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REMOVAL OF METALLIC CONTAMINANTS FROM INDUSTRIAL WASTE WATERS BY THE USE OF GREENSANDS, A PRELIMINARY REPORT

BY

NENAD SPOLJARIC
WILLIAM A. CRAWFORD

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REMOVAL OF METALLIC CONTAMINANTS FROM INDUSTRIAL WASTE WATERS BY THE USE OF GREENSANDS, A PRELIMINARY REPORT

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Nenad Spoljaric
Delaware Geological Survey

William A. Crawford
Department of Geology, Bryn Mawr College

INTRODUCTION

The Delaware Geological Survey, in cooperation with the U. S. Bureau of Mines, has investigated glauconite-bearing greensand deposits in Delaware for several years. The purpose of this effort is to find possible practical uses for this potentially important mineral resource. This report briefly describes the preliminary results of one phase of the study: application of greensands to the purification of industrial waste waters.

GLAUCONITE-BEARING GREENSANDS

The clay mineral glauconite is a hydrous alumino-silicate rich in ferric iron and containing significant amounts of potassium. Glauconite occurs as dark-, light-, or yellowish-green pellets usually 1 mm or less in size, as fillings of small fossil shells, or as coating on other grains. The Delaware glauconite-bearing greensands contain up to 80% glauconite; the remaining major constituents are quartz grains and calcium carbonate in fragments of fossils. The areal distribution of the Delaware greensands is shown in Figure 1. These deposits occur mostly in the subsurface. The principal exceptions are outcrops in the Middletown-Odessa area where greensands are most accessible.

METHOD OF STUDY

Samples of contaminated water from industrial effluent spiked with such components as arsenic, copper, and cyanide (see Appendix A) were used in each experiment. The flow chart

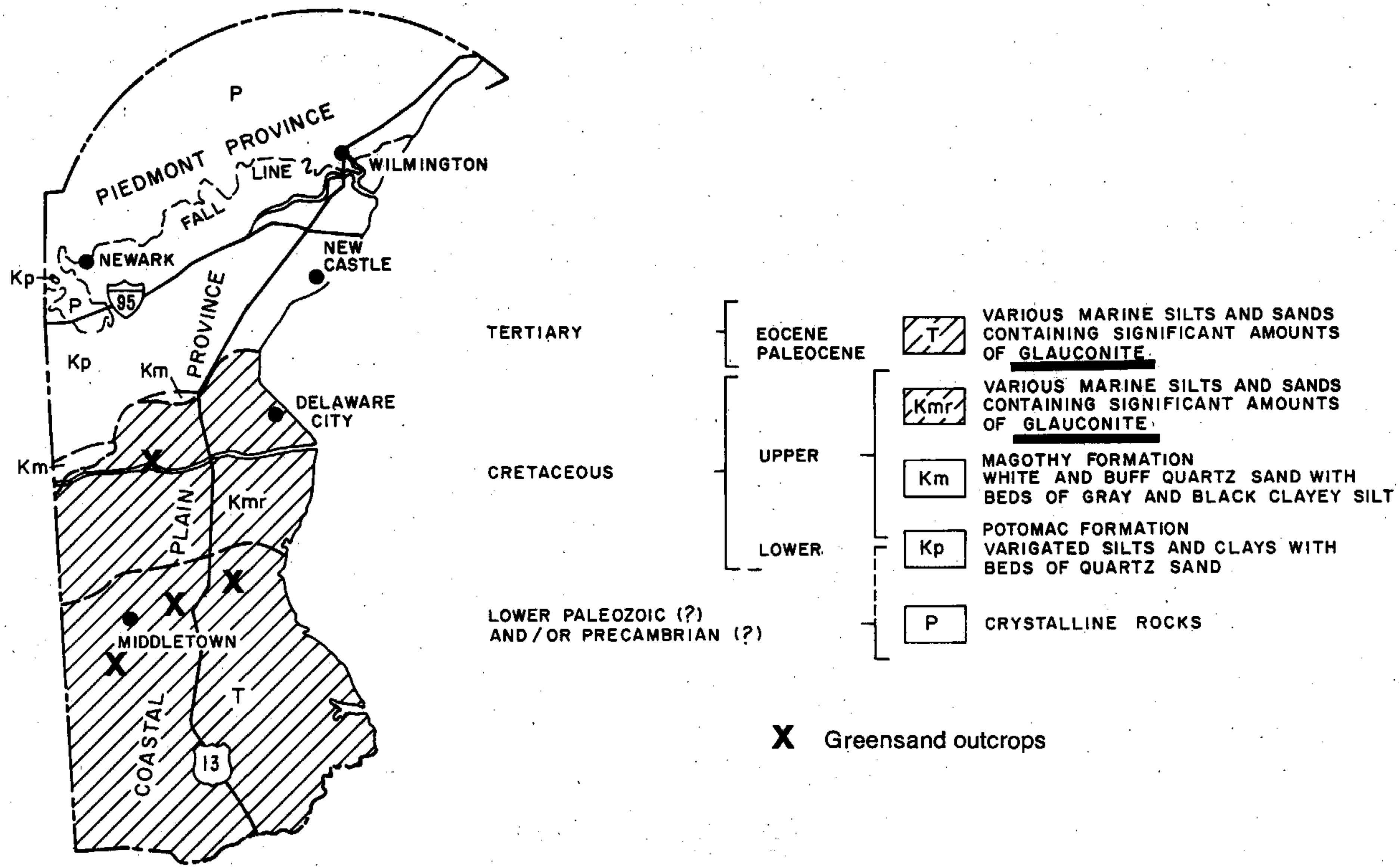


Figure 1. Map showing the areal distribution and outcrop locations of the greensands.

(Figure 2) shows the processing steps for each sample. Following the treatment the sub-samples were shipped to a commercial laboratory for chemical analyses. The treatment of one pint (0.473 liters) of sample with sodium hydroxide (NaOH) and another with nitric acid (HNO_3) acts as a preservative for analytical purposes and has nothing to do with the actual filtering process. The filtering system is composed of one filter containing greensand connected by a plastic tube to a second containing charcoal. A small suction pump was used to remove air from the tubes and help maintain the flow through the filters.

DISCUSSION OF RESULTS

The results of the chemical analyses (Appendix A) show the following general trends in the chemical changes of the samples of contaminated water after filtration:

1. The pH of the solution changes from strongly acid to neutral or slightly basic.

2. Concentrations of the metals (heavy metal ions) in solution are greatly decreased.

3. Concentrations of anions in solution are either unchanged or increased with the exception of cyanide and amonium which are greatly reduced in concentration.

