

New Jersey Geological Survey Technical Memorandum 98-1



Comprehensive Chemistry of Select Greensand from the New Jersey Coastal Plain

N.J. Department of Environmental Protection - Division of Science and Research

STATE OF NEW JERSEY

Christine Todd Whitman, Governor

Department of Environmental Protection Robert C. Shinn, Jr., Commissioner

Environmental Planning and Science Robert Tudor, Assistant Commissioner

Division of Science and Research Leslie J. McGeorge, Director

Geological Survey Haig F. Kasabach, State Geologist

NEW JERSEY DEPARTMENT OF ENVIRONMENTAL PROTECTION

The Department of Environmental Protection's mission is to assist the residents of New Jersey in preserving, sustaining, protecting and enhancing the environment to ensure the integration of high environmental quality, public health and economic vitality.

NEW JERSEY GEOLOGICAL SURVEY

The mission of the New Jersey Geological Survey is to map, research, interpret and provide scientific information regarding the state's geology and ground-water resources. This information supports the regulatory and planning functions of DEP and other governmental agencies and provides the business community and public with the information necessary to address environmental concerns and make economic decisions.

The New Jersey Geological Survey Technical Memorandum 98-1

Comprehensive Chemistry of Select Greensand from the New Jersey Coastal Plain

by

John H. Dooley

New Jersey Department of Environmental Protection Division of Science and Research Geological Survey P.O. Box 427 Trenton, NJ 08625-0427 1998 Printed on recycled paper

New Jersey Geological Survey Technical Memorandums are brief reports prepared for timely response to issues of concern. They are published by the New Jersey Geological Survey, P.O. Box 427, Trenton, NJ 08625-0427. This report may be reproduced in whole or part provided that suitable reference to the source of the copied material is provided.

Other Survey and Department maps and reports may be obtained from:

DEP Maps and Publications Sales Office P.O. Box 438 Trenton, NJ 08625-0438

A price list is available on request.

Use of brand, commercial, or trade names is for identification purposes only and does not constitute endorsement by the New Jersey Geological Survey.

CONTENTS

11 |1

																																						Pag	e
Introduction					•												•				•		•			•		•		۰.			 			•	 	•	1
Methods												•		÷																		•	 		•		 		3
Results							•																		•								 				 	. 4	4
Discussion												•		•						•							•						 				 , .	. 4	4
Major E	len	nen	nt (Эx	id	es	•					•		•										•									 				 , .	. 4	4 -
Trace E	lem	en	ts									•		•		. :		•				•				•		•					 				 	10)
Abbrevi	ate	d H	lis	to	гу	of	ſΑ	gr	iç	ult	ura	al	U	se	s (of	G	ree	ens	sai	nd	in	۱N	lev	W.	Je	rse	ey					 			•	 , .	1.	5
Conclusions																	•		•			•				•		•		•		•	 			•	 	1	7
Acknowledg	me	nt						• •						•			•		•			•	•				•					•	 			•	 	1	7
References							•		•••			•		•			•		•	•							•		 •		•		 		•		 •	18	3

FIGURES

Figure 1. Map of the New Jersey Coastal Plain showing location of the sample sites
greensand ($n = 7$, except for CaO where $n = 5$) normalized against (divided by)
the median concentration in glauconite reported in the literature
3. Plot of the ratio of major element oxides in New Jersey greensand compared to
arithmetic mean eastern United States soil
4. Plot of the arithmetic mean analyte concentration in greensand from the
Hornerstown and Navesink Formations divided by the median analyte
concentration for New Jersey soils
5. Plot of arithmetic mean analyte concentration in greensand from the Navesink
and Hornerstown Formations divided by the soil guideline for residences

TABLES

Table	1. Method and minimum detection limit in ppm, except where noted, for the
	analysis of minor and trace elements in greensand from New Jersey
	2. Concentration of elements in greensand from the New Jersey Coastal Plain
	physiographic province
	3. Concentration (in ppm) of lanthanide-series elements in greensand from the
	New Jersey Coastal Plain physiographic province
	4. Concentration of major elements (in wt %), on a dry basis, in greensand from
	the New Jersev Coastal Plain physiographic province
	5. Statistical summary of major element concentrations (in wt %), on a dry basis
	for greensand from the New Jersey Coastal Plain
	Statistical summary of major elements (in wt %) on a dry basis in greensand
	from the Homerstown and Neverink Formations in the New James Costal Disin
	10 In the Hornerstown and Navesink Formations in the New Jersey Coastal Flaim
	7. Concentration of minor and trace elements (in ppm) in greensand from the
	New Jersey Coastal Plain physiographic province
	8. Statistical summary of minor and trace-element concentrations (in ppm) for
	greensand from the Hornerstown and Navesink Formations in the New Jersey
	Coastal Plain province
	9 Proposed residential surface soil cleanup guidelines (in mm)
	Serve and the server

APPENDIX

Appendix 1. Cursory binocular microscopy description of the washed samples sent for											
geochemical analyses		. 19									

Comprehensive Chemistry of Select Greensand from the New Jersey Coastal Plain

Introduction

The New Jersey Coastal Plain physiographic province, figure 1, consists of sediments ranging in size from clay (for example, the Woodbury Clay) to gravel (for example, the Beacon Hill Gravel). Many of its geologic formations, particularly those that crop out in the Inner Coastal Plain, contain widely varying concentrations of the mineral glauconite, whose empirical formula may be written as:

 $(K,Na,Ca)_{1.2-2.0}(Fe^{+3},Al,Fe^{+2},Mg)_4[Si_{7.7.6}Al_{1-0.4}O_{20}](OH)_4 nH_2O.$ For example, the Hornerstown and Navesink Formations locally consist of essentially pure glauconite sand. Other geologic formations in the Coastal Plain contain little (Woodbury Clay) to no glauconite (Cohansey Sand). In sufficient amounts, glauconite imparts a greenish color to the formations in which it occurs. These glauconite-rich sediments are informally referred to as "greensands," which denotes unconsolidated glauconite-rich sand, and as "greensand marl" which is an inappropriate term found in the early literature.

