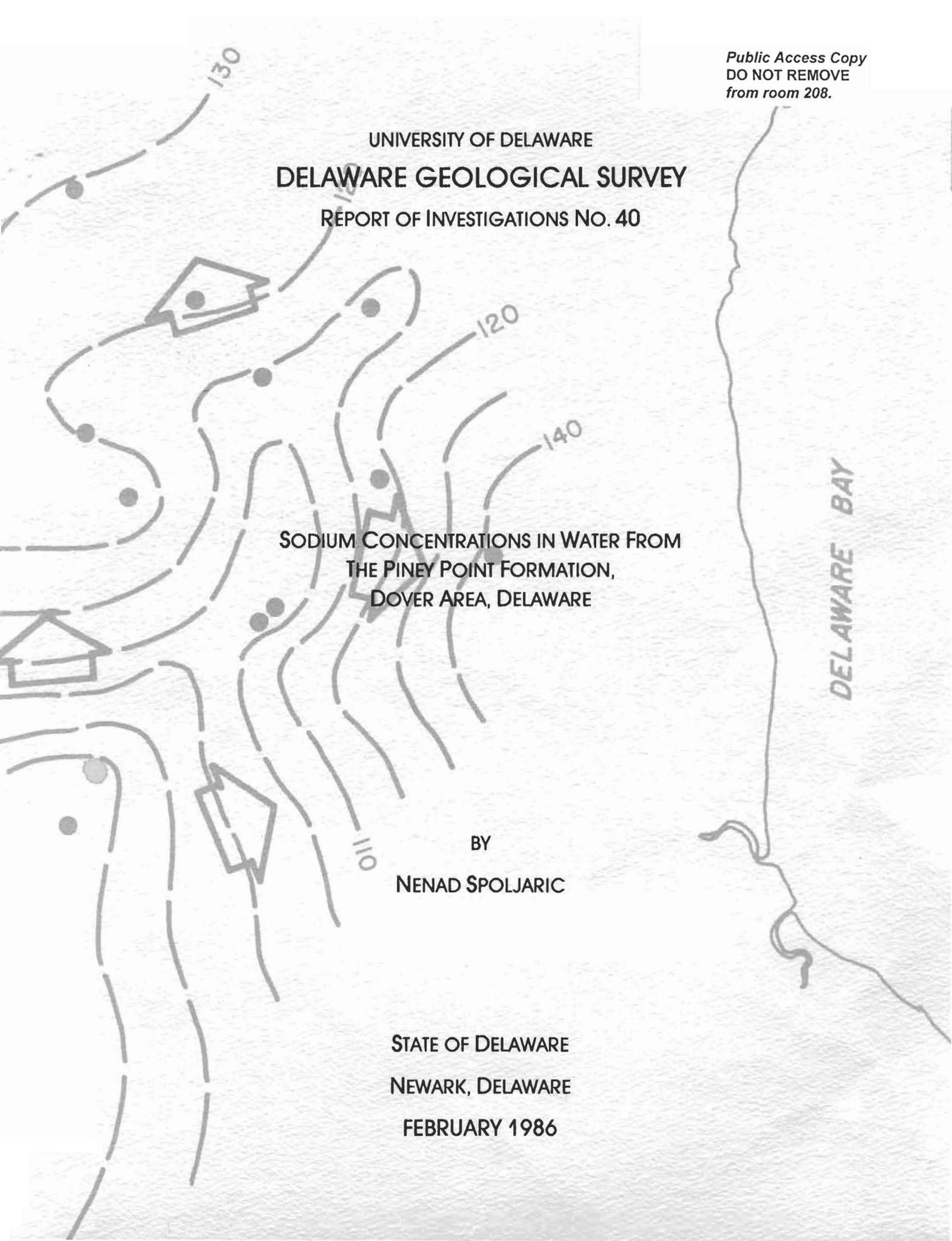


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UNIVERSITY OF DELAWARE  
**DELAWARE GEOLOGICAL SURVEY**  
REPORT OF INVESTIGATIONS No. 40

**SODIUM CONCENTRATIONS IN WATER FROM  
THE PINEY POINT FORMATION,  
DOVER AREA, DELAWARE**

BY  
**NENAD SPOLJARIC**

STATE OF DELAWARE  
NEWARK, DELAWARE  
FEBRUARY 1986

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## CONTENTS

	Page
ABSTRACT. . . . .	1
INTRODUCTION. . . . .	1
ACKNOWLEDGMENTS . . . . .	2
GEOLOGIC AND HYDROLOGIC CHARACTERISTICS OF THE PINEY POINT FORMATION . . . . .	2
PRESENT INVESTIGATION . . . . .	6
Methods. . . . .	6
Results. . . . .	6
DISCUSSION. . . . .	10
Sources and Characteristics of Sodium and Calcium. . . . .	10
Sodium. . . . .	10
Calcium . . . . .	11
CONCLUSIONS . . . . .	11
REFERENCES. . . . .	14