4. Total dissolved solids are generally decreased.

5. Hardness is increased.

As the metals are one of the major contaminants of industrial waste water, our study has been primarily concerned with them. The samples were analyzed for the following heavy metals: arsenic, cadmium, copper, chromium, lead, selenium, silver, and zinc. Figure 3a-c shows the results of the experiments. The samples illustrated in Figure 3a-c were run sequentially through the filter beds without changing or replenishing the filtering agents. No decrease in the capacity of the greensand to remove heavy metals from the waste water with time was noted. However, flushing the charged filter beds with distilled water (Appendix A) resulted in removal of portions of all of the heavy metal contaminants back in solution. Continued flushing may completely purge the filter beds of contaminants but our experiments did not last long enough to prove this. We are now exploring the feasibility of recovering some of the more valuable metals released in this manner.

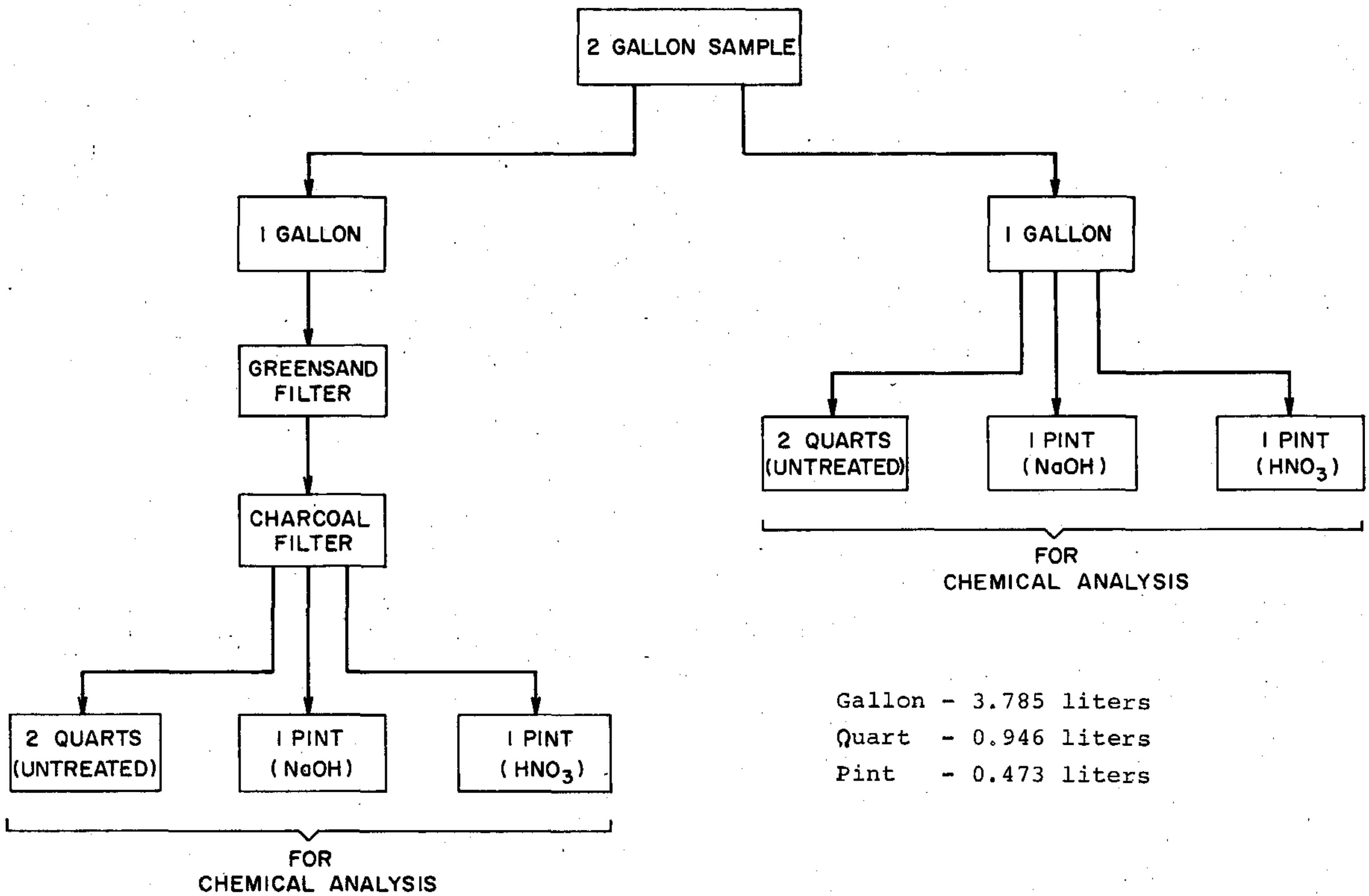


Figure 2. Flow chart of the filtration experiments.

