



1938

The occurrence and distribution of selenium in North Dakota ground waters

Hjalmer V. Peterson
University of North Dakota

Follow this and additional works at: <https://commons.und.edu/theses>

 Part of the [Geology Commons](#)

Recommended Citation

Peterson, Hjalmer V., "The occurrence and distribution of selenium in North Dakota ground waters" (1938). *Theses and Dissertations*. 229.

<https://commons.und.edu/theses/229>

This Thesis is brought to you for free and open access by the Theses, Dissertations, and Senior Projects at UND Scholarly Commons. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of UND Scholarly Commons. For more information, please contact zeinebyousif@library.und.edu.

**THE OCCURRENCES AND DISTRIBUTION OF SELENIUM
IN NORTH DAKOTA GROUND WATERS**

**A Thesis Submitted to the Graduate Committee of the
University of North Dakota in Partial Fulfillment
of the Requirements for the Degree of
Master of Arts**

by

**Hjalmer Victor Peterson, B. A.
" "
(University of North Dakota, 1936)**

Grand Forks, North Dakota

May 17, 1938

T1938
P48
Geol.

Grand Forks, North Dakota

May 17, 1938

This thesis, offered by Hjalmer V. Peterson as a part of the work required for the degree of Master of Arts, is hereby approved by the Committee under whom he has carried his work.

Chairman

First Minor

Second Minor

Director of Graduate Division

303901

ACKNOWLEDGMENT

The writer wishes to express his gratitude to Professor G. A. Abbott for suggesting this problem and for his helpful guidance and advice throughout the investigation.

TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	1
TABLE OF CONTENTS	11
INTRODUCTION	1
SELENIUM DISCOVERY AND HISTORY	5
PROPERTIES OF SELENIUM	5
EXPERIMENTAL	8
A. Details of the Horn Method for Selenium Determination	9
B. Details of the Distillation Method	10
APPARATUS AND REAGENTS	10
JUSTIFICATION OF THE CHOICE OF METHODS	11
THE GEOLOGIC HORIZONS	17
THE CORRELATION OF SELENIUM CONTENT OF WATERS WITH OTHER CONSTITUENTS	20
PROBABLE SOURCES OF THE SELENIUM FOUND IN THE DIFFERENT GEOLOGIC HORIZONS	20
PHYSIOLOGICAL EFFECTS OF SELENIUM	22
SUMMARY	24
BIBLIOGRAPHY	25

Introduction

A live stock malady, that the pioneers of certain districts of the semi-arid Great Plains erroneously called "alkali disease," has long been a problem of considerable importance. This condition was believed to have been caused by alkali water and spots in the soils of the region. Probably the first published account of the malady is the report of Madison,¹ who described its outbreak among the horses and mules of the cavalry troop at Fort Randall, Territory of Nebraska, in 1856. This early reference to the disease has acquired new interest from the fact that the region surrounding Old Fort Randall is in the area recently studied by various agencies to discover the cause of the malady.

All livestock is affected by the disease. The first symptoms observed are dullness and a lack of vitality in the animals. They lose weight, their coats become roughened, and they fail to respond to feeding even when given unaffected feed and water. The heart and liver are severely damaged in more advanced cases. Anemia is common and appears to be a characteristic accompaniment. The bones, especially the joints, are eroded and there is a pronounced disturbance of the calcium-phosphorus metabolism.² There are various gradations of the disease, from mild cases where the animals except in minor degrees show no ill effects, to very severe cases in which there is an alteration in the growth of horns, a sloughing-off of the hoofs, and a loss of hair from the switches of cattle; roughened coats, alterations in the hoofs and loss of hair from manes and tails of horses; and loss of hair in swine. After the sloughing-off of the hoofs in cattle and horses, the feet become so tender that many of the unfortunate animals are seen kneeling while they graze. This

gave rise to the term, "praying disease" by which the malady is known in some regions.

³Within the past few years it has been definitely established that the so-called "alkali disease" is a form of severe poisoning caused when animals feed on grasses, forages, and cereals that have absorbed the poisonous element selenium from the soil. The proposal to change the name of the malady to selenium poisoning has not been generally accepted, and the old term "alkali disease" will probably be retained to designate this type of selenium poisoning, because it is known that there are other types of selenium poisoning. "Alkali disease" is recognized as a chronic form of selenium poisoning and is the most prevalent type found in South Dakota and Nebraska. "Blind Stagers," a more acute type, is the variety most common in certain districts of Wyoming.

⁴Valuable facts that have been found by investigators are that notable concentrations of selenium in soils are associated with certain definite geological formations, and in soils derived therefrom, and that it is troublesome only in semi-arid regions. Investigations also show that wherever selenium is present in soils, plants absorb varying amounts ranging from traces to thousands of parts per million of the element. It is not definitely known how much selenium a soil may carry without being dangerous, but from investigations it appears that any soil containing over one-half part per million or any vegetation containing over four parts per million of selenium may be regarded as dangerous.

