

MOLYBDENUM IN SOILS, FORAGE CROPS AND WATER SUPPLY
IN THE SWAN RIVER VALLEY OF MANITOBA

A THESIS

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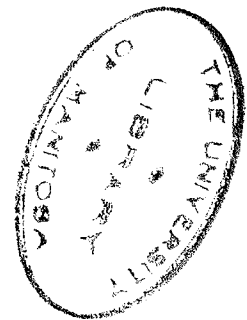
By

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ABSTRACT

A disorder of cattle, which has been reported to be caused by excessive amounts of molybdenum in forage, occurs in the southwestern portion of the Swan River Valley of Manitoba. Field and laboratory investigations, herein reported, indicate; that molybdenum in quantities toxic to cattle is contained in forage; that the minute quantities of molybdenum contained in the water supply has no contributing effect on the disorders encountered; that the levels of molybdenum in soils of the affected area are relatively high in molybdenum; and that Thunder Hill, an outlier of Porcupine Mountain might contain the source of the element.

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I. INTRODUCTION

A disorder of cattle has been known to exist for over forty years in the southwestern portion of the Swan River Valley of Manitoba. The disorder does not affect horses, pigs or sheep, but has damaging effects on young calves and milk cows during lactation. The disorder was particularly severe when cattle grazed on lush pasture or during seasons of heavy rainfall. Affected animals exhibit a severe and persistent diarrhea, anemia, excessive salt consumption, followed by a roughening of the coat, loss of coat color, loss of weight, and stiffness of the limbs. In severe cases death occurs. Characteristic of the disorder is that scouring ceases abruptly if the stock are removed to unaffected areas.

Agricultural officials and veterinarians became aware of these disorders about twenty-five years ago but, at that time, were unable to diagnose the condition or to suggest remedial or preventive measures. The many possible causes of the disorders that were postulated and later rejected included, poor feeding practices, phosphorus deficiency, parasitism, bacteria, poisonous plants, and selenium poisoning. Thus it became evident that the problem would not be resolved by any procedure other than an intensive study.

Some initial work was undertaken in 1947 when members of the Manitoba Department of Agriculture submitted soil samples, from the affected area, to the Soils Department of the University of Manitoba for examinations. Spectrographic analysis by Dr. Leech of the Botany Department of minor elements, including molybdenum, did not indicate any abnormality. Analysis of the samples for molybdenum was undertaken by E.A. Poyser of the Soils Department using Marmoy's thiocyanate stannous chloride method. He found varying amounts to be present, but not in the quantities reported to date, by early

investigators in other areas.

In the spring of 1948 members of the Animal Science Department in cooperation with the Provincial Department of Agriculture inaugurated an intensive study of the problem to determine the possibility of cobalt deficiency. However, feeding cobalt failed to cure or ameliorate the disorder. At this time a close relationship of the disorder to one that had been reported in England by Ferguson et al (12, 13) was brought to the attention of Cunningham and his associates, by members of the Soils Department. Ferguson had attributed the disorders to an excessive quantity of molybdenum in the pasturage. Further work by Cunningham et al (8) produced considerable evidence to show that excessive amounts of molybdenum in the pasturage was responsible for the disorders in the Swan River Valley.

Investigations herein reported were begun in 1951 by members of the Soils Department. The principal objectives of these investigations were; to supplement the studies of Cunningham et al (8) in respect of the quantities of molybdenum in forage found growing on soils in the toxic area; to determine the extent to which water might be responsible for causing the disorders; to determine the level of molybdenum in soils of the affected area; to determine the possible sources of the molybdenum found in the soils of the affected area; and to find out why, only a portion of one soil type, appeared to be a part of the affected area.

II. LITERATURE REVIEW

A. Occurrence:

In recent years considerable evidence has been compiled, which shows that an excessive amount of molybdenum in herbage will cause a severe disorder of cattle. The first case of molybdenum poisoning of cattle was reported in Somerset in England. Ferguson, Lewis and Watson (12, 13) investigating a condition referred to as "teartness" which affected ruminants, particularly young calves and fresh milk cows. Characteristic of the disorder was a severe and persistent diarrhea followed by a roughening of the coat, loss of coat color, loss of weight, decreased milk flow, and stiffness of the limbs. In severe cases death occurred. Further research by these workers definitely proved that the disease was caused by an excessive amount of molybdenum in forage grown on Lias clays high in molybdenum.

Britton and Goss (7) and Barshad (2) reported a similar disorder in the San Joaquin Valley of Central California, and attributed the cause to chronic molybdenum poisoning of the cattle. The findings of the American workers differed in one important respect from those in England, namely that the California soils contained very much less total molybdenum than the English soils. Toxic vegetation due to high molybdenum content has been found in several other states of the United States. Studies made by Stanfield (37) on toxic minerals in native vegetation, occurring on Cretaceous and Post-Cretaceous shales in Wyoming indicated that molybdenum in some instances was a contributing factor in the poisoning of livestock. Beath (6) made studies on the toxic vegetation growing on the salt wash sandstone member of the Morrison formation, which occurs in southeastern Utah and southwestern Colorado, and found that molybdenum sometimes occurred in toxic quantities.

From his studies, Beath concluded that the role of molybdenum in activating the poisonous character of indigenous vegetation was a minor one. Some cattle disorders also have been reported in the Florida Everglades area which led to investigations of molybdenum in grasses and peat. The results of the investigation indicated that the problem of molybdenum excess, per se, was rather small (15, 17, 20).

Instances of toxic vegetation due to high molybdenum content have been reported in New Zealand by Cunningham (9) and in South America by Robinson and Edgington (31) though in the latter case the role of molybdenum toxicity is not clearly established.

Walsh and O'Moore (42) in Eire have reported a unique case where an excessive amount of molybdenum in herbage might be a possible contributing factor in equine osteodystrophia. On farms where clinical rachitis occurred in foals and yearlings, the molybdenum content of the grazing herbage was within the range of 5.-25 p.p.m. The soil, developed on limestone, was of the type on which molybdenum induced copper deficiency had previously been identified. In this soil, the level of readily available molybdenum showed values that probably would cause excess molybdenum in the herbage.

In Canada instances of molybdenum toxicity also have been reported. A toxic area in eastern Ontario has been reported by Willis (45). Cunningham (8) presented evidence to substantiate the theory that toxic amounts of molybdenum in herbage were responsible for the disorder of cattle observed in the Swan River Valley of Manitoba. The symptoms of the disorder noted here were identical to those reported in Somerset and California, however, one manifestation of the disorder, an abnormal craving for salt, was reported by the author to be unique. He found that the affected animals would consume as much as 16 to 20 times their normal requirements of salt, depending upon the severity of the disorder.

B. Toxicity Limits:

Although there are many references in the literature to molybdenum poisoning in cattle, there are few references giving evidence that will permit a common fixed lowest toxic level of molybdenum in plants or in soils. In England Ferguson and his co-workers found that "teart" herbage contained from 20 to 100 p.p.m. of molybdenum whereas "non-teart" herbage contained less than five p.p.m. Mo. In the San Joaquin Valley of California Barshad (2) found that cattle scoured when fed Ladino clover containing 15 p.p.m. Mo. He also found that the succulence of the plants appeared to be of particular importance when molybdenum content ranged from 10 to 20 p.p.m. Britton and Goss (7) found that alfalfa containing as little as 10.3 p.p.m. Mo. caused a severe and persistent scouring in cattle in the Kern County of California. A report presented by Allcroft (1) suggested that still smaller quantities of molybdenum may be responsible in part, for copper deficiency which caused scouring of cattle in Cheshire. Where scouring occurred the blood copper values were found to be low although the pasture values were normal. However, the toxic vegetation contained from 6.9 to 9.0 p.p.m. Mo. Green (18) reported a case of bovine haematuria in South Australia which was suspected of being caused by long continued ingestion of molybdenum in quantities much smaller than those encountered in Somerset. Cunningham (8) found that the severity of the disorder encountered in the toxic area of the Swan River Valley of Manitoba varied with the molybdenum content of the herbage which ranged from 3.9 to 25.6 p.p.m. Mo. Thus it would appear that the toxic limit of 20 p.p.m. set by the English workers is too high for a universal standard, and it is believed, particularly by American investigators, toxicity may occur with much lower quantities.

The relationships between molybdenum content of soils and molybdenum

uptake by plants have been studied by Lewis (23, 24) in England, Barshad (2, 4, 5), Robinson et al (32, 33, 34, 35) and Evans et al (10, 11) in the United States.

Lewis (23, 24) has shown that the "teart" fields of Somerset were located on soils formed on the Lower Lias formation or from transported material from the formation. The molybdenum content was found to be concentrated in the uppermost, argillaceous, component of the formation. The soils developed on the Lower Lias formation in Somerset were clays, usually neutral to alkaline in reaction, often calcareous, in general poorly drained, and high in molybdenum. The soils developed on the transported Lower Lias materials were loams, usually better drained, and high in molybdenum. However, acid soils that were high in molybdenum were not considered to be potentially "teart." Calcareous alkaline soils that contained 2 to 3 p.p.m. Mo. in the surface horizons also were not considered to be potentially "teart". Further studies showed that the molybdenum content of the soils increased with depth and that molybdenum uptake by the plants might be greater, the greater the depth of penetration by the plant roots. Lewis, therefore, concluded that calcareous and alkaline soils which contained about 20 p.p.m. or more of molybdenum in the surface horizons were potentially "teart".

Work done in California by Barshad (2) showed that the molybdenum content of the soils in affected areas was not high. The content of molybdenum in the soils ranged from 1.5 to 10.0 p.p.m., a high percentage of which was soluble in water. The reason for the high solubility of the molybdenum in these soils was due principally to their alkaline reaction; under acidification, the water soluble molybdenum was found to be greatly reduced. Unlike Lewis, Barshad found that molybdenum was present in the greatest amounts in the surface horizons. In the soils with the highest

amounts it ranged from 10.0 p.p.m. in the surface foot to 5 p.p.m. in the fifth foot below the surface, and in the soils with the smallest amounts it ranged from 1.5 in the surface foot to 0.8 p.p.m. in the fifth foot below the surface. Barshad found that the molybdenum content of soils in the unaffected areas varied from a trace to 0.5 p.p.m. He quoted some figures from Vaneslow's unpublished work on the molybdenum content of California soils and showed that, in other unaffected areas, the molybdenum content of the soils ranged from 3 to 4 p.p.m.

Thus the presence of the relatively large amounts of total molybdenum in soil, in some cases, has been shown to be the primary cause of toxic vegetation. It is interesting to note the work that has been done by Robinson (34) with regard to the molybdenum status of soils. In a systematic survey of the total molybdenum in the soils of the United States, Robinson and his co-workers analyzed nearly 400 soil samples. The most remarkable conclusion that was drawn from these analyses was the nearly constant and relatively small quantity of molybdenum in these soils. Of the soils analyzed, 95% of them ranged between 0.6 and 3.5 p.p.m. Mo. A silt loam soil which contained 31.5 p.p.m. Mo. was found to be the only striking exception. Because of his findings Robinson cited work done by Evans and Purvis (10) and Barshad (2) in the United States, by Trelles and Amato (38) in Argentina, and by Vinogradov and Vinogradova (40) in Russia to substantiate his hypothesis that an average level for soil molybdenum may be considered as 2.5 p.p.m. Mo. Evans and Purvis (10) found that the molybdenum content of 18 New Jersey soils ranged from 0.8 to 3.3 p.p.m. with an average of 1.99 p.p.m. These soils had a wide range in parent material and texture, yet the molybdenum content of these soils was surprisingly uniform for a minor element. Barshad (2) determined the total molybdenum in 36 California soil

samples, which ranged from sandy loams to sandy clay loams, and found that they averaged 2.01 p.p.m. Mo. Robinson (34) who cited Trelles and Amato analyses of 187 Argentine soils and found these soils averaged 2 to less than 2 p.p.m. Mo. Vinogradov and Vinogradova (40) reported an average of 2.6 p.p.m. of molybdenum which was very uniformly distributed in Russian soils.

