presented in Part III, the following solids are assumed to be the solubility-controlling solids under aerobic and reduced conditions within the pH range of natural waters:

<u>Reducing</u>	<u>Oxidizing</u>
CdS	CdCO ₃
CuS	Cu ₂ (O ₃ (OH) ₂)
FeS \rightleftharpoons Fe(OH) ₃ \rightleftharpoons FeOOH \rightleftharpoons	Fe ₂ O ₃
MnS or MnCO ₃ \rightleftharpoons Mn(OH) _x \rightleftharpoons MnOOH \rightleftharpoons	MnO ₂
NiS	NiCO ₃
PbS	PbCO ₃
ZnS	ZnCO ₃

113. Due to the heterogeneous nature of the soil and groundwater interface, the redox and pH conditions, and thus the controlling solid, may vary at each site. Under normal undisturbed field conditions, saturated soils are mainly in a reduced state, Metal sulfides are likely to be the controlling solids. On the other hand, exposed unsaturated soils may be in an oxidized state. Therefore, calculations using both the reducing and oxidizing controlling solids are considered to encompass the entire range of those potentially encountered redox conditions.

114. Ligand species. Due to the complexity of natural water systems, it is difficult to include all ligand species which may be a factor in the trace metal ion solubilization. Model calculations will therefore include only those ligands whose concentrations were measured

for each sample. This will serve as a lower limit to the complexation effect. Any additional ligands would serve to increase the total metal concentration. The degree of increase is a function of the ligand concentration and the magnitude of the ligand formation constants. The quantity of unidentified ligand species also dictates the use of only measurable trace ligands.

115. Ligands selected for model calculations were chloride, hydroxide, bicarbonate-carbonate, sulfate, and sulfide. All anions were individually measured for each sample with the exception of sulfide. The original report demonstrated that, though hydrogen sulfide could be smelled in a few of the samples from identical locations, the sulfide was below the detection limit for the methods used (electrode and methylene blue photometric method). Thus, for the model calculation, total sulfide concentration, S_T , was assumed at 10^{-9} M or the acknowledged threshold of smell for hydrogen sulfide. In most samples, this value will represent the upper limit of the soluble sulfide anion concentration.

116. Activity coefficients (γ_i). The activity coefficients for the metal ions and their complexed species were calculated from the Guntelberg approximation derived from the Debye-Huckel equation:

$$\log \gamma_i = -0.5 Z_i^2 \left(\frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \right) \quad (10)$$

where μ = ionic strength = $\frac{1}{2} \sum_i Z_i^2 C_i$

C_i = molarity of the i^{th} type of ion

Z_i = the valence of charge

117. For simplicity, the average major ion concentrations for each site were used in calculating μ and γ_i . The results are given

in Table 4.

118. Model equations. Free metal ion concentration is governed by the solubility of the solid $M_p X_q$ as given by:

$$\left[M_f \right] = \left[\frac{(K_{sp}) M_p X_q}{\gamma_M^p \gamma_X^q (X_f)^q} \right]^{1/2} \quad (11)$$

where $[M_f]$ = concentration of free metal ions
 K_{sp} = solubility product
 γ = ion activity coefficient
 p, q = positive integers
 X_f = concentration of free anions

119. Due to the effects of complexation, the concentration of complexed metal ions in solution is given by:

$$\left[M_m L(i)_n \right] = \left[M\beta(i)_{nm} \right] \left[M_f \right]^m \left[L(i)_f \right]^n \frac{\gamma_M^m \cdot \gamma_{L(i)}^n}{\gamma_{M_m L(i)_n}} \quad (12)$$

120. The total metal concentration in the leaching solution is thus:

$$\begin{aligned} \left[M_t \right] &= \left[M_f \right] + m \sum_{n=1}^k \sum_{i=1}^j \left[M_m L(i)_n \right] \\ &= \left[M_f \right] + m \sum_{n=1}^k \sum_{i=1}^j \beta(i)_{nm} \left[M_f \right]^m \left[L(i)_f \right]^n \frac{\gamma_M^m \cdot \gamma_{L(i)}^n}{\gamma_{M_m L(i)_n}} \quad (13) \end{aligned}$$

where $[M_t]$ = total metal concentration
 k = number of ligands coordinated with M_h
 i = ligand species
 j = total number of ligands

$$\begin{aligned}
L(i)_f &= \text{free concentration of } i^{\text{th}} \text{ ligand} \\
n,m &= \text{composition of the complex } M_m L(i)_n \\
\beta(i)_{nm} &= \text{overall formation constant of complex } M_m L(i)_n
\end{aligned}$$

121. Solubility products and formation constants are temperature-dependent parameters. For example, samples collected at Grand Haven and Sayreville during the winter would likely be of different temperature than samples collected during the summer for the same sites. For simplicity, all calculations were performed assuming a constant temperature of 12°C. Generally, this assumption would not affect either of the values by more than 5 percent as illustrated by the following:

<u>Metal</u>	<u>log K_s, 12°C</u>	<u>log K_s, 25°C</u>
CdS	27.0	26.1
cus	35.4	35.2
PbS	27.7	26.6
ZnS	22.6	22.8

122. Mdel calculation. An example of the model calculations necessary to determine the free metal and complexed ion concentrations is presented in the following discussion using well HB as an example. Important solubility products of the trace metals used in this example calculation are included in Table 5. Relevant metal-ligand formation constants are contained in Table 6. Values are molar concentrations (excluding activities) for the example (HB). Graph presentation of all samples is presented in Appendix B. Results of such calculations are presented in Appendix C. An example of the calculations is presented as follows:

<u>Sample</u>	<u>pH</u>	<u>pOH</u>	<u>Chloride</u> <u>mole</u>	<u>Alkalinity</u> <u>mole</u>	<u>Sulfate</u> <u>mole</u>	<u>Ion Activities</u>	
						<u>Mono-</u> <u>valent</u>	<u>Di-</u> <u>valent</u>
HB	7.4	6.6	210	0.45	0.80	0.71	0.25

123. The free concentration of zinc (Zn_f) is given by:

$$Zn_f = \frac{K_s ZnS}{\gamma_{Zn} \gamma_{S^{=}} [S^{=}]}$$

where $S^{=} = S_T \left\{ K_2 [H^+]^2 + K_1 [H^+] + 1 \right\}^{-1}$ (14)

$$= S_T \left\{ K_2 [H^+]^2 \right\}^{-1}$$

or $Zn_f = \frac{10^{-22.60} 10^{-7.4} 2}{(0.25) (0.25) 10^{-30}} \text{ mole}$

$$= 6.37 \times 10^{-7} \text{ mole}$$

$$= 41.66 \mu\text{g/l}$$

124. The concentration of complexed zinc (Zn_T) is given by:

$$Zn_{\text{complexed}} = Zn_f \times \left[10^{0.43} \frac{[Cl^-]}{\gamma_{Cl^-}} + 10^{0.61} \frac{[Cl^-]^2}{\gamma_{Cl^-}^2} \right.$$

$$+ 100.53 \frac{[Cl^-]^3}{\gamma_{Cl^-}^3} + 10^{0.20} \frac{[Cl^-]^4}{\gamma_{Cl^-}^4} + 10^{4.4} \frac{[OH^-]}{\gamma_{OH^-}} \quad (15)$$

$$+ 10^{12.89} \frac{[OH^-]^2}{\gamma_{OH^-}^2} + 10^{14.4} \frac{[OH^-]^3}{\gamma_{OH^-}^3} + 10^{15.5} \frac{[OH^-]^4}{\gamma_{OH^-}^4}$$

$$\left. + 10^{2.37} \frac{[SO_4^{=}]}{\gamma_{SO_4^{=}}} \right]$$

$$= 3.0 (Zn_f)$$

$$= 124.3 \mu\text{g/l}$$

$$\begin{aligned} \text{Zn}_T &= \text{Zn}_f + \text{Zn}_{\text{complexed}} \\ &= 165.9 \text{ } \mu\text{g/l} \end{aligned}$$

125. Results. The results of the solubility equilibrium model calculations and the corresponding measured values are presented in Appendix C. Graphic display of these data is illustrated in Appendix B. Mercury was not included in the calculations because most of the analyzed values were comparatively small ($< 1 \text{ } \mu\text{g/l}$), and various studies have indicated sorption is the most important factor in controlling mercury concentrations.

126. Wherever values from field studies fall on the straight line (calculated value), or do not deviate too much from the line, the equilibrium mechanism is considered to be the major controlling factor in regulating metal concentration in solution. The line is a good indication that the controlling solid chosen for the redox condition at a particular site is likely to represent actual field conditions. It also indicates that any alternate ligand species do not exist at high concentrations, i.e., the effects of complexation have been adequately represented by the model.

127. The specific field sites represented by points on the graph are frequently grouped together with respect to each of the three modeled sites. Points lying below the line would indicate an under-saturated condition possibly caused by adsorption, a nonequilibrium stage, or the nonexistence of the assumed controlling solid. In general, for all of the carbonate-controlling graphs, the calculated or

theoretical trace metal values are much greater than the analyzed values. These values would therefore represent the upper concentration limit for the appropriate redox condition. Values actually encountered in these upper ranges could impact groundwater quality.

128. Majority of the data points for the sulfide-controlling graphs lie on either side of the straight line, indicating that this is more representative of the actual field conditions. The variability of the calculated values in reference to the analyzed values indicates additional complexes as well as adsorption as possible influencing factors or localized environment. Calculated trace metal values which are lower than analyzed values where sulfides are the assumed controlling solids may be attributable to the arbitrary selection of the sulfide concentration (see Part III). In many locations, the sulfide concentrations are likely to be much lower than the value employed in the free metal calculation, thus elevating the theoretical free metal values.

129. Under reduced conditions, the controlling solids for various metals were assumed to be CdS, CuS, FeS or FeCO_3 , MnCO_3 , NiS, PbS, and ZnS. As previously mentioned, with sulfides assumed as controlling solids, trace metal model calculations are usually within two orders of magnitude of the measured values. This would indicate that, in the field environment sulfides could be the controlling solids for cadmium, nickel, lead, and zinc. The exception is CuS. Predicted values of CuS were always many orders of magnitude lower than the analyzed results. As discussed in Part III, copper forms strong complexes with organic ligands. Should the concentration of organic ligands in the

samples be known, the theoretical values could be closer to the analyzed results.

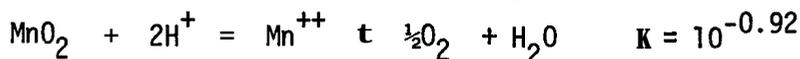
130. For Fe and Mn, initial solubility calculations from FeS ($K_{sp} = 10^{-16.9}$) and MnS ($K_{sp} = 10^{-15.7}$) indicated that soluble iron and manganese should be on the order of 10^7 and 10^8 higher than the measured values. When considering $FeCO_3$ and $MnCO_3$ as the controlling solids in the reducing environment, the data show that the theoretical and measured results are much closer than the sulfide-predicted values (see Appendix C).

131. Due to these conditions, it may be reasonable to assume that field environments were reduced enough so that iron and manganese existed in the +II oxidation state (as opposed to the +III and +IV states) and that there was insufficient sulfide to precipitate these metals as metal sulfides. Conditions favoring the formation of Fe and Mn carbonates necessitate high pH and alkalinity and moderate to low redox. All of these conditions can be the case of most groundwater samples.

132. Controlling solids selected for the various metals under aerobic or oxidizing conditions were $CdCO_3$, $Cu_2CO_3(OH)_2$, $Fe(OH)_3$, MnO_2 , $NiCO_3$, $PbCO_3$, and $ZnCO_3$. With the exception of iron and manganese, analysis of all remaining metals indicates lower measured values than corresponding predicted values. This information serves to substantiate previous evidence that a reducing environment should exist beneath the dredged material disposal sites. Additionally, the model calculations for these metals would serve as the upper concentration limit for the measured samples, with adsorption as the single most important mechanism which reduced the actual concentration.

133. It is well known that iron and manganese are less soluble in an oxidized environment than in a reduced environment. Iron usually will exist in the forms of FeOOH , $\text{Fe}(\text{OH})_3$, and Fe_2O_3 in an oxidized environment. Manganese may exist as MnOOH or MnO_x where x ranges from 1.1 to 2. The solubility of these solids would serve as the lower concentration limits for the samples analyzed.

134. The mineralogy of manganese in an oxidized environment is not easily characterized. It has been suggested that the following reaction may be the controlling mechanism for MnO_2 solubility:



135. Simple solubility calculations indicated that the predicted manganese values would be orders of magnitude lower than the measured values (assumed dissolved oxygen = 8 mg/l):

$$\begin{aligned} [\text{Mn}^{++}] &= \frac{10^{-0.92} [\text{H}^+]^2}{M_n^{++} [\text{O}_2]^{\frac{1}{2}}} [\text{H}^+]^2 \\ &= \frac{10^{-0.92} (0.37)^2}{0.78 (0.25 \times 10^{-3})^{\frac{1}{2}}} [\text{H}^+]^2 \quad (16) \\ &= 10^{-0.13} [\text{H}^+]^2 \text{ moles} \\ &= 10^{7.86} [\text{H}^+]^2 \mu\text{g/l} \end{aligned}$$

$$7 \times 10^{-3} \text{ to } 7 \times 10^{-9} \mu\text{g/l for pH} = 5 \text{ to } 8$$

136. Subsequently, no model calculations were performed for manganese in an oxidized environment.

Conclusions

137. Theoretical models can help define the potential concentration

levels of pollutants in groundwater. The dilution and solubility equilibrium models provide information on the controlling mechanisms for pollutant transport and possible contamination levels based on these mechanisms.

138. The dilution model shows that dilution is a dominant factor in regulating sodium and chloride concentrations. Potassium plots also correlate well for the Sayreville and Pinto Island sites. Though trends for calcium and manganese concentrations show that dilution could be a controlling factor, plots were variable. Plots for trace metals result in no observable trends.

139. Solubility equilibrium model calculations have demonstrated that by assuming a controlling solid for the appropriate redox condition, possible trace metal concentrations at a specific location may be predicted from various water quality parameters. The fundamental considerations for the model include the controlling solid solubilities and increases in trace metal concentrations due to complexing ligands.

140. Results indicate that, in general, the carbonate solubilities serve as the upper concentration limits for cadmium, copper, lead, nickel, and zinc. Carbonate and hydroxide solubilities serve as the respective upper and lower concentration limits for iron; likewise, the carbonate and oxide solubilities can determine the upper and lower concentration limits for manganese. With metal sulfides serving as the assumed controlling solids under reduced environmental conditions, the predicted trace metal concentrations were remarkably close to the measured values for cadmium, copper, lead, nickel, and zinc. Metal sulfide

calculations which were orders of magnitude below the saturation limit may be due to the arbitrary selection of sulfide concentrations for each sample, or that equilibrium was not attained.

141. Adsorption may further reduce the predicted concentrations and inclusion of other ligands may increase the predicted concentrations. More information in these two areas is needed to provide better insight into the system

PART V: CONCLUSIONS

142. Water quality degradation from the disposal of dredged material can be categorized in terms of surface and groundwater impairment. The purpose of this study was to assess the potential degradation of groundwaters from this disposal practice.

143. Results from the groundwater study indicated that an increase in the level of dissolved solids is quite likely. Among those identified were chloride, sodium and potassium. The degree to which these ions may impact groundwater is a factor of the disposal setting; a freshwater disposal environment may be more sensitive than a saline environment. Dilution appears to be the major controlling factor for these three ions.

144. Calcium and magnesium in the groundwater represent another water quality problem primarily due to their contribution to water hardness. Calcium concentrations in the groundwaters were found to be affected by dissolution of calcite and ion exchange. Magnesium transport was suspected to be controlled by ion exchange and dissolution of magnesium solids. Dilution also seemed to regulate their concentrations in groundwater.