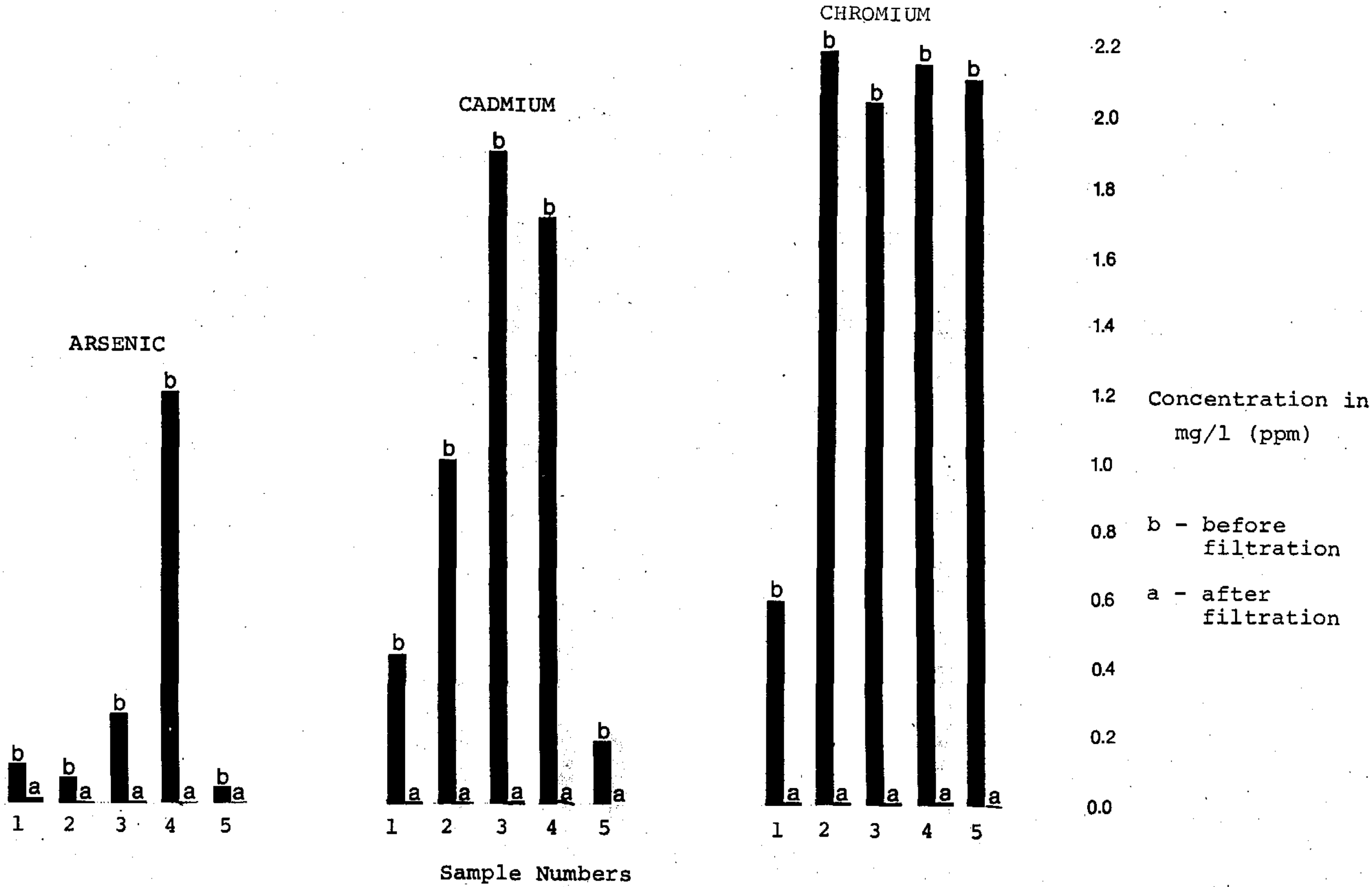


Figure 3a. Results of chemical analyses of heavy metals in industrial waste water before and after filtration through the filtering system.

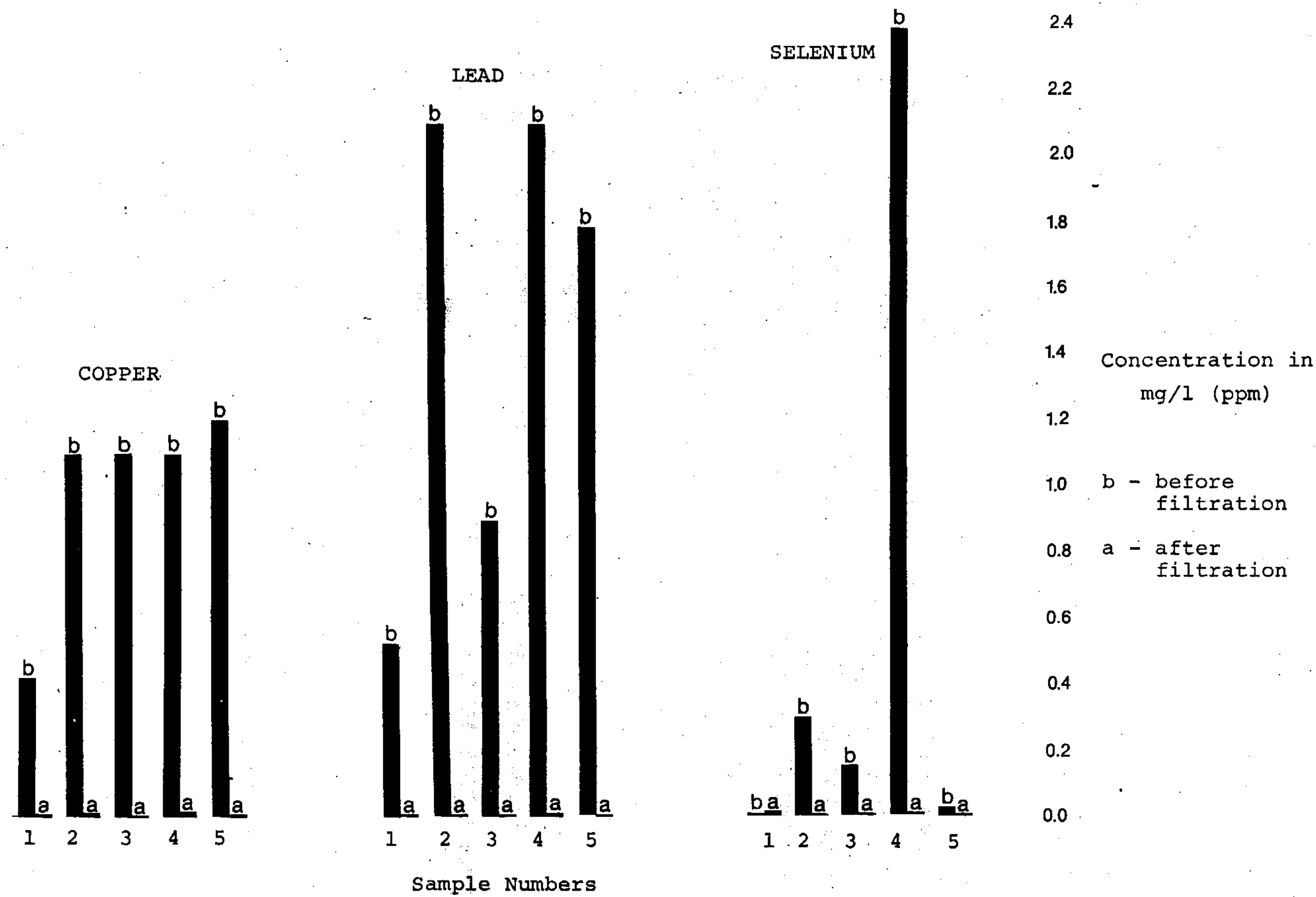
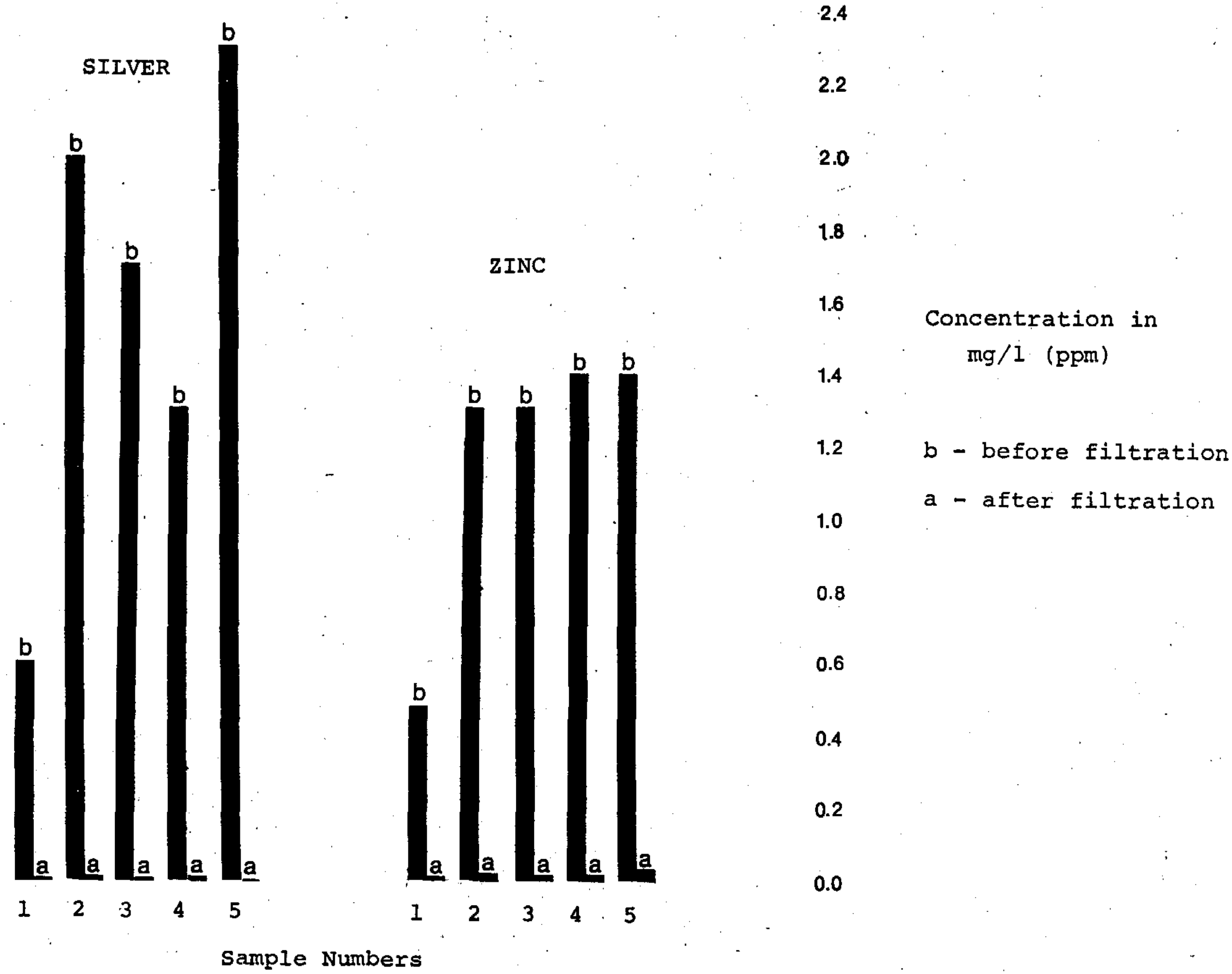