Robinson (34) cited the work of Bertrand on 20 European soils in contrast to the findings of the American, Russian, and Argentine investigators. These soils ranged from 4.3 to 69 p.p.m. total molybdenum with an average of 27.8 p.p.m. However, Robinson, who was able to obtain eight samples from the same areas found that the total molybdenum content ranged from a trace to 1 p.p.m. The figures reported by Robinson were verified by the Atomic Energy Commission in the United States using a neutron activation method and found that a composite these European soils averaged 0.28 plus or minus 0.01 p.p.m. There was still further evidence to support the lower figures found by the American workers. On "teart" pastures of Somerset, where the soil was found to be alkaline and high in molybdenum, the vegetation was high in the element and the cattle suffered from Molybdenosis. In France, Bertrand found that the molybdenum content of the vegetation was low and the soils were generally alkaline in reaction, which should have made the vegetation high in molybdenum. However, instances of molybdenosis of cattle were not reported from these areas.

C. Nature of Soil Molybdenum:

From the foregoing information it would appear that, except for a few isolated cases, the molybdenum content of soils was found to be quite low and uniform in distribution. For this reason, the nature of soil molybdenum, particularly in borderline cases of molybdenosis, required

investigation. Thus Barshad (4, 5) undertook to determine the nature of the molybdenum in certain California soils in an attempt to obtain a clearer understanding of the relationships between soils and uptake of the element by plants. The result of his experiments showed that a large part of the total molybdenum in these soils was water-soluble and that solubility of soil molybdenum was increased as the pH of the soil increased. He also found that the solubility of the various molybdenum minerals in water, acid or base differed from that of soil molybdenum. The main differences in solubility were found in acid solutions. Whereas the soil molybdenum is least soluble in acid, the solubility of the molybdenum minerals is either greatest in acid or greater than in water. These differences in solubility between soil molybdenum and molybdenum minerals led Barshad to suggest that the molybdenum in these soils, was present not as a distinct mineral, but rather partly as a soluble molybdate salt, partly as a component of soil organic matter, and partly as an absorbed exchangeable anion (MoO_4) on the clay exchange complex.

D. Soil Reaction and Availability of Soil Molybdenum:

The effects of soil treatments on the availability of soil molybdenum to plants have been studied by a number of workers, notably Barshad (4, 5), Robinson et al (33, 35) Evans et al (11) in the United States, Lewis (23, 24) in England, Oertal et al (27) in Australia. All have observed the close relationship between soil pH and uptake of molybdenum in plants.

Oertal et al (27) who studied the responses of subterranean clover to molybdenum noted that optimum pH for maximum uptake of molybdenum occurred at a pH of 7.9. The Australian workers have suggested, like Barshad in California, a parallelism between PO_4 and MoO_4 availability to plants. That

is, just as sufficient phosphate for optimum growth may be released from soil by increasing the OH concentration, so it appeared that a similar anion exchange is involved in the case of MoO_4 . Fertilizer work in Australia by Oertel et al also indicated a marked response by subterrean clover to changes in soil pH and molybdate uptake. They found a marked decrease in molybdenum uptake by the plants after a pH value of 8.0 had been reached.

Another striking instance of the important relationship between the pH value of the soil and molybdenum uptake by plants was the work done by Willis (46) on samples taken from a toxic area in Ontario. He found that molybdenum content of these soils did not necessarily bear any relation to that in the plant unless the pH value exceeded 7.0. When the pH value exceeded 7.0 the plants growing in soils which contained as little as 1 p.p.m. Mo. may contain as much as or more than 20 p.p.m.

E. Other Factors Affecting Availability of Molybdenum:

Other factors also have been found to have a considerable effect on the accumulation of molybdenum in toxic amounts in herbage. Among the more notable are botanical composition of the herbage, age of the plants, and the effects of seasons. Both Barshad (2) and Lewis (23, 24) found that legumes tended to absorb considerably more molybdenum than did non-legumes, particularly when grown on soils high in soluble molybdenum. Barshad even found considerable differences in molybdenum content among different varieties of the same plants when grown on the same soil and harvested at the same time. Both workers have found that total molybdenum content of the herbage increased with age, which accounted for the fact that older pastures were considered to be more toxic than younger ones. Both in Somerset and in California, it was found that, as the grazing season advanced from spring to

fall, the severity of the disorders also increased, until frost killed the herbage. A similar relationship of season to severity of the disorder was reported by Cunningham (8) in the Swan River Valley of Manitoba. Barshad (2) found that all herbage, whether high or low in molybdenum, showed two-fold to threefold increase in molybdenum from spring to fall. The effects of the growing season from year to year also have had a considerable effect on the severity of the disorder. Cunningham found that the disorders were particularly severe during seasons of heavy rainfall.

III. INVESTIGATIONAL PROCEDURES:

A. Field Investigations:

Field investigations were undertaken in late July of 1953. The objectives of the investigations were; to study the area, particularly the upper Valley Plain of the Swan River Valley of Manitoba; to compare the different soil types found in the area; and primarily to make a systematic collection of water, plant, and soil samples for laboratory investigations.

1. General Description of the Project Area:

(a) Location and Extent:

The area covered in this report included most of the land lying within Townships 34-35, and Ranges 28-29W in the municipality of the Swan River. This area embodies approximately 90,000 acres. (See Map 1).

(b) Physical Features and Surface Geology:

According to Tyrrell (39) the Swan River Valley is a preglacial valley which cut through the Cretaceous plateau of the Duck and Porcupine Mountains, most probably, during the Pliocene Age. He also stated that during the glacial period the valley was ascended by a lobe of the great glacier of the Winnipeg basin. After the glacier receded most of the lower portion of the valley was occupied by a wide bay of Glacial Lake Agassiz as evidenced by the occurrence of numerous strand lines.

According to Wallace (41), when the glacier receded it left a relatively thin deposit of glacial till on the floor of the valley which had subsequently been buried, to a great extent, under deltaic and shallow lacustrine deposits. (See Maps 2 and 3). These deposits range in texture

from gravelly sandy loams on the west to silty clays and clays on the east; indicating that the large flow of water carrying the alluvial material was from west to east. The deltaic and lacustrine nature of the deposits indicated that Lake Agassiz did not recede before the time of their deposition. Although most of these deltaic deposits were carried in from the west, some of them were products of erosion from the neighboring highlands. When Lake Agassiz finally receded the topography of the deltaic deposits was changed by rapid erosion. Much of the deltaic deposits have been eroded by many stream channels until now the area, particularly in the western portion of the valley, has the form of a much dissected plain. (See Fig. 1).

Wallace (41) has separated the valley plain into two natural landscape areas, namely; the Upper Valley Plain to the west and the Lower Valley Plain to the east. These landscape areas lie between the heavily wooded slopes of the Porcupine Mountains to the north and the Duck Mountains to the south. The subdivision was based largely on marked differences in altitude and drainage conditions of the two areas. The Upper Valley Plain is well drained because of the relief and many drainage channels, whereas, the Lower Valley Plain is relatively flat and poorly drained. The line of subdivision is well defined in many places by a definite escarpment.

The valley plain rises gradually from its broad eastern limit, where it is approximately 900 feet above sea level, to the west and on to the Manitoba - Saskatchewan border where the elevation is between 1300 - 1400 feet above sea level. This gradual rise is broken by the occurrence of a escarpment, which separates the Upper Valley Plain from the Lower Valley Plain, and which is especially noticeable in Township 35, Range 28.

To the west, in Townships 35 and 36, Range 29, the Upper Valley Plain is interrupted by Thunder Hill, considered to be an outlier of Porcupine

Mountain. This striking topographical feature rises abruptly from the Upper Valley Plain to a height of over 1800 feet above sea level, see Figure 2.

According to Wickenden (45) "this hill is made up, in part, of large masses of shale belonging to the Ashville and Favel formations that were picked up by glaciers and deposited on this site. During transportation the shales were crumpled and folded to some extent. Folding has affected the beds down to 957 feet and the thickness of the Swan River Formation is much greater at this site than it is in undisturbed sections elsewhere. It is probable that the folding was caused by some force exerted near the surface, such as the Continental Glaciers. No other locality along the escarpment exhibits similiar folding, although there are many other localities where the bedrock could obstruct the ice as effectively." Over the surface of these shale deposits there is a thin layer of glacial till which constitutes the soil parent material.

(c) Drainage:

Drainage is generally toward the northeast which conforms to the general slope of the area. The Swan River and the Woody River constitute the two main drainage systems of the area. These two systems according to Wallace (41) are separated by a height of land extending from Thunder Hill northeastward across the area between the two rivers. The Swan River and its tributaries including Lobstick and Thunder Hill Creeks, drain the larger part of the area, which includes the north slopes of the Duck Mountains, the Upper Valley Plain, and Thunder Hill. The Woody River System drains a belt along the south slopes of Porcupine Mountain.

(b) Climate and Vegetaion:

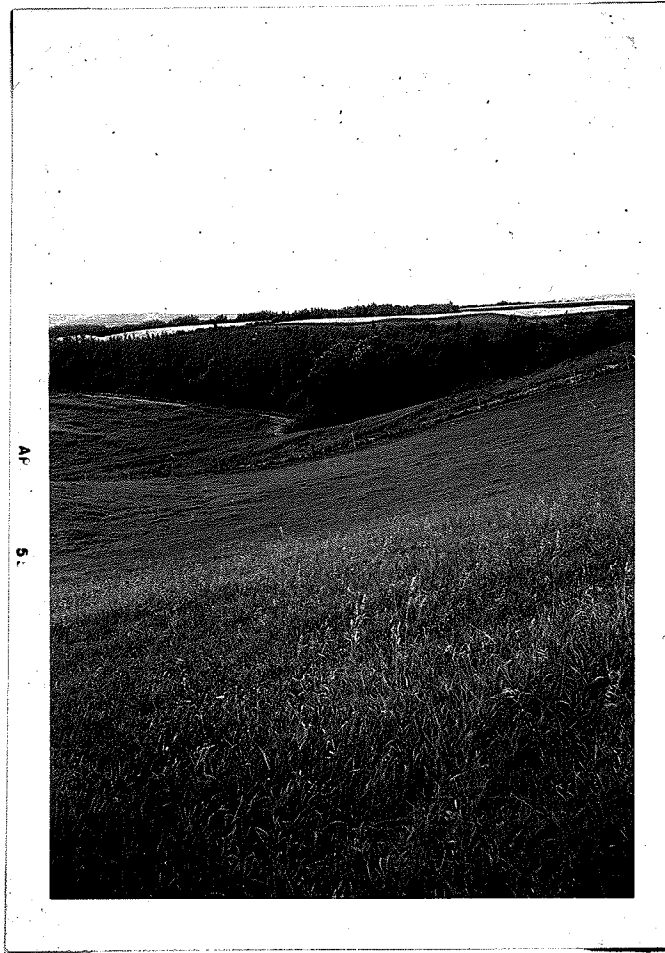


FIGURE 1.

Deeply eroded channels cut into the deltaic and shallow lacustrine deposits of the Upper Valley Plain. (Photo by R.A. Wallace, Soil Survey).



FIGURE 2.

Thunder Hill (background) rises abruptly from the Upper Valley Plain; location of the affected area is in the foreground. (Photo by R.A. Wallace, Soil Survey)

The meteorological data for the Swan River area is very incomplete, particularly for the Upper Valley Plain where the trouble area is centered. What little information that has been recorded is well summarized by Wallace (41). Variations in summer precipitation (April to October) recorded for twenty-four years ranged from 5.7 inches to 20.5 inches. These variations indicated a wide range in precipitation between wet and dry seasons. The temperature records indicated an annual mean of 32.8° F. and a seasonal mean temperature for the summer months of 51.1° F.

The wide variation in precipitation between wet and dry seasons according to Wallace (41) has had a definite effect on the native vegetation. In seasons of above average rainfall, woods have invaded considerable portions of what was formally a grassland area.

(e) Soils:

In the Upper Valley Plain area, particularly where molybdenosis is a problem, there are four soil types, which by their proximity to the area, bear some relationship to the problem. (See Map 1). These soils range from blackearth to grey-wooded soils. A generalized description of these soils appear below.