145. Of the trace metals analyzed, manganese and possibly iron pose the greatest impact upon groundwater quality. The majority of the analyzed samples were found to contain manganese and iron concentrations higher than the recommended EPA drinking water quality standards. Controlling mechanisms for these two constituents indicated that the solubility of the metal carbonates regulates the observed values. Disposal of dredged material could create environmental

conditions (pH and Eh) that are favorable for the formation of carbonate solids, which are among the most soluble species of iron and manganese solids.

146. Copper, cadmium, lead, nickel, mercury, and zinc groundwater concentrations were found to exist in levels which do not present water quality problems. By utilizing carbonate solubilities for the upper concentration limit and sulfide solubilities for the lower, most concentrations were nearer the calculated sulfide solubilities. Complexation and precipitation/dissolution are believed to represent the major controlling factors. Equilibrium solubility equations showed that carbonate solubilities represented the upper concentrations values for cadmium, copper, lead, nickel, and zinc. The lower concentration limits for manganese and iron were regulated by oxide and carbonate solubilities. Many of the observed lower concentrations were assumed to be due to adsorption on soil particles while the inclusion of soluble organic ligands may account for the higher concentrations.

147. Levels of potassium, total organic carbon, sodium, nitrate, chloride, magnesium, calcium, alkalinity, lead, iron, and manganese appeared to affect indigenous groundwaters as a result of the disposal of dredged material. The observed concentrations, however, did not represent a hazard to the water quality.

148. Analyses of chlorinated hydrocarbons (e.g., PCB's, DDT, DDE, and DDD) revealed that concentrations were below the detection limits in nearly all samples. Chlorinated hydrocarbons are not expected to pose a water quality problem due to their strong affinity to clay and organic matter.

149. Dilution and equilibrium solubility modeling appeared to be satisfactory for partially explaining the observed values for certain constituents in groundwater samples.

150. Review of the data from the groundwater sampling program in addition to the earlier sampling effort, provided several apparent observations:

- a. Manganese and iron represent potential groundwater impairment problems; the degree is based primarily upon the hydrological system characteristics and groundwater use.
- b. Dilution may be used to explain the observed concentrations of Cl, Na, Mg, and K.
- c. Solubility models can be used to provide boundary concentration values for the trace metals.
- d. Chlorinated hydrocarbons do not represent a groundwater quality problem in the hydrological settings studied. A near-to-surface groundwater could provide a transport mechanism from the upper soil layers and subsequently pose a potential problem.
- e. Disposal of saline dredged material into a freshwater environment could impact groundwater quality, especially when porous soils are present.

Appendix A.
Groundwater Analysis for Selected Parameters
at the Four Case Study Sites

Appendix A (Continued)

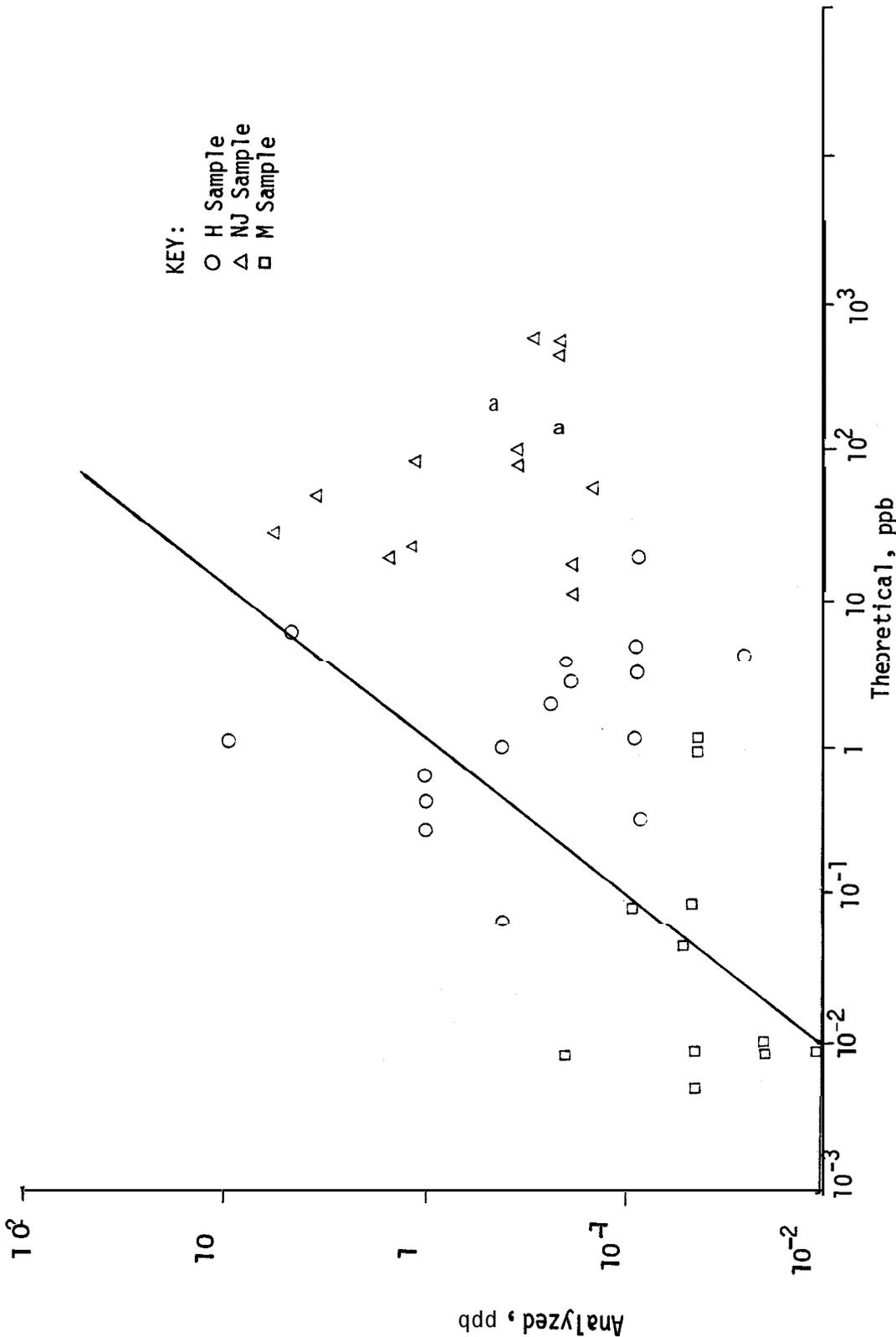
Sample Code	pH		Chloride, ppm		Alkalinity, ppm		TC, ppm		TOC, ppm		TIC, ppm		TKN	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B
PI-B	6.9	7.4	59	69	35	56	100	70	35	50	65	20	2.6	0
PI-C	7.3	7.5	212	165	25	30	70	80	38	50	32	30	2.8	13.3
PI-D	6.9	7.3	100	249	13	25	28	65	16	55	12	10	2.5	2.8
PI-H	7.4	7.4	72	100	25	28	90	90	55	45	35	45	1.0	0
PI-OM	6.8	6.8	509	400	19	28	35	50	20	40	15	10	4.2	11.2
PI-I	7	7.5	55	55	187	56	85	75	63	50	22	25	11.7	97.5
	<u>Organic N</u>		<u>Ammonia N</u>		<u>Nitrate</u>		<u>Nitrite</u>		<u>Phosphate, ppm</u>		<u>Sulfate, ppm</u>		<u>T-Phosphorus, ppm</u>	
PI-B	0	0	2.6	0	0.32	0.26	0.16	0.139	0	0	206	165	0.06	0.64
PI-C	0	7	2.8	12.6	7.6	0	0.006	0.027	0.875	1.03	194	341	1.35	1.4
PI-D	0	0	2.5	2.8	0.14	0	0.005	0.022	0.688	1.74	98	113	0.15	0.06
PI-H	0	0	1	0	0.26	0	0.004	0.033	0	0.078	53	57	0.06	0.05
PI-ON	0	0	4.2	11.2	6	0.119	0.35	0.003	0.013	0.781	31	27	0.04	0.126
PI-I	1.5	2.5	10.2	35	0.44	0.559	0.008	0.042	0.031	0	84	26	0.1	0.3
	<u>Na, ppm</u>		<u>K, ppm</u>		<u>Ca, ppm</u>		<u>Mg, ppm</u>							
PI-B	54	62	20	27	82	94	42	39						
PI-C	190	199	23	31	23	22	31	49						
PI-D	8	12	13	12	36	47	14	15						
PI-H	71	254	13	14	58	86	15	22						
PI-ON	153	116	18	14	36	29	27	19						
PI-I	53	50	14	10	51	36	17	14						

NA = 5, 26/79; 8 = 7/7/79

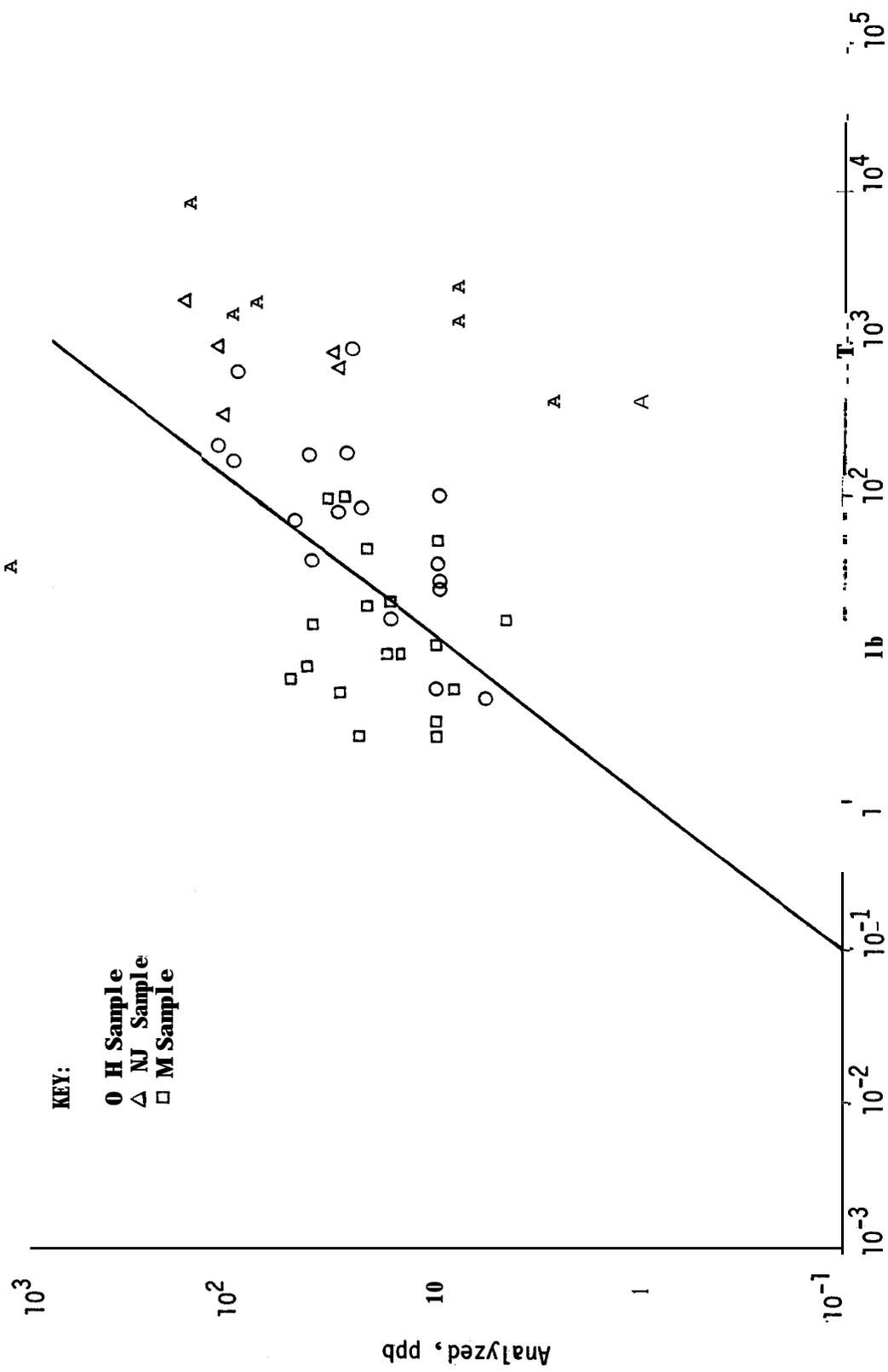
NS = not sample; ND = not detectable; MD = well destroyed; NA = not analyzed

Appendix B.

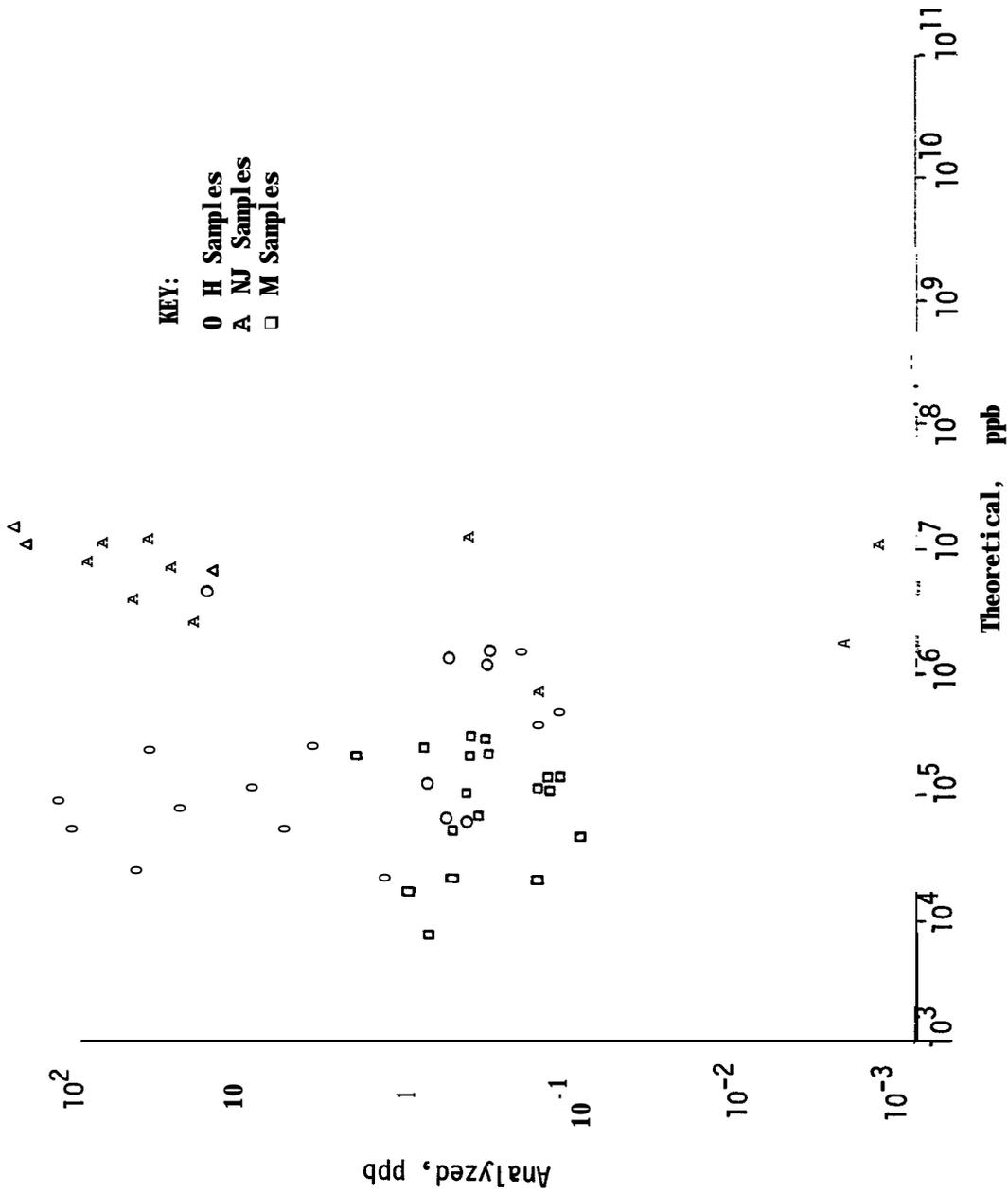
**Solubility Equilibrium Graphs for Cd, Cu, Fe, Mn,
Ni, Pb, and Zn**



