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**PRELIMINARY STUDY OF ARSENIC CONCENTRATIONS
IN GROUND WATER AND BEDROCK
IN NORTHEASTERN SOUTH DAKOTA**

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INTRODUCTION

North Dakota Investigation

In 1979, the North Dakota State Department of Health sampled municipal water supplies for inorganic parameters and found that several public water supplies in southeastern North Dakota exceeded the maximum contaminant level for arsenic. The maximum contaminant level is set by the United States Environmental Protection Agency at 50 micrograms per liter (United States Environmental Protection Agency, 1994). The public water supplies at Lidgerwood, Wyndmere, and Rutland, North Dakota, all exceeded the maximum contaminant level for arsenic. The limit was exceeded occasionally at Wyndmere and Rutland and consistently at Lidgerwood. Aqueous arsenic has no visible color, taste, or odor, and small amounts of arsenic can be toxic to humans. Consequently, the potential health hazard of the water in this area was investigated. It was found that arsenic concentrations ranged from 0 to 1.56 milligrams per liter, and it was determined that 1,719 persons were at an increased risk of chronic arsenosis from contaminated ground water (Roberts and others, 1985).

In the fall of 1987, the state of North Dakota contacted South Dakota and Minnesota about the possibility of investigating the distribution of arsenic in the tri-state region. A joint meeting was held and it was decided that all three states would: 1) review existing data, 2) obtain new data, as time and financing allowed, and 3) meet again in about a year to review all data.

Purpose

The state of South Dakota initiated a preliminary investigation in Marshall and Roberts Counties to: 1) determine if anomalous concentrations of arsenic were present in the ground water and 2) determine the natural arsenic concentration of the bedrock in the area. This information could be used to evaluate possible health hazards. The primary purpose of this report is to present the data gathered in South Dakota.

Health Concerns

Arsenic is a naturally occurring element present in minor amounts both in water and rocks. Small amounts of arsenic can be toxic to humans but toxicity varies with different oxidation states of arsenic. Chronic arsenosis results from long-term exposure to elevated levels of arsenic. The quantity ingested and the length of time since ingestion are also important factors that affect toxicity.

Arsenic in Rocks

Arsenic is naturally concentrated in some mineral and rock types. For example, arsenic readily substitutes for silicon, ferric iron, and aluminum in silicate minerals (Onishi and Sandell, 1955). As a result, arsenic concentrations tend to be higher in rock types that contain an abundance of volcanic glass or aluminosilicate minerals and in igneous rocks containing iron oxide. Sedimentary rocks

generally contain higher concentrations of arsenic than igneous and metamorphic rocks (Welch and others, 1988).

Cretaceous age shales and till are the most common lithologies of the study area in South Dakota. Till, a component of glacial drift, is the nonsorted, nonstratified sediment deposited by glaciers. Till contains sand to boulder-sized clasts in a very compact, silty, clay-rich matrix reflecting the predominance of shale in the local Cretaceous bedrock of South Dakota. The till and shales of southeastern North Dakota contain 5 to 21 parts per million of arsenic (Roberts and others, 1985). According to Welch and others (1988, page 334):

"The capacity of a sediment to retain and concentrate arsenic is generally controlled primarily by grain size (Horowitz, 1984), because smaller grain sizes have a greater surface area and a greater adsorption capacity per unit weight. Clay minerals, organic matter, and iron and manganese oxides, which commonly occur as coatings on sediments, commonly adsorb trace elements such as arsenic."

Arsenic in Ground Water

The geochemistry of arsenic is complex and is affected by a number of different factors including pH, Eh, solution composition, complexing ions, aqueous mineralogy, reaction kinetics, and the hydraulics of the ground water system. The major geochemical processes that control aqueous concentrations are adsorption and desorption processes associated primarily with clay minerals, chemical transformations, ion exchange, and microbial action.

The source of arsenic in ground water is generally attributed to the arsenic concentration of various rock types. High concentrations in ground water are generally associated with one of four geochemical environments: 1) basin-fill deposits of alluvial-lacustrine origin, particularly in semiarid environments, 2) volcanic deposits, 3) geothermal systems, and 4) uranium and gold-mining areas (Welch and others, 1988). Insufficient hydrogeologic information was available to indicate that the rock types and sediments in North Dakota were the major source of arsenic contamination (Roberts and others, 1985).