## FIGURES

Figure 1. Location of the study area . . . . .	3
Figure 2. Thickness distribution of the Piney Point Formation in the study area . . . . .	5
Figure 3. Graph of negative correlation between $\text{Na}^+$ and $\text{Ca}^{+2}$ . . . . .	8
Figure 4. Areal distribution of sodium concentration in the ground water of the aquifer of the Piney Point Formation. . . . .	12

## TABLES

Table 1. Chemical Analyses . . . . .	7
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# SODIUM CONCENTRATIONS IN WATER FROM THE PINEY POINT FORMATION, DOVER, DELAWARE

## ABSTRACT

In the greater Dover area sodium concentrations in ground water from the glauconitic Piney Point Formation commonly exceed 100 parts per million. Investigation of chemical characteristics of the water, and statistical analyses of the results, show that these high concentrations are due to a natural ion-exchange process. Calcium in water replaces sodium in the mineral glauconite and causes the sodium enrichment in ground water.

The mass of sodium in the glauconite fraction of the Piney Point Formation was calculated to be about 14,500 tons. Most of this sodium is available for exchange by calcium. However, as a result of extensive pumpage of water from the Piney Point Formation, a large cone of depression has developed which causes sodium-enriched water from the formation outside of the study area to be drawn into the greater Dover area. Thus, the actual mass of sodium available for the exchange process greatly exceeds 14,500 tons.

At present there is no method to stop or reverse this natural process. Sodium is considered generally safe for human consumption. Therefore, people who are on low-sodium or sodium-free diet are advised either to utilize appropriate filters to remove sodium from drinking water or to look for alternate sources of water suitable for their diet.

## INTRODUCTION

This study was initiated in response to reports by the State Division of Public Health (R. B. Howell, personal communication) of abnormally high sodium content in some ground-water samples taken from the aquifer of the Piney Point Formation in the City of Dover and surrounding area. Concentrations in excess of 100 parts per million (ppm) have been recorded.

Sodium is an essential nutrient in the diet of higher animals and humans because it regulates the composition of body fluids. The depletion of sodium may result in serious health problems. Some of the symptoms are lassitude, muscle cramps, and mental disorders (Lindsay, 1968). Too much sodium poses a hazard

for people with special health conditions requiring consumption of low-sodium or a sodium-free diet (R. B. Howell, personal communication).

This dual importance of sodium in human consumption makes it necessary to investigate high sodium concentrations in ground water in the greater Dover area in more detail.

The purpose of the present study is to attempt to explain both the source of the sodium and the process responsible for its anomalously high concentrations. It will also report the major present trends of sodium increase and discuss possible future trends.

#### ACKNOWLEDGMENTS

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I also thank my colleagues R. R. Jordan, T. E. Pickett, J. H. Talley, and K. D. Woodruff, Delaware Geological Survey, for reviewing the original manuscript.

#### GEOLOGIC AND HYDROLOGIC CHARACTERISTICS OF THE PINEY POINT FORMATION

The Piney Point Formation is one of the most readily recognizable units in central Delaware. It was first identified in Delaware in a well at the Dover Air Force Base (Je32-04) by Rasmussen *et al.* (1958). In the present study area (Figure 1) the formation is primarily composed of medium-grained sand that coarsens upward through the section.

The sand is a glauconitic greensand due to the presence of about 30-35% of the mineral glauconite in the sand. The other common mineral is quartz, also about 35% of the sand. Quartz tends to be more abundant in the upper part of the formation (Benson, *et al.*, 1985).