Distinct soils develop from the weathering of glauconite in areas where these formations crop out or are near the land surface. The New Jersey Department of Environmental Protection (NJDEP) Site Remediation Program's (SRP) data for several sites in Monmouth and Gloucester Counties indicate that elevated concentrations of arsenic, beryllium, cadmium and/or chromium occur in glauconite-bearing soils or in soils developed from glauconite (Kevin Schick, written communication, 1997). It is unknown whether these metals are natural occurring, anthropogenic, or a combination of the two. Discriminating natural (lithogenic) background from anthropogenic contamination dictates the course of action the Department will take.

Because of the prevalence of greensand in the Coastal Plain, it is essential that the Department understand its chemical composition. A comprehensive literature review revealed that the concentration of most minor- and trace-element constituents, some of which are regulated contaminants [As, Be, Cr, Pb, for example] in glauconite, are not known. To fill this data gap, the New Jersey Geological Survey (NJGS) is investigating the chemical constituents in pristine greensands from the New Jersey Coastal Plain. This report does not purport to be a comprehensive chemical characterization of New Jersey's glauconite-bearing formations, but rather focuses on the chemical characterization of the glauconite found therein. This data report provides the most comprehensive chemical characterization of greensand yet published. A brief discussion of the results of this investigation is presented in the context of residential soil cleanup guidelines and their implications for the Department.



Figure 1. Map of the New Jersey Coastal Plain showing location of the sample sites.

Methods

A total of seven greensand samples were collected from areas considered to be unaffected by anthropogenic inputs. Two samples of greensand were collected on June 11, 1996 from the Inversand Company pit at Sewell, New Jersey [figure 1]. Those from the lower Hornerstown Formation, designated as Hornsew, and from the upper Navesink Formation, designated as Navesew, were dug from a freshly exposed face in the working wall of the pit. A greensand sample, designated as Hornsdel, was collected on June 21, 1996 from the lower Hornerstown Formation in the Delta Lee pit near Perrineville, New Jersey. The greensand sample designated as Navemarl was collected on June 21, 1996 from the middle Navesink Formation on a fresh exposure along the bank of Big Brook Creek near Marlboro, New Jersey. Samples HornsBRC, NaveBRC and MarshBRC were obtained from cores taken from the Bass River corehole in March 1997. HornsBRC (1248 ft. below grade), NaveBRC (1280 ft. below grade) and MarshBRC (1430 ft. below grade) are samples from the Hornerstown, Navesink and Marshalltown Formations, respectively. All samples were collected and stored in new, precleaned glass bottles with a lined metal or polythene screw cap.

An aliquot of each specimen was put in an 80-mesh, brass, ASTM Standard Testing sieve and rinsed with copious amounts of doubly-distilled, deionized water at the NJGS laboratory. The rinse removed the clay, silt and very fine sand. The washed aliquots were oven dried at 50°C for approximately 6 hours. Binocular microscopy was used for a cursory examination of each aliquot sent for chemical analysis and the results are reported in Appendix 1. Additionally, binocular microscopy aided in the removal of much of the remaining nonglauconite mineral constituents (for example, quartz, bioclasts, etc.).

The aliquots were placed in new, precleaned glass vials fitted with lined polythene screw caps for shipment to XRAL Activation Services Incorporated for geochemical characterization. The major elements (that is Si, Al, Ca, etc.), expressed as oxides, were measured by X-ray fluorescence (XRF) methods with a minimum detection limit (MDL) of 0.01 percent. The minor and trace analytes, methods of analysis, and method detection limits are presented in Table 1.

Table 1. Method and minimum detection limit in ppm, except where noted, for the analysis of minor and trace elements in
greensand from New Jersey. Analytical methods are: AAS, atomic absorption spectroscopy; ICP, inductively coupled
plasma; ICP/MS, inductively coupled plasma/mass spectrometry; INAA, instrumental neutron activation analysis;
XRF, x-ray fluorescence; CVAAS, cold vapor atomic absorption spectroscopy; DCP, direct coupled plasma.

AAS		ICP		ICP/MS		INAA		XRF		Others		
Analyte	MDL	Analyte	MDL	Analyte	MDL	Analyte	MDL	Analvte	MDL	Analyte	Method	MDI.
Cd	0.2	Ag	0.1	Bi	0.5	As	0.1	Ba	50	Cl	coulometry	50
In	0.5	В	10	T1	0.1	Au	2 ppb	Nb	2	Hg	CVAAS	5 ppb
		Be	1	La	0.1	Br	1	Rb	2	Mn	DCP	2
	i	Со	1	Ce	0.1	Cr	2	Zr	1	S	Leco	0.005%
		Cu	0.5	Pr	0.1	Cs	0.5			LOI	gravimetry	0.01%
		Ga	0.1	Nd	0.1	Hf	0.2					
1		Ge	10	Sm	0.1	Sb	0.1	1				
1		Li	1	Eu	0.05	Se	1					
		Mo	1	Gd	0.1	Ta	0.5			ļ		
		Ni	1	ТЪ	0.1	Th	0.2					
•		РЪ	2	Dy	0.1	U	0.1			1		
		Sc	0.05	Ho	0.05	Ŵ	1					
		Sr	1	Er	0.1							
		V	2	Tm	0.1							
		Y	1	Yb	0.1			1				
		Zn	0.5	Lu	0.05							

LOI is loss on ignition.

Results

Chemical data for the seven greensand samples are tabulated in Tables 2 and 3. In Table 2, data for major element oxides, that is those analytes reported in percentage, include loss on ignition (LOI). Loss on ignition is the weight loss which results from heating the sample to a high temperature after preliminary drying at a temperature just above the boiling point of water. The weight loss upon drying is called free moisture (adsorbed water), whereas that which occurs above the boiling point for water is called loss on ignition (Thrush, 1968, p. 659). To facilitate a rational comparison among samples having a wide range in structural water (LOI) content, it is necessary to eliminate LOI from the analysis. A standard practice among geochemists is to subtract the LOI from the sum of oxides and recast the oxide data to 100 percent. The recast data for the major element oxides are shown in Table 4. Unless specified otherwise, discussion of major element oxides is restricted to the recast data in Table 4.