In South Dakota the selenium occurs in soils that have been formed by the weathering and disintegration of the Pierre Shale, a formation that comes to the surface in those areas. It is known to carry selenium in

amounts that vary widely according to different geological horizons of the strata, ranging from less than one part per million to as high as forty parts.

⁵In North Dakota the Pierre Shale probably underlies the entire State except in the Red River Valley, which however contains blue clay derived from it. In the eastern half of the state, the Pierre lies immediately below the glacial drift, except in the Turtle Mountains where it is capped by an outlier of the Fort Union formation. West of the Missouri escarpment it is generally deeply buried under younger sedimentary formations and comes to the surface only in two small areas, one along the Missouri River near the South Dakota boundary and the other in the valley of the Little Beaver Creek in the southwest corner of the State. The fact that the Pierre does not form the surface soils in North Dakota explains the absence of "alkali disease" among the livestock in the State.

In a large portion of North Dakota most of the deeper wells penetrate or pass through the Pierre Shale formation. The Shale proper is nearly impervious to the passage of water, but some wells obtain their water from the weathered or jointed parts of the formation or from the imbedded aquifer of sandstone and gravel.

From a consideration of these conditions, Professor G. A. Abbott suggested the possibility to the writer, that waters in prolonged contact with selenium-bearing formations might be found to carry appreciable amounts of selenium. His suggestions was strengthened by the statements of many farmers and veterinarians that cattle and horses watered from certain brackish wells "did not do well." The animals became thin,

often anemic and offered little resistance to the scourge of tuberculosis.

Accordingly an investigation of the occurrence and distribution of selenium in the ground waters of the state was undertaken by the writer with Professor Abbott's active cooperation in the hopes that information obtained might indicate whether or not selenium presents a hygienic problem in this State.

Having on hand a very large and representative collection of ground water samples gathered during the recent survey of municipal water supplies, attention was first directed toward the examination of waters used for human consumption. Thus, most of the analyses included in this report have been made upon municipal supplies. It is understood that municipalities naturally try to obtain the best available water supplies, and that these waters are not representative of the more brackish waters considered unfit for human use, but used for watering livestock. A limited number of these stock wells have been examined, but not enough to justify general conclusions concerning them.

Selenium Discovery and History

To give a better understanding of the problems involved in this investigation, a brief summary of the history, occurrence and properties of selenium is included.

⁶In 1817, J. J. Berzelius reported a red, pulverulent substance that collected on the floors of the lead chambers when certain copper pyrites were roasted to produce sulfur dioxide in the manufacture of sulphuric acid. During the subsequent years, he examined in some detail the chemical properties of the new element which he named "selenium" from the Greek word signifying the moon.

Selenium is widely distributed on the earth's crust, but occurs usually only in small quantities. Of the known elements, selenium ranks about fiftieth in abundance. It is not usually found in its native state, but the selenitellurium of Honduras finds the two sister elements practically free.⁷ It is invariably found replacing sulfur in ores, forming isomorphous compounds with lead, silver, copper and mercury. Some of these ores are clausthalite, $PbSe$; berselianite $(Cu, Ag, Fl)_2Se$; naumannite, $(Ag_2, Pb)Se$; tiemannite, $HgSe$; lehrbrachite, $(Pb, Hg)Se$; onofrite, $Hg(Se, S)$ and curcairite $(Ag, Cu)_2Se$. It is found also in small quantities in many varieties of pyrite and chalcopyrite. By roasting the minerals, all the selenium is volatilized and subsequently deposited as a mud from which it is extracted with potassium cyanide and precipitated with acid.



Properties of Selenium

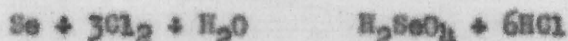
As does sulfur, selenium exists in several allotropic forms.

L-Selenium, the vitreous modification, dissolves in carbon disulfide. Red B-selenium is obtained by reducing a cold solution of selenious acid with sulphurous acid. It is less soluble in carbon disulfide than the L-variety. By heating red selenium with hot water, it is changed to dark gray selenium which is insoluble in the disulfide.

On being heated in air, selenium burns with a bluish flame, forming white, crystalline selenium dioxide. Selenium forms only one oxide and two acids, selenious acid, H_2SeO_3 , and selenic acid, H_2SeO_4 . When selenium is heated in hydrogen, gaseous hydrogen selenide, H_2Se , is formed.

Selenious acid is obtained in the form of long, colorless, needles by oxidizing the element with nitric acid and by dissolving the anhydride formed in water. On standing in air, the acid is reduced to the element. It is dibasic and forms salts in which the hydrogen atoms are replaced by metals. The acid salts are all soluble in water, but the neutral salts, except those of the alkalis, are insoluble.