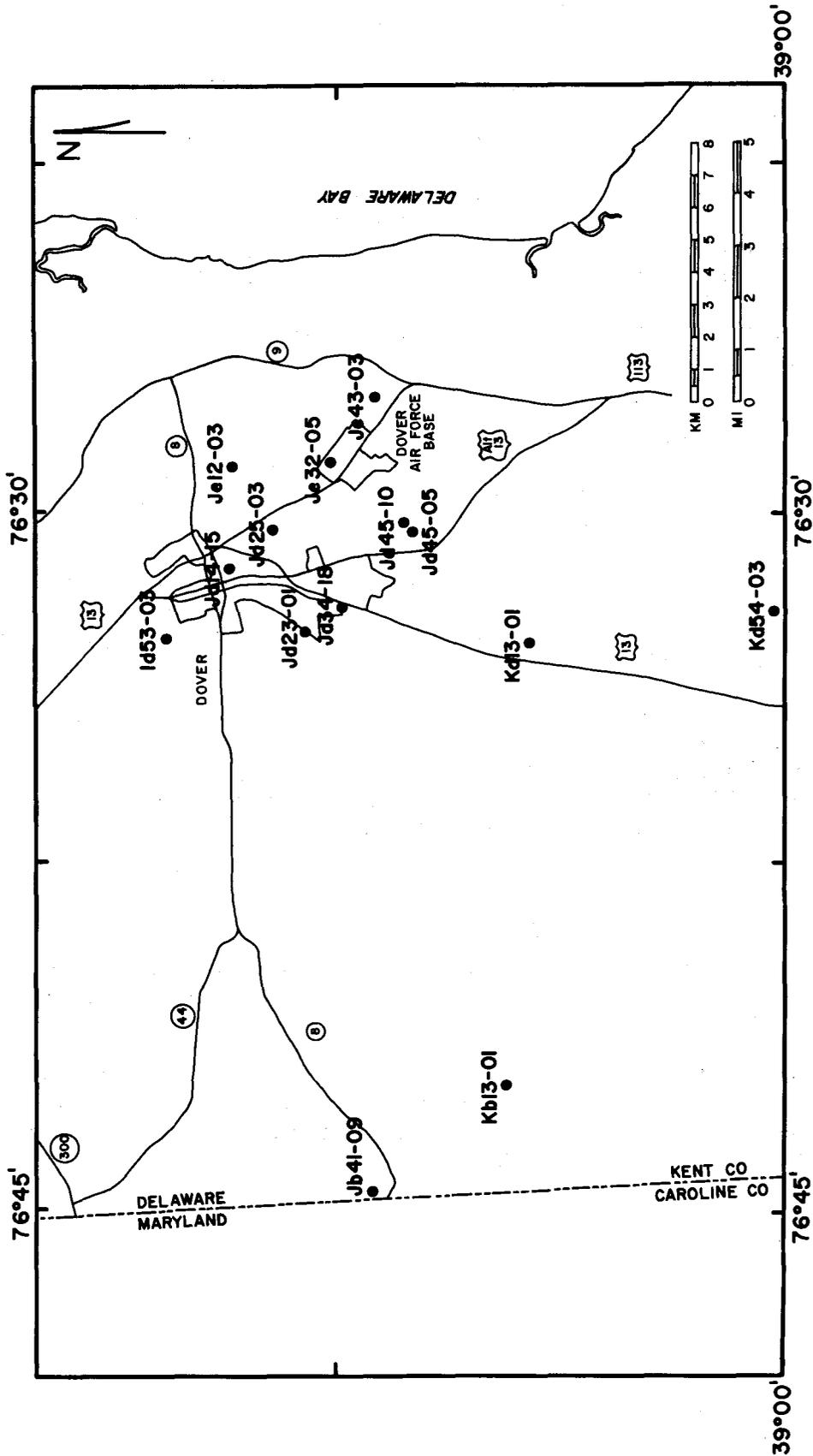


Figure 1. Location of the study area. Water samples for chemical analyses were obtained from the wells shown on the map.

The glauconite is usually both finer-grained and better sorted than quartz. It is primarily developed in roughly spherical, polylobate forms although elongate, platy pellets are also present. The color of the glauconite is usually dark green and the pellets display typical microcrystalline texture.

The Piney Point Formation ranges in age from middle Eocene to late Oligocene and is believed to represent a regressive prograding shelf sand (Benson *et al.*, 1985). The thickness distribution is shown in Figure 2 (Spoljaric *et al.*, 1976).

In most of the study area the entire Piney Point Formation is a usable aquifer. In fact, it is the main source of water supply for the City of Dover and surrounding communities.

Before pumping, the hydrologic system of the aquifer was in equilibrium and the aquifer was recharged from overlying aquifers in updip areas. Water moved laterally through the aquifer and was discharged in the downdip areas (Leahy, 1979).

Pumping has resulted in the development of a large cone of depression centered around Dover. The aquifer is recharged by vertical leakage through adjacent confining beds and overlying aquifers in updip areas (Leahy, 1979).