Discussion

Major Element Oxides

The greensand samples sent for analysis contain as much as a few volume percent of other minerals (Appendix 1). Other investigators have gone to great lengths to isolate glauconite from the other constituent minerals usually associated with greensand deposits. Chemical analyses for major element oxides in the isolated glauconite have been reported in the literature.

	Navesink			-	Hornerstown	Marshalltown		
Analyte	Marlboro	Sewell	Bass River	Sewell	Delta Lee	Bass River	Bass River	
<u>%</u>	- 47 20	47 70	40.50	£0.00	10.00	50.00	TO 10	
A1202	47.30	47.70	48.50	50.00	48.60	50.90	50.60	
A1203	0.87	1.50	6.95	7.90	9.67	7.50	8.17	
	2.75	2.02	5.10	SU.UI	<0.01 2.64	2.18	3.49	
Na2O	0.15	5.45 0.11	4.41	4.04	2.04	4.32	3.52	
K20	7.67	7 70	676	0.09	0.14	0.32	0.25	
Fe2O3	23.30	24.20	0.70	8.24 22.00	0.21	7.31	7.22	
Ma	25.50	24.20	. 19.00	22.00	20.90	20.30	19.30	
Cr2O3	0.01		0.01	0.01	0.01	<0.01	<0.01	
	0.02	0.05	0.02	0.07	0.19	0.07	0.03	
P205	0.00	0.05	2.00	0.00	0.30	0.08	0.06	
	0.88 9.10	0.50	2.43	7 90	0.09	1.20	1.92	
LOI	0.10	1.15	0.00	7.80	11.10	0.00	5.70	
mg/kg								
Ag	≪0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	
As	25	31	12	12	27	7.1	22	
Au	<2	<2	<2	<2	<2	<2	<2	
В	530	560	520	520	350	540	600	
Ba	100	110	50	80	9 0	50	80	
Be	6	5	5	7	.8	8	5	
Bi	<0.5	<0.5	<0.5	<0.5	1.5	<0.5	<0.5	
Br	3	5	4	4	3	3	4.	
Cd	1.2	≪0.2	<0.2	<0.2	<0.2	<0.2	<0.2	
Cl	50	<50	<50	50	70	<50	60	
Co	4	5	14	5	18	12	15	
Cr	130	130	130	380	1000	400	150	
Cs	1.6	3.4	2.3	3.0	5.1	5	2.7	
Cu	<0.5	1.7	2.6	6.7	8.3	1	3.8	
Ga	18	14	30 ·	14	14	23	18	
Ge	<10	<10	<10	<10	<10	<10	<10	
Hſ	<0.2	0.6	0.6	<0.2	1.6	1.7	0.6	
Hg	0.010	0.011	0.042	0.013	0.006	0.007	0.017	
In	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	
Li	27	25	54	35	16	39	31	
Мо	<1	<]	3	<1	<1	<1	2	
Nb	2	3	<2	2	9	<ż	<2	
Ni	17	19	30	21	48	46	32	
Pb	<2	<2	13	3	31	8	19	
Rb	206	224	156	255	250	195	185	
S	1950	3740	3170	740	1090 .	390	2290	
Sb	0.8	1.1	1.1	1.5	7.7	1.6	0.8	
Sc	4	5	7	7	24	13	10	
Se	<1	<1	<1	<1	<1	<}	<]	
Sr	85	46	214	2	5	110	197	
Ta	<0.5	⊲0.5	⊲0.5	<0.5	0.8	<0.5	<0.5	
Th	1.6	1.5	2.4	1.3	20	4.2	11	
T1	⊲0.1	<0.1	<0.1	0.2	<0.1	<0.1	0.1	
U	.3.5	3.4	6.5	4.4	11.3	5.1	5.2	
V	69	99	54	110	650	100	100	
W	<1	<1	1	<1	<1	1	2	
Y	21	14	71	33	46	58	- 70	
Zn	70	84	86	200	370	96	56	
Zr	10	12	33	18	74	34	36	

 Table 2. Concentration of elements in greensand from the New Jersey Coastal Plain physiographic province.

••

LOI is loss on ignition.

۱ſ ۱I

	-	Navesink	-		Hornerstown		Marshalltown
Analyte	Marlboro	Sewell	Bass River	Sewell	Delta Lee	- Bass River	Bass River
La	21.9	15.5	50.1	40.5	69.4	50.8	72.8
Ce	77.8	57.2	101.0	122.0	256.0	124.0	245.0
Pr	6.0	4.3	12.0	12.0	20.0	13.0	23.0
Nd	24.9	17.6	48.7	47.2	83.6	56.2	93.9
Sm	5.9	4.3	10.2	9.8	18.9	11.9	20.0
Eu	1.21	0.85	2.3	2.06	3.6	2 66	46
Gd	5.4	3.5	10.2	8.6	14.0	11.4	19.0
Tb	0.7	0.5	1.5	1.1	2.0	17	2.8
Dy	3.9	2.7	8.5	6.1	10.6	91	13.8
Но	0.69	0.47	1.74	1.08	1.85	1.68	2 40
Er	1.8	1.3	4.5	2.8	4.8	4.6	61
Tm	0.2	0.1	0.5	0.4	0.6	0.5	0.1
Yb	11	1.0	3.5	2.0	3.8	3.2	4.8
Lu	0.18	0.11	0.51	0.26	0.38	0.48	۹.۵ ۵ 69
Sum	151.68	109.43	255.25	255.90	489.53	291.22	509.78

 Table 3. Concentration (in ppm) of lanthanide-series elements in greensand from the New Jersey Coastal Plain physiographic province.

 Table 4. Concentration of major element oxides (in wt percent), on a dry basis, in greensand from the New Jersey Coastal Plain physiographic province.