Selenic acid is obtained in solution by conducting chlorine into water which contains the element of selenious acid.



The acid is dibasic and behaves similarly to a peroxide, evolving chlorine when boiled with concentrated hydrochloric acid, being reduced to selenious acid.

^BSelenium can be separated from all elements except arsenic by distillation with bromine in hydrobromic acid. This is the basis of one of the quantitative determinations of the element.

The form of the selenium with which this problem is chiefly concerned

is the selenite. The particular form is not known, but it is undoubtedly that of selenite ion although selenate ion may be present. ⁹Selenites are by far the more toxic of the two types.

Selenium salts are very toxic and act poisonously on the body as a whole. They are much more poisonous but they may be likened to arsenic and antimony in their toxic effects.

Experimental

The value of this research is largely dependent on the analytical methods used for the determinations. Some methods of analysis used by various analysts are practical where higher values of selenium than those found in ground waters are concerned. Some of these are titration methods; others gravimetric or colorimetric. ¹⁰In the former the selenium is titrated with potassium cyanide after previous treatment with cold, saturated sodium sulfide. ¹¹Another titration method is iodometric. ¹²A practical gravimetric method of determining selenium is to treat the selenized solution with hydrazine hydrochloride and concentrated hydrochloric acid. Boil until the deposit becomes black, filter, wash, dry at 110°C and weigh. ¹³Another method used for the determination of selenium gravimetrically is to treat a known small amount of the material with 0.3 ml of fuming nitric acid and then treat further with water and concentrated hydrochloric acid. Sulfur dioxide is passed in when the mixture is brought to boiling. Black selenium is filtered, washed, dried at 110°C and weighed. ¹⁴A practical colorimetric method for determinations of selenium is to add thiourea to hydrochloric acid solutions of the materials to be tested and compare with standards. This method was occasionally used as a check method in the survey. There are many more of these methods but suffice it to say that they are not practical for the determination of small quantities of selenium found in waters.

It was decided for this survey to use a colorimetric method.

¹⁵Selenized sulphuric acid when cooled develops a green color changing to blue when a few drops of 3% aqueous solution of codeine sulphate is added

to it. The depth of color shows by comparison with standards, the quantity of selenium present.

Two methods were used for treatment of the waters to bring them into the condition where the codeine sulphate could indicate the selenium. ¹⁶One was the method of Horn and the other⁵ a distillation method. A modified Kjeldahl digestion apparatus was used to digest the sulphuric acid in both methods. Batteries of Kjeldahl flasks were connected to one large central filter flask, partially filled with water by means of glass tubing and small bulb tubes. The suction flask was in turn connected to a water vacuum pump. Thus the sulfur trioxide fumes given off were absorbed in the water in the suction flask preventing any from escaping into the room.

A. Details of the Horn Method for Selenium Determinations

Exactly 100 ml. samples of the waters to be tested are added to the Kjeldahl flasks and slowly evaporated. To the residue after evaporation is added 10 ml. of concentrated sulphuric acid. The liquid is then digested until it becomes colorless. It is cooled and two drops of 3% codeine sulphate solution are added to it. The liquid is then poured into matched Nessler tubes and diluted up to the 10 ml. mark with dehydrated concentrated sulphuric acid. Standards are made up with selenious acid solution (made by dissolving 0.0163 gram of selenious acid in a liter of distilled water. 1 ml. of this solution is equivalent to 0.01 mg. of selenium). Definite measured amounts are placed in Kjeldahl flasks with 10 ml. of concentrated sulphuric acid. These are treated in the same manner as the samples. The standards and the samples are allowed to stand for 30 minutes after which reading are made by comparing the depths of the blue colors of the samples

with those of the standards.

Calculations: The number of mls. of standard $\times 0.01$ to 10 gives the parts per million of selenium.

B. Details of the Distillation Method:

This method is used for colored and highly mineralized waters where the Horn Method is not practical. The principle of the method is that the selenium is separated from all elements except arsenic by distillation with a mineral halogen acid. Hydrobromic acid is recommended but hydrochloric acts as well. In this method the selenium must be in, or converted into, the hexivalent condition before distillation in order to insure its distillation with the acid. Bromine is used to do this in most cases.

An all Pyrex glass distillation apparatus is used because bromine reacts with rubber or cork stoppers.

To exactly 100 ml. of the sample of water to be examined is added enough sodium peroxide to make the liquid definitely alkaline. The solution is then evaporated to dryness. The residue is taken up in concentrated hydrochloric acid and a small amount of bromine is added. The solution is placed in the distillation flask. To the condenser of the apparatus is attached an adapter which dips just below the surface of a few mls. of bromine water in the receiving flask. Heat is applied to the flask and from 30 to 50 mls. of the distillate are collected. Sulfur dioxide gas produced by the action of an acid on a sulphite is then passed into the distillate until the color due to bromine is completely discharged. The solution is then placed in a Kjeldahl flask and treated as in the Horn method.