Based on the results of a 23-day test, and assuming leaky artesian conditions, Leahy (1976) determined that the transmissivity of the aquifer and its storage coefficient are 4,100 ft<sup>2</sup>/d (or 31,000 gal/d/ft) and  $3 \times 10^{-4}$  respectively. Employing different methods, Leahy was also able to determine that vertical conductivity of the confining bed ranges between  $4 \times 10^{-5}$  and  $9 \times 10^{-5}$  ft/d, and specific storage between  $3 \times 10^{-6}$  and  $6 \times 10^{-6}$ /ft.

These summary results should be taken with caution because the values vary throughout the study area. Additional information can be obtained from Leahy (1976, 1982).

In 1985 pumpage from the Piney Point in the greater Dover area was about 3 million gallons of water per day (Phillip Cherry and Caroline Webber, Department of Natural Resources and Environmental Control; personal communication).

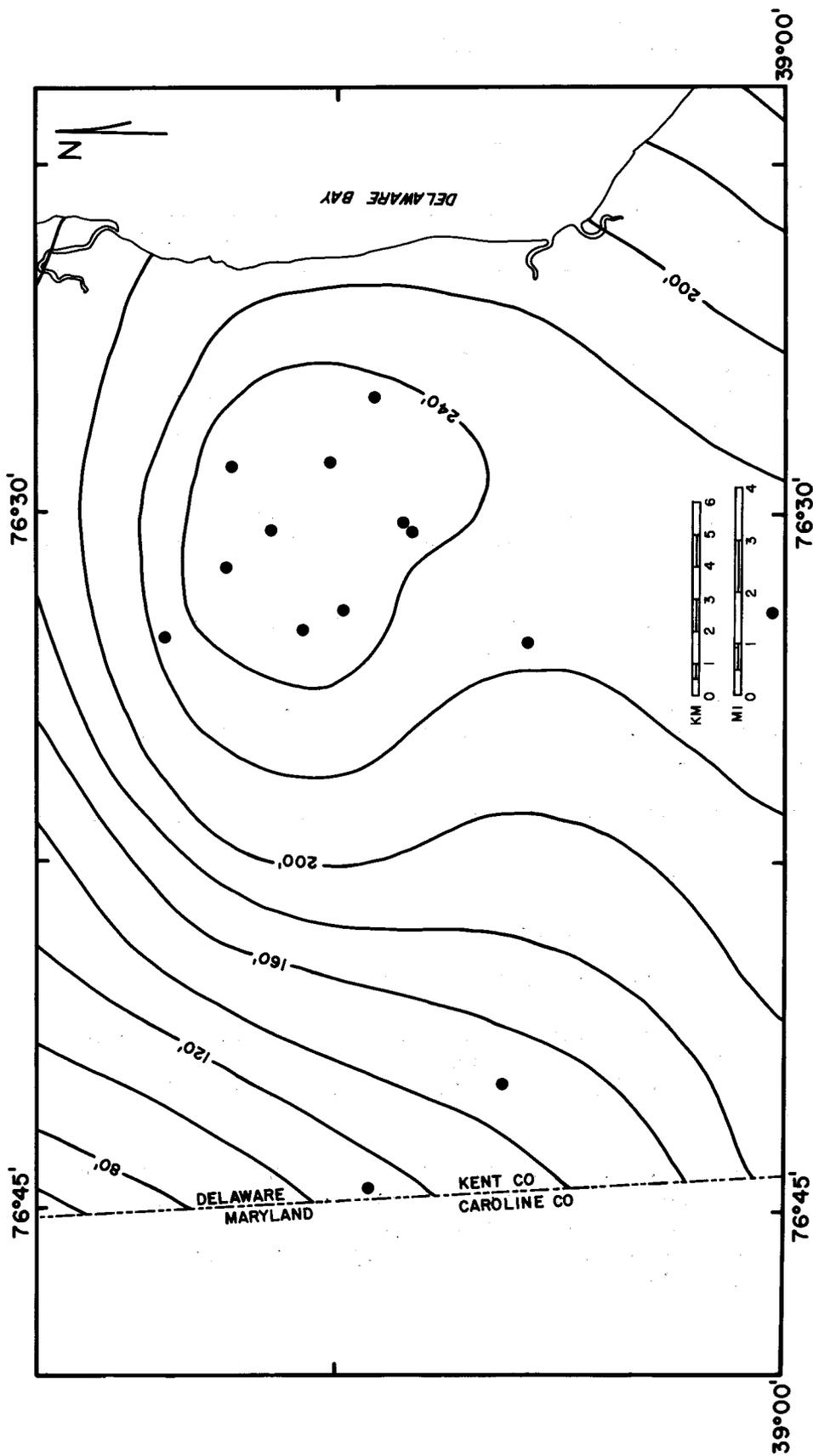


Figure 2. Thickness distribution of the Piney Point Formation in the study area. (Thickness contours in feet: Spoljaric, et al., 1976.)