	_	Navesink			Hornerstown		Marshalltown
Analyte	Marlboro	Sewell	Bass River	Sewell	Delta Lee	Bass River	Bass River
SiO2	51.27	51.48	51.60	54.03	54.73	54.05	53.51
Al2O3	7.45	7.33	7.38	8.60	10.82	7.96	8.64
CaO	2.96	1.71	5.48	<0.01	<0.01	2.31	3.69
MgO	3.56	3.49	4.68	4.37	2.96	4.59	3.72
Na2O	0.16	0.12	0.29	0.10	0.16	0.34	0.26
K2O	8.31	8.40	7.18	8.90	7.29	7.76	7.64
Fe2O3	25.25	26.34	20.81	23.77	23.39	21.55	20.41
MnO	<0.01	<0:01	<0.01	< 0.01	<0.01	<0.01	< 0.01
Cr2O3	0.02	0.12	0.02	0.08	0.21	0.07	0.03
TiO2	0.07	0.05	0.06	0.06	0.34	0.08	0.06
P2O5	0.95	0.97	2.60	0.09	0.10	1.27	2.03

These chemical data from the literature have been recast on an LOI-free basis to facilitate comparison with the chemistry for greensands from New Jersey. The recast data from the literature will appear in an NJGS Report following the conclusion of this investigation. A graphical comparison of major element oxides for New Jersey greensand normalized against those reported in the literature for glauconite is shown in Figure 2. With the exception of TiO₂, CaO and P₂O₅, the major element oxides in New Jersey greensand are essentially identical to those reported in the literature for the glauconite isolates.



Figure 2. Graphical depiction of the median analyte concentration in New Jersey greensand (n = 7, except for CaO where n = 5) normalized against (divided by) the median analyte concentration in glauconite reported in the literature (n = 47). Recast data used for the calculation.

The relative TiO₂ depletion in greensand from New Jersey suggests that the literature values for TiO₂ may be biased on the high side, perhaps because titanium minerals were not efficiently removed during the magnetic isolation of glauconite. Glauconite and ilmenite $(Fe^{+2}TiO_3)$ are paramagnetic. Perhaps the literature values for TiO₂ represent a situation where titanium-bearing minerals (for example, rutile, anatase, ilmenite) acted as a substrate around which glauconitization occurred. Alternatively, the depositional environment where the New Jersey greensand developed was such that free titanium was not available for incorporation into the glauconite crystal lattice. The manner and conditions of glauconite development are somewhat enigmatic; therefore, a comprehensive discussion of the topic is beyond the scope of this technical memorandum.

The mineral glauconite is always low in calcium (Deer and others, 1965), and phosphorus or the phosphate anion (PO_4^{-3}) is not accommodated in its crystal lattice. The relative calcium and phosphate enrichment of New Jersey greensand results from mineral impurities. Binocular microscopic examination of the samples reveals that brownish, in part mottled with green hues, smooth textured, rice-shaped sand grains, which are interpreted to be feces (coprolites) from marine organisms, occur in the greensand. X-ray diffraction analysis of these brownish sand grains demonstrate that they consist mainly of fluorapatite (Ca₅(PO₄)₃F, the mineral apatite) and carbonate-hydroxylapatite (Ca₁₀(PO₄)₃(CO₃)₃(OH)₂, the mineral dahllite). These apatite-group minerals account for the significant portion of phosphate and calcium reported in analyses for glauconite. Linear regression analysis for CaO versus P₂O₅ yields a correlation coefficient of 0.92 at the 95 percent confidence level -- further indicating that apatite-group minerals occur in the greensand samples. Greensand from the Hornerstown Formation at Sewell and Perrineville (Delta Lee) has calcium and phosphate concentrations <0.01 percent and ~0.10 percent, respectively. In this case, the phosphate likely is associated with iron which forms the dark green to dark blue mineral vivianite (Fe₃⁺²(PO₄)₂8H₂O) which visually can resemble glauconite.



Figure 3. Plot of the ratio of major element oxides in New Jersey greensand compared to arithmetic mean eastern U.S. soil. Data for eastern U.S. soils are from Shacklette and Boerngen (1984). The arbitrary value of 10⁻³ was chosen to offset samples with concentrations at or below the 0.01 percent MDL (minimum detection limit).

The enrichment or depletion of major element oxides in New Jersey greensand relative to their concentration in an arithmetic mean eastern United States soil, where the number of observations (n) ranges from 156 for SiO₂ to 541 for Cr_2O_3 , may aid in deciphering chemical signatures in soils that contain glauconite. The ratio of major element oxides in New Jersey greensand to arithmetic mean eastern U.S. soil is shown in Figure 3. Relative to mean eastern U.S. soil, clearly greensand is enriched in calcium (except for the samples of the Hornerstown Formation from Sewell and Perrineville), magnesium, potassium, iron, chromium and phosphate. The calcium and phosphate enrichment in greensand is due to apatite-group minerals. Magnesium, potassium and iron are major constituent elements in the glauconite crystal lattice and, therefore, their concentrations are expected to be high relative to median U.S. soil. Silicon, aluminum and sodium concentrations in greensand are similar to those in eastern U.S. soil. With the exception of greensand from the Hornerstown Formation at Perrineville, titanium is low by nearly an order of magnitude in greensand.

A statistical summary for the major element oxide concentrations in the seven greensand samples is in Table 5. The small standard deviation (Table 5) and tight cluster of points around Si, Al, Mg, K and Fe (Figure 3) are consistent with the limited variability in major constituent elements in the crystal lattice of the mineral glauconite. A large standard deviation for the major constituent elements comprising glauconite strongly suggests that other minerals are admixed. Indeed this is the case for the greensand samples analyzed.

				Standard	Arithmetic	
Analyte	Minimum	Maximum	Median	Deviation	Mean	N
SiO2	51.27	54.73	53.51	1.47	52.94	7
Al2O3	7.33	10.82	7.96	1.24	8.31	7
CaO	1.71	5.48	2.96	1.46	3.23	5
MgO	2.96	4.68	3.72	0.65	3.91	7
Na2O	0.10	0.34	0.16	0.09	0.20	7
K2O	7.18	8.90	7.76	0.63	7.93	7
Fe2O3	20.41	26.34	23.39	2.26	23.07	7
Cr2O3	0.02	0.21	0.07	0.07	0.08	7
TiO2	0.05	0.34	0.06	0.10	0.10	7
P2O5	0.09	2.60	0.97	0.93	1.14	7

 Table 5. Statistical summary of major element oxide concentrations (in wt percent), on a dry basis, for greensand from the New Jersey Coastal Plain.

N = number of observations at or exceeding the MDL.