Arsenic may also be concentrated in water supplies through nonnatural means such as the application of arsenic-laced bait to the land surface or the improper disposal of arsenic-containing compounds. Reportedly large amounts of arsenic-laced grasshopper bait were used in the Dakotas during the 1930s and 1940s. It has been suggested that contamination from bait could be the source of the arsenic contamination. However, no bait-disposal sites were confirmed in southeastern North Dakota, and remnant contamination at one known application site did not occur. It was concluded that bait alone could not be the sole source of contamination in southeastern North Dakota (Roberts and others, 1985).

PHYSICAL SETTING

Geography

The study area (fig. 1) is located in northeastern South Dakota. Topographically, the study area is dominated by the northernmost part of the Coteau des Prairies, a flat-iron shaped highland constructed by successive glaciations. The Coteau des Prairies separates the James River basin to the west from the Minnesota River basin to the east. To the north, the Coteau des Prairies bisects a portion of the Red/Rainy River basin. Both the James and Minnesota basins drain to the Gulf of Mexico but the Red/Rainy basin drains to Hudson Bay.

Climate

Northeastern South Dakota has a continental-type climate characterized by long cold winters and warm summers. The average annual temperature in the study area is 44°F and the average annual precipitation is 21 inches (Spuhler and others, 1971).

Geology

The oldest (Precambrian) rocks of northeastern South Dakota consist primarily of granitic rocks interspersed with small areas of metamorphic rocks. Samples collected during an investigation of Marshall County (Koch, 1975) indicate the presence of fresh granite as well as highly weathered granite. The highly weathered granites contained feldspars and accessory minerals that have been altered to a green clay containing quartz (Koch, 1975).

Bedrock above the Precambrian surface consists of up to 1,000 feet of Cretaceous rocks, from the Dakota Formation (sandstone) to the Pierre Shale (fig. 2). Many Cretaceous shales in South Dakota contain volcanic ash layers. No Tertiary rocks have been found in the study area. Pleistocene glacial drift up to 1,000 feet thick caps the Cretaceous sequence in most of the study area.

Geologic studies of Marshall and Day Counties have been published and are recommended for more detailed information about the geology of and near the study area (Koch, 1975; Leap, 1988). An investigation of the geology and water resources of Roberts County is currently in progress (Tomhave, in prep.). Additional information about Richland County, North Dakota, is available in Baker (1967), and the geology of Ransom and Sargent Counties is available in Bluemle (1979).

Hydrogeology

The study area contains several major aquifers. An aquifer is defined as a formation from which water may be obtained in useful quantities. The primary bedrock aquifer is the sandstone of the Dakota Formation. To a lesser extent, the Greenhorn Limestone and the limestone of the Niobrara Formation may be utilized. The glacial drift within the study area contains many aquifers. Glacial aquifers consist primarily of sand or sand and gravel which was deposited as outwash from melting glacial ice.

For additional information on the water resources of the study area please refer to Hedges and others (1982), Koch (1975), and Leap (1988). For additional information north of the South Dakota study area (in North Dakota) please refer to Baker and Paulson (1967) and Armstrong (1982).

METHODS

Sisseton Core

In May and June 1988, continuous core samples were collected in a test hole from a depth of 7 to 1,085 feet below land surface at a location near Sisseton (fig. 1). The legal location of the coring site is SE SE SW SE sec. 25, T. 126 N., R. 52 W. The core hole was permanently plugged in the fall of 1989.

Five-foot channel samples were obtained from the core. A channel sample is a composite sample of 5 feet of core. Depending on the hardness of the rock, samples were collected continuously by either shaving the outside length of the core or hand drilling through the interior of the core. The brazing alloy, masonry drill shanks, and masonry drill bits used for drilling samples did not contain arsenic (Carl Shumaker, Jr., Vermont American Company, written communication, 1989).