Whitesand Association:

The Whitesand Soil Association consists of coarse textured soils on smooth gently sloping glacial outwash. This association occurs along both sides of the Swan River in Saskatchewan and extends as far east as range 29 in Manitoba. The typical associate is a blackearth soil characterized by coarse textures, which range from gravelly or cobbly sandy loams, as reported by Mitchell et al (26) in Saskatchewan, to sandy loams in Manitoba.

The average depth of the well drained Whitesand soil may range from 18 inches to 24 inches. The black "A" horizon specked with white silica grains is generally neutral to mildly alkaline in reaction, very friable and slightly cemented when dry. In deep slightly degraded profiles a weak, dark brown cloddy-columnar "A"₂ horizon may be present. The brown to dark greyish brown "B" horizon is usually neutral to mildly alkaline and may exhibit weak columnar structure, breaking moderately easy into weakly developed fine granular aggregates. The lower part of this horizon generally grades into a thin, calcareous, transitional layer between the "B" and "C" horizons. The brownish - yellow "C" horizon is usually structureless, loose, and moderately calcareous.

Davidson Association:

The Davidson Soil Association consists of medium textured soils developed on smooth, gently sloping, deltaic sand and fine sand deposits. The typical associate is a grey-black soil characterized by medium textures, which range from sandy loams to very fine sandy loams. The average depth of the solum of the well drained associate is about 15 inches. The very dark grey "A"₁ horizon is generally structureless, loose, and neutral in reaction. The dark grey "A"₂ horizon, which is not strongly developed in many cases, is single grained, loose and generally slightly alkaline in reaction. The light yellowish-brown limecarbonate horizon is structureless, loose and moderately calcareous. The less well drained members of this association may or may not have a well developed "A"₂ horizon depending largely on drainage position.

Kenville Association:

The Kenville Soil Association consists of medium to fine textured soils developed on deltaic and shallow lacustrine deposits. These deposits, originally very gently sloping, have become subjected to geological erosion, and are much dissected. This soil association has been separated into a light and heavy phase. The lighter textured deposits are considered to be deltaic in nature, the heavier sediments, deltaic and lacustrine in nature. The typical heavy phase soil is a degrading blackearth and ranges in texture from loams to silty clays. The average depth of solum of the well drained member is about 18 inches, although depths of up to three feet also occur. The very dark grey "A₁" horizon is generally finely granular, friable and neutral to slightly acid in reaction. The dark to very dark grey "A₂" is finely granular to platy in structure, friable and neutral to slightly acid in reaction. The grey brown "B₁" horizon possesses a medium nutty structure of hard consistence and is slightly alkaline in reaction. The light greyish-brown "B₂" horizon has a coarse nutty structure of hard consistence and is slightly alkaline in reaction. The pale brown lime-carbonate horizon is finely granular, friable to hard, and calcareous. The light greyish-brown "C" horizon is finely granular, friable and calcareous. A great degree of variability in depth of "A" and "B" horizons exists and the "A" horizon commonly extends to tongued intrusions into the underlying horizons.

The light phase of the Soil association differs in several respects from the heavy phase. The texture range of the light phase is from a fine sandy loam to silty loams. In corresponding drainage positions it has a deeper profile, greater profile development, absence of tonguing, and a lack of uniformity in its textural profile. Because of the lighter textures these soils are more friable, and more acid in reaction.

Duck Mountain Association:

The Duck Mountain Soil Association consists of soils developed on irregular moderately sloping to irregular steeply sloping shaly boulder till. The typical associate is a well developed grey-wooded soil characterized by medium to heavy textures, which range from sandy loams to clay loams in the surface horizons and from clay loams to clays in the subsoil. The average depth of solum of the well drained member ranges from 18 inches to 24 inches. The dark to very dark brownleaf mat is generally well decomposed and neutral to slightly acid in reaction. The light grey "A"₂ horizon usually possesses a weakly platy structure, a friable consistence and a slightly acid reaction. The greyish brown "B"₂ horizon is medium blocky, moderately plastic and sticky, very hard when dry and slightly acid. The lower part of the "B"₂ horizon grades into a pale brown laminated, calcareous, lime-carbonate horizon. The light yellowish-brown "C" horizon is calcareous glacial till predominately of decomposed shale and may contain iron stones.

2. Extent and Severity of Molybdenosis of Cattle in 1953:

The relatively small toxic area found in the Upper Valley Plain of the Swan River Valley extends southeastward from Thunder Hill in the shape of a fan located in Township 35, range 30, to approximately the northwest corner of Township 34 range 28. In this area, where the disorder was obvious in 1951 (Figure 3, 4, 5), no visible evidence of molybdenum poisoning of cattle was encountered in 1953. This may have been the result of copper sulphate therapy instituted as a result of investigations by Cunningham et al (8).



FIGURE 3.

Black and white cow turning grey on affected pasture located southeast of Thunder Hill, (Photo by Prof. J.H. Ellis, 1951).



FIGURE 4.

Calf affected with scours on affected pasture located southeast of Thunder Hill, (Photo by Prof. J.H. Ellis, 1951).



FIGURE 5.

A healthy yearling Hereford, in unaffected area.
(Photo by Prof. J.H. Ellis, 1951).

3. Sampling Procedures:

To obtain more information about the source of possible high molybdenum content of soils in the toxic area and its relation to forage crops and water supply, a systematic collection of samples was undertaken in 1953. Water, plant, and soil samples were taken along three lines of traverse which began approximately at the Manitoba - Saskatchewan border and extended eastward through the center of the toxic area to approximately the middle of range 28. The first line of traverse crossed the top of the fourth tier of sections in Township 34, range 29, and Township 34, range 28. The third line crossed the top of the second tier of sections in Township 35, range 29, and Township 35, range 28. Through the center of the toxic area several north-south traverses were made to ensure that the sampling was representative and satisfactory.

B. Laboratory Investigations:

The total molybdenum was determined in water, plant and soil samples collected by the author in 1953 plus additional plant and soil samples collected by other members of the Manitoba Soil Survey in 1951. The content of water soluble molybdenum in the soil samples also was determined. The determination of the hydrogen ion concentration and its relation to the water soluble molybdenum in the soil samples was investigated. In addition a mineralogical study of the very fine sand fraction of the parent material of several soil samples was undertaken. The results of these investigations are outlined as follows.

1. The Total Molybdenum Content of Water:

The chief purpose of the water analysis was to determine if sufficient molybdenum was contained in the water supply to adversely effect cattle.

(a) Method:

The method used was a modification of the well known stannous chloride, thiocyanate method of Marmoy (25). A known volume of water, approximately 800 mls., was evaporated to dryness. The residue was taken up to 10 mls. of aqua regia, transferred to 100 ml. beaker and evaporated to dryness to destroy organic matter. This step was repeated until the organic matter was destroyed. The residue was then taken up in 10 mls. of HCl (conc.) and diluted to approximately 30 mls. The beaker was then covered with a watchglass and digested for several hours until all or nearly all of the residue was brought into solution. Care was taken to avoid loss of acid. The contents of the beaker were then filtered through a No. 42 Whatman filter paper into a 100 ml. volumetric flask and washed with hot water. When the filtrate was cooled it was diluted to volume.

A 50 ml. aliquot was placed in a 125 ml. separatory funnel and the following were added; 3 mls. of 10% KSCN, 1 ml. of 5N NaNO_3 , and 3 mls. of 10% SnCl_2 . The funnel was shaken manually for 30 seconds. The approximately 10 ml. of anhydrous ethyl ether were added, the funnel shaken manually for 30 seconds, and the ether layer separated from the aqueous solution. This step was repeated using 5 mls. of ether. The ether separations were collected in 25 ml. volumetric flask, diluted to volume, and then transferred to standardized cuvettes. Color transmittance readings were made using a Coleman Universal Spectrophotometer with the ultra-violet filter No. 11-124 at a wavelength of 460 mu. The readings were referred to a standard curve.

A standard solution of ammonium molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, was made by dissolving 0.368 gms. of the salt in a liter of distilled water. Then 20 mls. of this solution was diluted to 200 mls. to obtain a solution containing 20 p.p.m. Mo. A set of standards were made containing concentrations ranging from 0 to 10 p.p.m. Mo. Appropriate aliquots of these solutions were taken and the molybdenum extracted in the manner described above.

Regardless of the size of aliquot taken for the determination, the final concentration of HCl in the separatory funnel was adjusted to approximately 1N after all the reagents had been added. According to Willis (46) and Prince (29) 1N acid concentration gives maximum color development.

(b) Results and Discussion:

The results of the analysis on a total of 18 water samples and their distribution within the project area are given in Table 1 and Figure 2, respectively. The 18 samples are composed of 5 surface water and 13 well water samples. All of the samples were taken from sources used to supply the daily water requirements of livestock.

The results shown in Table 1 indicate that the level of molybdenum in the samples was low. The content of molybdenum was found to vary from 0.005 to 0.014 p.p.m., with an average content of 0.008 p.p.m. The differences in the level of molybdenum in water from the area, where, according to Cunningham et al (8), symptoms of molybdenum poisoning had been noted and water from outside the area, were not found to be significant. Well water within the area averaged 0.007 p.p.m. Mo. whereas, outside the area, it averaged 0.006 p.p.m. Mo. A comparison of surface drainage water samples showed that samples outside the toxic area contained as much as, or more

TABLE 1

The Total Content of Molybdenum in Well and Surface Drainage Water,
Collected in July, 1953 from the Project Area.

Location	Description of Source	ppm of Molybdenum
SW 17-35-29 W1	Deep well near barn	0.011*
NW 16-35-29 W1 SW 16-35-29 W1	Well water; composite sample	0.006*
NE 22-34-29 W1 SE 27-34-29 W1 SW 25-34-29 W1	Well water, composite sample	0.007*
NW 28-34-29 W1 SW 33-34-29 W1	Deep well water, composite sample	0.008*
SW 6-35-28 W1 SE 5-35-28 W1	Well water, composite sample	0.009*
NE 33-34-29 W1	Deep well in barn, water very milky in appearance but did not have any noticeable odor.	No trace*
NW 32-34-29 W1	Spring water from coarse sandy outwash near Swan River	0.006
NW 5-34-29 W1	Water from shallow well dug in dark grey acid shale.	0.011
NE 18-35-29 W1	Well water	0.005
NE 19-34-28 W1 SE 32-34-28 W1 NE 31-34-28 W1	Well water, composite sample	0.008
NE 11-35-29 W1	Well water	0.006
NE 7-35-28 W1	Well Water	0.006
NE 20-34-29 W1	Well water	No trace
NW 8-35-29 W1 CW 16-35-29 W1 SW 16-35-29 W1	Composite sample of drainage water from a tributary of Thunder Hill Creek.	0.011*
NE 33-34-29 W1	Slough water	0.011*
NW 7-35-29 W1	Slough water	0.012
NW 17-35-29 W1	Drainage from a tributary of Thunder Hill Creek	0.014
CN 9-35-28 W1	Slough water	0.012

* Samples taken from area in which symptoms of Molybdenum toxicity in cattle had been reported.