Apparatus and Reagents

All analyses were made in Pyrex, selenium-free glassware. The

colorimetric work was performed in carefully matched Nessler tubes and the standard selenium solution was added with EXAX-1 and 10 ml. pipettes graduated to hundredths and tenths, respectively. All reagents used were of certified purity. The acids, sulphuric and hydrochloric, were examined and found to be free from selenium.

Justification of the Choice of Methods

To justify the choice of methods used in this survey, tables are included showing the effect of interfering substances, Table A, the checks on the two methods used, Table B, and the sensitivity to known amounts of selenium added to natural waters, Table C.

Table A

Effects of Interfering Substances

Chlorides	present up to 6,000 p.p.m.	No interference
Sulfates	present up to 3,000 p.p.m.	No interference
Silicates	present up to 100 p.p.m.	No interference
Manganese	present up to 20 p.p.m.	No interference
Phosphates	present up to 5 p.p.m.	No interference
Nitrates	present up to 200 p.p.m.	No interference
Copper	present up to 5 p.p.m.	No interference
Iron	present up to 2 p.p.m.	*Slight interference

According to Horn, iron does not interfere in this method, but it has been discovered in this work that iron in higher concentrations interferes with the test to some extent. On waters that are high in iron content it is suggested that the bromine distillation method is used because it removes all elements that might interfere with the codeine test.

Quaternary Drift Waters

No.	City	Survey No.	County	Amount of Se. in ppm.
10	Rogers	M542	Barnes	Trace
11	Devils Lake	M305	Ramsey	0.15
12	Grenora	M353	Williams	0.35
13	Durton	M289	Traill	0.04
14	Hope	M551	Steele	0.05
15	Anamoose	M517	McHenry	0.02
16	Alice	M316	Cass	0.10
17	Linton	M553	Emmons	0.20
18	Luverne	M548	Steele	0.20
19	Hannaford	M545	Griggs	0.12
20	Strasburg	M561	Emmons	0.24
21	Souris	M614	Bottineau	0.80
22	Bergen	M616	McHenry	0.03
23	Tioga	096	Williams	0.30
24	Cando	M365	Towner	0.20
25	Grano	M420	Renville	0.10
26	Hankinson	M337	Richland	0.35
27	Fredonia	M311	Logan	0.30
28	Perth	M313	Towner	0.45
29	Wing	M239	Burleigh	0.10
30	Lakota	M259	Nelson	0.10
31	Montpelier	M310	Stutsman	0.10
32	Noonan	M242	Divide	0.05
33	McHenry	M123	Foster	0.08
34	Burdfield	M295	Wells	0.10
35	Buffalo	M117	Cass	0.09
36	Adams	M178	Walsh	0.07
37	Niagara	M112	Grand Forks	0.15
38	Tower City	M283	Cass	0.35
39	Edmore	M158	Ramsey	0.02
40	Sheyenne	M296	Eddy	0.70
41	Lawton	M114	Ramsey	0.02
42	Williston	098	Williams	0.25
43	Wolcott	M596	Ward	0.35
44	Dickey	M317	LaMoure	0.45
45	Ryder	M193	Ward	0.30
46	Bottineau	M587	Bottineau	0.25
47	Streeter	M567	Stutsman	0.30
48	Barton	M370	Pierce	0.25
49	Finley	M550	Steele	0.20
50	Dawson	M279	Kidder	0.80
51	Minnewaukan	M635	Benson	0.12