Prior to grinding, the channel samples were split in approximately 20-ounce size samples. All samples were hand ground and passed through sieves down to a mesh size of 100. Geochemical analyses of every other 5-foot channel sample were completed by the United States Geological Survey. Some additional analyses for iron and manganese were completed by the South Dakota Geological Survey.

Water Samples

Municipal Water Supplies Database

The state of South Dakota analyzes water samples from each municipal water supply on a regular basis. Procedures for collection and preservation are documented with the Department of Environment and Natural Resources in Pierre. The results are presented annually in a bulletin published by the Office of Drinking Water, Department of Environment and Natural Resources entitled *South Dakota Public Water System Data*. The arsenic concentrations in municipal well water for the incorporated towns in Roberts County and Marshall County were reviewed.

National Uranium Resource Evaluation Database

The National Uranium Resource Evaluation program was established in 1973 by the federal government to: 1) complete a comprehensive assessment of uranium reserves in the United States as rapidly as possible, 2) identify areas favorable for uranium resources, and 3) develop new and improved technologies. One part of the program consisted of a hydrogeochemical and stream sediment reconnaissance survey. The specific objective of this portion of the program was to determine the distribution of uranium and associated elements in surface and ground waters and in

stream sediments. In South Dakota, this program was coordinated by the Nuclear Division of Union Carbide Corporation. Study areas were assigned to correlate with 1x2 degree 1:250,000 scale United States Geological Survey quadrangle maps. The area of the South Dakota arsenic investigation is included within the Milbank quadrangle (Arendt and others, 1981). Water sample collection and analysis procedures were outlined by Union Carbide in two publications (1978a, 1978b). In South Dakota, all water samples were collected in July 1978. The water quality data were reviewed.

South Dakota Geological Survey Database

The South Dakota Geological Survey frequently collects water samples in the course of hydrogeologic studies. Sample collection, preservation, and analytical procedures used in this project are outlined in an unpublished South Dakota Geological Survey draft report (Coker, 1984). The computerized South Dakota Geological Survey database was searched for all water quality analyses in the study area.

Forty new water samples were collected by the South Dakota Geological Survey from wells in the study area. Well locations are shown on figure 1 and are listed in appendix A. Wells with previous arsenic analyses were selected for sampling. All other sampling locations were chosen using the following criteria: 1) approximately uniform geographic distribution of sampling points, 2) use existing South Dakota Geological Survey or United States Geological Survey observation wells if possible (these wells were given preference over private wells because more information about the well was generally available), and 3) collect at least one sample from each aquifer (as defined by Hedges and others, 1982) in each drainage basin.

All 40 samples were collected, treated, and analyzed in accordance with Coker (1984). The samples were analyzed by the South Dakota Geological Survey laboratory in Vermillion for major and trace element concentrations.

RESULTS

Sisseton Core

A generalized stratigraphic description of the Sisseton core is shown in figure 2. On request, a more detailed description of the Sisseton core made by researchers at the University of Nebraska at Lincoln is available from the South Dakota Geological Survey.

Geochemistry screening scans of the core samples were designed to test for the presence or absence of arsenic at a level of 200 parts per million, the quantitation limit for this method. All of the samples contained less than 200 parts per million arsenic. The arsenic geochemical data and additional geochemical information are available from the South Dakota Geological Survey.

Water Samples

Municipal Water Supplies Database

Table 1 lists the arsenic concentrations in municipal well water for the incorporated towns in Roberts County. Table 2 lists the arsenic concentrations in municipal well water for the incorporated towns in Marshall County. The municipal water supply data indicate that all samples contained arsenic concentrations less than the maximum limit of 50 micrograms per liter for arsenic; the highest observed concentration was 14.0 micrograms per liter.