9

Though three chemical analyses of greensand each from the Hornerstown and Navesink Formations do not permit a rigorous statistical analysis, there are notable chemical differences between the two geologic formations. Reported in Table 6 are the results of a statistical analysis for each of the two formations. Based on the arithmetic mean, samples of the Hornerstown greensand have more Si, Al, Cr and Ti, and less total Fe and P than greensand from the Navesink Formation. The arithmetic mean concentration of Mg, Na and K is essentially identical in the two geologic formations.

Trace Elements

Trace elements are a suite of chemical elements which are not essential constituents in the crystal lattice of most minerals. Trace elements do not necessarily reside in the crystal lattice but rather may be adsorbed onto the crystal. Trace elements are among those whose concentrations in the various environmental media are regulated by state and federal agencies, for example As, Be, Cr and Pb. Trace element concentrations of the seven greensand samples are in Table 7. This discussion focuses on analytes regulated by the Department.

Table 6.	Statistical summary of major elements (in wt percent) on a dry basis
	in greensand from the Hornerstown and Navesink Formations in the
	New Jersey Coastal Plain.

					Arithmetic	
Analyte	Formation	Minimum	Maximum	Median	Mean	N
SiO2	Horn	54.03	54.73	54.05	54.27	3
	Nave	51.27	51.50	51.48	51.42	3
Al2O3	Horn	7.96	10.82	8.60	9.13	3
	Nave	7.33	7.45	7.38	7.39	3
MgO	Horn	2.96	4.59	4.37	3.97	3
	Nave	3.49	4.68	3.56	3.91	3
Na2O	Horn	0.10	0.34	0.16	0.20	3
	Nave	0.12	0.29	0.16	0.19	3
K2O	Horn	7.29	8.90	7.76	7.98	3
	Nave	7.18	8.40	8.31	7.96	3
Fe2O3	Horn	21.55	23.77	23.39	22.90	3
	Nave	20.81	26.34	25.25	24.13	- 3
Cr2O3	Horn	0.07	0.21	0.08	0.12	3
	Nave	0.02	0.12	0.02	0.05	3
TiO2	Horn	0.06	0.34	0.08	0.16	3
	Nave	0.05	0.07	0.06	0.06	3
P2O5	Horn	0.09	1.27	0.10	0.49	3
	Nave	0.95	2.60	0.97	1.51	3

Horn = Hornerstown Formation; Nave = Navesink Formation.

	_	Navesink			Marshalltown		
Analyte	Marlboro	Sewell	Bass River	Sewell	Delta Lee	Bass River	Bass River
Ag	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
As	25	31	12	12	27	7.1	22
Au	<2	<2	<2	<2	<2	<2	<2
В	530	560	520	520	350	540	600
Ba	100	110	50	80	90	50	80
Be	6	5	5	7	8	8	5
Bi	<0.5	<0.5	<0.5	<0.5	1.5	<0.5	<0.5
Br	• 3	5	4	4	3	3	3
Cd	1.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Cl	50	<50	<50	50	70	<50	60
Со	4	5	14	5	18	. 12	15
Cr	130	130	130	380	1000	400	150
Cs	1.6	3.4 ·	2.3	3.0	5.1	5.0	2,7
Cu	<0.5	1.7	2.6	6.7	8.3	1.0	3.8
Ga	18	14	30	14	14	23	18
Ge	<10	<10	<10	<10	<10	<10	<10
Hf	<0.2	0.6	0.6	<0.2	1.6	1.7	0.6
Hg	0.010	0.011	0.042	0.013	0.006	0.007	0.017
In	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Li	27	25	54	35	16	39	31
Mo	<1	<1	3	<1	<]	<1	2
Nb	2	3	<2	2	9	<2	<2
Ni	17	19	30	21	48	46	32
Pb	<2	<2	13	3	31	8	19
Rb	206	224	156	255	250	195	185
S	1950	3740	3170	740	1090	390	2290
Sb	0.8	1.1	1.1	1.5	7.7	1.6	0.8
Sc	4	5	7	7	24	13	10
Se	<1	<1	<1	<1	<1	<1	<1
Sr	85	46	214	2	5	110	197
Ta	<0.5	<0.5	<0.5	<0.5	0.8	<0.5	<0.5
Th	1.6	1.5	2.4	1.3	20	4.2	11
Tl	<0.1	<0.1	<0.1	0.2	<0.1	<0.1	0.1
U	3.5	3.4	6.5	4.4	11.3	5.1	5.2
V	69	99	54	110	650	100	100
W	. <1	<1	1	<1	<1	1	2
Y ·	21	14	71	33	46	58	70
Zn	70	84	86	200	370	96	56
Zr	10	12	33	18	74	34	36

 Table 7. Concentration of minor and trace elements (in ppm) in greensand from the New Jersey Coastal Plain physiographic province.

.

					Arithmetic	
Analyte	Formation	Minimum	Maximum	Median	Mean	Ν
As	Horn	7.1	27	12	15	3
	Nave	12	31	25	23	3
В	Horn	350	540	520	470	3
_	Nave	520	560	530	537	3
Ba	Horn	50	90	80	73	3
	Nave	50	<u> </u>	100	87	3
Be	Horn	7	8	8	8	3
	Nave	5	6	5	5	3
Br	Horn	3	4	3	3	3
_	<u>Nave</u>	3	5	4	4	3
Co	Hom	5	18	12	12	3
	Nave	4	14	5	. 8	3
Cr	Horn	380	1000	400	593	3
_	Nave	130	130	130	130	3
Cs	Hom	3.0	5.1	5.0	4.4	3
-	Nave	1.6	3.4	2.3	2.4	3
Cu	Horn	1.0	8.3	6.7	5.3	3
_	Nave	1.7	2.6	2.2	2.2	2
Ga	Hom	14	23	14	17	3
	Nave	14	30	18	21	3
Hg	Hom	0.006	0.013	0.007	0.009	3
	Nave	0.010	0.042	0.011	0.021	3
Li	Horn	16	39	35	30	3
	Nave	25	54	27	35	3
Nı	Hom	21	48	46	38	3
-	Nave	17		19	22	3
Pb	Hom	3	31	8	14	3
Rb	Hom	195	255	250	233	3
<u> </u>	Nave	156	224	206	195	3
8	Horn	390	1090	740	740	3
a 1	Nave	1950	3740	<u>3170</u>	2953	3
Sb	Horn	1.5	7.7	1.6	3.6	3
~	Nave	0.8	<u>1,1</u>	1.1	1.0	3
Sc	Horn	7	24	13	15	3
a	Nave	4	7	5	5	3
ər	Hom	2	110	5	39	3
	Nave	46	214	85	115	3
In	Hom	1.3	20.0	4.2	8.5	3
	Nave	1.5	2.4	1.6	1.8	3
U	Hom	4.4	11.3	5.1	6.9	3
v	Nave	3.4	6.5	3.5	4.5	
v	HOM	100	650	110	287	3
v	Nave		99	69	74	3
Y	Hom	33	58	46	46	3
-	Nave	14	71	21	35	3
Zn	Horn	96	370	200	222	3
-	Nave		86	84	80	3
<u>L</u> r	Hom	18	74	34	42	3
	Nave	10	33	12	18	3