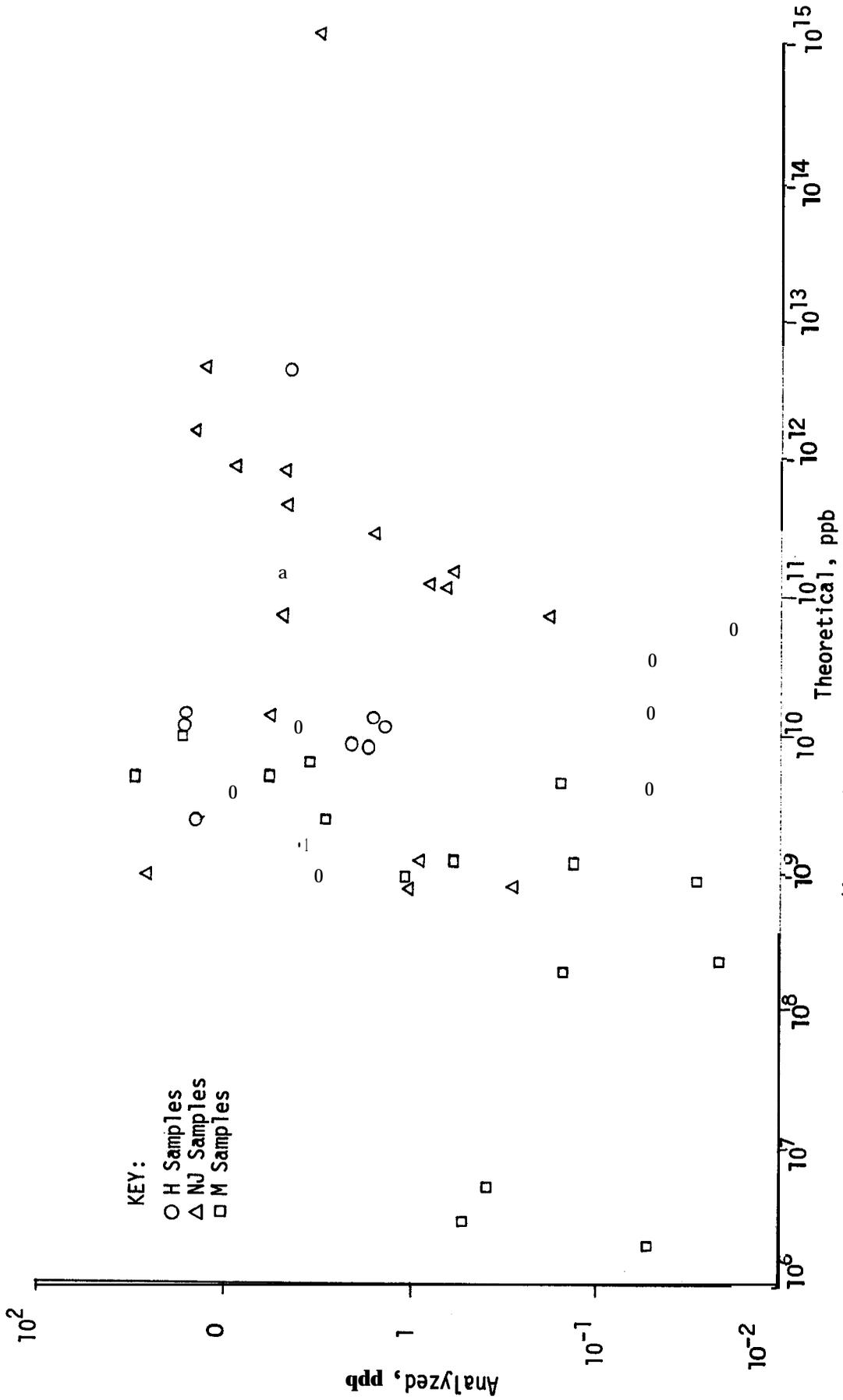
Appendix B. Theoretical Cd Concentration versus Analyzed Cd Concentration: CdS Control.



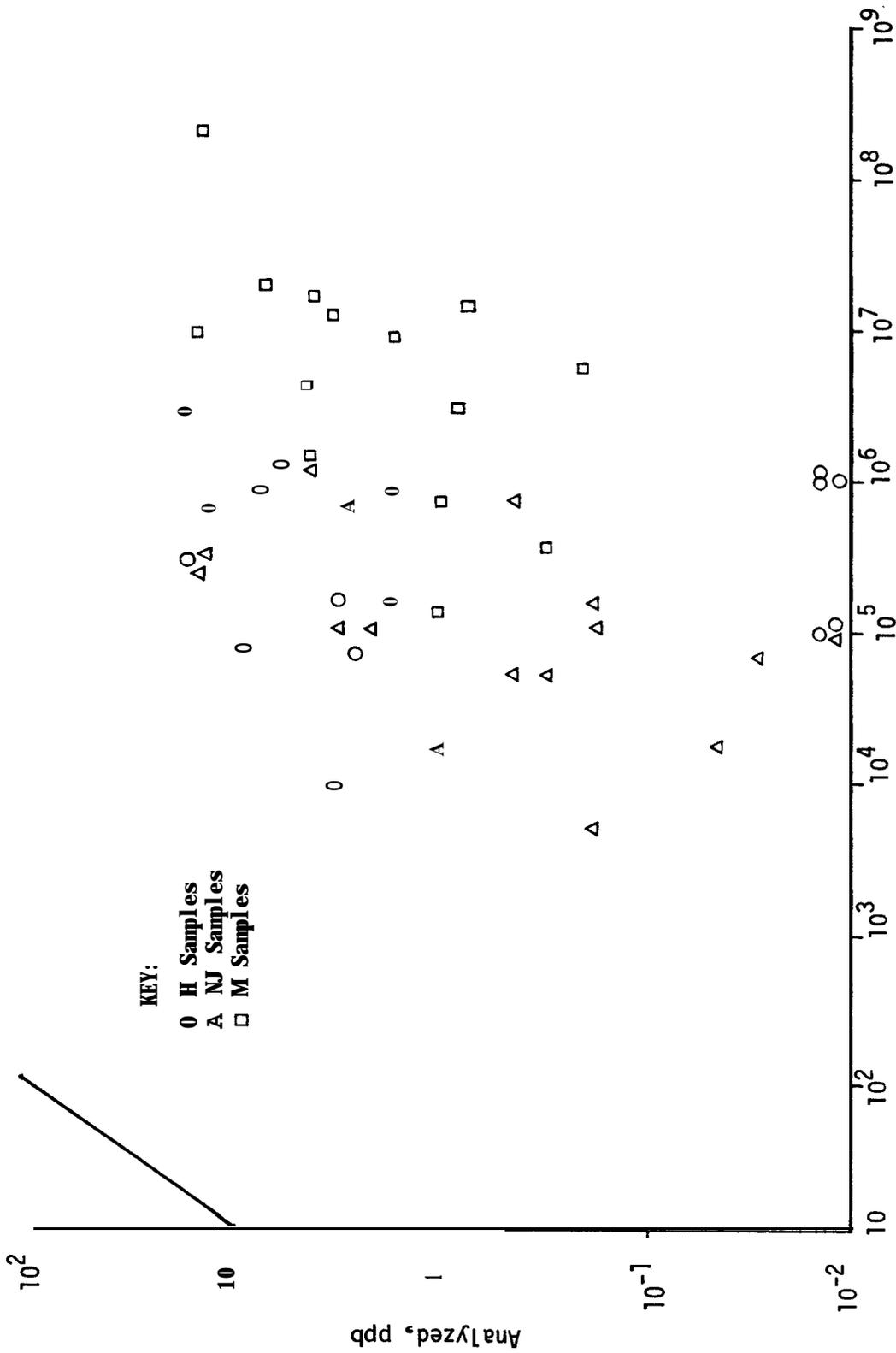
Appendix B. Theoretical Cu Concentration versus Analyzed Cu Concentration: $\text{Cu}_2\text{CO}_3(\text{OH})_2$ Control.



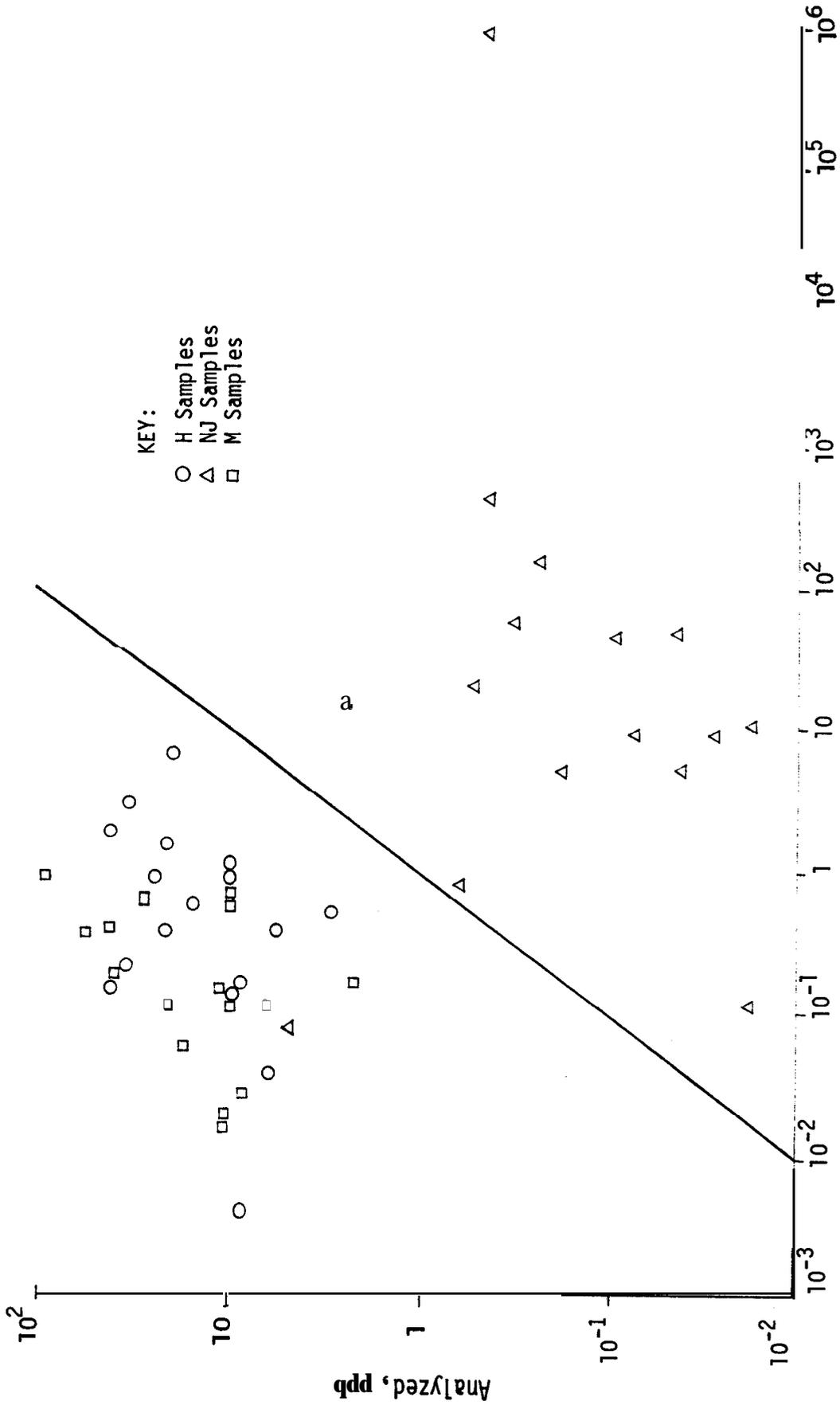
Appendix B. Theoretical Fe Concentration versus Analyzed Fe Concentration: FeCO₃ Control.



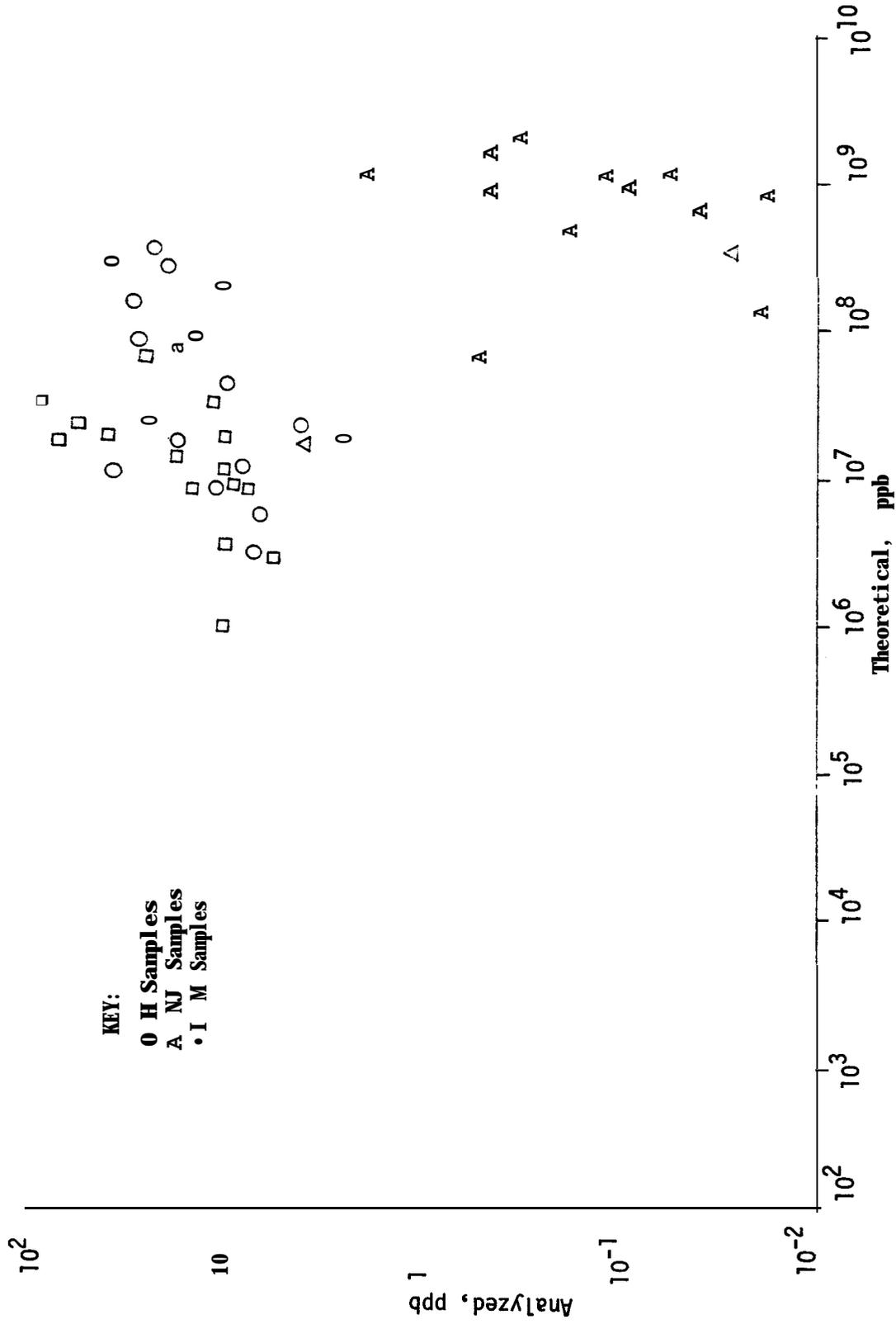
Appendix B. Theoretical Mn Concentration versus Analyzed Mn Concentration: MnS Control.