Fort Union Waters

52	Killdeer	M252	Dunn	0.08
53	Crosby	M261	Divide	0.07
54	McClusky	M87	Sheridan	0.35

Fort Union Waters

No.	City	Survey No.	County	Amount of So in num.
55	Beach	N35	Golden Valley	0.05
56	Belfield	N528	Stark	0.40
57	Parshall	N463	Hountrail	0.20
58	Scranton	N43	Bowman	0.40
59	Richardton	N84	Stark	0.50
60	Dunn Center	N508	Dunn	0.45
61	Garrison	N421	McLean	0.30
62	Van Hook	N467	Hountrail	0.55
63	Boula	N523	Mercer	0.40
64	Blaisdell	N529	Hountrail	0.12
65	Blaisdell	N578	Hountrail	0.10
66	Haynes	N584	Adams	0.10
67	Reeder	N357	Adams	0.10
68	Leith	N326	Grant	0.18
69	Mott	N228	Hettinger	0.09
70	Elgin	N237	Grant	0.10
71	Halliday	N221	Dunn	0.05
72	Alexander	N513	McKenzie	0.20
73	Milton	N273	McLean	0.02
74	Bowman	N490	Bowman	0.03
75	New Salem	N499	Morton	0.45
76	Ransom	N512	McKenzie	0.15
77	Medora	N496	Billings	0.15
78	Northgate	028	Burke	0.10
79	Hebron	N502	Morton	0.15
80	Des Lacs	N472	Ward	0.10
81	Portal	038	Burke	0.15
82	Dickinson	N518	Stark	0.05
83	Kenmare	N147	Ward	0.10
84	Arnegard	N511	McKenzie	0.35
85	Carson	N582	Grant	0.07
86	Golva	N534	Golden Valley	0.05
87	Lehr	N146	McIntosh	0.07
88	Dodge	N506	Dunn	0.50
89	Wabek	N625	Hountrail	0.05
90	Sanish	N524	Hountrail	0.03
91	Benedict	N21	McLean	0.30

Dakota Sandstone Waters

92	Lidgerwood	N433	Richland	0.15
93	Loda	N617	Benson	0.10
94	Verona	N401	LaMoure	0.20
95	Clifford	N236	Trail	0.40
96	Lisbon	N151	Ransom	0.02

Dakota Sandstone Waters

No.	City	Survey No.	County	Amounts of Se in ppm.
97	Iudden	M157	Dickey	0.07
98	Reynolds	M291	Grand Forks	0.10
99	Portland	M255	Traill	0.08
100	Fullerton	M398	Dickey	0.10
101	Forman	M639 Sp.	Sargent	0.20
102	Sheldon	M539	Ransom	0.30
103	Rutland	M441	Sargent	0.45
104	Grand Forks	Bridgeman-Russell	Grand Forks	0.20
105	Grand Forks	M607	Grand Forks	0.20
106	Langdon	M583	Cavalier	0.20

Alluvial Deposit Waters

107	Galces	M402	Dickey	0.20
108	Valley City	M286	Barnes	0.10
109	Jamestown	M122	Stutsman	0.35
110	Minot	M637	Ward	0.30
111	Zap	M504	Mercer	0.40
112	Hazen	M272	Mercer	0.35
113	Stanton	M503	Mercer	0.10
114	Cavalier	M91	Pembina	0.07

Lake Agassiz Waters

115	Winto	M612	Walsh	0.20
*116	Hamilton	M378	Pembina	2.00
117	Neche	M639	Pembina	0.25
118	Hoople	M590	Walsh	0.08
119	Thompson	M288	Grand Forks	0.10

Pierre Shale Waters

120	Galio	M628	Cavalier	0.20
121	Munich	M626	Cavalier	0.20
122	Ashley	M633	McIntosh	0.45
123	Wales	M413	Cavalier	0.15
124	Polcin	M352	Nelson	0.07
125	Cleveland	M277	Stutsman	0.10
126	Helcoma	M245	Cavalier	0.15
127	Staricweather	M265	Ransom	0.04
128	Cooperstown	M36	Griggs	0.08
129	Loma	M532	Cavalier	0.07
130	Michigan	M600	Nelson	0.10
131	Adams	M175	Walsh	0.35
132	Rock Lake	M630	Towner	0.30

*Not considered in average.

Lance Waters

No.	City	Survey No.	County	Amount of Se. in mm.
133	Hague	M562	Emmons	0.10
134	Braddock	M557	Emmons	0.40
135	Newburg	M183	Bottineau	0.05
136	Drake	M522	McHenry	0.10
137	Hazelton	M559	Emmons	0.03
138	Carbury	M188	Bottineau	0.04
139	Goodrich	M276	Sheridan	0.10
140	Flasher	M481	Morton	0.40
141	Tuttle	M238	Kidder	0.10
Fox Hills				
142	Hettinger	M101	Adams	0.10
143	Zeeland	M566	McIntosh	0.13
144	Bordulac	M604 (No well schedule)	Foster	6.00 (unchecked because of lack of sample)
145	Dunseith	G146 (No well schedule)	Rolette	0.2
146	Washburn	M203 (River Water)	McLean	0.1
147	Grand Forks	City Water	Grand Forks	0
148	Grafton	Special (Paleozoic)	Walsh	0.2
149	Voltaire	M619 (Lake Souris)	McHenry	0.45

The Geologic Horizons

In order to give a better understanding of the various water bearing formations in the State, a brief description of the various geologic horizons from which waters used in this survey are obtained is essential. There are eight horizons of interest.

(1) The Quaternary or Glacial Drift includes two or more stages of glacial deposits and consists of two classes of materials, stony clay or till, deposited by the ice, and beds of silt, sand and gravel laid down by the waters of the melting ice of the glaciers. The drift usually consists of typical boulder clay.