Table 8. Statistical summary of minor and trace-element concentrations(in ppm) for greensand from the Homerstown and NavesinkFormations in the New Jersey Coastal Plain province.

Hom = Homerstown Formation; Nave = Navesink Formation.

N = number of observations at or exceeding the MDL.

.

٠,

A statistical summary of trace element data for the Hornerstown and Navesink Formations is in Table 8. Based on this limited dataset, greensand from the Hornerstown Formation is enriched in Cr, Cu, Ni, Sb, V and Zn, relative to the arithmetic mean concentration for the Navesink Formation. The arithmetic mean concentration of As and Hg in greensand from the Navesink Formation is greater than that for the Hornerstown Formation. Arithmetic mean concentrations for Ba and Be are nearly the same in both geologic formations.

To evaluate how the concentration of the regulated analytes in greensand compares to New Jersey soils in general, the arithmetic mean analyte concentrations for greensand are divided by the median analyte concentrations in soils from New Jersey as reported by Fields and others (1993). When the analyte concentration in the greensand equals that for New Jersey soils, the ratio equals unity (10^0 or 1). If the ratio is either greater than or less than unity, the analyte concentration for the greensand is either enriched or depleted, respectively, relative to median New Jersey soil. The results of this evaluation are shown in Figure 4.



Figure 4. Plot of the arithmetic mean analyte concentration in greensand from the Hornerstown (Horners) and Navesink Formations divided by the median analyte concentration for New Jersey soils. Data for New Jersey soils are from Fields and others (1993). Data for the Marshalltown (Marshall) Formation are from one sample.

Of the regulated analytes shown in Figure 4, only copper concentrations are similar (Hornerstown Formation) or slightly depleted (Marshalltown and Navesink Formations) relative to median soil for New Jersey. Nickel concentrations in greensand range from 3.4 to 5.9 times the median concentration in New Jersey soil for the Navesink and Hornerstown Formations, respectively. Zinc concentrations in greensand range from 1.7 to 6.8 times the median concentration for New Jersey soils. Arsenic, beryllium and vanadium are enriched by nearly an order of magnitude over the median concentration in soils from New Jersey. Relative to the median New Jersey soil, chromium is highly enriched (17.3 to 79 times) in greensand. Therefore, in areas of the Coastal Plain province with significant concentrations of glauconite, and perhaps in soils developed from glauconite-rich sediments, it is necessary to account for the metals contribution from glauconite. Note that it is not known how trace metal concentrations are modified during soil-forming processes (pedogenesis) that involve glauconite. It is expected that research will be initiated to address this question in the future.

The NJDEP has proposed a set of guidelines for residential surface soil cleanup standards (Table 9). The mean trace analyte concentration for greensand from the Hornerstown and Navesink Formations and its concentration in the Marshalltown Formation is divided by the residential surface soil cleanup guideline in order to evaluate how greensand compares with this proposed guideline. The results are shown in Figure 5. Clearly, the arithmetic mean concentration for beryllium and chromium in greensand from all three formations, and the arsenic concentration in greensand from the Navesink and Marshalltown Formations, exceed the proposed residential soil cleanup guideline. The arithmetic mean concentration for arsenic and vanadium in greensand from the Hornerstown Formation is slightly below the proposed guideline.

Analyte	Guideline		
As	20		
Ba	700		
Be	1		
Cd	1		
Cr	100		
Cu	600		
Hg	14		
Ni	250		
Pb	400		
Sb	14		
Tl	2		
V	370		
Zn	1500		

Table 9. Proposed Residential Surface Soil Cleanup Guidelines (in ppm).

14



Figure 5. Plot of the arithmetic mean analyte concentration in greensand from the Navesink and Hornerstown (Horners) Formations divided by the soil guideline for residences. Data for the Marshalltown (Marshall) Formation are for one sample. The arbitrary value of 10^{-4} was chosen to offset the Pb concentration at less than the detection limit in the Navesink Formation from those samples with quantitated concentrations.

It is rare for a native soil to consist entirely of glauconite, so for typical soils in the New Jersey Coastal Plain, which may contain only trace amounts of glauconite, the natural (lithogenic) background concentration should be below the proposed soil cleanup guideline for all these analytes. Glauconite weathering in soil may produce other clay minerals and iron oxyhydroxide phases such as goethite (FeO(OH)). These weathering products are capable of retaining many trace elements via surface complexation or incorporation into crystal lattices. Therefore, the concentration of trace metals in soils developed from glauconite-rich sediments, or soils having significant amounts of glauconite, may approach guideline concentrations for residential cleanup. This emphasizes the importance of geologic factors that may strongly influence the interpretation of the results of any site assessment. This has a direct bearing on subsequent actions implemented by the Department.

Abbreviated History of Agricultural Uses of Greensand in New Jersey

Greensand has been used for a variety of purposes which include uses as diverse as fertilizer and soil conditioner, catalysts, water softener, a source of potash (potassium), the brick industry, green paint pigment, and a coloring agent for glass. In particular, its use as a fertilizer

and soil conditioner by agriculturists in southern New Jersey has been significant. Greensand was extensively excavated and used in agriculture as a fertilizer and soil conditioner from the late 1700's to the early 1900's (Markewicz and Lodding, 1983). Additionally, greensand has been used as a nonpoisonous dusting agent for plants (Markewicz and Lodding, 1983). According to Mansfield (1923), the Marshalltown Formation "has been dug for fertilizer," the Navesink Formation "has been extensively dug [with spades and grubbing hoes (Cook, 1868)] for fertilizer throughout much of the marl belt," and the Hornerstown Formation "has been extensively dug and used as a fertilizer."