Table 1. Arsenic concentrations in municipal wells in the incorporated towns in Roberts County

Town	Concentration (in micrograms per liter)	Date sampled
Corona	<1.0	09/14/82
	<1.0	11/04/85
New Effington	<1.0	09/02/81
	1.6	09/25/84
Peever	3.8	09/14/81
	<1.0	06/11/85
Rosholt	5.8	02/10/82
	<1.0	04/02/85
Sisseton	3.1	02/01/83
	2.3	03/18/86
Summit	<1.0	10/28/81
	<1.0	11/29/84
Wilmot	1.5	09/09/81
	<1.0	09/27/84

Table 2. Arsenic concentrations in municipal wells in the incorporated towns in Marshall County

Town	Concentration (in micrograms per liter)	Date sampled
Britton	1.5	06/07/83
	<1.0	06/25/85
Eden	14.0	01/09/78
	14.0	12/19/83
Lake City	7.3	01/08/79
	7.9	11/05/83
Langford	1.3	10/30/80
	6.3	11/07/83
Veblen	<1.0	07/30/81
	3.7	12/05/84

National Uranium Resource Evaluation Database

No violation of the drinking water standard was observed in the water samples collected for the National Uranium Resource Evaluation from the Milbank quadrangle. As shown in table 3, the maximum arsenic concentration observed was 28.7 micrograms per liter and most of the samples (316 out of 346) had arsenic concentrations below the detection limit of 0.5 micrograms per liter.

Table 3. National Uranium Resource Evaluation data, Milbank quadrangle

<u>Statistical Parameter</u>	<u>Arsenic Value</u>
minimum value	<0.5 micrograms per liter
maximum value	28.7 micrograms per liter
mean	3.6 micrograms per liter
median	<0.5 micrograms per liter
standard deviation	4.53

From Arendt and others (1981)

South Dakota Geological Survey Database

The computerized South Dakota Geological Survey database was searched for all water quality analyses in the study area. Arsenic analyses were found to have been completed on only three samples prior to 1987. All three samples were collected from observation wells. Two of the three samples were collected from the same well. Arsenic concentrations of these three analyses ranged from <0.5 to 12.0 micrograms per liter.

The 40 new samples collected and analyzed by the South Dakota Geological Survey ranged in value from <1.0 to 69 micrograms per liter arsenic. Two samples from different wells exceeded the United States Environmental Protection Agency's limit of 50 micrograms per liter. Nineteen of the analyses contained between 10 and 50 micrograms per liter arsenic. Nineteen analyses contained less than 10 micrograms per liter arsenic. All water quality results are stored in a computerized data management system at the South Dakota Geological Survey in Vermillion, South Dakota. A list of the wells sampled by the South Dakota Geological Survey in order by legal location is given in appendix A.

SUMMARY

In summary, although some arsenic was detected in ground water samples from northeastern South Dakota, the results of this investigation did not reveal high levels of arsenic in ground water similar to those in southeastern North Dakota. The Sisseton core analyses yielded concentrations less than 200 parts per million arsenic. The meeting initially proposed to occur in about 1 year after inception of the project was never held.

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Figure 1. Locations of the study area, the Sisseton coring site, and wells sampled by the South Dakota Geological Survey.