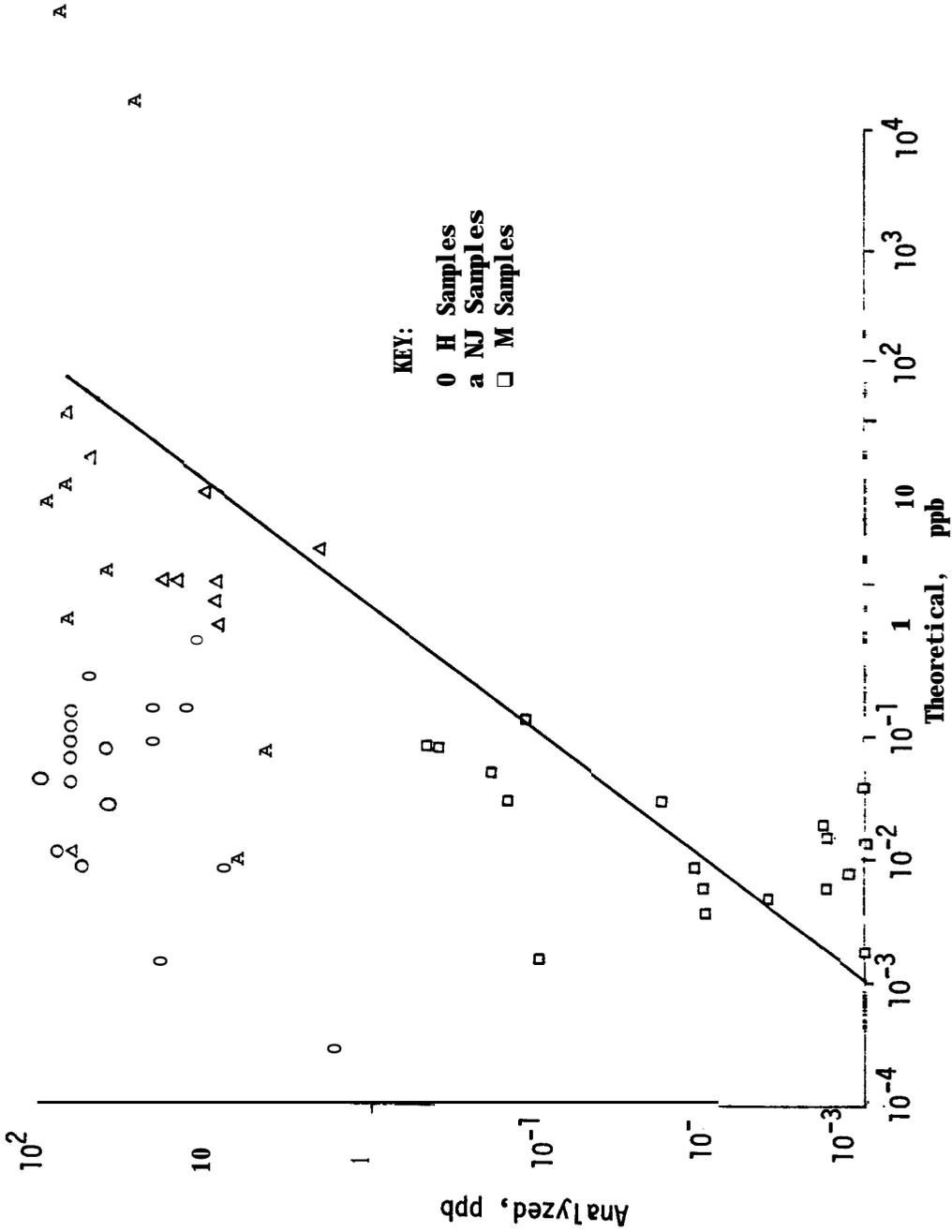
Appendix B. Theoretical Mn Concentrations versus Analyzed Mn Concentrations: MnCO₃ Control.



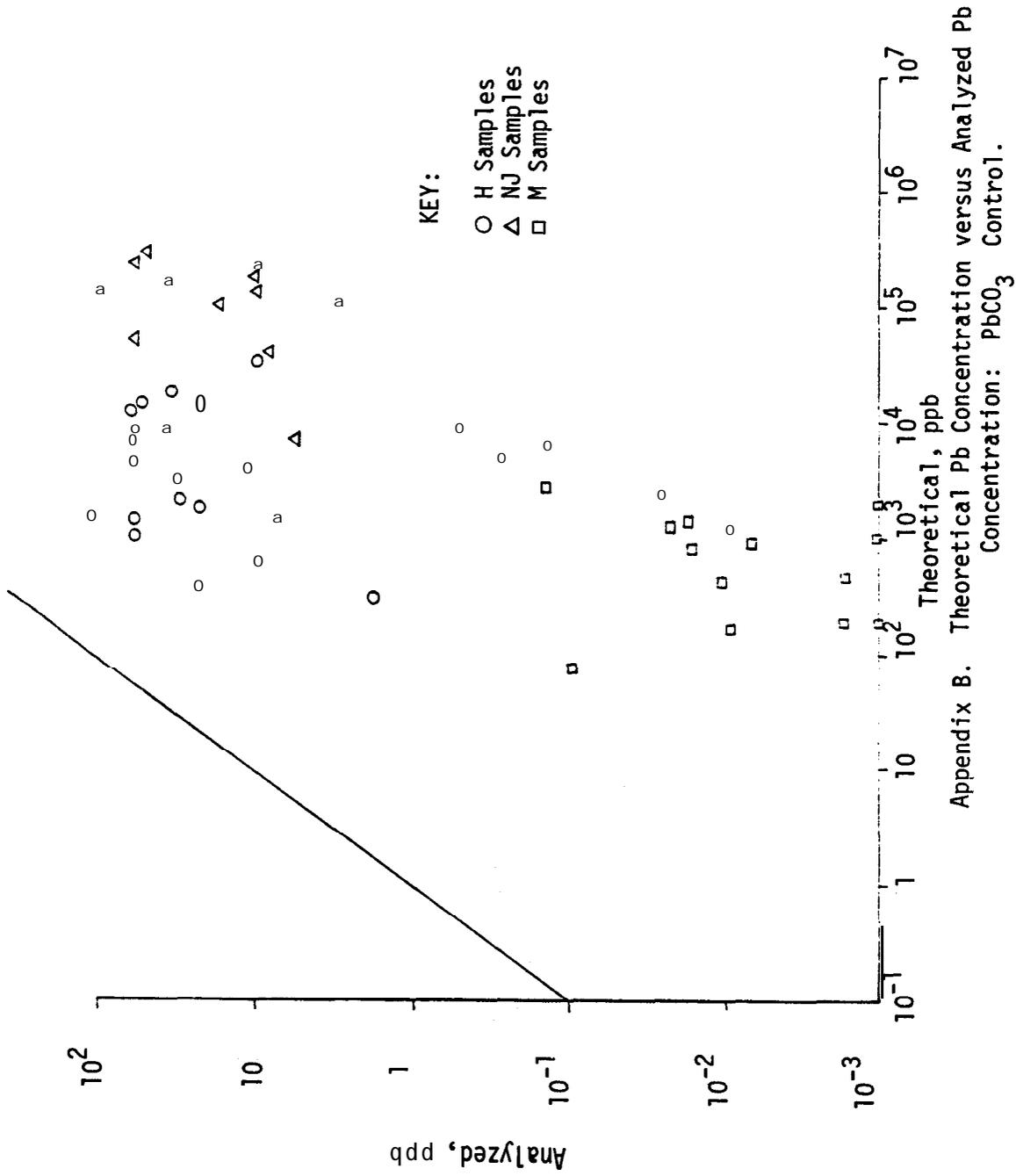
Appendix B. Theoretical Ni Concentration versus Analyzed Ni Concentration: NIS Control.

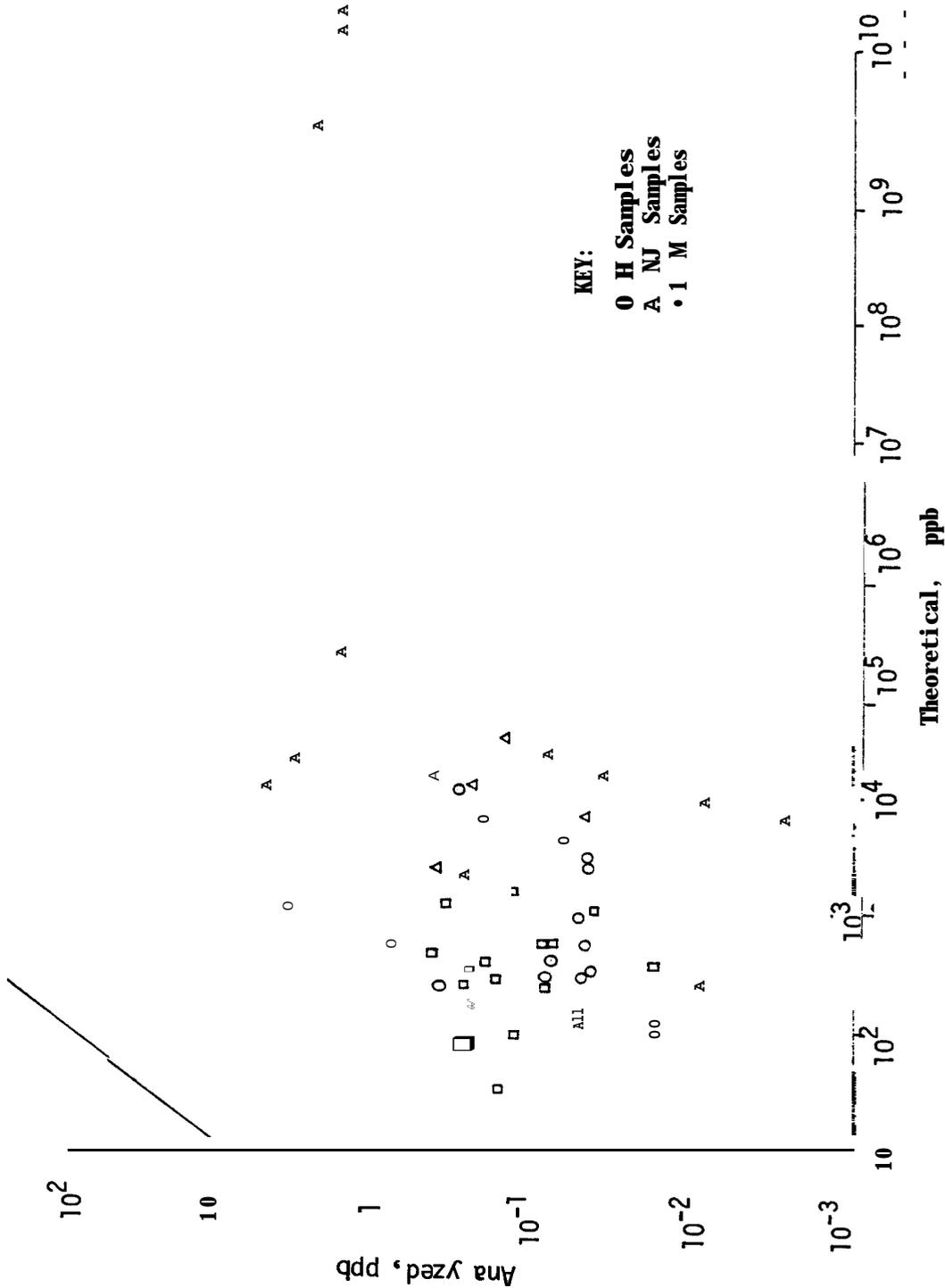


Appendix B. Theoretical Ni Concentration versus Analyzed Concentration: NiCO₃ Control.



Appendix B. Theoretical Pb Concentration versus Analyzed Pb Concentration: PbS Control.





Appendix B. Theoretical Zn Concentration versus Analyzed Zn Concentration: ZnS Control.

Appendix C.

Results of Solubility Equilibrium Concentrations

Appendix C.
Results of Solubility/Equilibrium Concentrations

Sample	Equilibrium Concentration of Cd (ppb)						Analyzed Cd
	Free Cd CdCO ₃	CdS	CdCO ₃	Grand Haven Complexed Cd CdCO ₃	CdS	Total Cd CdCO ₃	
MA	63.28	0.0253	1.22E2	.0487	1.353E2	0.0680	1
MB	14.28	0.0101	8.30E1	.0587	97.28	0.0688	.5
MD	4.49	0.0011	7.52E1	.0184	79.69	0.0195	.2
MF	95.99	0.0063	5.31E2	.0348	6.27E2	0.0411	.5
MK	54.18	0.0067	2.68E2	.0331	3.222E2	0.0398	.5
MPW	20.01	0.0016	7.93E1	.0063	99.31	0.0079	2
2MA	88.79	0.0101	6.94E3	.7919	7.029E3	0.8020	.5
2MB	42.04	0.0101	7.28E1	.0175	1.148E2	0.0276	ND
2MD	89.92	0.0042	7.41E1	.0035	1.640E2	0.0077	.1
2MF	149.72	0.0063	1.52E4	.6461	1.535E4	0.6524	.05
2MK	39.57	0.0042	3.94E1	.0042	78.97	0.0084	.5
2MPW	57.66	0.0026	4.58E1	.0030	1.635E2	0.0056	.5
3MA	39.57	0.0160	3.64E3	1.479	3.679E3	1.4950	.4
3MB	39.23	0.0101	1.25E2	.0323	1.642E2	0.0424	ND
3MD	13.83	0.0067	1.10E1	.0053	24.83	0.0120	ND
3MF	147.24	0.0160	1.53E4	1.669	1.545E4	1.6850	.037
3MK	49.79	0.0067	6.25E1	.0084	1.223E2	0.0151	ND
3MPW	50.81	0.0041	8.21E1	.0066	1.329E2	0.0107	ND

Ω

{Continued}

(Sheet 1 of 42)

Cd (continued)

Sample	Free Cd		Grand Haven Complexed Cd		Total Cd	Analyzed Cd
	CdCO ₃	CdS	CdCO ₃	CdS		
4MA	348.44	11.0160	7.35E3	.3375	7.598E3	0.3535
4MB	348.44	0.0760	1.05E3	.0485	1.398E3	0.0645
4MD	62.83	0.0027	2.18E1	.0009	84.63	0.0035
4ME	23.83	0.0001	1.46E3	.0065	1.484E3	0.0066
4MK	98.91	0.0042	3.08E1	.0013	1.297E2	0.0055
4MPW	50.69	0.0007	2.70E1	.0004	77.69	0.0011

(Continued)

Cd (Continued)

Sample	Free Cd		Houston ComptExed Cd		Total Cd		Analyzed Cd
	CdCO ₃	CdS	CdCO ₃	CdS	CdCO ₃	CdS	
HB	81.84	9.0031	1.72E4	.6513	1.72E4	6.65	10
HC	17.96	0.0012	3.78E3	.2524	3.79E3	0.25	10
HD	28.54	0.0124	3.17E3	1.376	3.19E3	1.39	50
HE	22.86	0.0078	3.04E3	1.037	3.06E3	1.04	70
HDSPW	28.77	0.0124	1.08E3	.4634	1.11E3	0.47	10
DFPW	47.10	a 0029	2.28E2	.0140	2.75E2	0.01	40
2HB	23.24	0.0313	3.36E3	4.520	3.38E3	4.55	.3
2HC	33.49	0.0124	6.74E3	2.496	6.77E3	2.51	2
2HD	36.68	0.0124	3.39E3	1.147	3.42E3	1.16	.8
2HF	124.95	0.0313	1.66E4	4.157	1.67E4	4.19	1
2HOSPW	260.35	0.1244	5.55E3	2.698	5.91E3	2.82	.8
2DFPW	103.76	0.0288	1.04E3	.2899	1.14E3	0.32	ND
3HB	109.99	0.0078	3.00E4	2.127	3.01E4	2.13	2
3HC	138.42	0.0124	4.01E4	3.595	4.02E4	3.61	2
3HD	87.42	0.124	1.37E4	19.54	1.38E4	19.6	1
3HDSPW	58.29	0.0049	3.66E3	.3075	3.72E3	0.31	.8
3DFPW	4.25	0.0001	5.40E1	.0013	58.2	0.00	ND
3HF	109	0.0078	1.86E4	.1320	1.87E4	1.33	1