Cook (1868) states that in the late 1700's to early 1800's "it is not uncommon for farmers to use two hundred and fifty cart loads" of glauconite-rich sediments (so-called marls) per acre of ground in the vicinity of Holmdel and Marlboro, Monmouth County. Regrettably the volume of greensand in a cartload can not be determined. Cook (1868, p. 446) writes, "In fact there is scarcely a limit to the amount of such marl applied except the expense of excavation and distribution over the surface. In the districts where the marl outcrops on every farm more is used than in those neighborhoods where it is not found, and to which it must be hauled -- perhaps several miles. Transportation influences to a great degree the amount used."

By about the 1850's it was discovered that sediment with lower concentrations of glauconite applied to fields provided the same crop yield. However, by this time, railroads rather than carts were hauling the glauconite "south to more sandy districts" (Cook, 1868). According to Cook (1868, p. 451), "the use of marl has been very much increased in the southern part of the state through the operations of the West Jersey Marl and Transportation Company. It is distributed along various connecting railroad lines to a wide scope of country."

Cook (1868, p. 461) estimated that the greensand used in the state, principally within and near the greensand districts, is "very near one million tons as the annual amount used." General annual application rates for greensand in the 1860's were: 100 to 400 bushels per acre for most forage crops; 5 to 30 tons per acre for potatoes; 2.5 tons per acre for buckwheat; and 5 to 30 tons per acre for wheat, rye, oats and corn. An annual estimate of the metal burden to soil due to the application of a million tons of greensand in the coastal plain, assuming glauconite (including phosphate and carbonate minerals) comprises 85 percent of the greensand, and using arithmetic mean concentrations from this study, is: 16.5 tons As, 68 tons Ba, 5.4 tons Be, 281 tons Cr, 3.4 tons Cu, 25.5 pounds Hg, 25.5 tons Ni, 12.8 tons Pb, 1.8 tons Sb, 144 tons V, and 116 tons Zn. An application rate of 10 tons per acre or ~300 bushels per acre for pure glauconite sand roughly equates to ~1 pound per square foot of soil. Assuming there is 85 percent glauconite in the greensand fertilizer, an effective density of 2.0 grams per cubic centimeter, and the glauconite is evenly distributed in the top foot of soil, the chromium added to the soil annually is calculated at 5.4 micrograms Cr per gram of soil using the 400 ppm median Cr concentration for the Hornerstown Formation.

Although the use of greensand as a fertilizer was replaced by manufactured fertilizers during the late 1800's, glauconite is still recommended as a mulch, top dressing mixture, and additive to soil for gardens, potted plants, and vegetable starting plots. The usual application

£

now is from 1 to 10 pounds per 100 square feet (Markewicz and Lodding, 1983).

Conclusion

Based on the results of this investigation, it can be concluded that:

1. The median major-element oxide concentration for seven samples of greensand from the New Jersey Coastal Plain is similar to that reported in the literature for glauconite.

2. The relative enrichment of calcium (CaO) and phosphorus (P_2O_5) in New Jersey greensand compared to glauconite reported in the literature results from apatite-group mineral impurities. The glauconite crystal lattice does not accommodate phosphorus.

3. The enrichment in magnesium, potassium and iron for New Jersey greensand relative to the arithmetic mean eastern United States soil is expected in that these are major constituent elements in the glauconite crystal lattice.

4. The limited dataset for greensand from the Hornerstown and Navesink Formations suggests that the Hornerstown has more silicon, aluminum, chromium, copper, nickel, antimony, vanadium and zinc, and less total iron, phosphorous, arsenic and mercury than greensand from the Navesink. Magnesium, sodium, potassium, barium and beryllium concentrations are essentially identical in the samples from these two geologic formations.

5. Relative to the median analyte concentration in 80 New Jersey soils, the greensand samples are moderately to highly enriched in arsenic, beryllium, chromium, nickel, vanadium and zinc. Copper concentrations are similar to those in the median New Jersey soil.

6. The arithmetic mean concentration for beryllium and chromium in greensand samples from the three geologic formations, and the arsenic concentration in greensand from the Navesink and Marshalltown Formations, exceed the proposed guidelines for residential soil cleanup. However, native soils in southern New Jersey typically contain only a trace, if any, of glauconite, so most soil developed from glauconite-rich sediments should meet compliance with these soil guidelines.

7. The historic use of large quantities of greensand as a fertilizer/soil conditioner in the New Jersey Coastal Plain has resulted in large quantities of metals, some of which are regulated contaminants, being redistributed over this physiographic province while the impact on environmental quality remains undefined.

Acknowledgment

11

Dr. Peter Sugarman and Lloyd Mullikin of the NJGS are kindly thanked for their logistical support, expertise and collection of some of the greensand samples. Inversand Company is thanked for permission to sample their pit. Zehdreh Allen-Lafayette is acknowledged for preparing Figure 1. The manuscript was significantly improved by thorough reviews by Richard Dalton, Dr. Peter Sugarman, Dr. Larry Muller, Irving (Butch) Grossman, Thomas Seckler and Haig Kasabach.

References

Cook, G. H., 1868, Geology of New Jersey: New Jersey Geol. Survey, Trenton, N. J. 899 p.

Deer, W. A., Howie, R. A., and Zussman, J., 1965, Rock-forming minerals, volume 3 - sheet silicates: London, England, Longmans, Green and Co., p. 35 - 41.

Fields, T. W., McNevin, T. F., Harkov, R. A., and Hunter, J. V., 1993, A summary of selected soil constituents and contaminants at background locations in New Jersey: Trenton, N.J., Dept. of Environmental Protection, 43 p.

Mansfield, G. R., 1923, Potash in the greensands of New Jersey: New Jersey Geol. Survey Bull. 23, Trenton, N. J., 146 p.

Markewicz, F. J., and Lodding, W., 1983, Glauconite, *in* Lefond, S. J., ed., Industrial Minerals and Rocks, 5th ed., v. 2, p. 745 - 756.