(2) Alluvial Deposits are found in practically all larger valleys of the State. The deposits consist largely of gravel, sand and silt which in some places reach a depth of 150 feet. These deposits are often thought of as disintegration products of the drift.

(3) The Fort Union Formation underlies practically all of the Missouri Plateau and has an outlier in the Turtle Mountains. It has a maximum thickness of about 1300 feet. Its chief constituents are numerous beds of shale, lignite coal and sandstone from which water supplies are obtained. Many waters from this formation are brownish in color due to the presence of organic matter.

(4) The Dakota Sandstone probably underlies the entire State except for small areas in the Red River Valley. It does not come to the surface at any point. It is probably the best water-bearer of the various formations in the State. It consists of very poorly cemented sandstone interbedded with thin layers of shale and clay. It is known to have a depth of

more than 2000 feet in certain areas. ¹⁷Two separate flows have been recognized coming from this horizon. One is the Dakota Sandstone flow itself and the other the Lakota Sandstone flow. The first is softer and not as highly mineralized as the Lakota flow.

(5) The Lance Formation underlies the Fort Union and comes to the surface in two areas in the State, the first in Morton and Sioux Counties, and the second in Burleigh and Emmons Counties. The formation is chiefly composed of gray sandstone, shale, and beds of lignite. The maximum thickness is about 900 feet.

(6) The Pierre Shale probably underlies the entire State except in the Red River Valley, which, however, contains a blue clay derived from it. It lies directly below the drift in the eastern part of the State, but west of the Missouri escarpment it is usually covered with younger sedimentary rocks. It is largely made up of thin layers of very impervious, dark blue-gray shale. It is estimated to have a maximum depth of about 1100 feet.

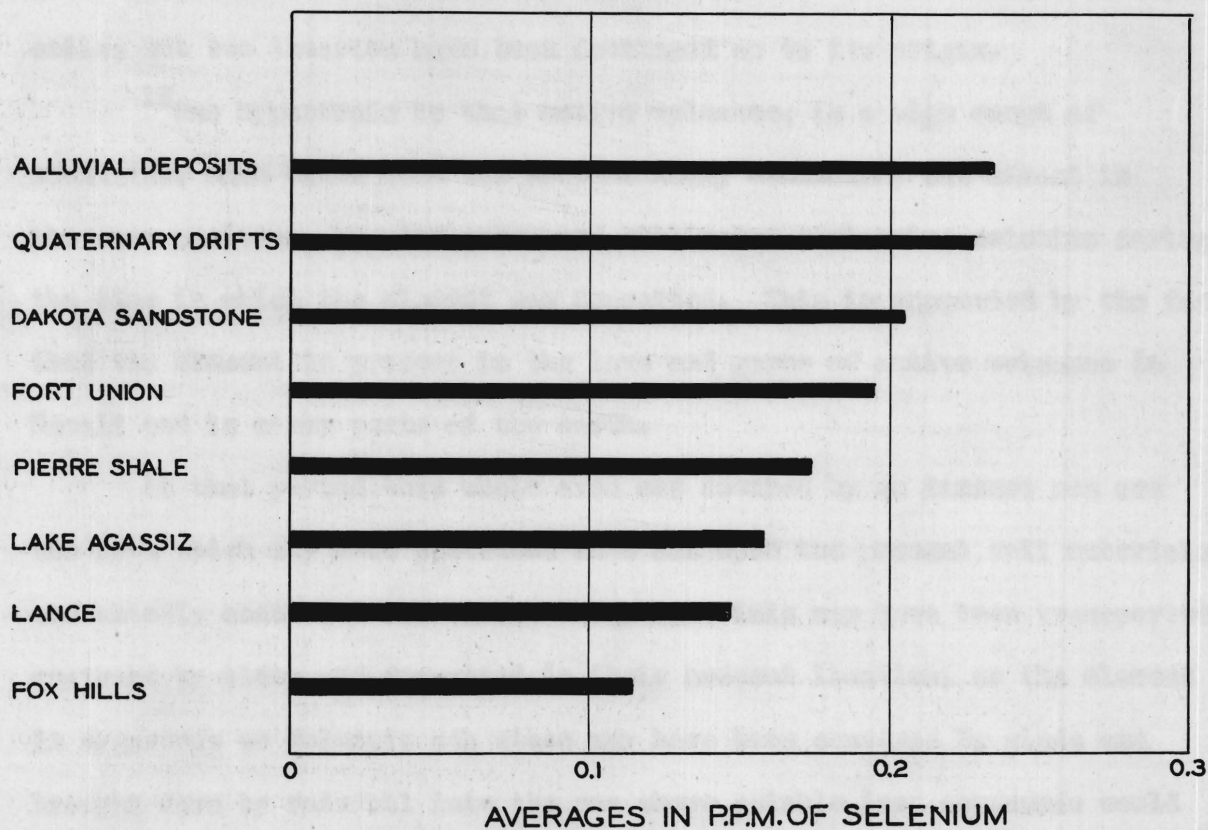
(7)¹⁷Lake Agassiz Deposits are the lacustrine and clayey silts that underlie an extensive area of the eastern portion of the State. Most of the deposits are a mixture of fine sand and clay. The Shesenne, Elk Valley, and Pembina deltas on the western edge of the basin, however, are chiefly composed of sand and gravel.