R ge. 28

R ge. 29

R ge. 30

Tp. 35

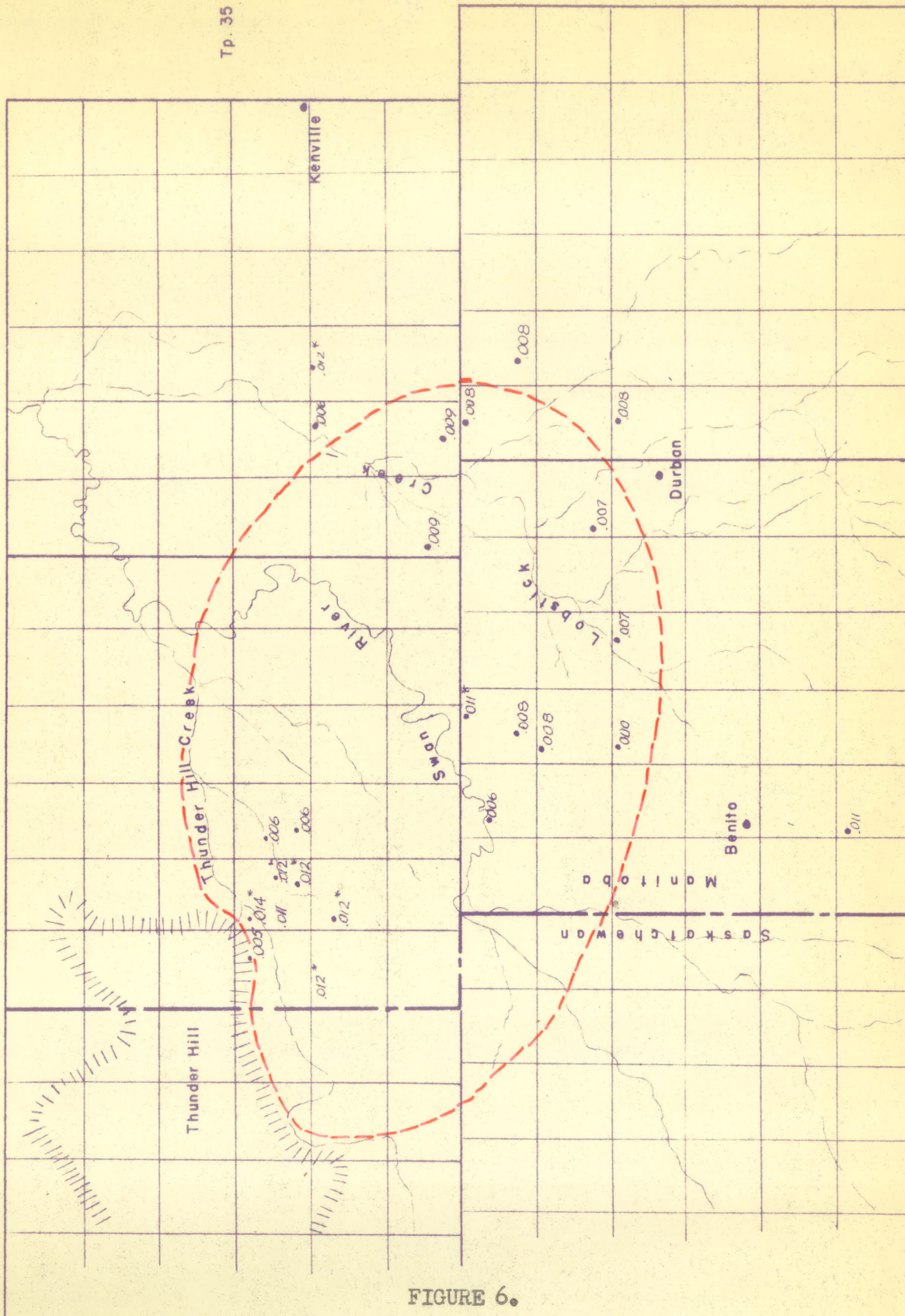


FIGURE 6.

Location of water samples, analysed for total molybdenum and molybdenum content expressed in p.p.m. (* surface drainage water).

molybdenum (range from 0.012 to 0.014 p.p.m.) than samples from within the toxic area (range from 0.011 to 0.012 p.p.m.).

Although differences in molybdenum content of samples inside and outside the affected area were not significant, almost twice as much molybdenum was present in surface drainage waters than in well water (see Table 1). The well water samples varied from 0 to 0.011 p.p.m. Mo., whereas the surface water samples varied from 0.011 to 0.014 p.p.m. Mo. The higher molybdenum content in the samples of surface water was probably due to contamination with suspended material containing molybdenum. However, because the cattle ingested the water containing this suspended material it is believed that its presence did not detract from the results of the analysis.

A cow which consumes 15 gals. of water with 0.014 p.p.m. Mo. and 30 lbs. of dry weight forage with 10 p.p.m. Mo. each day would have an intake of 0.000021 lbs. of Mo. from water and 0.0003 lbs. of Mo. from forage. In other words, water could be the source of only 0.07% as much Mo. as the forage. Thus it would seem that in general the molybdenum content of the water supply in the affected area is not sufficient to affect cattle adversely.

The only conclusion to be drawn from the data in Table 1 and Figure 6 is that relatively uniform and minute quantities of molybdenum are found in both well water and surface drainage water, regardless of location within or without the affected area.

2. The Total Molybdenum Content of Plants:

The purpose of the plant analysis was, to supplement studies of Cunningham et al (8) in respect of the quantities of molybdenum in herbage grown on soils in the Swan River Valley. Approximately forty plant samples were collected within the space of one week, thus obtaining plants of uniform

development for comparison. Plants samples taken in the summer of 1951 by Dryden of the Manitoba Soil Survey Staff made it possible to obtain comparative information regarding the effect of season on the content of molybdenum in the pasturage. The sampling technique also made it possible to make comparisons of different plant species.

(a) Method:

The stannous chloride thiocyanate method of Marmoy (25) was used for determining the total molybdenum content of the plant samples. The method for extracting the molybdenum consisted of transferring 2 gms. of plant material to a sillimanite dish and igniting it in a muffle furnace at 450° C. When cooled the ash was moistened with a few drops of water. Then 10 mls. of aqua regia was added and evaporated to dryness on a hot plate, taking care to avoid sputtering. The ash was ignited a second time at 450° C and when cooled 10 mls. of concentrated HCl were added. The ash was warmed, transferred to a 100 ml. beaker, diluted to approximately 30 or 40 mls. boiled for a few minutes and filtered through a No. 42 Whatman filter paper into a 100 ml. volumetric flask.

The procedure for developing and measuring color was identical to that used in the water analysis.

(b) Results and Discussion:

The results of the plant analysis as shown in Tables 2 and 3 indicate that toxic quantities of molybdenum were found in samples from the affected area. Eight out of 42 samples collected in 1953 from affected parts of the project area showed molybdenum contents above 10 p.p.m. which is the lower limit of toxicity set by Barshad (2) and 1 sample which showed

a content of molybdenum equal to 20 p.p.m. which is the lower limit of toxicity set by Ferguson et al (13). In the samples collected in 1951, only 2 out of 23 samples were found to contain molybdenum above the lower toxic limit of 10 p.p.m. and none above the 20 p.p.m. limit. The average molybdenum content of affected herbage was found to be somewhat lower than that found by Cunningham (8) in plants from the same area in 1948 and 1949. The relatively low quantities of molybdenum found in herbage in the affected area of the Swan River Valley as compared to other problem areas suggest that the area is only moderately affected. Furthermore, Cunningham (8) noted the disorder in cattle was mild in 1948 and 1949 but that in previous years the cattle were much more severely affected.

The effect of growing season on the molybdenum content of pasturage was found to be considerable. The average molybdenum content of 9 plants collected in 1948 and 1949 by Cunningham et al (8) varied from an average of 11.1 p.p.m. to 8.5 p.p.m., respectively. The 23 plants collected in 1951 by Dryden (see Table 2) averaged 4.93 p.p.m. Mo., whereas, the average of 42 plants collected by the author in 1953 (see Table 3) was found to be 7.16 p.p.m. Mo.

It was observed in the affected area, and likewise in California and Somerset, that certain species of pasture plants were more toxic and contained greater quantities of molybdenum than others. In the Somerset and California investigations, legume pastures were found to absorb the largest amounts of molybdenum. In the Swan River area, however, legumes were not found to be more toxic than non-legumes. Cunningham found that of 29 samples, collected from the area in 1948 and 1949, the molybdenum content averaged 6.4 p.p.m. for alfalfa and 13.5 p.p.m. for brome grass. A similar situation was found to exist in 1951 and 1953. Of 23 samples collected in 1951 by Dryden the molybdenum content averaged 3.87 p.p.m. for alfalfa, and

TABLE 2

Total Molybdenum Content of Plants Collected July, 1951.

Location	Plant Description	ppm of Molybdenum
NW 33-34-29 W1	Alfalfa	3.75*
SW 7-35-29 W1	Alfalfa	1.87*
NW 34-34-29 W1	Alfalfa	2.50*
SW 6-35-28 W1	Alfalfa	1.25*
SE 13-35-29 W1	Alfalfa	1.87
SE 13-34-29 W1	Alfalfa	4.37
NW 29-35-29 W1	Alfalfa	3.12
NE 29-35-28 W1	Alfalfa	10.00
CE 19-35-29 W1	Alfalfa	5.00
SE 33-34-29 W1	Yellow Blossom Sweet Clover	3.12*
NW 33-34-29 W1	Yellow Blossom Sweet Clover	8.12*
SW 27-34-29 W1	Brome	8.75*
SW 17-35-29 W1	Brome	1.25*
NE 9-35-29 W1	Brome	6.87
CE 21-35-29 W1	Brome	13.75
SW 17-35-29 W1	Alfalfa, Brome	3.12*
NW 24-34-29 W1	Alfalfa, Brome	3.12*
SE 3-35-28 W1	Alfalfa, Brome	2.50
SE 4-35-28 W1	Alfalfa, Brome	8.75
SE 28-35-29 W1	Yellow Blossom Sweet Clover and Wild Oats	3.75
CE 31-34-29 W1	Yellow Blossom Sweet Clover and Timothy	8.75
GN 33-34-28 W1	Brome, Timothy, Kentucky Bluegrass	3.12
SW 16-35-29 W1	Wheat Second Year After Brome Pasture	6.87*

* Samples taken from area in which symptoms of molybdenum toxicity in cattle have been reported.

TABLE 3

Total Molybdenum Content of Plants Collected in July, 1953.

Location	Plant Description	ppm of Molybdenum
SW 17-35-29 W1	Alfalfa	5.62*
SW 17-35-29 W1	Alfalfa	4.37*
NW 23-34-29 W1	Alfalfa	9.37*
NE 33-34-29 W1	Alfalfa	5.00*
SE 8-35-29 W1	Alfalfa	2.50*
NE 17-35-29 W1	Alfalfa	3.12
SW 20-35-29 W1	Alfalfa	15.16
SE 18-35-29 W1	Yellow Blossom Sweet Clover	6.25*
SE 28-34-29 W1	Yellow Blossom Sweet Clover	2.50*
NW 28-34-29 W1	Yellow Blossom Sweet Clover	4.37*
SW 33-34-29 W1	Yellow Blossom Sweet Clover	5.00*
NE 33-34-29 W1	Yellow Blossom Sweet Clover	13.75*
NE 7-35-29 W1	Yellow Blossom Sweet Clover	3.12
SE 21-34-29 W1	Yellow Blossom Sweet Clover	2.50
SE 29-34-28 W1	Yellow Blossom Sweet Clover	2.50
SE 4-35-29 W1	Yellow Blossom Sweet Clover	2.50
SE 8-35-29 W1	White Blossom Sweet Clover	2.50*
SW 17-35-29 W1	Brome	13.12*
SE 8-35-29 W1	Brome	18.75*
SW 35-34-29 W1	Brome	2.50*
SE 2-35-29 W1	Brome	10.62*
NE 35-34-29 W1	Brome	7.75*
SW 4-35-29 W1	Brome	13.75
NW 10-35-29 W1	Brome	7.75
NE 7-35-28 W1	Brome	5.62
SW 16-35-28 W1	Brome	9.37
NE 20-34-29 W1	Brome	3.75
NE 31-34-28 W1	Brome	3.75
SE 7-35-29 W1	Brome	11.87
NW 8-35-29 W1	Glyceria	1.87*
NW 8-35-29 W1	Brome, Alfalfa	5.00*
NE 22-34-29 W1	Brome, Alfalfa	6.50*
SE 27-34-29 W1	Brome, Timothy, Couch, Alfalfa	3.12*
NW 33-34-29 W1	Alfalfa, Timothy	5.62*
NW 12-35-30 W1	Alfalfa, Timothy, Brome	20.00
NE 19-34-28 W1	Brome, Red Clover	3.12
NE 35-34-29 W1	Timothy, Couch	18.12*
SW 6-35-28 W1	Timothy, Brome, Kentucky Bluegrass	9.37*
NW 31-34-29 W1	Red Top, Kentucky Bluegrass	6.87
NE 11-35-29 W1	Red Top, Timothy, Kentucky Bluegrass	4.37
SW 5-35-29 W1	Wild Pea Vine	8.12
NW 11-35-29 W1	Wild Pea Vine	4.37

* Samples taken from area in which symptoms of molybdenum toxicity in cattle have been reported.