COPPER
LEAD
SELENIUM
b
a
1
2
3
4
5
Sample Numbers
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Concentration in mg/l (ppm)
b - before filtration
a - after filtration

Figure 3b.



SILVER
ZINC
b
a
1
2
3
4
5
Sample Numbers
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
Concentration in mg/l (ppm)
b - before filtration
a - after filtration

Figure 3c.

Separate sets of filtration runs were made in the laboratory using solutions consisting of distilled water spiked with various compounds each containing contaminant ion of interest (Appendix B and C). The results show that solutions spiked with 100 mg/liter of Ba, Ca, Mg, and K and passed through a greensand filter bed picked up other contaminants from the filter bed (Fig. 4a); the solutions spiked with 100 mg/liter of Al, Cr, Fe, Mn, and Na did not pick up significant amounts of contaminants (Fig. 4b).

Filtration of a strongly acidic, strongly basic, and neutral solutions through a greensand filter bed indicates that Ba, Ca, Mg, and K were added to the solutions with a small amount of Al in the acidic solution and some Fe in the basic solution (Fig. 4c). These are the elements one would expect to find in the filtrate if both the acidic and basic solutions are destroying the glauconite in the filter bed. The neutral solution (distilled water) did not remove any ions from the greensand bed suggesting that the greensand from the outcrop is in a neutral state and has been thoroughly flushed with rain water.

Figure 5 illustrates the results of passing 5 different solutions spiked with 100 mg/liter of Ba, Fe, Na, and K through a greensand filter bed. In runs 1 through 4 the concentration of each of the spiked contaminants was significantly reduced but some K and Na were added to the filtrates. K and Na are two of the most easily removed cations from the glauconite structure. In run 5 the solution contained 100 mg/liter of all 4 contaminants (Ba, Fe, K, and Na). The greensand filter bed demonstrates a preference for the removal of Fe followed by Ba, K, and Na from solution.

CONCLUSIONS

The greensand tested has a capacity to remove many heavy metal contaminants from industrial waste waters. The process responsible for this capacity is not yet understood; however, the fact that the same metals can be easily released back into distilled water suggests that some metal cations are adsorbed on the surface of glauconite pellets rather than exchanged within the glauconite crystal structure.

A more detailed study on a large scale is not only desirable but necessary so that the potential of greensand may be evaluated for possible practical applications. It may be possible to utilize this mineral resource and at the same time to relieve one of the major environmental problems we are facing today: water pollution.