33

(Continued)

(Sheet 3 of 42)

Cd (continued)

Sample	Free Cd		Houston Complexed Cd		CdCO ₃	CdS	CdCO ₃	CdS	Total Cd CdCO ₃	Analyzed Cd
	CdCO ₃	CdS	CdCO ₃	CdS						
4HB	46.48	0.0313	9.75E3	6.567	9.79E3				6.60	
4HC	151.35	0.0197	3.40E4	4.424	3.41E4				4.44	
4HD	73.64	0.0785	8.16E4	8.698	8.16E4				8.77	
4HF	232.39	0.0313	2.70E4	3.637	2.72E4				3.67	
4HSPW	460.13	0.0785	1.90E4	3.241	1.94E4				3.31	
40FPW	149.18	0.0072	1.69E3	.0814	1.84E3				0.09	
5HB	73.36	0.0124	2.00E4	3.380	2.01E4				3.39	
5HC	45.93	0.0313	1.02E4	6.934	1.02E4				6.96	
5HD	25.73	0.005	3.54E3	.6879	3.56E3				0.69	
5HF	136.70	0.0313	1.66E4	3.808	1.67E4				3.84	
5HSPW	108.30	0.0785	4.56E3	3.305	4.66E3				3.38	
50FPW	38.11	0.0046	4.55E2	.0549	4.93E2				0.06	

Cd (Continued)

Sample	Free Cd		Sayreville Complexed Cd		Total Cd		Analyzed Cd
	CdCO ₃	CdS	GdCO ₃	CdS	CdCO ₃	CdS	
NJA	295.6	0.1113	7.08E4	26.64	7.10E4	26.75	50
NJB	57c.c	0.1763	1.91E5	58.24	1.91E5	58.42	36
NJC	2939.3	1.112	5.68E5	214.9	5.71E5	216.01	5
NJF	1238.7	0.1690	1.38E5	18.86	1.39E5	19.03	14
NJPW	142.7	0.0042	4.96E3	.1461	5.10E3	0.15	
NJJ		401662.0		4.919E6		5320662	3
2NJA	1043.1	0.1113	3.66E5	39.09	3.67E5	39.20	2
2NJB	866.6	0.4429	3.04E5	155.5	3.05E5	155.94	2
2NJC	8597.5	1.763	2.84E6	582.8	2.85E6	584.56	2
2NJF	5190.6	0.4244	2.59E5	21.14	2.64E5	21.56	4
2NJPW	50.13	0.0027	1.75E3	.0941	1.86E3	0.097	
2NJJ		40166.0		7.474E5		787566	16
3NJA	329.3	0.0443	8.43E4	11.35	8.46E4	11.39	2
3NJB	737.3	0.2795	2.59E5	98.16	2.60E5	98.44	3
3NJC	659.8	1.112	4.33E4	72.98	4.40E4	74.09	3
3NJF	2408.7	0.4244	2.69E5	47.35	2.71E5	47.77	2
3NJPW	241.7	0.0042	6.64E3	.1154	6.88E3	0.119	
3NJJ				3.104E6		2.77E5	13

(Continued)

(Sheet 5 of 42)

Cd (continued)

Sample	Free Cd		Sayreville Complexed Cd		Total Cd		Analyzed Cd
	CdCO ₃	CdS	CdCO ₃	CdS	CdCO ₃	CdS	
4NJA	2342.4	0.1763	7.28E5	54.77	7.30E5	54.95	
4NJB	4663.5	0.7020	1.44E6	218.0E2	1.44E6	21800.7	
4NJC	928.4	0.4429	2.38E5	113.4	2.39E5	113.84	
4NJF	355.2	0.0424	3.27E4	3.922	3.31E4	3.96	
4NJP							
4NJJ		25343.0		1.533E5		178643	
5NJA	159.6	0.0702	3.57E4	15.68	3.59E4	15.75	
5NJB	121.4	0.0111	3.32E4	3.038	3.33E4	3.05	
5NJC	166.4	0.1763	5.17E4	54.77	5.19E4	54.95	
5NJD	729.5	1.112	1.52E5	231.38	1.53E4	232.49	

Equilibrium Concentration of Cu (ppb)

Sample	Free Cu		Grand Haven		Total Cu		Analyzed cu
	$\text{Cu}_2\text{CO}_3(\text{OH})_2$	cus	$\text{Cu}_2\text{CO}_3(\text{OH})_2$	Complexed Cu cus	$\text{Cu}_2\text{CO}_3(\text{OH})_2$	cus	
MA	6.75	5.4E-12	5.24	4.19E-12	12.0	9.59F-12	5
MB	2.54	2.1E-12	2.95	2.43E-12	5.49	4.53L-12	50
MD	.680	9.0E-13	1.77	2.34E-12	2.45	3.24E-12	10
MF	5.88	1.36E-12	8.70	2.01E-12	14.6	3.37E-12	20
MK	4.06	1.4E-12	2.66	9.16E-13	6.72	2.32E-12	20
MPW	1.64	3.5E-13	1.40	2.98E-13	3.04	6.48E-13	30
2MA	6.35	2.1E-12	43.2	1.43E-11	49.5	1.64E-11	10
2MB	4.37	2.1E-12	6.03	2.89E-12	10.4	4.99E-12	50
2MD	4.67	9.0E-13	2.57	4.95E-13	7.23	1.39E-12	10
2MF	7.35	2.1E-12	61.4	1.73E-11	68.7	1.94E-11	40
2MK	3.10	9.0E-13	2.92	8.48E-13	6.01	1.75E-12	50
2MPW	3.13	5.6E-13	1.33	2.39E-13	4.45	7.99E-13	7
3MA	4.75	3.4E-12	42.5	3.01E-11	47.2	3.35E-11	30
3MB	4.22	2.1E-12	11.5	6.46E-12	15.7	85.6E-12	30
3MD	2.05	1.4E-12	1.05	7.13E-13	3.10	2.11E-12	10
3MF	9.21	3.4E-12	76.2	2.77E-11	85.4	3.11E-11	40
3MK	3.90	1.4E-12	4.36	1.56E-12	8.25	2.96E-12	20
3MPW	3.29	8.8E-13	1.38	3.70E-13	4.67	1.25E-12	40

Cu (Continued)

Sample	Free Cu		cus	Grand Haven Complexed Cu		Total Cu		Analyzed cu
	$\text{Cu}_2\text{CO}_3(\text{OH})_2$	$\text{Cu}_2\text{CO}_3(\text{OH})_2$		$\text{Cu}_2\text{CO}_3(\text{OH})_2$	CuS	$\text{Cu}_2\text{CO}_3(\text{OH})_2$	CuS	
4MA	14.1	3.4E-12	68.3	1.64E-11	82.4	1.98E-11	1.98E-11	
4MB	6.72	3.4E-12	8.42	4.26E-12	15.1	7.66E-12	7.66E-12	
4MD	3.48	5.7E-13	4.38	3.90E-13	7.85	9.6E-13	9.6E-13	
4MF	1.04	2.16E-14	32.3	1.19E-13	33.3	1.41E-13	1.41E-13	
4MK	4.89	9.0E-13	3.13	5.76E-13	8.02	1.48E-12	1.48E-12	
4MPW	2.07	1.4E-13	2.50	1.69E-13	4.57	3.09E-13	3.09E-13	

(Continued)

(Sheet 8 of 42)

Cu (Continued)

Sample	Free Cu		Houston Complexed Cu		Total Cu		Analyzed cu
	$\text{Cu}_2\text{CO}_3(\text{OH})_2$	cus	$\text{Cu}_2\text{CO}_3(\text{OH})_2$	cus	$\text{Cu}_2\text{CO}_3(\text{OH})_2$	cus	
HB	5.00	6.7E-13	85.2	1.10E-11	90.2	1.17E-11	10
HC	1.48	2.7E-13	29.6	5.25E-12	31.1	5.52E-12	10
HD	4.17	2.7E-12	38.1	2.43E-11	42.3	2.7E-11	10
HE	3.33	1.7E-12	38.2	1.78E-11	41.5	1.95E-11	10
HOSPW	4.55	2.7E-13	26.7	1.58E-12	31.3	1.85E-12	10
OPFW	3.10	2.46E-14	2.65	2.10E-14	5.75	4.56E-14	10
2HB	15.0	6.7E-12	161	7.01E-11	176	7.68E-11	30
2HC	4.52	2.7E-13	66.8	3.85E-12	71.3	4.12E-12	60
2HD	4.73	2.7E-13	35.6	2.01E-12	40.3	2.28E-12	50
2HF	11.0	6.7E-12	145	8.67E-11	160	9.34E-11	100
2HOSPW	17.8	26.7E-12	62.1	9.31E-11	79.9	1.19E-10	30
2OFPW	7.30	16.9E-12	6.63	1.58E-11	13.9	9.27E-11	20
3HB	7.30	1.7E-12	142	3.14E-11	149	3.31E-11	130
3HC	9.18	2.7E-13	185	5.15E-12	194	5.42E-12	50
3HD	5.80	1.06E-12	216	3.92E-11	222	4.03E-11	30
3HOSPW	5.31	1.7E-12	75.8	2.42E-11	81.0	2.59E-11	40
3OFPW	.415	2.45E-14	4.53	2.67E-13	4.94	2.92E-13	6
3HF	7.30	1.7E-12	138	3.14E-11	145	3.31E-11	100

Cu (Continued)

Sample	Free Cu		cus	Houston Complexed Cu		cus	Total Cu Cu ₂ CO ₃ (OH) ₂	cus	Analyzed cu
	Cu ₂ CO ₃ (OH) ₂	Cu ₂ CO ₃ (OH) ₂		Cu ₂ CO ₃ (OH) ₂	Cus				
4HB	6.70	100	6.7E-12	9.64E-11	107	1.03E-10			
4HC	10.8	173	4.2E-12	6.46E-11	184	6.88E-11			
4HD	10.6	89.2	16.9E-12	1.34E-10	100	1.51E-10			
4HF	15.0	185	6.7E-12	8.15E-11	100	8.82E-11			
4HSPW	26.6	173	16.9E-12	1.10E-10	100	1.27E-10			
40FPW	6.95	8.43	1.55E-12	1.88E-12	15.0	3.43E-12			
5HB	6.69	128	2.7E-13	4.90E-12	134	5.17E-12			
5HC	6.66	105	6.7E-12	1.03E-10	112	1.09E-10			
5HD	3.14	38.0	1.06E-12	1.26E-11	41.0	1.37E-11			
5HF	11.5	172	6.7E-12	9.92E-11	183	1.06E-10			
5HSPW	12.9	77.7	16.9E-12	1.02E-10	91.0	1.19E-10			
50FPW	3.13	4.00	9.7E-13	1.24E-12	7.00	2.21E-12			

(Continued)

(Sheet 10 of 42)

Cu (Continued)

Sample	Free Cu		cus	Sayreville Complexed Cu		Total CuS	Cu ₂ CO ₃ (OH) ₂	cus	Analyzed cu
	Cu ₂ CO ₃ (OH) ₂	Cu		Cu ₂ CO ₃ (OH) ₂	Cu				
NJA	24.3		2.39E-11	447	2.41E-12	471	2.63E-11	1	
NJB	38		3.79E-11	966	9.11E-10	1004	9.49E-10	7	
NJC	136		239E-12	1979	3.36E-9	2115	3.59E-9	7	
NJF	49.3		36.3E-12	420	3.05E-10	469	3.41E-10	3	
NJPW	6.67		9.12E-13	28.4	3.87E-12	35.1	4.78E-12	--	
NJJ	--		544E-15	--	1.15E-12	--	1.69E-12	45	
2NJA	45.5		2.39E-11	1134	5.58E-10	1180	5.82E-10	270	
2NJB	58.7		95.1E-12	1598	2.44E-9	1657	2.54E-9	80	
2NJC	261		37.9E-12	8373	1.16E-8	8636	1.19E-8	200	
2NJF	127		91.2E-12	531	3.79E-10	658	4.70E-10	40	
2NJPW	3.51		5.75E-13	16.1	2.63E-12	19.6	3.21E-12	--	
2NJJ	--		8.63E-6	00	1.96E-5	--	2.82E-5	300	
3NJA	20.3		9-51E-12	447	2.01E-10	467	2.11E-10	110	
3NJB	48.2		60E-12	1298	1.54E-9	1346	1.58E-9	100	
3NJC	64.4		239E-12	764	2.82E-9	828	3.06E-9	138	
3NJF	86.6		91.2E-12	736	7.63E-10	823	8.54E-10	40	
3NJPW	8.68		9.12E-13	31.5	3.31E-12	40.2	4.22E-12	1300	
3NJJ	--		54.4E-6	--	8.22E-5	--	1.37E-4	--	

(Continued)

(Sheet 11 of 42)

Cu (Continued)

Sample	Free Cu		CuS	Savreville Complexed Cu		Cu ₂ CO ₃ (OH) ₂	CuS	Cu ₂ CO ₃ (OH) ₂	Total Cu cus	Analyzed Cu
	Cu ₂ CO ₃ (OH) ₂	CuS		Cu ₂ CO ₃ (OH) ₂	CuS					
4NJA	76.6	3.79E-11		171	7.96E-10	1782		1782	8.34E-10	
4NJB	108	151E-12		2573	3.40E-9	2681		2681	3.55E-9	
4NJC	60.7	95.1E-12		1743	1.88E-9	1804		1804	1.98E-9	
4NJF	18.7	9.12E-12		136	6.55E-11	155		155	7.46E-11	
4NJP	--	--		--	--	--		--	--	
4NJJ	--	5.4E-6		--	6.38E-6	--		--	1.18E-5	
5NJA	15.9	15.0E-12		262	2.38E-10	278		278	2.53E-10	
5NJB	8.74	9.12E-13		202	2.02E-11	211		211	2.11E-11	
5NJC	20.4	3.79E-11		489	8.60E-10	509		509	8.89E-10	
5NJD	67.8	239E-12		1507	5.18E-9	1575		1575	5.42E-9	

(Continued)

(Sheet 12 of 42)

Equilibrium Concentration of Fe (ppb)