(8) The Fox Hills Sandstone Formation is of little importance in this State. It is a soft, yellow to gray sandstone which underlies the Lance formation and comes to the surface only in the banks of the Missouri near its exit from the State and in the banks of small streams of that region.

Average Selenium Values for the Different Geologic Horizons

Horizon	No. of Waters	Average in ppm.	High Value	Low Value
Quaternary Drift	51	0.228	0.80	0.02
Fort Union	40	0.195	0.55	0.02
Pierre Shale	13	0.174	0.45	0.07
Dakota Sandstone	15	0.205	0.45	0.02
Alluvial Deposits	8	0.234	0.40	0.10
Lance	9	0.147	0.40	0.03
Lake Agassiz	4	0.158	0.25	0.07
Fox Hills	2	0.115	0.13	0.10

Graph of the Average Selenium Values for the
Different Geologic Horizons
Average in ppm. of Se



The Correlation of Selenium Content of Waters with Other Constituents

Efforts that have been made to correlate the selenium values with other mineral constituents in the waters examined in this survey have met with little success. It is indeed safe to say that selenium contents of waters cannot be tied up with other constituents. It was thought that the selenium would correlate the calcium contents but the supposition was proved incorrect.

Probable Sources of the Selenium Found in the Different Geologic Horizons

As has been shown in this investigation and soil surveys in other States, there is selenium in varying quantities in practically every horizon. It is difficult to discover the exact source of the element in these soils, but two theories have been developed as to its origin.

¹⁸One hypothesis is that active volcanoes, in a high range of mountains, much older than the present Rocky Mountains, but almost in the same position, erupted gases and sublimates containing selenium during the time in which the element was deposited. This is supported by the fact that the element is present in the lava and gases of active volcanoes in Hawaii and in other parts of the earth.

At that period this whole area was covered by an immense sea and the lava which may have protruded into and upon the present soil materials undoubtedly contained selenium. These materials may have been transported eastward by tides and deposited in their present location, or the element in a gaseous or volcanic ash state may have been conveyed by winds and brought down by rainfall into the sea where soluble iron compounds would

react with it to form insoluble iron salts. These would be deposited at the bottom along with other sedimentary materials. The latter theory is strengthened by the fact that ferric hydroxide absorbs and precipitates selenium from dilute solutions.

¹⁹Another theory is that the mountains mentioned above were made up of selenium containing materials. The materials were deposited in the bottom of the sea and transported eastward by tides to their present location. Either theory may be partially or wholly correct but the theory that the selenium was transported by winds and deposited is supported by the fact that the shale formations which carry high seleniums also contain bentonite which is thought to be derived from volcanic ash.

Selenium compounds both organic and inorganic, at any rate, are present in the geological formations. They probably have been converted into the more soluble state by weathering and oxidation. In this condition the compounds have more easily been dissolved in the ground waters and absorbed by the plants of the selenium endemic regions. ³This conclusion has been borne out by the fact that corn grown on Pierre Shale, in which there has been very little or no oxidation or weathering due to its imperviousness, contains very little selenium in contrast to Pierre clay soils of the same selenium content and the fact that ²⁴areca exist in highly seleniferous soils of Puerto Rico and Hawaii that do not produce toxic vegetation.

Physiological Effects of Selenium

A brief discussion of the toxic effects of selenium in man and lower animals is included to show that there is a potential hazard in being continually exposed to the element. It is doubtful, however, if the low concentrations of selenium found in the waters investigated in this survey would cause any serious physiological effects.

The experimental work of a number of investigators on the effects on animals of ingested compounds of selenium was shown²⁰ that soluble selenium compounds are toxic producing both chronic and acute physiological effects. The toxic effects are in direct proportion to the amount of the element consumed. The acute effects may be summarized as consisting primarily of cellular destruction and later pathological changes throughout the organism. The ingestion of small amounts of selenium over a long period of time results in pathological changes in the liver and kidneys and abnormal functional weaknesses.

²¹In conducting experimental work on the action of small amounts of selenium salts on animals, it was concluded that the toxic salts are cumulative in their effects though much of the selenium is detoxified in some animals.