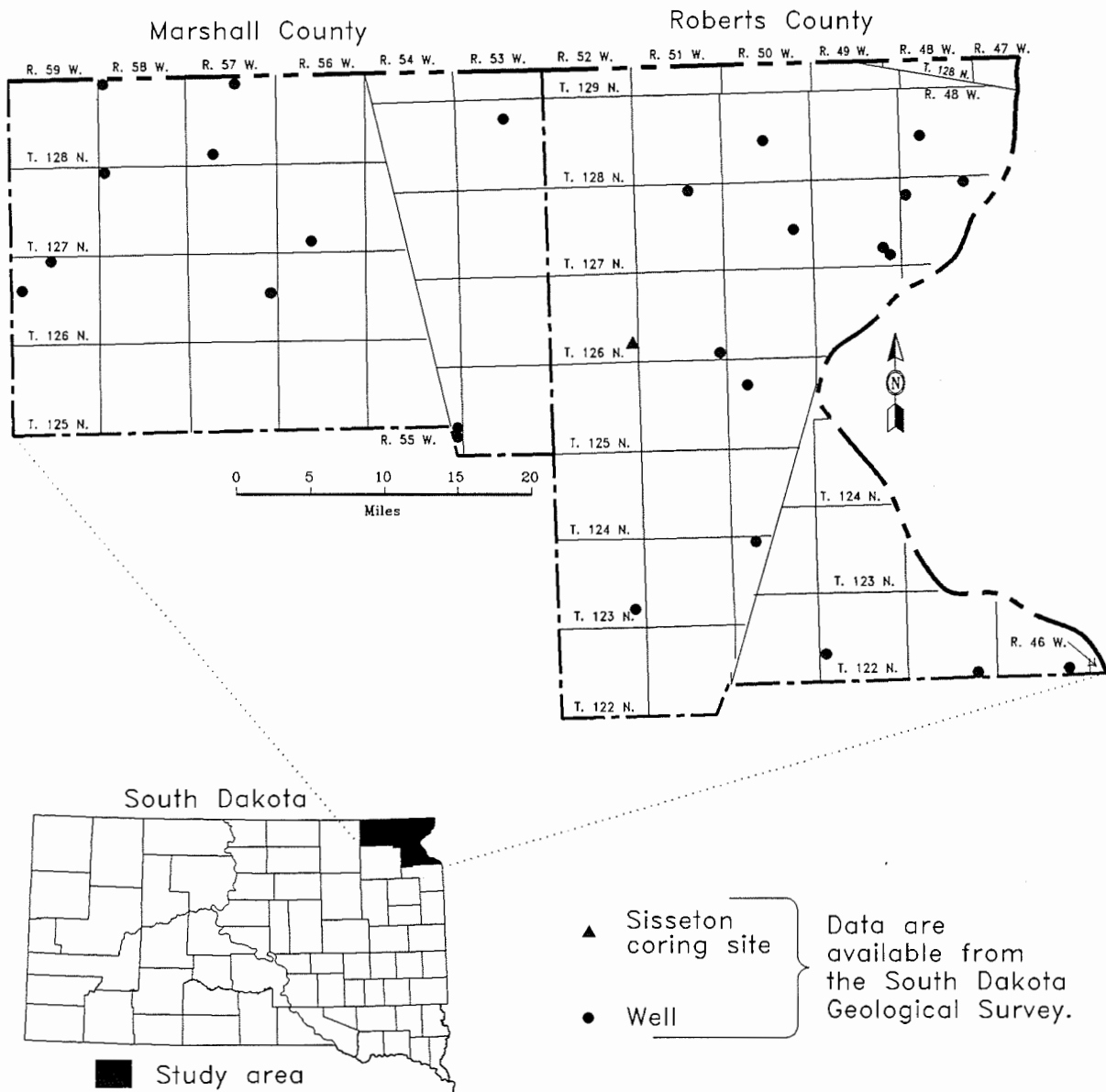
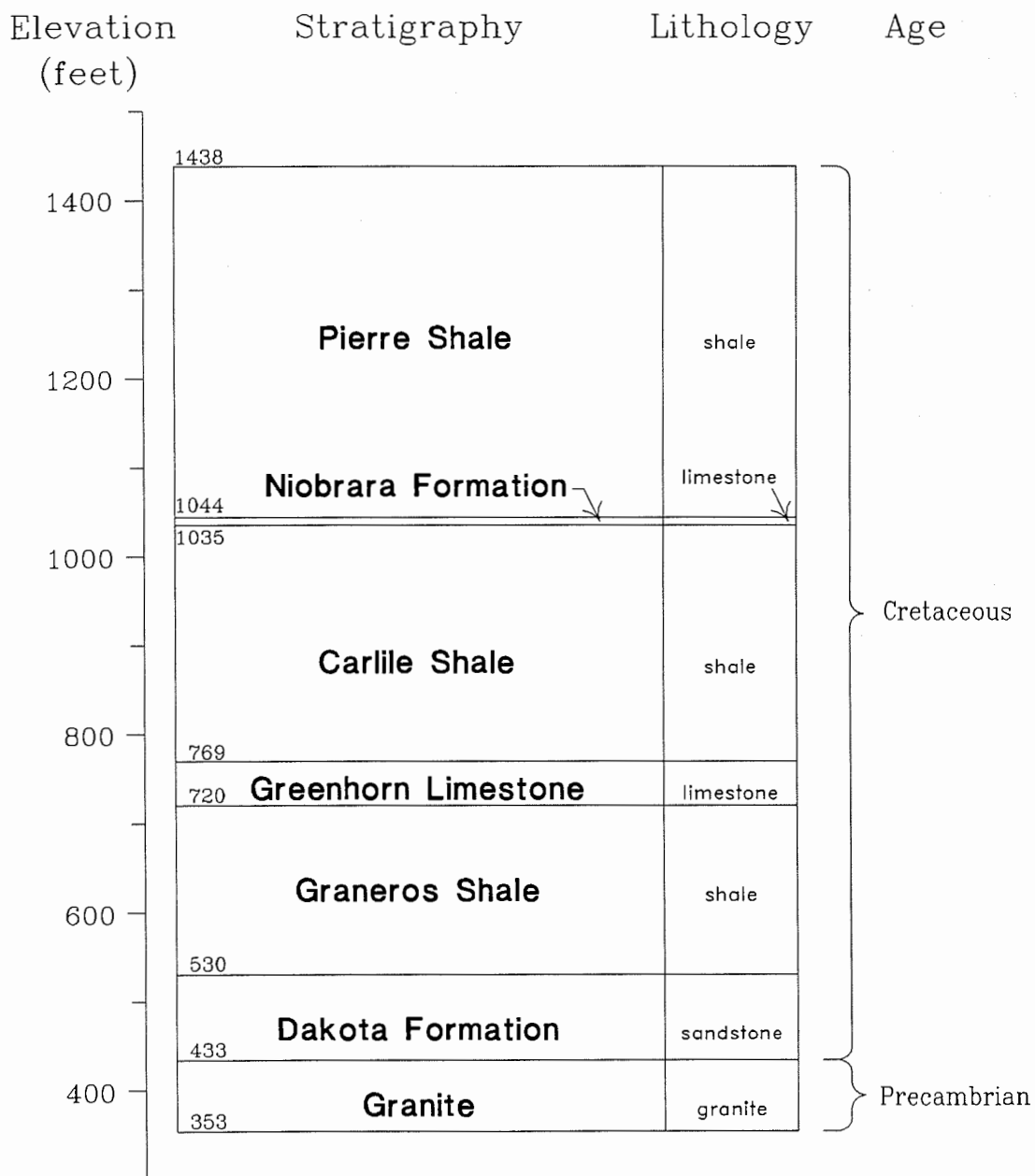