7.41 p.p.m. for brome grass. Of 42 samples collected in 1953 by the author the molybdenum content averaged 6.56 p.p.m. for alfalfa, 4.72 p.p.m. for yellow blossom sweet clover and 9.05 p.p.m. for brome grass. According to Cunningham legume pastures in the area were reported to have been more toxic than non-legumes in seasons of high precipitation and that during dry seasons they are no more dangerous than non-legumes. Although the analyses of plants sampled in four different years have shown striking fluctuations in the average content of molybdenum in both legumes and non-legumes, the relative relationship between them have not changed. In consideration of the facts revealed by the analyses, it seems probable that, in the Swan River area, brome grass accumulates more molybdenum than alfalfa. The fact that legumes pastures have been reported in the past to be more toxic than non-legume pastures in seasons of high rainfall has not been substantiated by analytical evidence.

Figure 7 shows the relationship between content of molybdenum and source of plant material. The plants high in molybdenum were found chiefly in an area which extends from the southeast corner of Thunder Hill in a fan shaped manner to approximately the north west corner of Township 34, Range 28. With one exception, the level of molybdenum diminished the further the plants are from Thunder Hill. In general, the plants that were high in molybdenum were found to be located on soils of the Kenville Association. However, there are notable exceptions because the sample highest in molybdenum is located on the Whitesand Soil Association near the foot of Thunder Hill. The distribution of plants high in molybdenum, indicates that Thunder Hill might have been the source of materials from which the molybdenum is derived.

3. The Total Molybdenum Content of Soils:

Soil analyses were conducted; first to determine the level of total molybdenum in soils where plants high in molybdenum have grown; second to determine the possible source of the element and finally to study the relationship of soil molybdenum to toxic vegetation. Of the different soil types involved, analyses were made on twelve profile samples, nine of which represent the Kenville, one the Whitesand, one the Davidson, and one the Duck Mountain Soil Associations.

(a) Method:

Several methods were tried before adopting a method outlined by Willis (46) which is a modification of methods by Ferrin and by Evans, Purvis and Bear. The method used consisted of weighing 2.5 gms. of air dried 100 mesh soil into a platinum crucible and heated in a muffle furnace at 500° C for three hours to destroy organic matter (care was taken to avoid the use of higher temperatures which might have involved loss of molybdenum). Samples which contained large amounts of organic matter were heated for longer periods. After the crucibles were cooled 5 mls. of distilled water, 10 mls. of 48-50% HF and 0.5mls. concentrated H₂SO₄ were added. The crucibles were heated gently on a sandbath, and stirred occasionally with a platinum wire, until dried. (Caution was required in order to prevent over heating and loss of material due to spattering especially when the samples were near dryness). The addition of water and hydrofluoric acid was repeated, and again taken to dryness. The crucibles were then placed in a cold muffle furnace and heated to 350° for one hour to drive off residual H₂SO₄ in the form of SO₃ fumes. The crucibles were removed, and after they were cooled 10 mls. of 6N HCl and 5 mls. of distilled water were added. The crucibles were heated gently on a sandbath to loosen the residue. Contents of the

crucible were then transferred to 150 ml. beaker and washed with hot distilled water. Another 10 mls. of 6N HCl were added to the beaker, covered with a watchglass and digested at a low temperature until all of the residue was in solution. This digestion required approximately two hours and care was taken during that time to avoid any loss of acid. The contents were then filtered through a No. 42 Whatman filter paper into a 100 ml. volumetric flask, washed and diluted to volume.

A 50 ml. aliquot taken for the determination was placed in a 125 ml. separatory funnel, and in succession the following reagents were added; 3 mls. of 10% KSCN, 1 ml. of 5N NaNO₂, 1 ml. of FeCl₃·6H₂O, (49 gms. Fe Cl₃·6H₂O per liter of H₂O) and 5 mls. of freshly made 10% SnCl₂ (10 gms. of SnCl₂ dissolved in 10 ml. of conc. HCl and diluted to 100 ml H₂O). On the addition of these reagents the final concentration of HCl in the funnel was approximately 1N. The funnel was then shaken manually for approximately 30 seconds. About 10 mls. of anhydrous ethyl ether were added, the funnel shaken manually for another 30 seconds and the ether separated from the aqueous solution. This step was repeated using 5 mls. of ether. The ether separations were collected in a 25 ml. volumetric flask and diluted to volume. The ether separations were then transferred to standardized cuvettes and the color transmittance readings were made using a Coleman Universal Spectrophotometer with an ultra-violet filter at a wavelength of 460 mμ.

The method used here differed slightly in several respects, from the method outlined by Willis. The color was extracted with ethyl ether in place of the preferred isopropyl ether. The color is more stable and losses due to evaporation are less when iso-propyl ether is used. Lack of a suitable mechanical shaker necessitated shaking the separatory funnels by hand. Also a Coleman Universal Spectrophotometer was used in place of an

Evelyn Colorimeter. Finally the use of redistilled water and recrystallized chemicals was not found to be necessary.

This method was found to be much superior to the fusion methods using sodium carbonate outlined by Robinson (30), (33) and Prince (29). The greatest disadvantage of the fusion method is the contamination of the anhydrous sodium carbonate with large and variable quantities of molybdenum, a problem encountered by Robinson et al (33). Washington (44) advocated the use of monohydrated sodium carbonate for fusion purposes because this salt usually has less molybdenum than the anhydrous salt. However, the monohydrated sodium carbonate also was found to contain too much molybdenum for this work.

A modification of a method by Perrin (28), that was developed by the Chemistry Division of the Science Service of the Canada Department of Agriculture, at Ottawa, was used as a check on the hydrofluoric acid method employed in this laboratory. In this method, molybdenum was extracted by the use of perchloric acid.

The molybdenum was then determined by a modification of the thiocyanate method. Citric acid was used to separate molybdenum and iron from other elements in solution. These two elements were extracted alternately with ether and water. Color was developed by adding potassium thiocyanate and stannous chloride successively and then extracted with iso-amyl alcohol. This method although more precise proved to be time consuming and costly. However, the method is superior to the hydrofluoric acid method for determining the molybdenum content of samples high in iron.

To check the method adopted for the determination of molybdenum in soils, several samples were sent to the laboratories of the Chemistry Division, Science Service, Ottawa, where the molybdenum content of the

samples were determined by a perchloric acid modification of the Perrin method. A comparison of these results with determinations made by the hydrofluoric acid modification used by the author is given in Table 4.

TABLE 4

A Comparison of Molybdenum Determinations by Different Methods.

Sample No.	Sample Description	Ottawa* Method	Hydrofluoric Acid Method
57	Indurated Concretionary Iron	134.00	-
78	B Horizon of Kenville Assoc.	4.47	5.75
93	" " " "	1.95	2.75
126	" " " "	2.19	1.25

* Analysed by the Chemistry Division, Science Service, Ottawa.

(b) Results and Discussion:

The analytical results of the soil samples obtained from the project area are shown in Table 5. The data indicate that the average level of molybdenum in soils of the problem area is considerably higher than the average level of 2.5 p.p.m. reported by Robinson and Alexander (34). With the exception of the concretionary iron sample, the average level of molybdenum in the soil samples analyzed, ranged from 1.25 to 7.75 p.p.m. In the soil profile with the highest amount, the level of molybdenum was 5.25 p.p.m. in the surface horizon and 11.75 p.p.m. in the subsoil or parent material. In the two soil profiles with the lowest amount, the level of molybdenum throughout the profile remained constant at 1.25 p.p.m.

Samples from a soil profile obtained immediately east of the affected area were found to contain from 3.25 p.p.m. in the surface horizon to 2.75 p.p.m. in the subsoil or parent material. A composite sample obtained from the Newdale Association approximately 6 miles west of Hamiota, and outside the Swan River area, contained 2.75 p.p.m. Thus the molybdenum level in the soils from two sites outside the affected area are comparable to Robinson's average value of 2.5 p.p.m. Although soils reported in Table 5 did not reveal high levels of molybdenum, the amounts present are sufficient to account for the intake of toxic quantities by the forage here produced. The level of molybdenum in the soils of the Swan River Valley are similar to those in California where Barshad (2) found that the total amount of molybdenum in the soils of the affected areas was not excessively high and that a large percentage of it was soluble in water. Apparently, factors other than total molybdenum in the soil are responsible for toxic vegetation in the Swan River area.

Figure 8 shows the location of the soils analysed and the average content of molybdenum in the respective soil horizons of the various profiles.

TABLE 5

Total Molybdenum, pH, and Calcium Carbonate of Soils by Horizon Depths.

Location	Soil Association	Depth or Horizon (Depth)	ppm. of Mo.	Average Level of Mo. in ppm *	pH	CaCO ₃ **
SW 17-35-29 W1	Kenville ***	0- 6"	7.50	7.63	6.7	-
		6- 9"	6.25		6.5	-
		9-16"	8.25		5.8	-
		16-29"	7.75		5.7	-
		29-34"	8.25		7.3	+++
		38-50"	7.75		7.3	++
SW 17-35-29 W1	Kenville ***	0- 6"	5.25	5.25	5.5	-
		6- 8"	3.75		5.9	-
		8-13"	3.75		5.3	-
		13-25"	5.25		5.5	-
		25-33"	5.75		7.3	+++
		33-50"	7.75		7.2	+++
SE 33-34-29 W1	Kenville ***	0- 8"	8.25	7.05	6.9	-
		8-15"	5.25		6.2	-
		15-24"	5.75		5.8	-
		24-36"	7.75		6.6	-
		36"+	7.75		7.3	+++
SE 33-34-29 W1	Kenville ***	0- 8"	4.25	3.95	7.2	-
		10-18"	3.75		7.3	-
		18-24"	5.25		7.3	+++
		30-36"	3.75		7.3	+++
		36"+	2.75		7.3	+++
NW 14-34-30 W1	Gravel Outwash:		4.25	4.25	7.9	++
		(Horizon):				
SE 19-35-29 W1	Duck Mountain	A	2.75	2.56	7.0	+
		B	2.75		7.1	++
		C	2.50		7.6	+++
		D	2.50		7.4	++
SW 17-35-29 W1	Kenville	A	2.75	3.58	6.8	-
		B	4.25		6.3	-
		C	3.75		7.4	++

Cont'd.

TABLE 5 CONT'D.

Total Molybdenum, pH, and Calcium Carbonate of Soils by Horizon Depths.

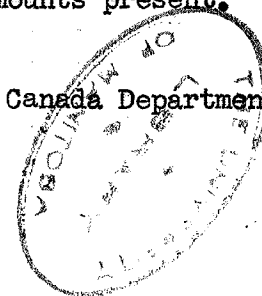
Location	Soil Association	Depth or Horizon	ppm. of Mo.	Average Level of Mo. in ppm *	pH	CaCO ₃ **
		(Horizon):				
SE 8-35-29 W1	Kenville	A	5.25	7.75	5.9	-
		B	5.75		6.2	-
		C	11.75		7.2	+++
NE 11-35-29 W1	Davidson	A	1.25	1.25	5.9	-
		B	1.25		5.9	-
		C	1.25		7.1	+++
SW 16-35-28 W1	Kenville	A	3.25	2.92	7.1	+
		B	2.75		7.1	+
		C	2.75		7.5	+++
NE 20-34-29 W1	Whitesand	A	2.25	3.25	6.3	-
		B	2.25		6.5	-
		C	5.25		7.5	+++
SW 33-34-29 W1	Kenville	A	2.25	2.75	6.7	-
		B	3.75		6.3	-
		C	2.25		7.5	+++
NE 33-34-29 W1	Kenville	A	1.25	1.25	6.7	-
		B	1.25		6.1	-
		C	1.25		7.3	+++
NW 32-34-29 W1	Concretionary Iron ****		134.00	134.00	7.7	-
SE 18-14-24 W1	Newdale	Composite Sample	2.25	2.25	7.5	++

* Arithmetic averages of molybdenum in respective horizons, i.e.; not the weighted averages.

** Presence of free carbonate was determined qualitatively, by the use of dilute HCl. The symbols are as follows: - None present; + Slight amounts present; ++ Moderate amounts present; +++ Large amounts present.