²²In a field study of the effects of selenium on humans in the selenium endemic regions of South Dakota and Nebraska, the investigators concluded that the excretion level of selenium in man is a fairly reliable index of the availability of the element. It was discovered on analyzing urine specimens from 100 subjects that the concentrations of selenium varied from 0.02 to 0.198 mg. per 100 ml. This affords definite proof

of the absorption of the element by humans who come in direct contact with it. A large percentage of the subjects showed gastric or intestinal dysfunctions, which, as well as the few cases of liver (hepatic) dysfunctions, were probably a result of continual selenium ingestion.

²³In another field study, bad teeth, a yellowish coloration of the skin, skin eruptions, chronic arthritis, diseased nails of fingers and toes, and protracted gastro-intestinal disturbances were noted. Most of these may be directly attributed to the continual selenium ingestion of the subjects.

Summary

1. The significance of selenium as it is related to the "alkali disease" is discussed.
2. Analytical methods for the determination of selenium are reviewed and satisfactory methods are described.
3. The selenium contents of various ground waters of the State according to the Geologic Horizons are given.
4. The various Geologic Horizons of North Dakota are briefly discussed and the average selenium results for the horizons shown.
5. There is no direct correlation of the selenium content with any other element in the waters.
6. The probable sources of the selenium are discussed.
7. A brief resume of the physiological effects of selenium is included.
8. A bibliography of the literature is appended.

Bibliography

1. Madison, T. G. Sanitary Report. Fort Randall, in Cellidge, R. H. Statistical Report on Sickness and Mortality in Army of the U.S. Jan. 1855 to Jan. 1860, Washington, Ex. Doc. 52: 37-41(1860).
2. Franke, K. W., T. D. Rice, A. G. Johnson and H. W. Schoening. Report on A Preliminary Field Survey of the So-Called "Alkali Disease" of Livestock. U. S. D. A. Circular 320(1934).
3. Bulletin 311, Alkali Disease or Selenium Poisoning, South Dakota Agricultural Experiment Station, May 1937.
4. Knight, H. G. Selenium and Its Relation to Soils, Plants, Animals, and Public Health. Sigma XI Quarterly, March 1937.
5. Simpson, H. E. Geology and Ground Water Resources of North Dakota. U. S. Geological Survey Water-Supply Paper, 598, 38-39 (1929).
6. Neller, A Comprehensive Treatise on Inorganic and Theoretical Chemistry. Vol. X.
7. Treadwell, Hall. Analytical Chemistry. Vol. I.
8. Robinson, W. O., H. C. Dudley, K. T. Williams, and H. G. Byers. Determination of Selenium and Arsenic by Distillation. J. Ind. Eng. Chem. Anal. Ed. 6, 274(1934).
9. Joachimoglu, G. and W. Hirose. Z. Biochem. 125: 5-11(1921).
10. Benesch, E., Chem. Ztg. 52: 878-9(1928).
11. Berg, R. and H. Tortelbaum. Ibid 52: 142(1928).
12. Benesch, E., and E. Erdheim. Ibid 54: 954(1930)
13. Drew, H. D. and C. R. Porter. Journal of the Chemical Society 2091-5(1929).
14. Falciola, P. Ann. Chim. Applicata. 357-8(1927).
15. Schmidt, Ernst. Archiv der Pharmazie, V. 252, 161(1914).
16. Horn, H. J. Qualitative Method for Selenium in Organic Compounds. J. Ind. Eng. Chem. Anal. Ed. 6: 34-5(1934).
17. Abbott, G. A., and F. W. Veedisch, Report on Municipal Ground Water Supplies of North Dakota, North Dakota Geological Survey. Bulletin 11 (In press) (1938).

18. Byers, H. G., K. T. Williams, and H. W. Lakin. Selenium in Hawaii and Its Probable Source in the United States. *J. Ind. Eng. Chem.* 28: 821-3(1936).
19. Beath, O. A., H. F. Eason, and C. S. Gilbert. Selenium and Other Toxic Minerals in Soils and Vegetation. *Wyo. Expt. Station Bull.* 206(1935).
20. Dudley, H. C. Selenium as a Potential Industrial Hazard. *Public Health Reports.* Vol. 53, 8: 282(1938).
21. Smith, M. I., E. F. Stohlman and R. D. Lillie. The Toxicology and Pathology of Selenium. *Journal of Pharmacology and Exp. Ther.* 60, 449(1937).
22. Smith, M. I., B. B. Westfall. Further Field Studies on the Selenium Problem in Relation to Public Health. *Public Health Reports.* Vol. 52. 40: 1375(1937).
23. Smith, M. I., K. W. Franke, and B. B. Westfall. Selenium Problem in Relation to Public Health. *Public Health Reports.* Vol. 51: 1489(1936).
24. Lakin, H. W., K. T. Williams, and H. G. Byers. "Nontoxic Seleniferous Soils. *J. Ind. Eng. Chem.* 30, 599-600(1938).