Shacklette, H. T., and Boerngen, J. G., 1984, Element concentrations in soils and other surficial materials of the conterminous United States: U. S. Geological Survey Professional Paper 1270, 105 p.

Thrush, Paul W., ed., 1968, A dictionary of mining, mineral, and related terms: Washington, D.C., U.S. Dept. of the Interior, Bureau of Mines, p. 659

p

Appendix 1

Cursory binocular microscopy description of the washed samples sent for geochemical analyses.

<u>Navesew</u> - greensand from the upper Navesink Formation in the Inversand Company pit at Sewell, N.J. The sample consists of a dark gray to dark grayish green glauconite sand/clay mixture. This washed aliquot of the sample revealed some rather well-indurated, medium gray, clay balls (up to 8 mm in diameter) which contain quartz and glauconite clasts with some of these aggregates being very pyritic. These clay balls are suspected to be related to the bioturbated structures. This sample contained a moderate amount of pyrite and abundant clay \pm phyllosilicates with much of it surrounding or filling voids in the glauconite grains. Very sparse quartz sand/silt. Dark brown, marine(?) fossil fragments rather abundant.

<u>Navemarl</u> - greensand from the middle Navesink Formation in Big Brook Creek (@ Hillsdale Road) near Marlboro, N.J. Very dark green to black, unconsolidated glauconite sand. Most of the glauconite sand grains have very light gray phyllosilicates (?) infilling the grain fractures/sutures. Very minor trace of pyrite and a trace of marine fossil fragments, that is spicules, mollusca fragments, elongate (rice-shape) phosphatized feces, foraminifera, and a minute shark tooth. Some clay aggregates contain glauconite inclusions. Note that some quartz sand/silt remains in the sample. Much of the quartz sand is transparent, with minor frosted quartz grains, predominantly medium to very fine grained, angular, some subangular; occasional larger quartz sand is subround to round. Occasional green-stained quartz sand. Abundant macerated fossil mollusca fragments the size of silt to very fine sand. Some complete depauperate mollusca.

<u>NaveBRC</u> - greensand from the Navesink Formation obtained from the Bass River Corehole(1,280 feet below grade). Glauconite is bluish green to occasionally black. Two to three percent of washed sample consists of foraminifera, which generally are fragmented though some are complete, and accompanied by mollusca fragments (some depauperate fauna). Extremely sparse transparent, angular, very fine to medium quartz sand. Sparse (<<1 percent), very well indurated, very coarse to coarse sand to very fine pebble-size aggregates of glauconite (medium to very fine sand) clasts which are very deep green to almost black, many of which are translucent, cemented (and matrix-supported) in a medium- to dark-gray submicroscopic matrix. Some of these aggregates also contain transparent quartz clasts the glauconite clasts in size. These aggregates react with moderate vigor in 1:5 HCl to release silt-size platelets and clasts of translucent (due to small size of particles) glauconite \pm quartz (?) silt and a significant quantity of very fine pyrite/marcasite silt. Trace constituents include brownish phosphatic clasts (≤ 1 percent). Sample sent for analysis corresponds essentially to what is reported above although eight glauconite/carbonate aggregates and three relatively large (carbonate) marine fossils were removed.

<u>Hornsew</u> - greensand from the lower Hornerstown Formation in the Inversand pit at Sewell, N.J. Essentially pure (\geq 99.5%), unconsolidated glauconite sand with traces of very fine sand to silt-size quartz, pyrite, clay and ± feldspars (?). These trace constituents were culled by hand (under

ń

binocular magnification) from the bulk sample.

<u>Hornsdel</u> - greensand from the lower Hornerstown Formation in the Delta Lee pit near Perrineville, N.J. Sample taken approximately 0.5 meter above contact with the Navesink Formation. Essentially an argillaceous ("dirty") greensand even after rinsing with copious amounts of doubly distilled deionized water.

HomsBRC - greensand from the Hornerstown Formation obtained from the Bass River Corehole (1,248 feet below grade). Glauconite is mainly green with some bluish-green grains. Regardless of grain size, fractured and broken clasts have very dark green to black cores -- black to very dark green cores range from waxy to matte luster, cryptocrystalline, no apparent cleavage and no change in fracture/break character across the boundary between the green skin (rind) and black to very dark green core. Some outer surfaces of the glauconite grains have very dark green to black color showing through the green skin. This may represent areas where the lighter green skin has been eroded (that is the younger, less crystallized, light-green mineral has weathered away exposing the better crystallized very dark green glauconite (?)) or areas absent of verdissement, that is the process leading to the development of green facies. Contact between the green rind and very dark green to black core generally is gradational over a short distance -- approximately 50 percent of all glauconite grains have thin green skins with very dark green to black cores where skin:core ratio is ~1:4 - whereas the other 50 percent have skin:core ratios >1:4. Trace constituents in the sample include various foraminifera of which some are fresh and whole and others are fragmented and chambers broken open; shark tooth fragments; clayballs (?); phosphatized, rice-shaped, smooth, light to dark brown to black fecal pellets; and extremely sparse quartz clasts. Sample sent for chemical analysis is very clean with ~1 percent impurities such as foraminifera, phosphate clasts and feces, very few quartz clasts, and clayballs (?).

<u>MarshBRC</u> - greensand from the Merchantville Formation obtained from the Bass River Corehole (1,430 feet below grade). Glauconite is blue green to dark bluish. Approximately 1 percent of the sample consists of foraminifera which are whole and fragmented, and mollusca fragments. Approximately 3 percent of sample is transparent (some greenish incipient glauconite(?)), angular to subangular, very fine to fine quartz sand to very coarse quartz silt. Approximately 0.5 percent is pyrite with some marcasite with a bright metallic, silvery luster. Most of the pyrite is oxidized (dark gold with some iridescence due to oxide staining). Some glauconite clasts encase pyrite, have pyrite inclusions, or have pyrite-filled cracks. Some bioturbation features (for example feeding traces; tubules) are completely replaced by submicroscopic to microscopic framboidal pyrite. Sample sent for analysis has ~1 percent foraminifera and mollusca fragments, and ~2 percent quartz sand and significant pyrite.

ſ