*** Samples collected by R. Dryden in July, 1951.

**** Analysis made by the Chemistry Division, Science Service, Canada Department of Agriculture, Ottawa, 1954.



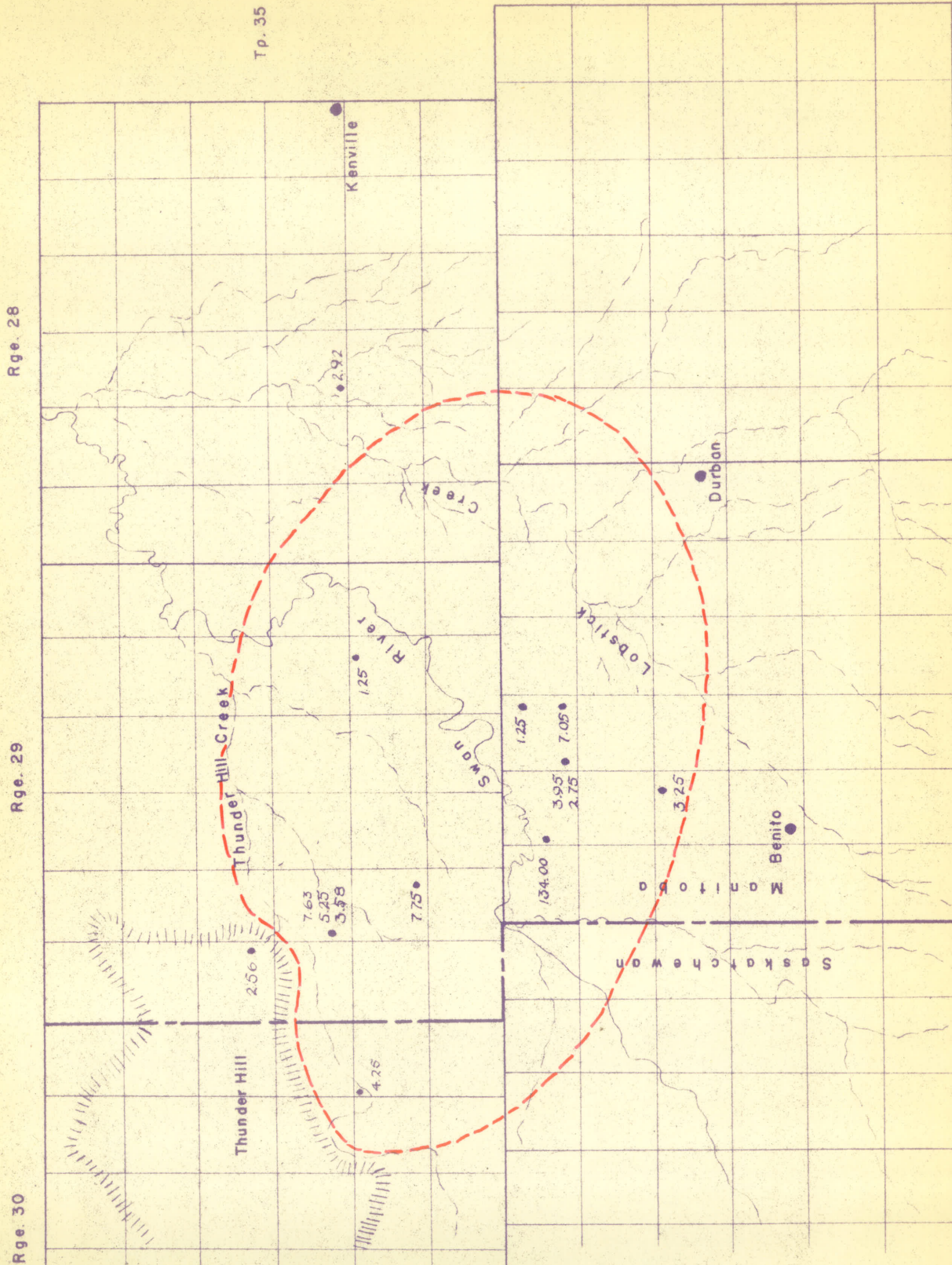


FIGURE 8.

Location of soil samples analysed for total molybdenum, and average molybdenum content expressed in p.p.m.

The soils highest in molybdenum appear to concentrate in an area just southeast of Thunder Hill. This agrees with the results of the plant analyses. The distribution of soils high in molybdenum suggests that erosional products high in molybdenum may have been washed out in an alluvial fan southeastward from Thunder Hill. The presence of soils relatively high in molybdenum south of the Swan River at this point suggests that the material could have been deposited before the river had cut through the deltaic and shallow lacustrine deposits. (See Maps 2 and 3).

4. Soil Reaction and Water-Soluble Molybdenum:

Barshad (4) and Lewis (24) noted that large variations in molybdenum content of different plant species were due to the amount of water-soluble molybdenum in the soil and to a number of other related factors. Hence it was decided to conduct an investigation of the relationship of pH to water-soluble molybdenum in soils.

(a) Methods:

Water-soluble molybdenum was determined using a modification of the method outlined by Barshad (4). The method consisted of adding distilled water to a weighed air dried soil sample that had first been passed through a 2 mm. sieve. In this instance 250 mls. of water were added to 50 gms. of soil. The mixture was shaken for half an hour and allowed to stand until the soil settled to the bottom of the container to obtain a clear supernatant liquid. However, it was found that by adding 2 or 3 drops of dilute HCl to the mixture, followed by centrifuging a clear liquid free from colloidal clay was readily obtained, hence this procedure was adopted. Approximately 200 mls. of clear liquid were recovered and evaporated to dryness. The

residue was then ignited in a muffle furnace at 450° C for 3 hours to destroy soluble organic matter. The residue was taken up in 20 mls. of 6N HCl, diluted to about 30 or 40 mls., digested until it came into solution, filtered through a Whatman No. 42 filter paper into a 100 ml. volumetric flask, washed, cooled, and diluted to volume.

A 50 cc. aliquot was used for the determination. The procedure for developing and measuring the color was identical to that used in determining the total molybdenum of soils.

The pH values of the respective soils were determined by the use of a Coleman Model 3 Electrometer equipped with a glass electrode, after a method proposed by Reed and Cummings (36). The pH determinations were made on samples that were moistened with just enough distilled water to give a continuous water film between the glass and calomel electrodes. This condition was obtained when a paste was made to contain water slightly above the upper plastic limit. Several readings were made to insure reliable measurements.

(b) Results and Discussion:

The water soluble molybdenum found in the soils studied are reported in Table 6. In contrast to the condition reported by Barshad (4), the levels of water-soluble molybdenum in the Swan River soils are not very high. The water-soluble in percent of total molybdenum in these various soil horizons ranged from 0.8% to 14.99%, whereas the percentage of water-soluble molybdenum in the California soils ranged from 11% to 67% of the total. Barshad inferred from these and other results that molybdenum in the California soils is present not as a distinct mineral, but rather, partly as a soluble molybdate salt, partly as a component of the organic matter, and partly as an

TABLE 6

Total and Water Soluble Molybdenum, Water Soluble Molybdenum in Percent of Total, pH, and Calcium Carbonate of Soils by Horizon Depths.

Pro- file No.	Location and Soil Description	Depth or Horizon (Depth)	Total Mo. in ppm.	Water Soluble Mo. in ppm.	Water Soluble Mo. in Percent of Total	pH	CaCO ₃
I.	:SW 17-35-29 W1 :Kenville :Association	: 0- 6"	: 7.50	: .281	: 3.75	: 6.7	: -
		: 6- 9"	: 6.25	: .156	: 2.50	: 6.5	: -
		: 9-16"	: 8.25	: .125	: 1.52	: 5.8	: -
		: 16-29"	: 7.75	: .156	: 2.01	: 5.7	: -
		: 29-34"	: 8.25	: .156	: 1.89	: 7.3	: +++
		: 38-50"	: 7.75	: .187	: 2.41	: 7.3	: +++
II.	:SE 33-34-29 W1 :Kenville :Association	: 0-8 "	: 4.25	: .187	: 4.40	: 7.2	: -
		: 10-18"	: 3.75	: .156	: 4.16	: 7.3	: -
		: 18-24"	: 5.25	: .187	: 3.56	: 7.3	: +++
		: 30-36"	: 3.75	: .156	: 4.16	: 7.3	: +++
		: 36"+	: 2.75	: .156	: 5.67	: 7.3	: +++
III.	:NW 14-34-30 W1 :Gravel		: 4.25	: .156	: 4.40	: 7.9	: ++
IV.	:NW 32-34-29 W1 :(Concretionary) :Iron) :(Horizon):		: 134.00	: 1.08	: .81	: 7.7	
IV.	:SE 19-35-29 W1 :Duck Mountain :Association	: A	: 2.75	: .187	: 6.80	: 7.0	: +
		: B	: 2.75	: .187	: 6.80	: 7.1	: +
		: C	: 2.50	: .125	: 5.00	: 7.6	: +++
		: D	: 2.50	: .187	: 7.48	: 7.4	: ++
V.	:SE 8-35-29 W1 :Kenville :Association	: A	: 5.25	: .156	: 2.97	: 5.9	: -
		: B	: 5.75	: .156	: 2.71	: 6.2	: -
		: C	: 11.75	: .187	: 1.59	: 7.2	: ++
VI.	:NE 11-35-29 W1 :Davidson :Association	: A	: 1.25	: .156	: 12.48	: 5.9	: -
		: B	: 1.25	: .187	: 14.96	: 5.9	: -
		: C	: 1.25	: .187	: 14.96	: 7.1	: +++
VII.	:SW 16-35-28 W1 :Kenville :Association	: A	: 3.25	: .281	: 8.65	: 7.1	: +
		: B	: 2.75	: .219	: 7.96	: 7.1	: +
		: C	: 2.75	: .187	: 6.80	: 7.5	: ++
VIII.	:NE 20-34-29W1 :Whitesand :Association	: A	: 2.25	: .156	: 6.93	: 6.3	: -
		: B	: 2.25	: .125	: 5.56	: 6.5	: -
		: C	: 5.25	: .125	: 2.38	: 7.5	: ++
IX.	:NE 33-34-29 W1 :Kenville :Association	: A	: 1.25	: .156	: 12.48	: 6.7	: -
		: B	: 1.25	: .156	: 12.48	: 6.1	: -
		: C	: 1.25	: .187	: 14.96	: 7.3	: +++

absorbed exchangeable anion.

The soil horizon samples of profile I. and profile VII. are the well drained and imperfectly drained members of the Kenville Association, respectively. The less well drained member is both calcareous and alkaline in reaction and contains from 6.8% to 8.6% water-soluble molybdenum. The well drained member, which is very slightly acid in the surface horizons and slightly alkaline and calcareous in the subsoil, contains from 1.52% to 3.75% water-soluble molybdenum.

5. Minerological Study of Soil Parent Materials:

A minerological study was made of the very fine sand fraction of the parent material of three Kenville soils and one Duck Mountain soil. The primary objective of this investigation was to note if there was any variation in the minerological composition of the respective parent materials.

(a) Method:

The very fine sand fraction from 10 gms. of soil was used for this study. The sample was obtained by dispersing the soil sample in a mechanical stirrer with 10 mls. of 3% Na_2CO_3 for ten minutes. The dispersed sample was passed through a 300 mesh sieve to obtain the sand fraction which was then separated into, coarse, medium, fine and very fine sand. The very fine sand fraction was separated into light and heavy minerals using the bromoform (S.G. = 2.89) separation as described by Krumbein and Pettijohn (22). After this separation each sample was mounted in Canada Balsam and allowed to dry. Between 300 and 700 particles of minerals were identified on each slide under a petrographic microscope.

(b) Results and Discussion:

The percent of heavy and light minerals in the parent material of a Duck Mountain and three Kenville soils are given in Table 7. These percentages indicated that the light minerals with a specific gravity of less than 2.89 constitute, by far, the major suite of the very fine sand fraction. The light minerals constitute from 90.3 to 95.7 percent (by weight) of the total fraction. The heavy minerals on the other hand constituted from 4.3 to 9.7 percent of the total.