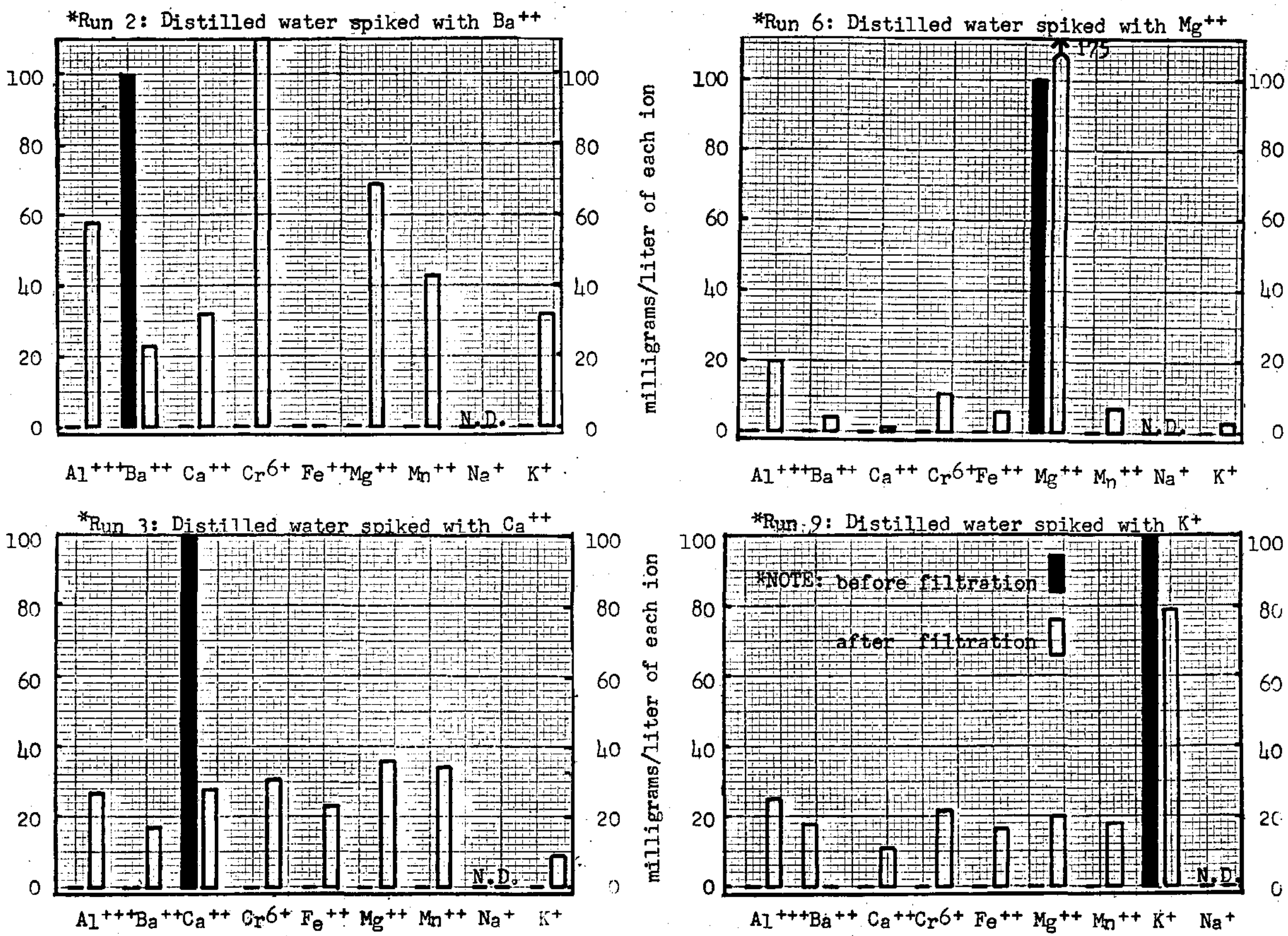
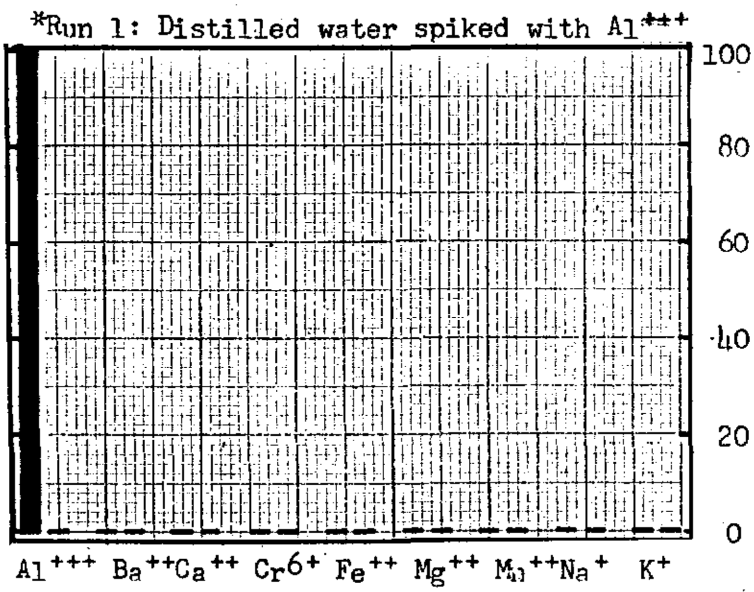
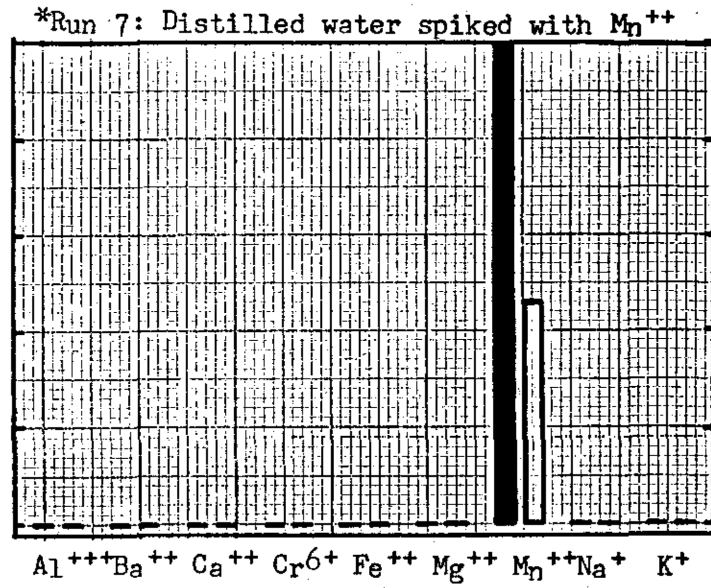
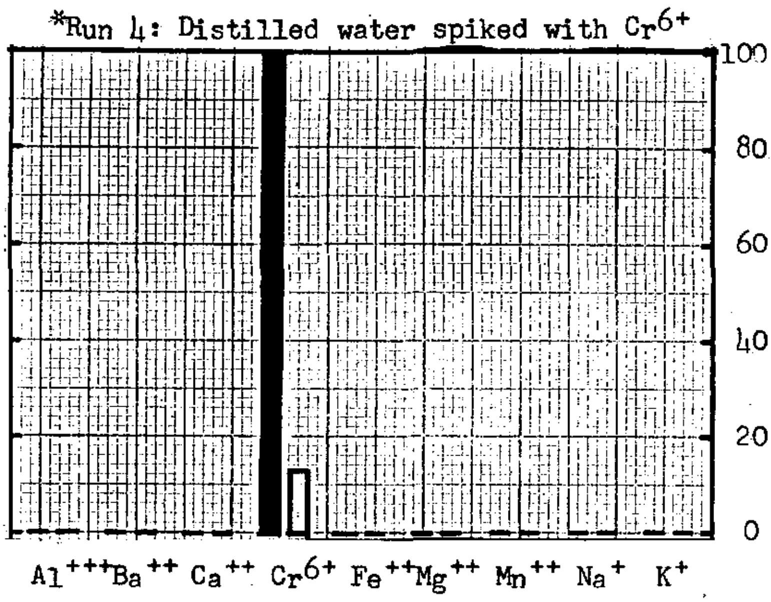
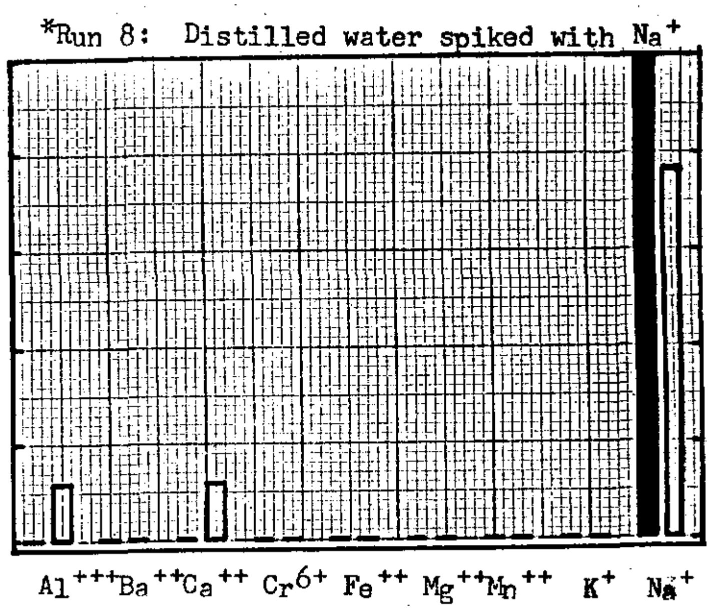