Figure 2. General stratigraphy of the Sisseton core.



APPENDIX A

List of South Dakota Geological Survey water sample locations

All locations of water samples collected by the South Dakota Geological Survey are listed in order by legal location according to a numbering system based on the federal land survey system used in South Dakota.

The location consists of township, range, and section numbers separated by hyphens, followed by a maximum of four letters that indicate, respectively, the 160-, 40-, 10-, and 2½-acre tract in which the water sample was collected. A serial number following the last letter is used to distinguish between data points in the same tract. An "R" following the serial number indicates that the sample was collected on reservation land. The sample locations are listed by smallest township number, then the smallest range number, the smallest section number, and then by quarter section: NE = A; NW = B; SW = C; SE = D. A comparison of a legal location and a location is as follows. A legal location of NW SE NE SW sec. 08, T. 106 N., R. 52 W. is the same as a location of 106N-52W-08CADB.

Please contact the South Dakota Geological Survey if a copy of a computerized water quality analysis is needed.

122N-47W-35DDCD	127N-48W-07BBBB 1R
122N-48W-35DDDD 2	127N-48W-07BBBB 2R
122N-49W-30BBBB	127N-49W-26DDDD R
123N-52W-25CCCC R	127N-49W-36BBBB R
124N-50W-05AAAD R	127N-50W-23AAAA
125N-50W-08CCCC 2	127N-51W-03AAAA R
125N-50W-08CCCC 3	127N-56W-33BBC 2
125N-54W-25ACC	127N-58W-06BBBB
125N-54W-25DBB	128N-48W-20BBBB R
126N-51W-36DCCC R	128N-50W-21AABA R
126N-57W-13DDDD	128N-53W-10BBBB R
126N-59W-04AAAA	128N-57W-03BBBB 2
126N-59W-18AAAD 1	128N-57W-32ADB
127N-48W-02BBBB R	128N-58W-06BBBB