Sample	Free Fe			Grand Haven Complexed Fe			Total Fe	Analyzed Fe
	FeCO ₃	Fe(OH) ₃	FeCO ₃	Fe(OH) ₃	FeCO ₃	Fe(OH) ₃		
MA	5.23E4	2.71E-9	8.03E4	4.16E-9	1.33E5	6.87E-9	.2	
MB	1.18E4	6.78E-10	1.50E4	8.63E-10	2.68E4	1.54E-9	.6	
MD	3.15E3	2.26E-11	3.97E3	2.86E-11	7.12E3	3.08E-10	.9	
MF	7.93E4	3.41E-10	1.45E5	6.23E-10	2.24E5	9.64E-10	.5	
MK	4.47E4	3.58E-10	1.45E4	1.16E-10	5.92E4	4.74E-10	.1	
MPW	1.73E4	4.46E-11	1.03E4	3.22E-11	2.76E4	7.68E-11	.2	
2MA	7.35E4	6.78E-10	1.73E5	1.65E-9	2.47E5	2.33E-9	.4	
2MB	3.48E4	6.78E-10	1.01E5	1.97E-9	1.36E5	2.65E-9	.17	
2MD	7.43E4	1.79E-10	5.23E4	1.26E-10	1.27E5	3.05E-10	.17	
2MF	1.24E5	3.41E-10	1.82E5	5.47E-10	3.06E5	8.88E-10	.4	
2MK	3.27E4	1.49E-10	6.17E4	2.81E-10	9.44E4	4.30E-10	.55	
2MPW	4.77E4	8.90E-11	1.51E4	3.32E-11	6.28E4	1.22E-10	.5	
3MA	3.27E4	1.35E-9	2.01E5	8.44E-9	2.34E5	9.79E-9	2.5	
3MB	3.24E4	6.78E-10	2.46E5	5.14E-9	2.78E5	5.82E-9	.72	
3MD	1.14E4	3.58E-10	9.79E3	3.07E-10	2.12E4	6.65E-10	1.1	
3MF	1.23E5	1.35E-9	2.07E5	2.47E-9	3.30E5	3.82E-9	.5	
3MK	4.12E4	3.58E-10	1.09E5	9.43E-10	1.50E5	1.30E-9	.17	
3MPW	4.20E4	1.78E-10	1.83E4	9.45E-11	6.03E4	2.73E-10	.5	

Fe (Continued)

Sample	Free Fe		Grand Haven Complexed Fe		Total Fe	Analyzed Fe
	FeCO ₃	Fe(OH) ₃	FeCO ₃	Fe(OH) ₃		
4MA	2.88E5	1.35E-9	2.61E6	1.23E-8	2.90E6	1.36E-8
4MB	6.53E4	1.35E-9	1.66E5	3.43E-9	2.31E5	4.78E-9
4MD	5.20E4	9.00E-11	4.23E4	7.32E-11	9.43E4	1.63E-10
4MF	1.87E4	3.41E-10	4.65E4	8.68E-10	6.52E4	1.21E-9
4MK	8.18E4	1.79E-10	9.06E4	1.98E-10	1.72E5	3.77E-10
4MPW	4.19E4	2.04E-11	4.31E4	2.56E-11	8.50E4	4.60E-11

(Continued)

(Sheet 14 of 42)

Fe (Continued)

Sample	free Fe		Fe(OH) ₃	FeCO ₃	Houston Complexed Fe		FeCO ₃	Total Fe FeCO ₃	Total Fe Fe(OH) ₃	Analyzed Fe
	FeCO ₃	Fe(OH) ₃			FeCO ₃	Fe(OH) ₃				
1B	6.77E4	1.0E-10	1.32E5	2.36E-10	2.00E5	3.36E-10	130			
1C	9.38E3	2.51E-11	1.78E4	5.77E-11	2.72E4	8.28E-11	50			
1D	2.36E4	8.01E-10	4.35E4	1.60E-9	6.71E4	2.40E-9	30			
1F	1.89E4	4.0E-10	2.16E4	5.39E-10	4.05E4	9.39E-10	100			
1HSPW	2.81E4	8.01E-10	2.13E5	5.96E-9	2.41E5	6.76E-9	40			
1RFPW	3.89E4	1.03E-10	1.28E4	2.56E-11	5.17E4	2.66E-9	6			
21B	1.92E5	3.19E-9	1.64E5	3.47E-9	3.56E5	6.66E-9	.2			
21C	2.77E4	8.01E-10	3.39E4	1.29E-9	6.16E4	2.09E-9	.6			
21D	3.03E4	8.01E-10	2.30E4	7.00E-10	5.33E4	1.50E-9	.5			
21F	1.03E5	3.19E-9	1.06E6	3.35E-8	1.16E6	3.67E-8	.4			
21HSPW	2.15E5	2.51E-8	1.17E6	1.37E-7	1.39E6	1.62E-7	.4			
20FPW	8.58E4	1.62E-9	2.63E4	3.27E-10	1.12E5	1.95E-9	.8			
31B	9.09E4	4.0E-10	1.38E5	8.34E-10	2.29E5	1.23E-9	4.7			
31C	1.14E5	8.01E-10	1.81E5	1.77E-9	2.95E5	2.57E-9	9.4			
31D	7.23E4	2.01E-10	3.76E6	1.05E-8	3.83E6	1.07E-8	17			
31HSPW	4.82E4	4.0E-10	1.13E6	9.42E-9	1.18E6	9.82E-9	.6			
30FPW	3.52E3	1.46E-8	2.47E4	5.54E-8	2.82E4	7.00E-8	1.6			
31F	9.09E4	4.0E-10	1.59E6	7.10E-9	1.68E6	7.50E-9	.3			

Fe (Continued)

Sample	Free Fe		Houston Complexed Fe		Total Fe		Analyzed Fe
	FeCO ₃	Fe(OH) ₃	FeCO ₃	Fe(OH) ₃	FeCO ₃	Fe(OH) ₃	
4IB	3.84E4	3.19E-9	450E4	5.02E-9	8.34E4	8.21E-9	
4IC	1.25E5	1.59E-9	1.67E5	2.83E-9	2.92E5	4.42E-9	
4ID	6.09E4	1.27E-8	6.03E4	1.45E-8	1.21E5	2.72E-8	
4IE	1.92E5	3.19E-9	2.12E6	3.58E-8	2.31E6	3.89E-8	
4IDSPW	3.80E5	1.27E-8	3.75E6	1.26E-7	3.13E6	1.38E-7	
40FPW	1.23E5	4.08E-10	1.24E5	2.28E-10	2.47E5	6.36E-10	
5IB	6.06E4	8.01E-10	9.32E4	1.69E-9	1.54E5	2.49E-9	
5IC	3.79E4	3.19E-9	4.89E4	5.50E-9	8.68E4	8.69E-9	
5ID	1.20E5	2.01E-8	3.64E5	6.54E-8	4.84E5	8.55E-8	
5IE	1.13E5	3.19E-10	1.93E6	5.50E-8	2.04E6	5.81E-8	
5IDSPW	2.17E5	1.27E-8	1.81E6	1.06E-7	2.03E6	1.19E-7	
50FPW	3.15E4	2.05E-10	1.53E4	6.63E-11	4.68E4	2.71E-10	

(Continued)

(Sheet 16 of 42)

Fe (Continued)

Sample	Free Fe			Sayreville Complexed Fe			Total Fe		Analyzed Fe
	FeCO ₃	Fe(OH) ₃	FeCO ₃	Fe(OH) ₃	FeCO ₃	Fe(OH) ₃	FeCO ₃	Fe(OH) ₃	
NJA	2.45E5	2.45E-8	1.61E6	1.73E-7	1.86E6	1.97E-7	1.86E6	1.97E-7	.003
NJB	4.76E5	4.89E-8	5.60E6	6.11E-7	1.04E7	6.60E-7	1.04E7	6.60E-7	40
NJC	2.43E6	7.8E-7	9.21E6	3.24E-6	1.16E7	4.02E-6	1.16E7	4.02E-6	.002
NJF	1.02E6	4.58E-8	1.52E6	7.52E-8	2.54E6	1.21E07	2.54E6	1.21E07	2 2
NJPW	1.18E5	1.80E-10	3.28E5	5.03E-18	4.46E5	1.80E-10	4.46E5	1.80E-10	.14
NJJ	--	1.74E-12	--	6.42E-12	--	8.16E-12	--	8.16E-12	284
2NJA	8.63E5	2.45E-8	5.96E6	1.88E-7	6.82E6	2.13E-7	6.82E6	2.13E-7	3 2
2NJB	7.17E5	2.0E-7	9.82E6	2.90E-6	1.05E7	3.10E-6	1.05E7	3.10E-6	178
2NJC	3.27E5	1.55E-6	9.11E6	4.43E-5	9.44E6	4.59E-5	9.44E6	4.59E-5	159
2NJF	4.29E6	1.8E-7	6.16E6	2.66E-7	1.04E7	4.46E-7	1.04E7	4.46E-7	7 8
2NJPW	4.14E4	9.13E-11	1.03E5	2.29E-10	1.44E5	3.21E-10	1.44E5	3.21E-10	N D
2NJJ	--	5.17	--	14.1	--	19.3	--	19.3	138
3NJA	2.72E5	6.16E-9	3.68E6	8.65E-8	3.95E6	9.27E-8	3.95E6	9.27E-8	5 3
3NJB	6.10E5	9.74E-8	7.79E6	1.32E-6	8.40E6	1.42E-6	8.40E6	1.42E-6	8 5
3NJC	5.45E5	7.8E-7	1.05E7	1.51E-5	1.11E7	1.59E-5	1.11E7	1.59E-5	.5
3NJF	1.99E6	1.8E-7	2.93E6	2.93E-7	4.92E6	4.73E-7	4.92E6	4.73E-7	1 6
3NJPW	2.01E5	1.82E-10	5.04E5	4.59E-10	7.05E5	6.41E-10	7.05E5	6.41E-10	.2
3NJJ	--	82.3	--	151	--	233	--	233	.5

(Continued)

(Sheet 17 of 42)

Fe (Continued)

Sample	Sayreville					Total Fe FeCO ₃	Analyzed te
	Free Fe FeCO ₃	Fe(OH) ₃	FeCO ₃	Complexed Fe Fe(OH) ₃	Fe(OH) ₃		
4NJA	1.94E6	4.89E-8	1.15E-7	3.22E-7	1.34E7	3.71E-7	
4NJB	1.93E6	3.9E-7	2.03E7	4.37E-6	2.22E7	4.76E-6	
4NJC	7.68E5	2E-7	2.27E7	6.02E-6	2.35E7	6.22E-6	
4NJF	2.94E5	5.77E-9	4.25E5	9.01E-9	7.19E5	1.48E-8	
4NJP	--	--	--	--	--	--	
4NJJ	--	2.59E-8	--	5.83E-8	--	8.42E-8	
5NJA	1.32E5	1.23E-8	4.75E5	4.97E-8	6.07E5	6.20E-8	
5NJB	1.00E5	7.78E-10	1.18E6	9.64E-9	1.28E6	1.04E-8	
5NJC	1.38E5	4.89E-8	1.49E6	7.88E-7	1.63E6	8.37E-7	
5NJD	1.08E9	7.8E-7	2.39E10	1.73E-5	2.50E10	1.81E-5	

(Continued)

(Sheet. 18 of 42)

Equilibrium Concentration of Mn (ppb)

Sample	Free Mn			Grand Haven			Total Mn	Analyzed Mn
	MnCO ₃	MnS	MnCO ₃	MnCO ₃	Complexed Mn	MnCO ₃		
MA	5.23E4	2.11E9	5.05E4	2.2E9	2.2E9	1.03E5	4.31E9	.2
MB	1.18E4	7.27E8	9.93E3	8.9E8	8.9E8	2.17E4	1.62E9	--
MD	3.16E3	8.75E7	3.16E3	9.4E7	9.4E7	6.32E3	1.82E8	.15
ME	7.93E4	6.40E8	9.24E4	5.6E8	5.6E8	1.72E5	1.19E9	.2
MK	4.47E4	1.30E8	1.08E4	5.9E8	5.9E8	5.55E4	7.19E8	--
MPW	1.73E4	4.93E5	6.17E3	1.45E6	1.45E6	2.35E4	1.94E6	.05
2MA	7.35E4	2.84E9	2.56E5	8.9E8	8.9E8	3.30E5	3.73E9	17
2MB	3.48E4	1.60E9	6.29E4	8.9E8	8.9E8	9.77E4	2.49E9	2.5
2MD	7.44E4	1.38E8	2.79E4	3.7E8	3.7E8	1.02E5	5.08E8	.02
2ME	1.24E5	1.82E9	4.49E5	5.6E8	5.6E8	5.73E5	2.38E9	.5
2MK	3.27E4	4.22E8	3.74E4	3.7E8	3.7E8	7.01E4	7.92E8	.03
2MPW	4.77E4	3.07E5	6.58E3	2.3E6	2.3E6	5.43E4	2.61E6	.5
3MA	3.27E4	8.46E9	2.09E5	1.4E9	1.4E9	2.41E5	9.86E9	18
3MB	3.25E4	4.31E9	1.58E5	8.9E8	8.9E8	1.91E5	5.20E9	5
3MD	1.14E4	2.90E8	5.64E3	5.9E8	5.9E8	1.70E4	8.8E8	1
3ME	1.23E5	4.90E9	4.76E5	1.4E9	1.4E9	5.99E5	6.29E9	3
3MK	4.12E4	9.71E8	6.80E4	5.9E8	5.9E8	1.09E5	1.56E9	3.3
3MPW	4.20E4	8.52E5	1.02E4	3.6E6	3.6E6	5.22E4	4.45E6	.4

Mn (Continued)

Sample	Free Mn		Grand Haven Complexed Mn		Total Mn		Analyzed Mn
	MnCO ₃	MnS	MnCO ₃	MnS	MnCO ₃	MnS	
4MA	2.88E5	8.64E9	1.80E6	1.4E9	2.09E6	1.00E10	
4MB	6.53E4	2.25E9	1.06E5	1.4E9	1.71E5	3.65E9	
4MD	5.20E4	9.84E7	2.14E4	2.4E8	7.34E4	3.38E8	
4MF	1.97E4	1.74E7	4.36E4	8.9E6	6.33E4	2.63E7	
4MK	8.18E4	2.31E8	5.11E4	3.7E8	1.33E5	6.01E8	
4MPW	4.19E4	2.81E5	2.07E4	5.7E5	6.26E4	8.51E5	

(Continued)

(Sheet 20 of 42)

Mn (Continued)

Sample	Free Mn		Houston Com i		Total Mn		Analyzed Mn
	MnCO ₃	MnS	MnCO ₃	Mn MnS	MnCO ₃	MnS	
1B	6.76E4	2.7E8	4.36E5	1.94E9	5.54E5	2.21E9	15
1C		1.1E8	6.56E4	7.70E8	7.50E4	8.79E8	3
1D	2.36E4	1.1E9	9.71E4	4.52E9	1.20E5	5.62E9	--
1F	1.87E4	6.9E8	8.07E4	2.98E9	9.94E4	3.67E9	9
1HSPW	2.81E4	1.1E9	1.59E5	6.22E9	1.87E5	7.32E9	2
1FPW	3.89E4	1.0E22	5.52E3	6.86E20	4.44E4	1.07E22	--
2HB	1.92E5	2.7E9	8.81E5	1.24E10	1.07E6	1.51E10	.05
2HC	2.77E4	1.1E9	1.88E5	7.26E9	2.15E5	8.36E9	4.3
2HD	3.03E4	1.1E9	8.62E4	3.13E9	1.16E5	4.32E9	.05
2HF	1.03E5	2.7E9	1.06E6	2.79E10	1.17E6	3.06E10	.05
2HSPW	2.15E5	1.1E10	8.53E5	4.37E10	1.07E6	5.47E10	.02
2FPW	8.58E4	6.9E22	2.61E4	2.10E22	1.12E5	8.99E22	.03
3HB	9.09E4	6.9E8	8.19E5	6.21E9	9.10E5	6.90E9	2.1
3HC	1.14E5	1.1E9	1.10E6	1.06E10	1.21E6	1.17E10	6
3HD	7.23E4	4.4E8	2.73E6	1.66E10	2.8E6	1.71E10	19
3HSPW	4.82E4	6.9E8	7.99E5	1.14E10	8.4E5	1.21E10	8
3FPW	3.52E3	4.4E20	7.44E3	9.30E20	1.10E4	1.37E21	4
3HF	9.09E4	6.9E8	1.45E6	1.10E10	1.55E6	1.17E10	20

Mn (Continued)