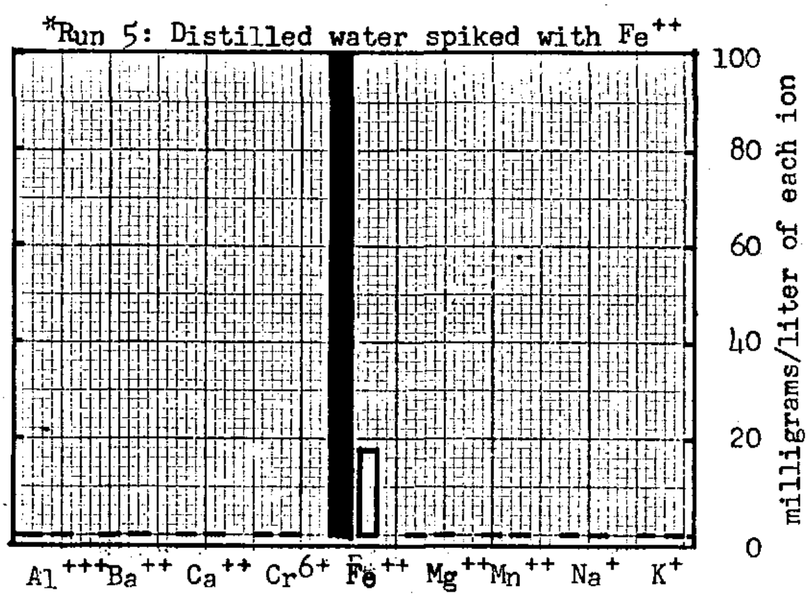
Figure 4a. Chemical analyses of distilled water solutions spiked with specific contaminants before and after filtration through the greensand.