The minerals and rock fragments identified in the light mineral suites of six soil parent materials together with the molybdenum content of the soil material from which the minerals were separated are given in Table 8. The data indicate that, with one exception, the bulk of the light minerals are composed of feldspar, limestone, quartz, shale and biotite in descending order of magnitude. The light minerals of the very fine sand fraction from the soil sample with 11.75 p.p.m. Mo. were found to have less feldspar, less limestone, as much quartz, and biotite and considerably more shale than the light minerals of the other soil samples. In this sample the shale, approximately 32 percent was found to almost equal the feldspar content approximately 36 percent.

The petrographic studies of the heavy mineral suite of the parent materials revealed a wide range of minerals as shown in Table 9. The data show that amphiboles, proxenes, iron oxides, chlorite, epidote and apatite are the dominant minerals. Zircon, leucoxene, staurite, tourmaline, biotite, rutile were few in numbers and in some samples several of these minerals were not present. However, the soil sample with a level of 11.75 p.p.m. Mo. was found to contain a lower percentage of amphiboles and pyroxenes (approximately 23 percent) and much higher percentage of limonite (approximately 43 percent)

TABLE 7

Percent by Weight of Heavy and Light Minerals* in the Very Fine Sand Fraction of the Parent Material of One Duck Mountain and Three Kenville Soils.

Location and Soil Association	Heavy Minerals Percent	Light Minerals Percent
SE 19-35-29 W1 Duck Mountain	4.3	95.7
SW 17-35-29 W1 Kenville	4.6	95.4
SW 16-35-28 W1 Kenville	9.7	90.3
SW 33-34-29 W1 Kenville	4.5	95.5

* Includes Limestone and Shale Rock Fragments.

TABLE 8

Percent of Feldspar, Quartz, Biotite, and Rock Fragments Contained in the Light Mineral Suites of Soil Parent Material. *

Location and Soil Association	ppm. of Mo.	Feldspar Percent	Quartz Percent	Biotite Percent	Limestone Percent	Shale Percent
SE 19-35-29 W1 Duck Mountain	2.25	48.7	12.4	4.9	22.0	12.0
SW 17-35-29 W1 Kenville	3.75	47.9	14.3	3.1	18.7	16.0
SE 8-35-29 W1 Kenville	11.75	36.1	13.4	2.3	16.2	32.0
SW 16-35-28 W1 Kenville	2.75	47.6	16.2	3.7	18.4	14.1
SW 33-34-29 W1 Kenville	2.25	50.8	11.0	2.6	21.8	13.8
SW 33-34-29 W1 Kenville	2.75	47.0	14.5	5.0	19.5	14.0
Means		45.9	13.9	3.3	18.9	18.0

* Identification of minerals by Dr. W.A. Ehrlich, Senior Pedologist, Manitoba Soil Survey Staff.

TABLE 9

Percent of Heavy Minerals and Rock Fragments in the Heavy Mineral Suites of Soil Parent Material.*

Location and Soil Association	ppm. Mo.	Amphiboles and Pyroxenes	Limonite	Leucoxene	Pyrite	Other Opaques	Apatite	Biotite	Chlorite	Epidote	Garnet	Others
SE 19-35-29 W1 Duck Mountain	2.25	31.6	3.5	3.5	3.4	26.4	2.7	-	1.5	2.4	16.4	8.6
SW 17-35-29 W1 Kenville	3.75	35.3	3.9	1.2	1.4	23.9	3.9	1.0	5.2	1.4	17.4	5.4
SE 8-35-29 W1 Kenville	11.75	23.4	42.9	1.1	5.9	16.4	1.9	1.4	.2	-	4.6	2.2
SW 16-35-28 W1 Kenville	2.75	39.2	4.2	1.1	1.3	25.5	3.1	.5	2.7	1.3	14.4	6.7
SE 33-34-29 W1 Kenville	2.25	49.1	12.5	2.8	2.9	18.2	4.6	.4	1.1	1.1	5.4	1.9
SW 33-34-29 W1 Kenville	2.75	39.8	7.0	1.3	.8	3.34	1.0	.3	3.5	1.0	7.2	4.7

* Identification of minerals by Dr. W.A. Ehrlich, Senior Pedologist, Manitoba Soil Survey Staff.

than any of the other samples.

The petrographic studies of the light and heavy minerals indicate a close association of molybdenum with iron oxides, particularly in the sample with 11.75 p.p.m. Mo. Goldschmidt (16) found that conspicuous amounts of molybdenum always occur in the oxidate precipitates in soils, such as the ferric minerals and especially manganese dioxide minerals. He also stated that, under strongly oxidizing conditions in the sedimentary cycle, molybdenum as the molybdate ion becomes rather mobile and may migrate in porous sands. According to Goldschmidt and to Hillebrande and Lundell (19), under reducing conditions molybdenum is precipitated, presumably as molybdenite and as a hydrated ferric molybdate. The migration of molybdenum as the oxidized molybdate ion and its subsequent fixation as the reduced hydrated ferric molybdate mineral probably may have occurred in the affected area of the Swan River Valley. The results of the analysis on the concretionary iron sample which was found to contain 134 p.p.m. of molybdenum (See Table 5) would support this hypothesis.

The petrographic studies also indicate that erosional products derived from Thunder Hill make up part of the parent material of the soils high in molybdenum. This conclusion is based on the presence of large amounts of shale in these samples. Samples located north of the Swan River and near Thunder Hill obviously contain more shale than samples found south of the river and further away from Thunder Hill. Therefore it is highly probable that the erosional products which presumably contain oxidized molybdate, were derived from localized areas in Thunder Hill.

IV. GENERAL DISCUSSION

Data in this report show that molybdenum in above normal and toxic quantities is contained in forage grown on a specific area in the Swan River Valley. However, the levels of molybdenum here are not as high as those found in some other areas by other workers. It has been shown by investigations, particularly in England and New Zealand, that the toxic limit in forage is dependent upon the ratio of molybdenum to copper content. In the "teart" pastures of Somerset, pathological effects in cattle resulted from excess molybdenum in the presence of normal copper supplies because the excess was high. In New Zealand, above normal levels of molybdenum were found insufficient to produce pathological effects unless the copper was below normal. Therefore, before a reliable estimation of molybdenum toxicity in the Swan River area can be made, information on the copper content and the molybdenum to copper ratio of the forage is essential. Hence studies of the copper content of forage should be initiated.

Another investigation that should be undertaken is the composition of the shales in Thunder Hill and in the parent material of the soils that are high in molybdenum. The presence of this shale suggests that the parent material of these soils is partly made up of erosional products derived from Thunder Hill. The chemical composition of the shale beds belonging to the Ashville and Favel formations exposed on Thunder Hill is unknown. The amounts of molybdenum they contain should be ascertained.

V. SUMMARY

The occurrence of a peculiar disorder of cattle in the southwestern portion of the Swan River Valley of Manitoba, known for over forty years, has been found to be caused by above normal concentrations of molybdenum in the pasturage.

The objectives of the field investigations initiated in 1951 by Dryden and carried out in 1953 by the author were; to note the extent and severity of molybdenosis in the affected area; to become familiar with the geology, soils, vegetation and other physical features of the affected area; and primarily to make a systematic collection of water, plant and soil samples for laboratory investigations.

Chemical analyses of the water, plant and soil samples were conducted to determine their total molybdenum content. The relation of soil pH and water-soluble molybdenum in soils was investigated to obtain more information as to the state of the molybdenum found in these soils. A microscopic study of the very fine sand fraction extracted from certain soils also was undertaken to obtain information in respect of the mineralogical composition of the soil parent material.

VI. CONCLUSIONS

1. Analyses of plants grown in 1951 and 1953 are in line with the results obtained by Cunningham in 1948 and 1949, that toxic quantities of molybdenum (above the lower limit set by Barshad, but below the limit by Ferguson et al) is contained in herbage grown in the Thunder Hill district of the Swan River Valley.
2. Plant analyses have shown that brome grass accumulates more molybdenum than does alfalfa.
3. The molybdenum content of pasture plants was found to vary greatly in different years.
4. The distribution of plants and soils high in molybdenum was found to be concentrated in an area just southeast of Thunder Hill.
5. The analyses of samples of water consumed by animals in the affected area showed that the molybdenum content ranged from a trace in well waters to a maximum of 0.014 p.p.m. in surface drainage water. Hence the waters ingested by cattle in the affected area do not contain sufficient molybdenum to affect cattle adversely.
6. The soil analyses have shown that the average level of molybdenum in soils of the affected area are definitely higher than the 2.5 p.p.m. that may be taken as the average level of molybdenum in soils.
7. The level of water-soluble molybdenum in all soils analysed was low and ranged from 0.8 to 14.9 percent. Results show that the alkaline and calcareous soils contained slightly more than the acid soils.
8. Mineralogical analyses of the soils high in molybdenum indicated that large amounts of hydrated ferric oxides and shale were present in their parent materials.

9. It is suggested that molybdenum in the soils of the affected area is a constituent of a hydrated ferric oxide, which was found to be only slightly soluble in water.
10. No striking evidence of molybdenosis was observed in the limited number of cattle seen during the field operations in the affected area in 1953.
11. Studies of the copper content of forage grown in the affected and the adjacent non-affected areas should be initiated; and the molybdenum content of the Ashville and Favel shale beds in Thunder Hill also should be ascertained.

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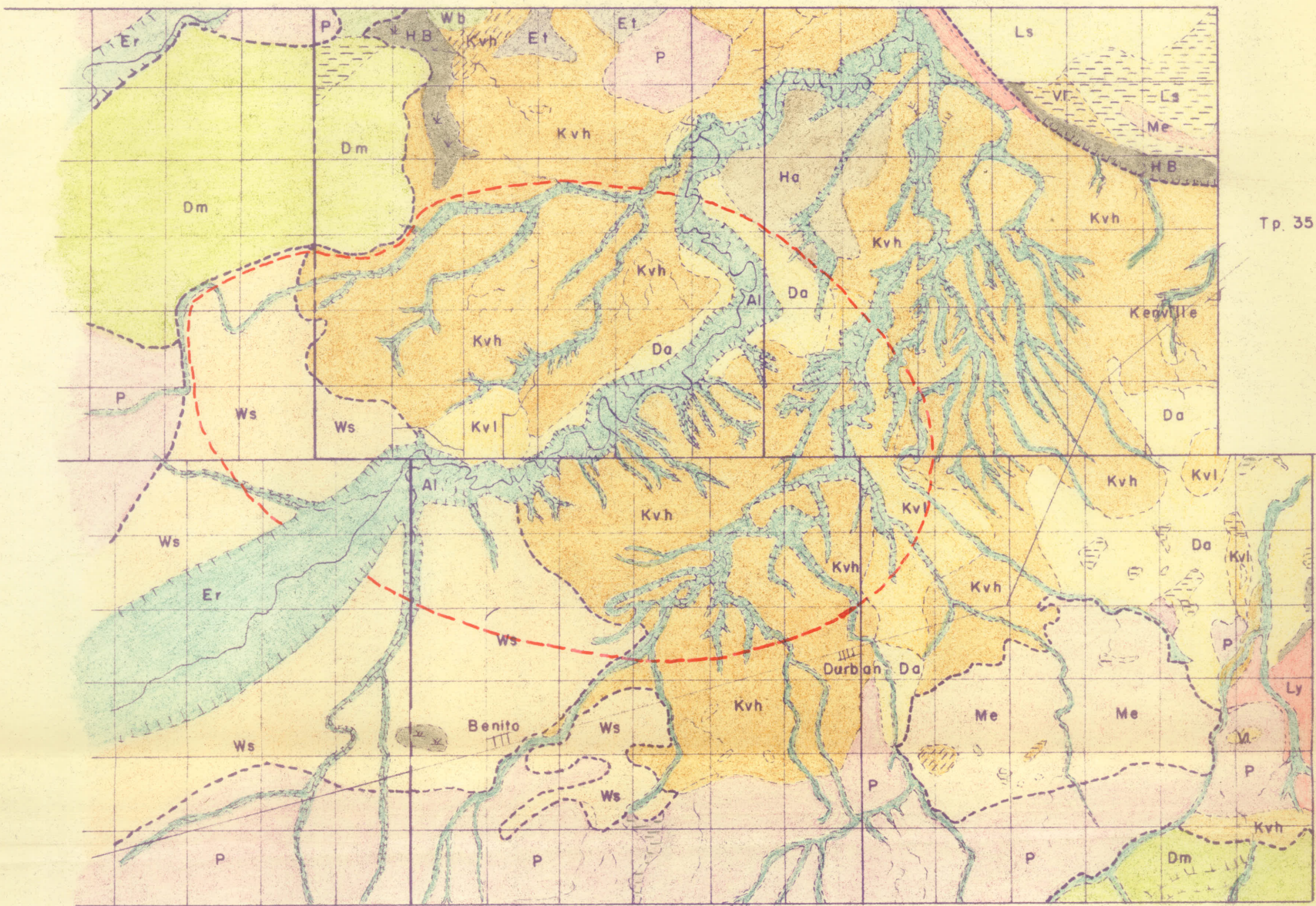
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SOIL MAP
of
PROJECT AREA