## PRESENT INVESTIGATION

### Methods

Samples of two liters of untreated water were collected from wells shown in Figure 1. Immediately after collection the samples were acidified with nitric acid to a pH of about 3. The original pH of all the samples was rather consistent and ranged between 7.9 and 8.1.

Chemical analyses were done by flame atomic absorption spectrophotometry. Each sample was analyzed for sodium (Na), potassium (K), calcium (Ca), and iron (Fe). To reduce various interferences the following treatments of the samples were performed prior to analysis.

To suppress ionization of sodium in air-acetylene flame, potassium chloride was added to give a final concentration of 2000 ppm potassium in all solutions.

To suppress potassium ionization, cesium nitrate was added to give a final concentration of 1000 ppm cesium in all solutions.

To overcome the interference by calcium ionization in nitrous oxide-acetylene flame, potassium in concentration of 5000 ppm was added to all solutions.

Iron was analyzed in air-acetylene flame and no suppressants were necessary.

### Results

Results of chemical analyses are shown in Table 1.

The results clearly show that sodium concentrations are not related to either iron or potassium content of the samples. However, a good negative correlation is apparent between Na and Ca concentrations.

Statistical analyses of Na and Ca data also indicate strong mutual dependence of the concentrations of the two cations, as shown by high correlation coefficient (0.8) and the two regression lines (without regard to the selection of independent and dependent variable; Figure 3).

Table 1  
Chemical Analyses\*

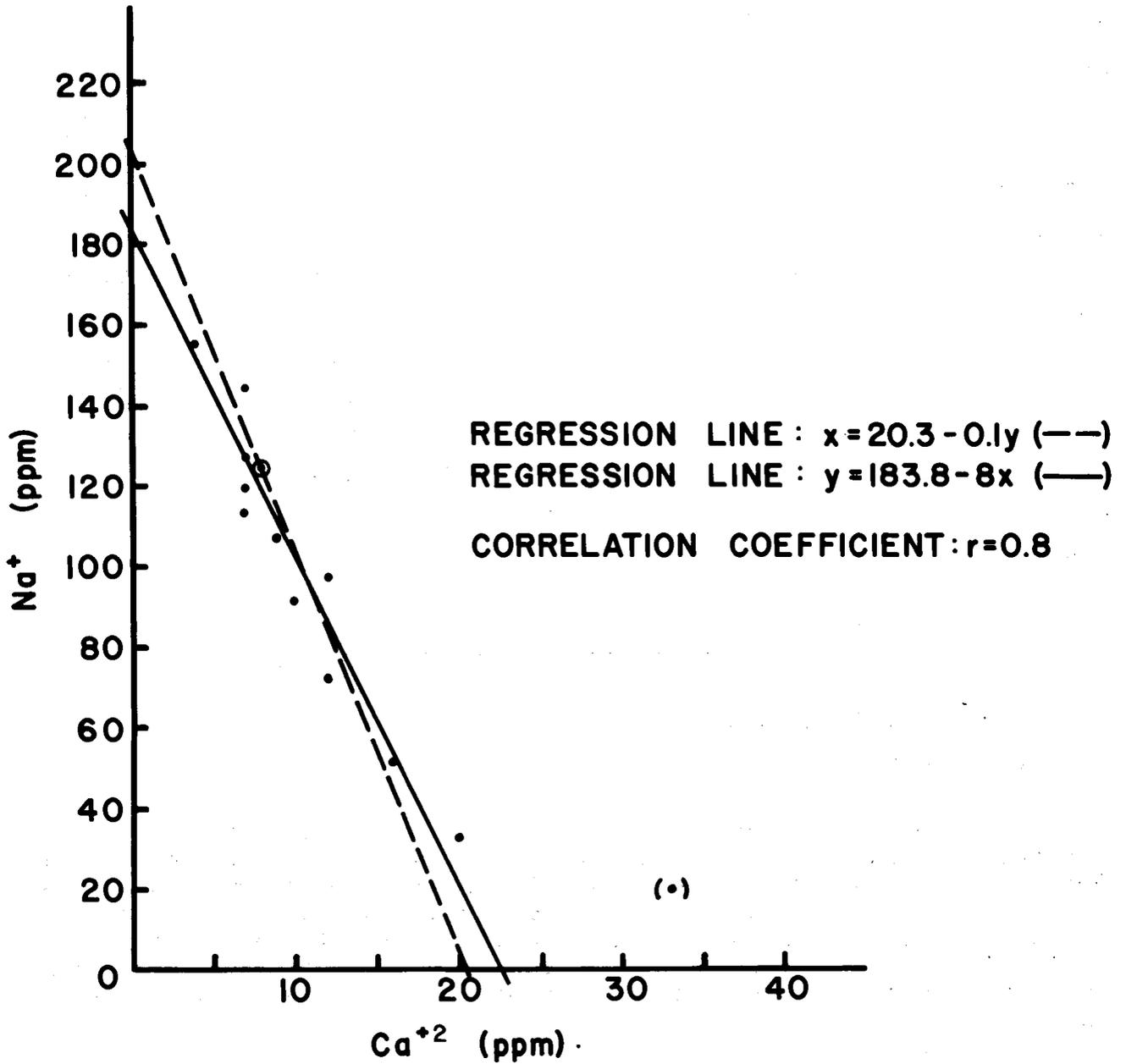
Well Number	Na	Ca	K	Fe
Id53-03	128	7	5.1	N/D**
Jb41-09	84	33	5.0	0.9
Jd14-15	125	8	5.2	0.3
Jd23-01	120	7	5.1	0.5
Jd25-03	33	20	2.4	2.5
Jd34-18	125	8	5.5	0.2
Jd45-05	98	12	6.7	0.05
Jd45-10	92	10	6.7	1.3
Je12-03	108	9	5.6	0.6
Je32-05	114	7	6.6	5.7
Je43-03	145	7	6.7	0.3
Kb13-01	157	4	4.9	0.2
Kd13-01	52	16	6.4	0.2
Kd54-03	73	12	6.5	0.05