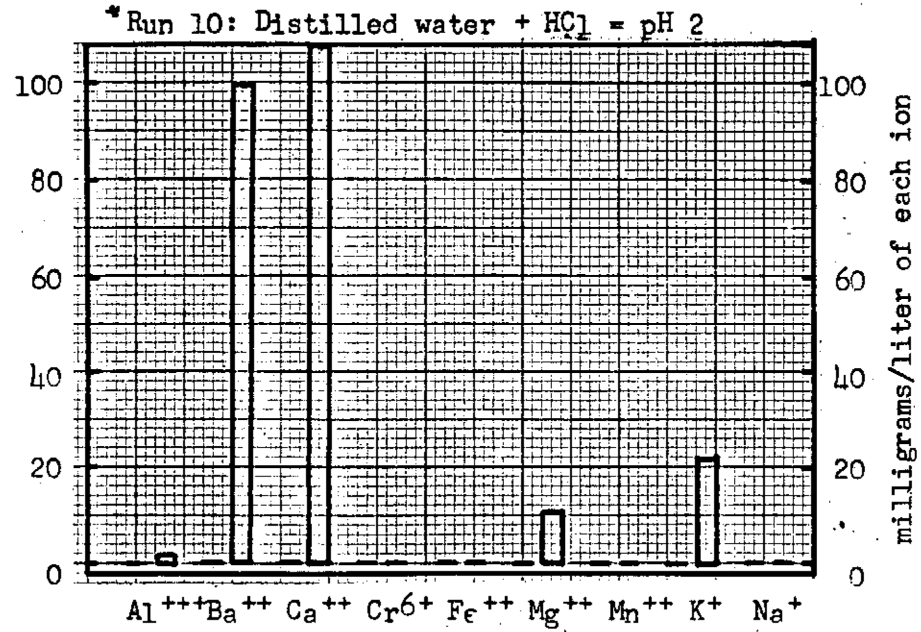


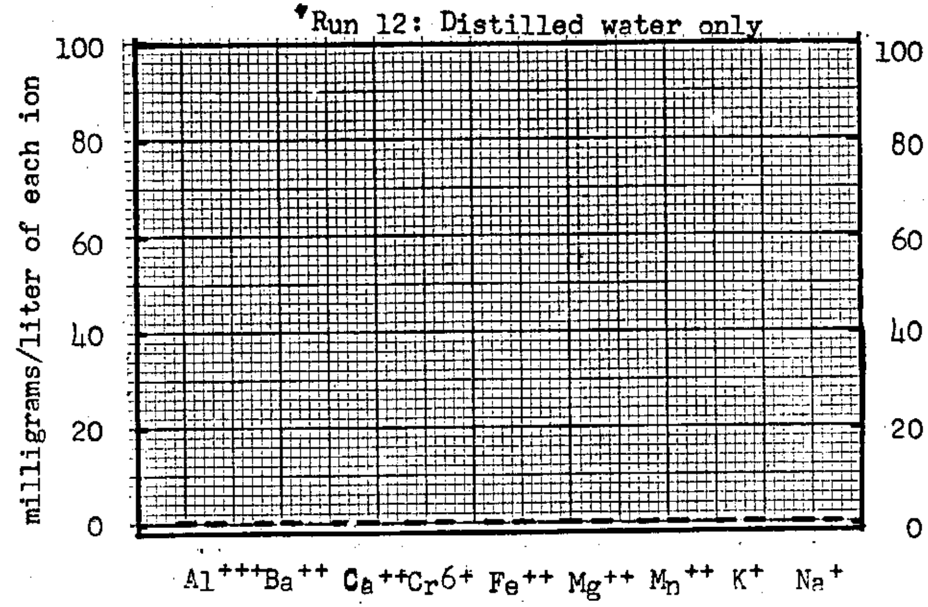


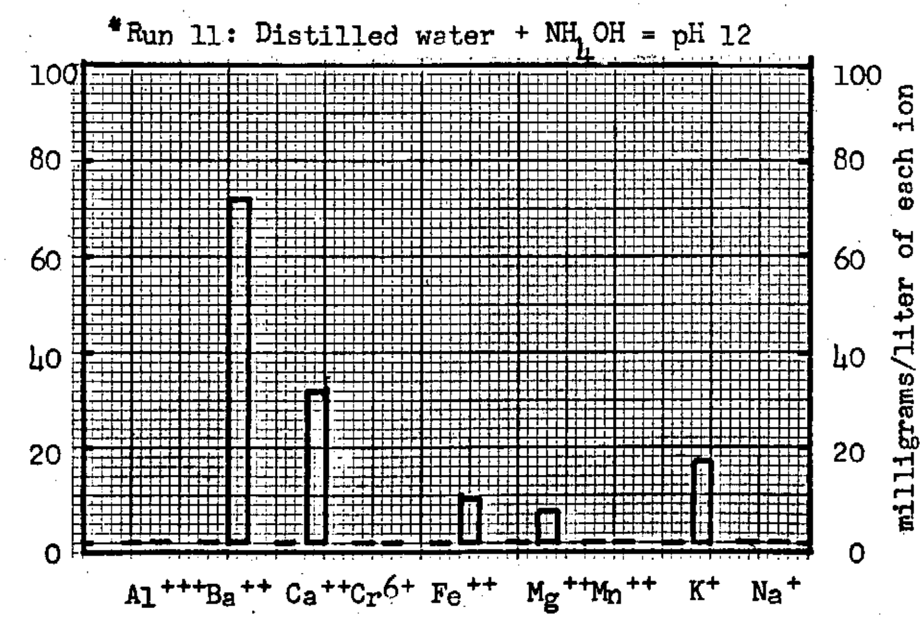
NOTE: before filtration ■

after filtration □

Figure 4b. Chemical analyses of distilled water solutions spiked with specific contaminants before and after filtration through the greensand.







*NOTE: before filtration after filtration

Figure 4c. Chemical analyses of distilled water solutions spiked with specific contaminants before and after filtration through the greensand.

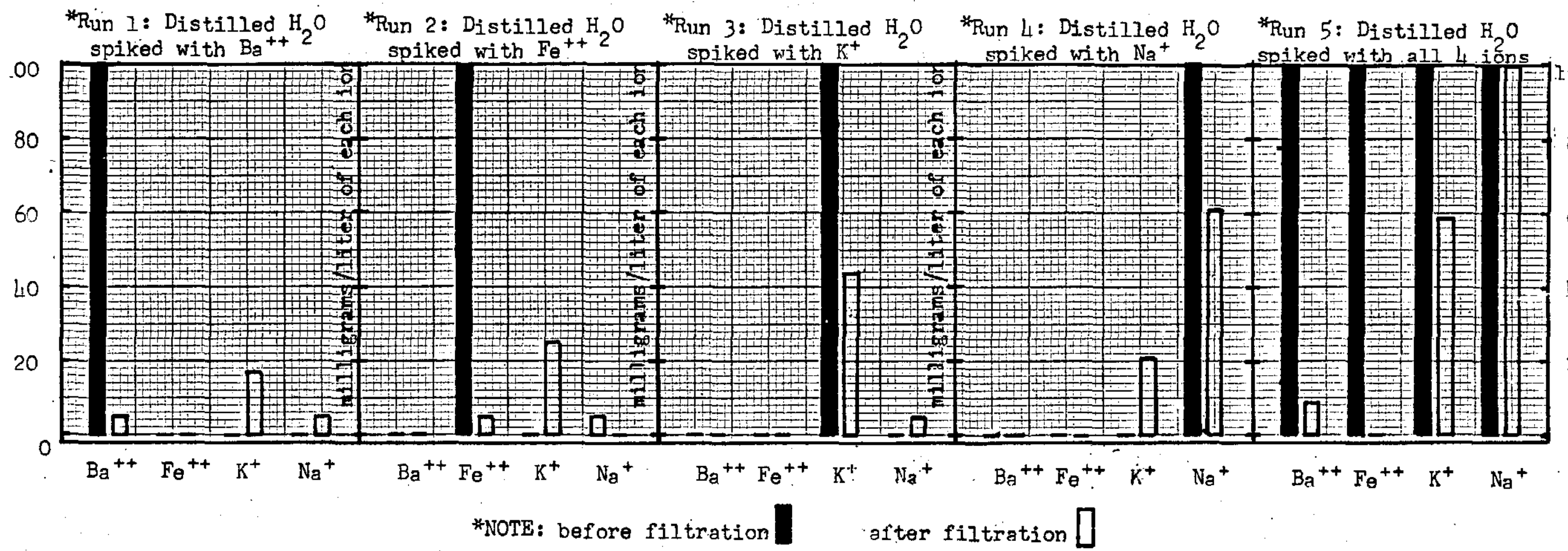


Figure 5. Chemical analyses of distilled water solutions spiked with chloride compounds before and after filtration through the greensand.

ACKNOWLEDGMENTS

We acknowledge the support provided by the U. S. Bureau of Mines under the Cooperative Agreement between the U. S. Bureau of Mines and the Delaware Geological Survey. C. D. Edgerton of the U. S. Bureau of Mines provided encouragement and counseling throughout the study, as did A. H. Harvey, Liaison Officer of the U. S. Bureau of Mines Region III.