Sample	Houston						Analyzed Mn
	Free Mn MnCO ₃	MnS	MnCO ₃	Complexed Mn MnS	MnCO ₃	Total Mn MnS	
4HB	3.84E4	2.7E9	2.65E5	1.86E10	3.03E5	2.13E10	
4HC	1.25E5	1.8E9	9.30E5	1.34E10	1.06E6	1.52E10	
4HD	6.09E4	6.9E9	2.22E5	2.22E10	2.83E5	3.21E10	
4HF	1.92E5	2.7E9	1.97E6	2.77E10	2.16E6	2.78E12	
4HSPW	3.80E5	6.9E9	2.78E6	5.05E10	3.16E6	5.74E10	
40FPW	1.23E5	2.8E22	6.57E4	1.49E22	1.89E7	4.29E22	
5HB	6.06E4	1.1E9	5.49E5	9.96E9	6.09E5	1.11E10	
5HC	3.79E4	2.7E9	2.78E5	1.98E10	3.16E5	2.25E10	
5HD	2.13E4	4.4E8	1.20E5	2.48E9	1.41E5	2.92E9	
5HF	1.13E5	2.7E9	1.62E6	3.87E10	1.73E6	4.14E10	
5HSPW	8.95E4	6.9E9	5.69E5	4.39E10	6.59E5	5.08E10	
50FPW	3.15E4	1.7E22	1.18E4	6.40E21	4.33E4	2.34F22	

(Continued)

(Sheet 22 of 42)

Mh (Continued)

Sample	Free Mh		Sayreville Complexed Mn		Total Mh		Analyzed Mh
	MnCO ₃	MnS	MnCO ₃	MnS	MnCO ₃	MnS	
NJA	2.45E5	9.88E9	2.78E6	1.12E11	3.03E6	1.22E11	.86
NJB	4.76E5	1.56E10	8.36E6	2.74E11	8.83E6	2.89E11	1.46
NJC	2.43E6	9.88E10	1.98E7	8.03E11	2.22E7	9.02E11	7.5
NJF	1.02E6	1.50E10	4.11E6	5.45E10	5.13E6	6.95E10	.22
NJPW	1.18E5	3.77E8	2.90E5	3.58E8	4.08E5	7.35E8	.32
NJJ	--	2.2E8	--	5.73E8	--	7.93E8	28.9
2NJA	8.63E5	9.88E9	1.30E7	1.48E11	1.38E7	1.58E11	5
2NJB	7.17E5	3.94E10	1.39E7	7.66E11	1.47E7	8.05E11	5
2NJC	7.11E6	1.56E11	1.99E8	4.36E12	2.06E8	4.52E12	16
2NJF	4.29E6	3.77E10	9.2E6	7.39E10	1.35E7	1.12E11	.7
2NJPW	4.14E4	2.38E8	9.22E4	4.97E8	1.34E5	7.35E8	1
2NJJ	--	3.6E15	--	7.58E15	--	1.12E15	4
3NJA	2.72E5	3.9E9	4.44E6	6.37E10	4.71E6	6.76E10	5.2
3NJB	6.10E5	2.48E10	1.15E7	4.67E11	1.21E7	4.92E11	4.4
3NJC	5.45E5	9.88E10	7.72E6	1.37E12	8.26E6	1.47E12	18
3NJF	1.99E6	3.7E10	8.01E6	1.34E11	1.71E11	1.71E11	.6
3NJPW	6.10E5	3.77E8	4.20E5	7.46E8	6.21E5	1.12E9	1
3NJJ	--	2.2E16	--	3.09E16	--	5.29E16	2

(Continued)

(Sheet 23 of 42)

Mn (-Continued)

Sample	Free Mn		MnS	Sayreville Complexed Mn		Total Mn		Analyzed Mn
	MnCO ₃	MnS		MnCO ₃	MnS	MnCO ₃	MnS	
4NJA	1.92E6	1.56E10	2.53E7	1.93E11	2.72E7	2.08E11	2.08E11	
4NJB	1.93E6	6.24E10	3.12E7	4.33E12	3.31E7	4.39E12	4.39E12	
4NJC	7.68E5	3.94E10	2.06E7	1.03E12	2.13E7	1.07E12	1.07E12	
4NJF	2.94E5	3.7E9	9.94E5	1.13E10	1.29E6	1.49E10	1.49E10	
4NJP	--	3.7E15	--	--	--	--	--	
4NJJ	--	2.2E15	--	3.43E15	--	5.63E15	5.63E15	
5NJA	1.32E5	6.24E9	1.18E6	5.15E10	1.31E6	5.77E10	5.77E10	
5NJB	1.00E5	9.88E8	1.57E6	1.48E10	1.67E6	1.57E10	1.57E10	
5NJC	1.38E5	1.56E10	2.25E6	2.41E11	2.39E6	2.57E11	2.57E11	
5NJD	6.03E5	9.88E10	1.22E7	1.94E12	1.28E7	2.04E12	2.04E12	

(Continued)

(Sheet 24 of 42)

Equilibrium Concentration of Ni (ppb)

Sample	Free		Grand Haven		Total Ni	Analyzed	
	NiCO ₃	NiS	NiCO ₃	Complexed Ni NiS			NiS
MA	8.11E6	0.240	8.96E6	0.266	1.71E7	0.506	60
MB	1.82E6	0.096	1.62E6	0.085	3.44E6	0.181	10
MD	4.89E5	0.010	4.23E5	0.009	9.12E5	0.019	10
MF	1.23E7	0.060	1.57E7	0.077	2.80E7	0.137	11
MK	6.94E6	0.064	1.37E6	0.013	8.31E6	0.076	9
MPW	2.57E6	0.016	8.02E6	0.006	1.06E7	0.021	10
2MA	1.14E7	0.096	2.71E7	0.211	3.85E7	0.307	390
2MB	5.39E6	0.096	1.13E7	0.201	1.67E7	0.296	60
2MD	1.15E7	0.040	5.00E6	0.536	1.65E7	0.576	10
2MF	1.92E7	0.060	3.20E7	0.100	5.12E7	0.161	20
2MK	5.07E6	0.040	6.76E6	0.054	1.18E7	0.094	20
2MPW	7.40E6	0.025	1.10E6	0.004	8.50E6	0.028	8
3MA	5.07E6	0.152	2.64E7	0.787	3.15E7	0.939	80
3MB	5.03E6	0.096	2.85E7	0.541	3.35E7	0.637	121
3MD	1.77E6	0.064	1.01E6	0.037	2.78E6	0.700	6
3MF	1.90E7	0.152	3.60E7	0.287	5.50E7	0.439	30
3MK	6.38E6	0.064	1.23E7	0.123	1.87E7	0.186	40
3MPW	6.25E6	0.039	1.71E6	0.010	8.23E6	0.049	15

Ni (Continued)

Sample	$\frac{\text{Free Ni}}{\text{NiCO}_3}$	NiS	$\frac{\text{NiCO}_3}{\text{NiCO}_3}$	$\frac{\text{Granulated Ni}}{\text{Complexed Ni}}$	$\frac{\text{NiCO}_3}{\text{NiCO}_3}$	$\frac{\text{Total Ni}}{\text{NiS}}$	$\frac{\text{Analyzed Ni}}{\text{Ni}}$
WA	4.47E7	0.152	3.10E8	1.05	3.55E8	1.20	
4XB	1.01E7	0.152	1.87E7	.281	2.88E7	.432	
4XD	8.06E6	0.025	3.93E6	.012	1.20E7	.038	
4XF	3.06E6	0.001	4.02E6	.001	7.08E6	.002	
4MK	1.27E7	0.040	9.37E6	.303	2.21E7	.070	
4MPW	6.50E6	0.006	3.83E6	.004	1.03E7	.010	

(Continued)

(Sheet 26 of 42)

Ni (Continued)

Sample	Free Ni		Houston Complexed Ni		Total Ni NiCO ₃	Analyzed Ni
	NiCO ₃	NiS	NiCO ₃	NiS		
HB	1.05E7	0.030	2.63E7	.074	3.68E7	10
HC	1.45E6	0.012	3.32E6	.027	4.77E6	7
HD	3.68E6	0.118	7.32E6	.024	1.10E7	8
HE	3.46E6	0.075	5.38E6	.116	8.84E6	10
HSPW	2.61E7	0.118	1.53E8	.692	1.79E8	10
OPW	4.35E6	0.027	3.84E5	.002	4.73E6	--
2HB	6.80E6	0.297	1.02E7	.447	1.70E7	3
2HC	4.70E6	0.118	9.66E6	.243	1.44E7	20
2HD	1.01E7	0.118	1.06E7	.124	2.07E7	5
2HE	1.67E7	0.297	1.44E8	2.76	1.61E8	33
2HSPW	7.24E7	1.18	3.06E8	5.00	3.78E8	28
20FPW	1.03E7	0.172	1.74E6	.029	1.20E7	40
3HB	1.41E7	0.075	3.67E7	.194	5.08E7	31
3HC	1.77E7	0.118	4.93E7	.330	6.70E7	15
3HD	5.93E6	0.047	2.38E8	1.89	2.44E8	39
3HSPW	9.34E6	0.075	1.69E8	1.35	1.78E8	23
30FPW	8.23E5	0.001	1.92E6	.003	2.74E6	8
3HE	2.99E6	0.075	1.82E7	1.06	2.12E7	28

(Continued)

(Sheet 27 of 42)

Ni (Continued)

Sample	Free Ni		Houston Complexed Ni		Total i NiS	Analyzed Ni
	NiCO ₃	NiS	NiCO ₃	NiS		
4HB	2.44E7	0.297	5.17E7	.629	7.61E7	.618
4HC	4.73E6	0.187	1.09E7	.431	1.56E7	1.82
4HD	4.72E7	0.746	6.78E7	1.07	1.15E8	2.99
4HF	3.72E7	0.297	3.37E8	2.69	3.74E8	6.49
4HSPW	1.31E8	0.746	1.01E9	5.75	1.14E9	.097
40FPW	3.44E6	0.069	1.43E6	.029	4.87E6	.433
5HB	3.71E6	0.118	9.88E6	.315	1.36E7	.972
5HC	8.27E6	0.297	1.88E7	.675	2.71E7	.187
5HD	6.98E6	0.047	2.07E7	.140	2.97E7	4.35
5HF	8.76E6	0.297	1.20E8	4.05	1.29E8	5.64
5HSPW	4.21E7	0.746	2.76E8	4.90	3.18E8	.053
50FPW	4.88E6	0.043	1.08E6	.010	5.96E6	

(Continued)

(Sheet 28 of 42)

Ni (Continued)

Sample	Free Ni		NiS	NiCO ₃	Sayreville Complexed Ni		NiCO ₃	Total Ni NiCO ₃	Analyzed Ni
	NiCO ₃	NiS			NiS	NiCO ₃			
NJA	3.80E7	1.06	1.06	2.43E8	6.77	2.81E6	7.83	0.03	
NJB	7.38E7	1.68	1.68	7.97E8	18.1	8.71E8	19.8	0.5	
NJC	3.77E8	10.6	10.6	1.54E9	43.3	1.92E9	53.8	0.37	
NJF	1.59E8	1.61	1.61	2.94E8	2.97	4.53E8	4.58	0.2	
NJPW	1.84E7	.040	.040	3.98E7	.087	5.82E7	.727	0.67	
NJJ	--	3.8E6	3.8E6	--	1.34	--	3.8E6	1.4	
ENJA	1.33E8	1.06	1.06	8.19E8	7.61	9.52E8	8.66	0.07	
2NJB	1.11E8	4.21	4.21	1.37E9	52.1	1.15E9	56.3	0.106	
2NJC	1.10E9	16.8	16.8	2.54E10	386	2.65E10	403	0.47	
2NJF	6.65E8	4.03	4.03	9.43E8	5.72	1.16E9	15.5	2.7	
2NJPW	6.42E6	.025	.025	1.22E7	.048	1.86E7	.074	4.2	
2NJJ	--	3.8E5	3.8E5	--	8.34E5	--	1.21E6	0.43	
3NJA	4.22E7	.421	.421	4.95E8	4.94	5.37E8	5.36	0.04	
3NJB	9.46E7	2.66	2.66	1.10E9	31.0	1.20E9	64.6	0.06	
3NJC	8.45E7	10.6	10.6	1.28E9	160	1.37E9	170	0.49	
3NJF	3.08E8	4.03	4.03	5.70E8	7.46	8.78E8	11.5	0.02	
3NJPW	3.10E7	.040	.040	9.73E7	.077	1.28E8	.117	0.018	
3NJJ	--	2.4E6	2.4E6	--	3.53E5	--	5.93E6	0.14	

(Sheet 29 of 42)

(Continued)

Ni (Continued)

Sample	Free Ni		Complexed Ni		Total Ni		Analyzed Ni
	NiCO ₃	NiS	NiCO ₃	NiS	NiCO ₃	NiS	
4NJA	3.00E8	1.68	1.88E9	10.5	2.18E9	12.2	
4NJB	2.99E8	6.67	2.93E9	65.4	3.23E9	69.7	
4NJC	1.19E8	4.21	2.85E9	101	2.97E9	105	
4NJF	4.56E7	.463	7.61E7	.773	1.22E8	1.24	
4NJP	--	--	--	--	--	--	
4NJJ	--	2.4E5	--	4.2E5	--	6.6E5	
5NJA	2.04E7	.667	8.26E7	2.70	1.03E8	3.37	
5NJB	1.56E7	.106	1.63E8	1.10	1.79E8	1.21	
5NJC	2.14E7	1.68	2.13E8	16.7	2.34E8	1.84	
5NJD	9.35E7	10.6	1.67E9	189	1.76E9	199	

(Continued)

(Sheet30 of 42)

Equilibrium Concentration of Pb (ppb)

Sample	PbCO ₃	Free Pb		Grand Haven		Total Pb		Analyzed Pb
		PbS	PbCO ₃	Complexed Pb	PbS	PbCO ₃	PbS	
MA	227	9.5E-3	810	0.0338	0.0338	1037	0.043	
MB	51.1	3.8E-3	174	0.0129	0.0129	225	0.017	
MD	13.7	399.2E-6	61.2	.0018	.0018	74.9	2.20E-3	
MF	344	2.4E-3	1599	0.0111	0.0111	1944	0.014	
MK	194	2.5E-3	248	0.0032	0.0032	442	5.70E-3	
MPW	72	614.1E-6	137	.00116	.00116	209	1.77E-3	
2MA	319	3.8E-3	3548	0.0423	0.0423	3867	0.046	
2MB	151	3.8E-3	987	0.0248	0.0248	1138	0.029	
2MD	322	158E-3	594	0.0029	0.0029	917	4.48E-3	
2MF	537	2.4E-3	6021	0.0269	0.0269	6558	0.029	
2MK	142	1.58E-3	614	0.0069	0.0069	756	7.48E-3	
2MPW	207	973.4E-6	891	0.0010	0.0010	1098	1.97E-3	
3MA	141	5.9E-3	2843	.1183	.1183	2985	0.124	
3MB	140	3.8E-3	2315	.0624	.0624	2456	0.066	
3MD	49.7	2.5E-3	104	0.0052	0.0052	153	7.70E-3	
3MF	532	5.9E-3	6190	0.0688	0.0688	6722	0.075	
3MK	178	2.5E-3	1044	0.0146	0.0146	1223	0.017	
3MPW	182	1.5E-3	229	.0019	.0019	412	3.4E-3	

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(Sheet 31 of 42)

Pb (Continued)

Sample	Free Pb		Grand Haven Complexed Pb		Total Pb		Analyzed Pb
	PbCO ₃	PbS	PbCO ₃	PbS	PbCO ₃	PbS	
4MA	1252	5.9E-3	25989	.1225	27241	0.128	
4MB	283	5.9E-3	1642	.0342	1926	0.04	
4MD	225	1.0E-3	477	0.0021	703	3.1E-3	
4ME	85.7	37.8E-6	1170	.0005	1256	5.38E-4	
4MK	355	1.58E-3	940	.0042	1295	5.78E-3	
4MPW	182	244.5E-6	505	.000679	688	9.24E-4	