\* parts per million (ppm)

\*\* not detected

Low potassium concentrations suggest that ground water is not the original sea water in which the Piney Point sediments were deposited. Thus, it appears that high sodium concentrations are due to a natural ion exchange process by which calcium from ground water replaces sodium in the Piney Point sediments releasing sodium in solution. However, for the process to be feasible, the sediments must contain minerals capable of exchanging sodium for calcium.

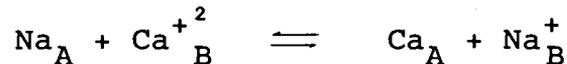
Figure 3. Graph of negative correlation between  $\text{Na}^+$  and  $\text{Ca}^{+2}$ .  
 In the regression line equations  $X = \text{Ca}^{+2}$  and  $Y = \text{Na}^+$ .  
 ⊙ Coincidence of two data points.  
 (.) Anomalous data point, possible contamination.



The most likely minerals with this ability are clays. The predominant sodium-bearing clay mineral present in sufficient amounts in the Piney Point Formation and having ion-exchange capacity is the glauconite.

It is, therefore, concluded that glauconites from the sediments and calcium from the ground water participate in the process.  $\text{Ca}^{+2}$  from ground water replaces sodium in the crystal structure of glauconite. Calcium is retained by the glauconite while sodium is released in ground water resulting in anomalously high  $\text{Na}^+$  concentrations. The exchange is possible because both sodium and calcium atoms are of similar sizes.

The precise mechanisms of cation exchange reactions are not well understood. It is known, however that the reactions involve the displacement of cations from mineral surfaces and their replacement by different cations from water solution. In the present case the exchange can be presented in the following simplified form:



Explanation:

(A) - in glauconite; (B) - in water solution.

How much longer can this Na-Ca exchange process continue? Making some very general assumptions, the amount of sodium in the Piney Point Formation can be estimated.

The volume of the Piney Point sediments, assuming an average thickness of the formation in the study area of 180 feet and porosity of 20 percent, is about 250 million  $\text{ft}^3$ . On the average, glauconite makes up about 33 percent of the sediments and its total volume is about 83 million  $\text{ft}^3$ . Assuming specific gravity of glauconite to be about 2.7, the mass of all the glauconite in the formation in the study area is about 6,300,000 tons. Taking into account the  $\text{Na}_2\text{O}$  contents of glauconite (0.14 to 0.48 weight percent) and atomic weights of sodium (22,9898) and oxygen (15,9994) it can be shown that the total weight of sodium in the Piney Point Formation in the study area is about 14,500 tons. It is also important to point out that because of the large cone of depression centered around Dover, continuous pumping draws in ground water from the Piney Point Formation outside of the study area. Thus, the total amount of sodium available for the exchange greatly exceeds the 14,500 tons calculated for the study area.