Rge. 30

Rge. 29

Rge. 28



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Tp. 35

Tp. 34

KEY TO SOILS

BLACK SOILS

- Ls Lenswood Association
- Me Meharry Association
- Ws Whitesand Association
- Vl Valley Association (Light Phase)

GREY WOODDED SOILS

- Dm Duck Mountain Association
- Wb Whitebeach Association

ORGANIC SOILS

- HB Half Bog

GREY-BLACK SOILS

- Et Etomami Association
- Ha Harlington Association
- Kvh Kenville Association (Heavy Phase)
- Kvl Kenville Association (Light Phase)
- P Pelly Association
- Da Davidson Association

LOCAL SOIL AREAS

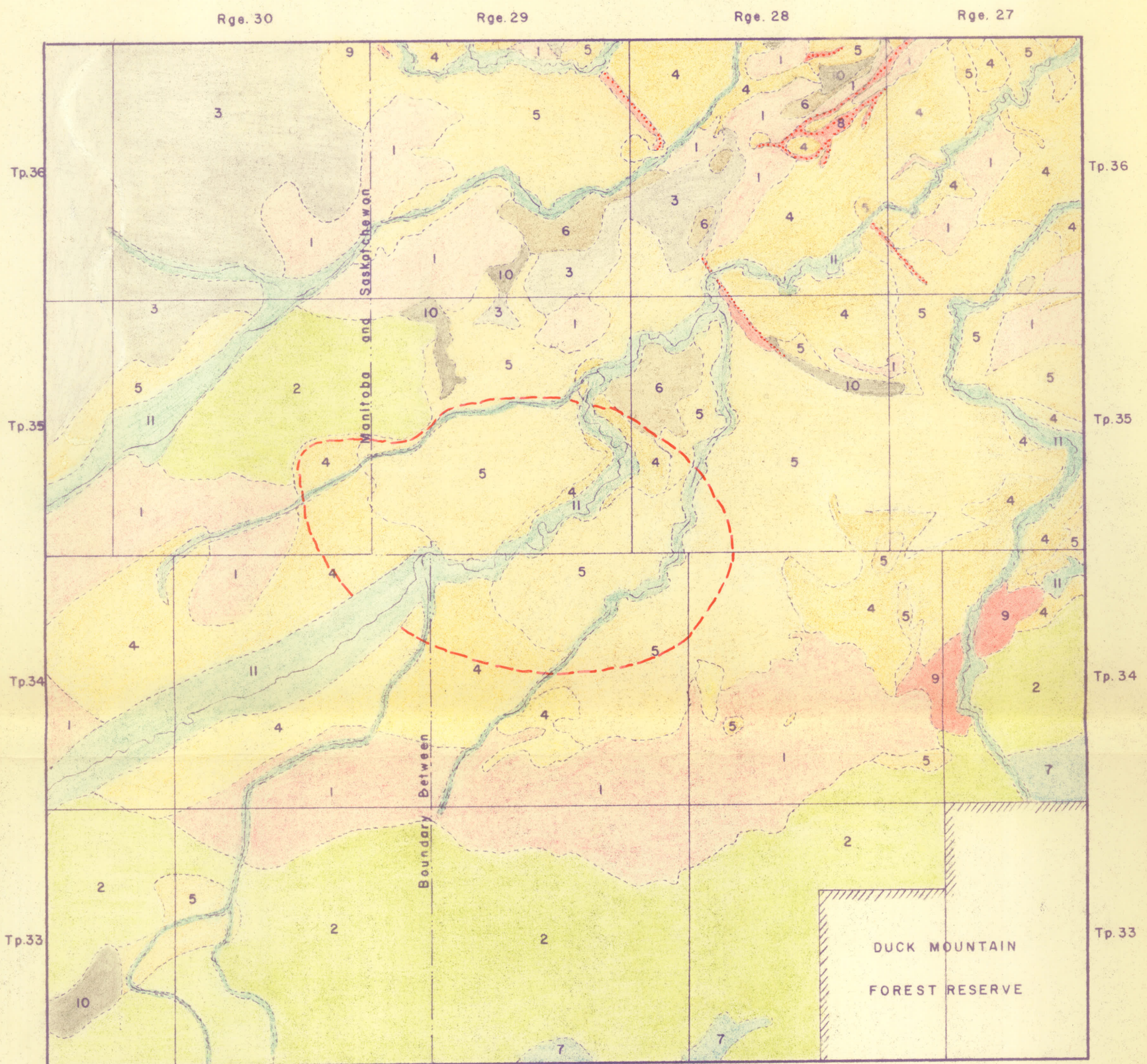
- Er Eroded Channels
- Al Alluvium

SYMBOLS

- Well Drained
- Meadow
- Transition

MAP 2.

MAP of SURFACE
GEOLOGICAL DEPOSITS



LEGEND

GLACIAL TILL:

- 1 Calcareous Boulder Till
- 2 Shaly Boulder Till
- 3 Boulder Clay

SHALE CLAY:

- 7

GRAVEL OUTWASH:

- 9

PEAT:

- 10

DELTAIC and SHALLOW LACUSTRINE DEPOSITS:

- 4 Sandy Textured Deposits
- 5 Medium Textured Deposits
- 6 Clay Textured Deposits

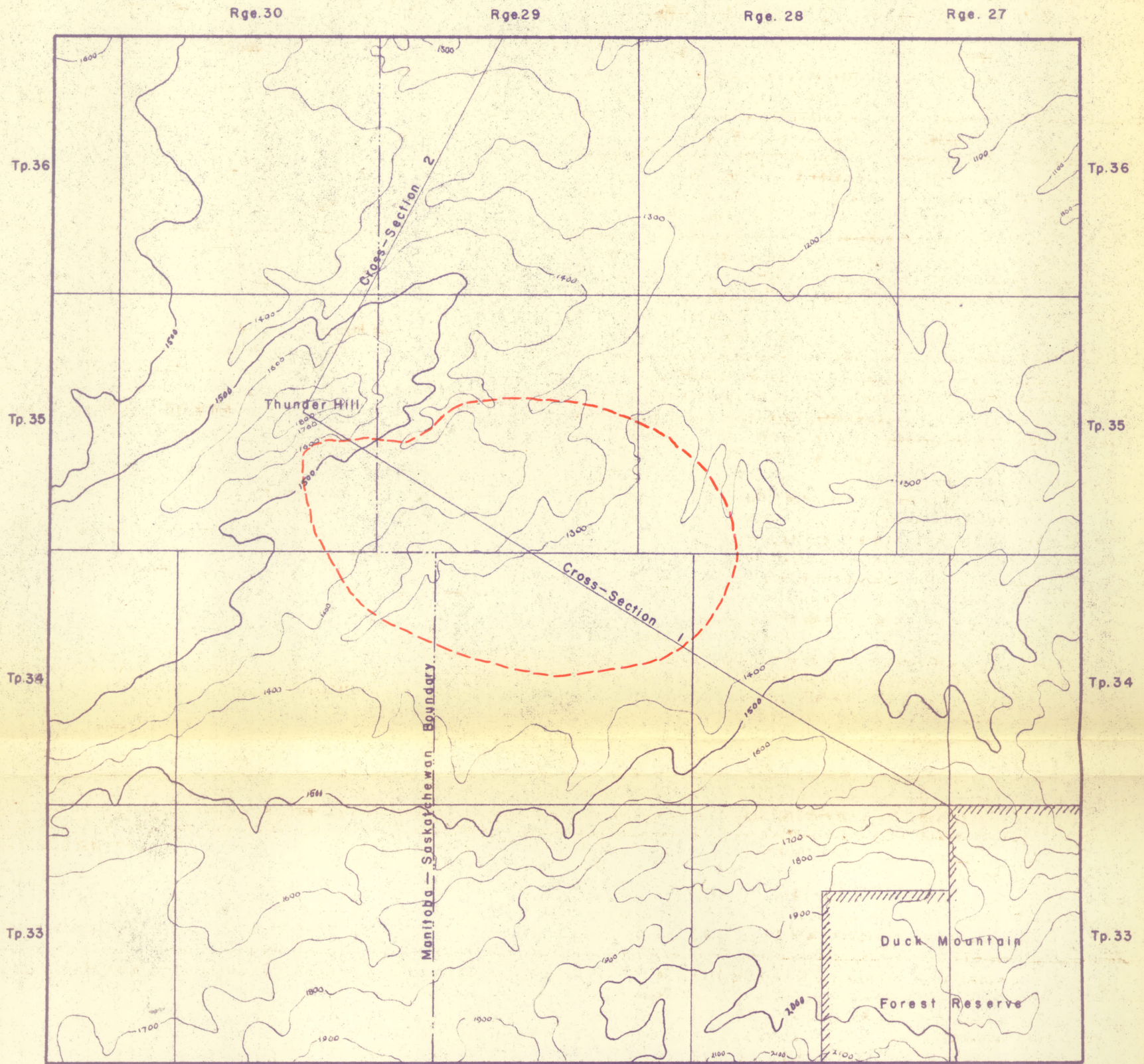
GRAVEL BEACHES:

- 8

RECENT ALLUVIUM:

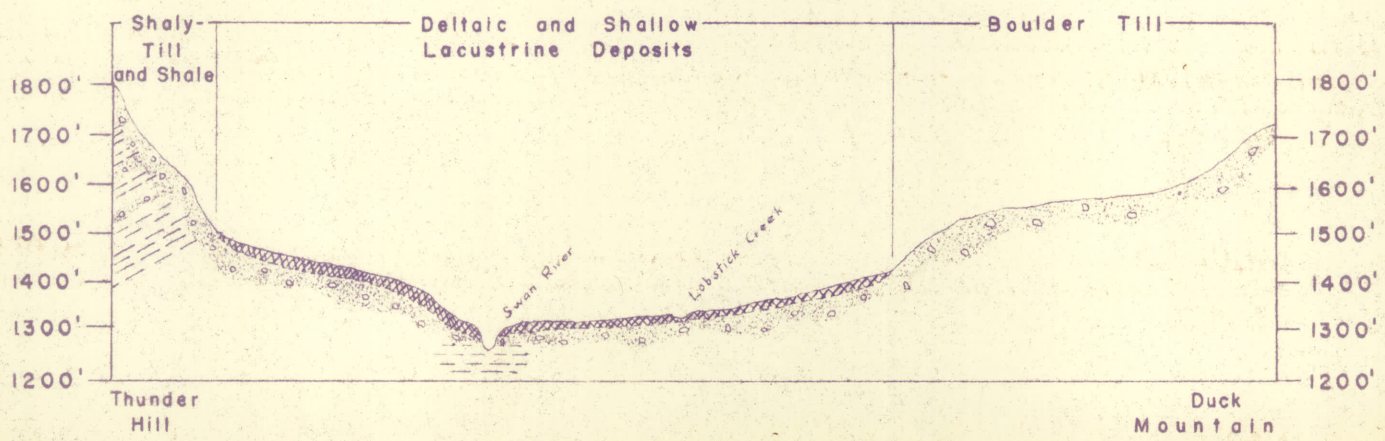
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MAP 3.
CONTOUR MAP AND CROSS-SECTIONS SHOWING
ELEVATION AND SURFACE GEOLOGICAL DEPOSITS



Contour Detail Showing Feet Above Sea Level From Sectional Maps No. 221, 171. Topographical Survey of Canada.

CROSS-SECTION 1. THUNDER HILL TO DUCK MOUNTAIN



CROSS-SECTION 2. THUNDER HILL TO PORCUPINE MOUNTAIN