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(Sheet 32 of 42)

Pb (Continued)

Sample	Free Pb		PbS	PbCO ₃	Houston Complexed Pb		PbS	PbCO ₃	Total Pb		Analyzed Pb
	PbCO ₃	PbS			PbS	PbCO ₃			PbCO ₃	PbS	
HB	293.8	1.17E-3	1.17E-3	6055	2.49E-2	6340.4	0.03	60	60	0.03	60
HC	4D.7	4.678E-4	4.678E-4	857	1.02E-2	898.6	0.07	60	60	0.07	60
HD	102.4	4.678E-3	4.678E-3	1296	5.94E-2	1398.4	0.06	60	60	0.06	60
HF	96.9	2.952E-3	2.952E-3	1256	3.85E-2	1353.2	0.04	100	100	0.04	100
HSPW	731.8	4.678E-3	4.678E-3	13960	8.92E-2	14692.7	0.10	20	20	0.10	20
OPFW	121.8	1.081E-3	1.081E-3	153	9.93E-5	275.1	1.18E-3	20	20	1.18E-3	20
2HB	190.5	1.175E-2	1.175E-2	2460	.153	2651.2	0.17	10	10	0.17	10
2HC	131.7	4.678E-3	4.678E-3	2368	8.68E-2	2500.3	0.10	40	40	0.10	40
2HD	283.2	4.778E-2	4.778E-2	2549	4.21E-2	2832.8	0.05	40	40	0.05	40
2HF	468.8	1.175E-2	1.175E-2	11126	.375	11595.0	0.39	50	50	0.39	50
2HOSPW	2028.8	4.678E-2	4.678E-2	26581	.613	88610.2	0.66	9	9	0.66	9
2OPFW	288.2'	6.823E-3	6.823E-3	374	1.17E-3	662.2	7.99E-3	7	7	7.99E-3	7
3HB	394.9	2.952E-3	2.952E-3	9334	7.57E-2	9729.6	0.08	60	60	0.08	60
3HC	497.1	4.678E-3	4.678E-3	12341	.128	12838.4	0.13	60	60	0.13	60
3HD	166.3	1.862E-3	1.862E-3	20204	3.94E-2	20371.2	0.04	40	40	0.04	40
3HSPW	261.7	2.952E-3	2.952E-3	14240	.160	14502.6	0.16	20	20	0.16	20
3OPFW	23.1	4.305E-5	4.305E-5	251	2.54E-4	274.5	2.97E-4	2	2	2.97E-4	2
3HF	83.7	2.95E-3	2.95E-3	4163	.167	4247.5	0.17	60	60	0.17	60

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(Sheet 33 of 42)

Pb (Continued)

Sample	Free Pb		PbS	PbCO ₃	Houston Complexed Pb		PbCO ₃	Total Pb		Analyzed Pb
	PbCO ₃	PbS			PbCO ₃	PbS		PbCO ₃	PbS	
4HB	431.8	1.175E-2	7900	,223	8332.5	0.23				
4HC	132.6	7.415E-3	2619	.153	2752.1	0.16				
4HD	1321.9	2.952E-2	13984	.313	15306.3	0.34				
4HF	1043.1	1.175E-2	33494	.378	34538.0	0.38				
4HOSPW	3670.1	2.952E-2	87548	.704	91218.8	0.73				
40FPW	96.4	2.716E-3	214	2.21E-3	310.9	4.93E-3				
5HB	104.1	4.678E-3	2510	.119	2614.9	0.13				
5HC	231.8	1.175E-2	4489	.238	4721.6	0.25				
5HD	195.7	1.862E-3	3410	3.26E-2	3606.2	0.035				
5HF	2453.9	1.175E-2	42769	.531	45218.1	0.54				
5HOSPW	1180.3	2.952E-2	24166	.613	25346.3	0.64				
50FPW	136.8	1.714E-3	252	4.39E-4	389.1	2.15E-3				

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(Sheet 34 of 42)

Equilibrium Concentration of Pb (ppb)

Sample	Free Pb		Sayreville Complexed Pb		Total Pb		Analyzed Pb
	PbCO ₃	PbS	PbCO ₃	PbS	PbCO ₃	PbS	
NJA	1.06E3	41.8E-3	3.47E4	1.37	3.58E4	1.41	3.58E4 .003
NJB	2.07E3	66.3E-3		3.49	1.11E5	3.55	40
NJC	1.06E4	418E-3	2.42E5	9.56	2.53E5	9.98	.002
NJF	4.45E3	63.5E-3	1.23E5	.738	1.27E5	0.80	22
NJPW	5.15E2	1.59E-3	4.59E3	.014	5.11E3	0.06	.14
NJJ	--	151E-3	--	1.30	--	1.45	284
2NJA	3.75E3	41.8E-3	1.67E5	1.87	1.71E5	1.91	32
2NJB	3.11E3	167E-3	1.83E5	9.80	1.86E5	9.97	178
2NJC	3.09E4	663E-3	2.66E6	57.2	2.69E6	57.8	159
2NJF	1.86E4	160E-3	1.26E5	1.08	1.45E5	1.24	78
2NJPW	1.79E2	1.00E-3	1.52E3	.009	1.70E3	0.01	ND
2NJJ		15.1E3	--	1.06E5	--	1.21E5	138
3NJA	1.18E3	16.6E-3	5.77E4	0.82	5.89E4	0.83	53
3NJB	2.65E3	105E-3	1.51E5	7.19	1.54E5	7.30	85
3NJC	5.28E3	418.3E-3	2.40E5	19.0	2.45E5	19.4	.5
3NJF	8.65E3	160E-3	9.99E4	1.84	1.09E5	2.00	16
3NJPW	8.71E2	160E-3	6.80E3	.013	7.67E3	0.01	.2
3NJJ	--	95.3E3	--	4.48E5	--	5.43E5	.5

(Continued)

(Sheet 35 of 42)

Pb (Continued)

Sample	Free' Pb		Sayreville Comptexed Pb		'Total' Pb		Analyzed Pb
	PbCO ₃	PbS	PbCO ₃	PbS	PbCO ₃	PbS	
4NJA	8.41E3	66.3E-3	3.21E5	2.53	3.29E5	2.60	
4NJB	8.39E3	264E-3	4.00E5	12.6	4.08E5	12.9	
4NJC	3.34E3	167E-3	2.75E5	13.7	2.78E5	13.9	
4NJF	1.28E3	9.5E-3	1.30E4	.097	1.43E4	0.11	
4NJP	--	--	--	--	--	--	
4NJJ	--	9.5E3	--	4.88E4	--	5.83E4	
5NJA	5.73E2	26.3E-3	1.44E4	.662	1.50E4	0.69	
5NJB	4.36E2	4.18E-3	2.06E4	.198	2.10E4	0.20	
5NJC	5.99E2	66.3E-3	2.89E4	3.20	2.95E4	3.27	
5NJD	2.62E3	60.5E-3	1.62E5	3.74	1.65E5	3.80	

Equilibrium Concentration of Zn (ppb)

Sample	Free Zn		Grand Haven Complexed Zn		Total Zn	Analyzed Zn	
	ZnCO ₃	ZnS	ZnCO ₃	ZnS			ZnCO ₃
MA	3.20E4	336	5.56E4	585	8.76E4	923	.05
MB	7.21E3	134	1.03E4	192	1.75E4	327	.2
MD	1.94E3	14.1	3.02E3	22.0	4.96E3	36.2	.02
MF	4.86E4	84.6	1.03E5	178.6	1.52E5	263	.1
MK	2.74E3	89.3	8.56E2	27.9	3.60E3	117	.15
MPW	1.02E4	21.7	6.62E3	14.1	1.68E4	35.9	.2
2MA	4.50E4	134	1.23E5	365	1.68E4	500	.5
2MB	2.13E4	134	7.14E4	449	9.27E4	584	.1
2MD	4.56E4	56.3	3.48E4	42.9	8.04E4	99.3	.3
2MF	7.59E4	84.6	1.32E5	147	2.08E5	232	.35
2MK	2.01E4	56.3	5.08E4	121	7.09E4	178	.13
2MPW	2.92E4	34.5	8.93E3	10.5	3.81E4	451	.22
3MA	2.00E4	212	1.44E5	1527	1.64E5	1.74E3	.2
3MB	1.98E4	134	1.75E5	1187	1.95E5	1.32E3	.39
3MD	7.01E3	89.3	6.59E3	83.9	1.36E4	173	.06
3MF	7.51E4	212.	1.48E4	418.2	8.99E4	631	.09
3MK	2.52E4	89.2	7.57E4	270	1.01E5	359	.3
3MPW	2.57E4	54.6	1.14E4	24.25	3.71E4	78.9	.26

Zn (Continued)

Sample	Free Zn		Grand Haven Complexed Zn		Total Zn ZnCO ₃	Total Zn ZnS	Analyzed Zn
	ZnCO ₃	ZnS	ZnCO ₃	ZnS			
4MA	4.54E4	212	4.72E5	2248	5.17E5	2.46E3	
4MB	1.03E4	212	3.00E4	618	4.03E4	831	
4MD	1.95E4	35.5	1.77E4	32.3	3.72E4	67.9	
4MF	1.21E4	1.34	1.67E5	18.5	1.79E5	19.9	
4MK	5.01E4	56.3	6.20E4	69.7	1.12E5	126,	
4MPW	2.57E4	8.66	3.25E4	10.9	5.82E4	19.6	

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(Sheet 38 of 42)

Zn (Continued)

Sample	Free Zn		Complexed Zn		Total Zn	Analyzed Ln	
	ZnCO ₃	ZnS	ZnCO ₃	ZnS			ZnCO ₃
HB	4.14E4	41.66	1.23E5	124.3	1.64E5	1.66E2	.02
HC	5.75E3	16.58	2.35E4	57.68	2.93E4	34.3	.02
HD	1.44E4	165.8	3.19E4	366.9	4.63E4	5.33E2	.8
HF	1.15E4	104.6	6.04E5	156.6	6.16E5	2.61E2	.14
HDSPW	1.72E4	165.8	4.07E5	1475.4	4.24E5	1.64E3	4
0FPW	2.38E4	38.33	5.83E3	9.382	2.96E4	47.71	
2HB	1.18E5	416.58	1.24E5	437.4	2.42E5	8.54E2	.06
2HC	1.69E4	165.8	2.77E4	271.4	4.46E4	4.37E2	.08
2HD	1.86E4	165.8	1.71E4	152.5	3.57E4	3.18E2	.1
2HF	6.33E4	416.58	7.32E5	5059.0	7.95E5	5.48E3	.26
2H0SPW	1.31E5	1658.4	8.30E5	10507.4	9.61E5	1.22E4	.14
20FPW	5.25E4	241.8	9.14E3	42.10	6.16E4	2.84E2	.06
3HB	7.90E4	104.6	1.74E5	230.6	2.53E5	3.35E2	.05
3HC	9.94E4	165.8	2.24E5	374.2	3.23E5	5.40E2	.05
3HD	6.27E4	66.02	3.85E6	4051.9	3.91E6	4.12E3	.07
3HF	5.57E4	104.6	1.15E6	2166.8	1.21E6	2.27E3	.05
3H0SPW	4.19E4	104.6	1.16E6	2893.7	1.20E6	2.99E3	.05
30FPW	2.16E3	1.526	1.65E4	11.68	1.87E4	13.21	.06

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(Sheet 39 of 42)

Zn (Continued)

Sample	Free Zn		ZnS	Houston Complexed : Zn		ZnS	Total Zn		Analyzed Ln
	ZnCO ₃	ZnCO ₃		ZnCO ₃	ZnS		ZnCO ₃	ZnS	
4IB	2.36E4	3.63E4	416.58	641.4	5.99E4	1.06E3	1.06E3		
4IC	7.67E4	1.36E5	262.8	467.6	2.13E5	7.30E2	7.30E2		
4ID	3.73E4	4.33E4	1046.4	1215.2	8.06E4	2.26E3	2.26E3		
4IF	1.18E5	1.53E6	416.58	5404.9	1.65E6	5.82E3	5.82E3		
4HSPW	2.33E5	2.69E6	1046.4	12062.2	2.92E6	1.31E4	1.31E4		
40FPW	7.56E4	4.41E6	96.29	56.16	4.49E6	1.53E2	1.53E2		
5IB	3.72E4	8.02E4	165.8	357.3	1.17E5	5.23E2	5.23E2		
5IC	2.33E4	3.97E4	416.58	709.8	6.30E4	1.13E3	1.13E3		
5ID	1.30E4	4.24E4	66.02	255.6	5.54E4	3.22E3	3.22E3		
5IF	6.93E4	1.39E6	416.58	8348.3	1.46E6	8.77E3	8.77E3		
5HSPW	5.49E4	5.35E5	1046.4	10202.9	5.90E5	1.13E4	1.13E4		
50FPW	1.93E4	6.01E3	60.75	18.91	2.53E4	79.66	79.66		

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(Sheet 400f 42)

Zn (Continued)

Sample	Free Zn		ZnS	Sayreville		ZnS	Total Zn		Analyzed Zn
	ZnCO ₃	.		ZnCO ₃	Comp _l exec Zn		ZnCO ₃	ZnS	
NJA	1.50E5		337.	1.19E6	2684	1.34E6	3.02E4	.02	
NJB	2.91E5		535	4.15E6	7640	4.44E6	8.18E3	"009	
NJC	1.49E6		3378	6.88E6	15602	8.37E6	1.89E4	3.1	
NJF	6.3E5		2252.	1.11E6	3985	1.74E6	6.24E3	.003	
NJPW	7.26E4		56.5	2.39E5	186	3.12E5	243	.01	
NJJ	1.51E8		8.96E9		3.87E10		1.27E10	1.8	
2NJA	5.28E5		337	4.54E6	2904	5.07E6	6.15E3	.07	
2NJB	4.39E5		1344	7.29E6	22329	7.73E6	2.37E4	.08	
2NJC	4.36E6		5353	1.45E8	177867	1.49E8	1.83E5	1.7	
2NJF	2.63E6		5657	4.07E7	9437	4.33E7	1.51E4	.04	
2NJPW	2.53E4		35.6	7.80E4	109	1.03E5	146	.06	
2NJJ	-		8.96E8		2.86E9		3.76E9	2.6	
3NJA	1.66E5		134	2.68E6	2172	2.85E6	2.31E3	.45	
3NJB	3.74E5		848	5.80E6	13136	6.17E6	1.39E4	.13	
3NJC	1.67E5		3378	3.79E6	76713	3.96E6	8.01E4	1.5	
3NJF	6.13E5		5657	7.73E5	9980	1.39E6	1.56E4	.52	
3NJPW	1.23E5		56.5	3.66E5	168	4.89E5	225	.32	
3NJJ	-		5.66E9		1.21E10		1.78E10	2.1	

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(Sheet 41 of 42)

Zn. (Continued)

Sample	Free Zn		Savreville Complexed Zn		Total Zn	Analyzed Zn
	ZnCO ₃	ZnS	ZnCO ₃	ZnS		
4NJA	1.19E6	535	8.74E6	3932	9.93E6	4.47E3
4NJB	1.18E6	2131	1.51E7	27271	1.63E7	2.94E4
4NJC	4.71E5	1344	1.65E7	47106	1.70E7	4.85E4
4NJF	1.80E5	565	3.02E5	950	4.82E5	1.52E3
4NJP	-					
4NJJ		5.66E8		1.49E9		2.06E9
5NJA	8.08E4	213	3.57E5	941	4.38E5	1.15E3
5NJB	6.16E4	33.7	8.83E5	484	9.45E5	518
5NJC	8.45E4	535	1.10E6	6981	1.18E6	1.23E3
5NJD	70E5	3378		87170	9.92E6	9.06E4

(Sheet 42 of 42)