Although the results of the above calculations are very inexact and general, we can conclude that an ample amount of sodium is available for Na-Ca exchange process to continue for a long time.

## DISCUSSION

### Sources and Characteristics of Sodium and Calcium

#### Sodium

The source of sodium in ground water of the greater Dover area is differentiated from other possible sources and ascribed to naturally occurring glauconite.

The most common sources of sodium in ground water are sodium-bearing minerals present in various rocks. Sodium is released from these minerals by percolating water during the weathering process. It is present in solution primarily in the form of  $\text{Na}^+$  ion. This form is most common in concentrations below about 1,000 ppm. However, if concentrations are considerably higher, a variety of very complex sodium ions may develop and remain stable in solution (Hem, 1985).

The actual concentration depends primarily on types of sodium-bearing minerals being weathered and chemical characteristics of percolating water. Although the sodium content of ground water is usually only a few parts per million, concentrations exceeding 100,000 ppm have been reported from some areas containing various sodium salts (Hem, 1985).

Some rocks are known to contribute sodium to ground water much more readily than the others. For example, in coarse-grained sediments of high porosity and permeability and containing Na-bearing minerals, sodium can be easily released in solution thus leaving the sediments poor in sodium. On the other hand, very fine-grained deposits, such as highly compacted clays with low porosity and low permeability, can retain sodium for long periods of time.

In recent years considerable amounts of sodium have been added to ground water by various human activities. A good example is the use of large amounts of salt ( $\text{NaCl}$ ) in winter for deicing roads and highways. Much sodium from this activity ends up not only in ground water but also in surface water.

Pumping of ground water by communities in coastal areas may bring about a change in hydraulic gradient and cause movement of sodium-rich sea water toward pumping wells in fresh-water aquifers.

Disposal of various chemical and other wastes containing sodium may also contribute significant amounts of sodium to ground-water supplies.

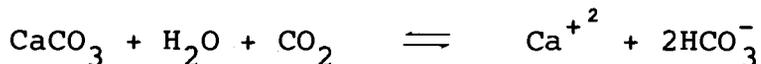
Although these are among the most important natural and artificial causes leading to higher than normal sodium concentrations in ground water, there are numerous other activities which individually may appear insignificant, but their cumulative affect could be considerable.

### Calcium

Calcium is present in rocks primarily as calcium carbonate, calcium sulfate, calcium phosphate, calcium-magnesium carbonate, and some other calcium-bearing minerals, primarily silicates.

Almost all natural waters contain either calcium carbonate or calcium sulfate or both. Many organisms concentrate calcium from water in their shells or skeletons. For example, calcium carbonate is formed in shells of many marine organisms, whereas calcium phosphate is a major component of the bones of animals.

Considerable amounts of calcium carbonate dissolve in water in the presence of carbon dioxide:



Unlike sodium, which does not have important precipitation reactions that can maintain low sodium concentration in water, calcium concentrations are controlled by specific carbonate precipitation reactions (Hem, 1985).

### CONCLUSIONS

The areal distribution of sodium concentrations in the study area is shown in Figure 4. The major trends of sodium increase are indicated by arrows.

Considering the fact that the aquifer is the most important source of water supply in the Dover area, and is being extensively pumped, the distribution and concentration of sodium