The industrial waste water samples for our experiments were provided by the Delaware Division of Environmental Control and we make special note of the help given by H. W. Otto and C. J. Anthony in securing the necessary samples.

The many beneficial discussions held with the members of the Delaware Geological Survey, R. R. Jordan, State Geologist, K. D. Woodruff, T. E. Pickett, and particularly J. C. Miller, former member of the Survey, are gratefully acknowledged.

APPENDIX A

Chemical analyses of the spiked industrial waste water samples before and after filtration through the filtering system

	SEQUENTIAL RUNS											
	Spiked Industrial Polluted Water										Distilled Water	
	Run 1		Run 2		Run 3		Run 4		Run 5		Run 6	
	Before Filtration	After Filtration	Before Filtration	After Filtration	Before Filtration	After Filtration	Before Filtration	After Filtration	Before Filtration	After Filtration	Before Filtration	After Filtration
Arsenic	117	18	720	3	260	2	1.2×10^3	3	42	<1	<1	290
Cadmium	430	5	910	6	1.9×10^3	5	1.7×10^3	12	180	<1	2	120
Chromium	600	7	2.2×10^3	10	2.04×10^3	9	2.16×10^3	21	2.1×10^3	<1	3	24
Copper	420	12	1.1×10^3	22	1.1×10^3	14	1.1×10^3	24	1.2×10^3	5	12	90
Lead	540	7	2.1×10^3	11	900	8	2.1×10^3	17	1.8×10^3	3	23	120
Selenium	5	10	300	<1	150	<1	2.4×10^3	2	23.8	<1	2	200
Silver	620	10	$2\ .\times 10^3$	19	1.7×10^3	12	1.3×10^3	20	2.3×10^3	2	4	210
Zinc	480	4	1.3×10^3	32	1.3×10^3	21	1.4×10^3	22	1.4×10^3	40	4	45
Bicarbonate	$5\ \times10^3$	130×10^3	none	74×10^3	none	68×10^3	none	58×10^3	none	52×10^3	n.d.	n.d.
Chloride	144×10^3	174×10^3	129×10^3	137×10^3	135×10^3	133×10^3	131×10^3	133×10^3	125×10^3	131×10^3	5×10^3	10×10^3
Cyanide	170	<50	<50	150	100	<50	50	<50	180	<50	<100	<100
Fluoride	80	4×10^3	60	3.4×10^3	50	3×10^3	60	1.8×10^3	50	2×10^3	20	310
Nitrate	60×10^3	72×10^3	69×10^3	205×10^3	79×10^3	260×10^3	74×10^3	235×10^3	81×10^3	265×10^3	500	8.7×10^3
Sulfate	127×10^3	142×10^3	153×10^3	181×10^3	167×10^3	79×10^3	203×10^3	212×10^3	158×10^3	161×10^3	38×10^3	48×10^3
Acidity	none	none	106×10^3	none	106×10^3	none	113×10^3	none	102×10^3	none	n.d.	n.d.
Alkalinity	5×10^3	162×10^3	none	74×10^3	none	68×10^3	none	58×10^3	none	52×10^3	n.d.	n.d.
Ammonium	20	20	2.16×10^3	80	2.68×10^3	240	1.5×10^3	80	260×10^3	20	<100	<100
Hardness	103×10^3	230×10^3	108×10^3	133×10^3	111×10^3	341×10^3	113×10^3	265×10^3	103×10^3	271×10^3	280	1.7×10^3
Iodine	20	60	80	5.12×10^3	30	990	30	220	20	30	n.d.	n.d.
TDS *	690×10^3	874×10^3	884×10^3	792×10^3	878×10^3	790×10^3	872×10^3	803×10^3	846×10^3	768×10^3	90×10^3	224×10^3
pH	3.8	8.2	4.6	7.3	4.7	8.2	4.7	7.8	4.7	7.4	5.8	4.8

All concentration units in micrograms/liter (ppb). *Total Dissolved Solids

APPENDIX B

Chemical analyses of distilled water solutions spiked with specific contaminants before and after filtration through the greensand.

DISTILLED WATER SPIKED WITH 100 mg/ liter OF:	Run No.	CONTENTS OF SOLUTION AFTER FILTRATION THROUGH GLAUCONITE FILTER BED								
		ALUMINUM	BARIUM	CALCIUM	CHROMIUM	IRON	MAGNESIUM	MANGANESE	POTASSIUM	SODIU
ALUMINUM only	1	0	58	27	0	0	20	0	25	12
BARIUM "	2	0	23	17	0	0	4	0	17.5	0
CALCIUM "	3	0	32	28	0	0	1	0	11	12
CHROMIUM "	4	0	110	31	13	0	11	0	22	0
IRON "	5	0	0	23	0	18	6	0	16.5	0
MAGNESIUM "	6	<1	69	36	0	0	175	0	20	0
MANGANESE "	7	0	43	34	0	0	7	46	18	0
SODIUM "	8	0	n.d.	n.d.	0	0	n.d.	0	n.d.	77
POTASSIUM "	9	0	32	9	0	0	3	0	79	0
ACID SOLN pH 2	10	2	100	108	0	0	11	0	22	0
BASE SOLN pH 12	11	0	74	32	0	9.5	7	0	17	0
DISTILLED WATER	12	0	0	0	0	0	0	0	0	0

The compounds used to spike the solutions were:

Al; $Al_2(SO_4)_3 \cdot 18H_2O$ — Mg; $MgSO_4$

Ba; $Ba(NO_3)_2$ — Mn; $MnCl_2$

Ca; $Ca(C_2H_3O_2)_2$ — K; $K_2Cr_2O_7$

Cr; $Cr(NH_4)(SO_4)_2 \cdot 12H_2O$ — Na; $CH_3COONa \cdot 3H_2O$

Fe; $FeSO_4 \cdot 7H_2O$

APPENDIX C

Chemical analyses of distilled water solutions spiked with chloride compounds before and after filtration through the greensand.

DISTILLED WATER SPIKED WITH 100 mg/liter OF:		Run No.	CONTENTS OF SOLUTION AFTER FILTRATION THROUGH GLAUCONITE FILTER BED			
			BARIUM	IRON	POTASSIUM	SODIUM
BARIUM	only	1	5	0	17	5
IRON	"	2	0	5	25	5
POTASSIUM	"	3	0	0	44	5
SODIUM	"	4	0	0	21	60.6
Ba, Fe, K, Na	all four	5	9	0	59	100

The compounds used to spike the solutions were:

Ba; $BaCl_2$ K; KCl

Fe; $FeCl_2$ Na; NaCl