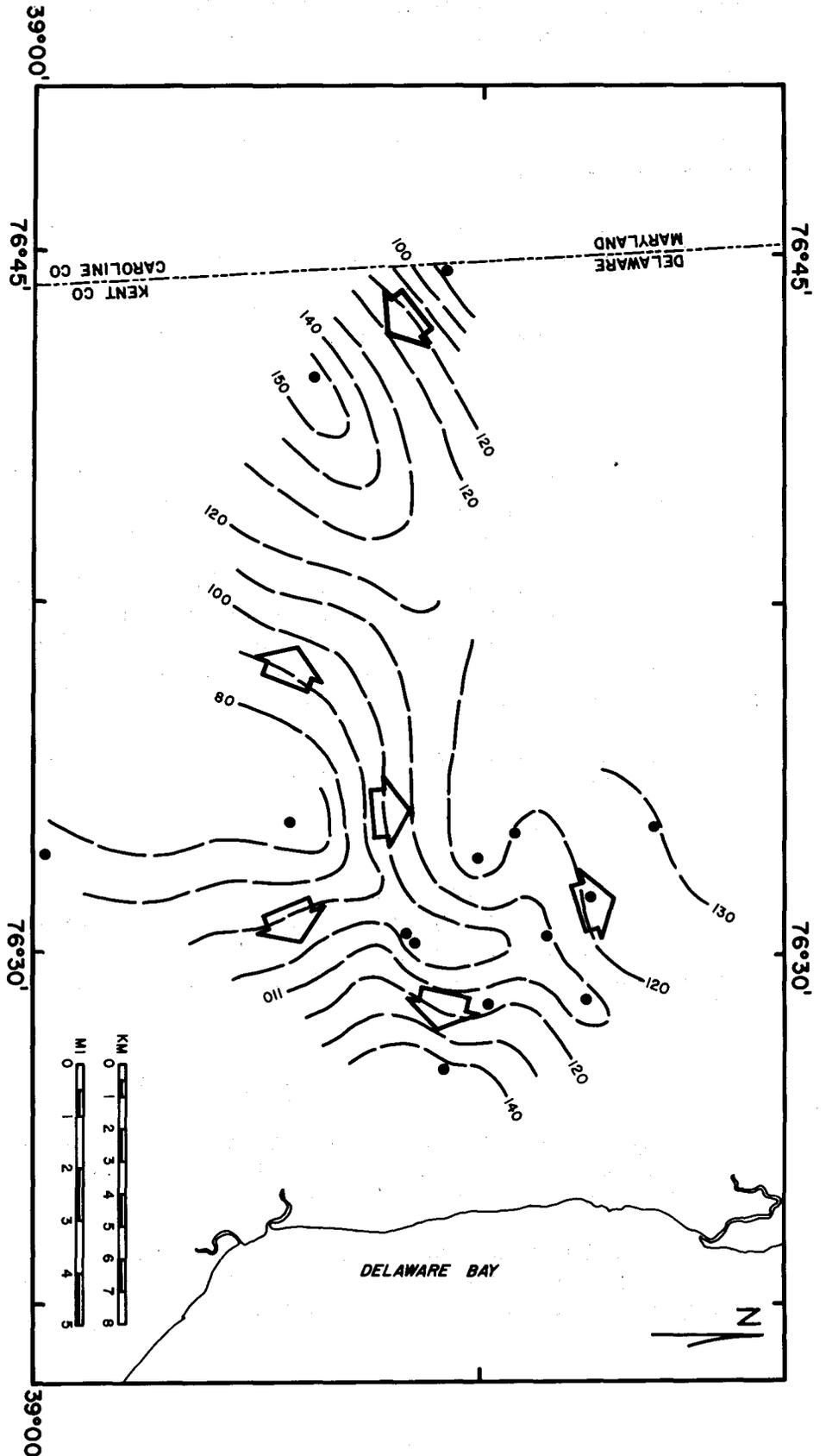


Figure 4. Areal distribution of sodium concentration in the ground water of the aquifer of the Piney Point Formation. Arrows indicate major trends of sodium increase.

occur in a constantly changing hydrologic system. Therefore, the map is simply a representation of the situation at the time when the study was conducted.

Cumulative affects of uneven pumpage and sediment transmissivities are most likely the main causes of continuing changes in both concentrations and trend directions of sodium distributions.

Based on the results of the present study it is impossible to predict future trends of sodium concentration. If indeed the trends are related to pumpage variability and sediment transmissivities, a more definitive relationship of these variables and sodium concentrations could be established by additional studies in the area conducted at predetermined time intervals in the future.

As pointed out elsewhere in this report, the high sodium concentrations are due to a natural cation exchange process. At the present state of knowledge there is nothing we can do to stop or reverse the process.

This Na-Ca exchange process is in fact quite common in many areas and results in natural softening of ground water. It is particularly prevalent in areas where clays are abundant (Lehr *et al.*, 1980). In the Piney Point Formation the clay occurs in permeable form (glauconite pellets) so that most of the unit also serves as a major aquifer.

The same process is employed in artificial water softening. If hard water containing  $\text{Ca}^{+2}$  is passed through a mineral Na-zeolite filter, Ca is retained by the zeolites and  $\text{Na}^{+}$  is released in solution.

The problem of relatively high sodium content in the eastern United States is much more common than usually assumed. Waters low in dissolved solids and in which calcium has been depleted and sodium increased through natural cation exchange processes, are indeed common in sediments of the Atlantic Coastal Plain (Hem, 1985).

For most people sodium is an essential nutrient in their daily diet. However, people whose health condition requires a low-sodium or sodium-free diet should look for alternate sources of drinking and cooking water, or utilize appropriate filters to remove sodium from the water.

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