COPPER AND MOLYBDENUM STATUS OF PASTURES IN EASTERN SASKATCHEWAN

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Introduction

In the last few years there has been an increasing demand from livestock producers, veterinarians, and SDA agricultural representatives for information on the copper status of pastures and soils in eastern Saskatchewan. Evidence has accumulated (Brockman, 1976) of cases where copper deficiency diagnosed in animals on the basis of hair color, blood copper levels and occasionally liver copper levels, has been confirmed by growth response to dietary copper supplementation. Brockman (1977) also collected 100 liver samples at random from animals slaughtered by local farmers and by Intercontinental Packers in Saskatoon and found 60% of the liver samples to be 10 ug/g D.M. or less. This suggests that copper deficiency may be a greater problem in Saskatchewan than we presently know.

Copper deficiency expresses itself in the animal in a variety of deficiency symptoms. These have been described (Christensen and Cochran, 1975) as loss of appetite in general but with a craving for salt, rough hair coat, reproductive failure and low hemoglobin. Copper deficiency was first observed in cattle in 1931 and since then many studies have been carried out. For instance, in 1952 Marsden quoted 828 references and gave levels of deficient blood copper (below 1 ug of Cu/ml) and liver copper (normal values above 100 ug/g D.M. with recorded values as low as 5 ug/g). In the same review it was noted that copper levels could be adequate in forage, but that copper deficiency symptoms could occur in the animal because of the high intake of molybdenum. Interest in molybdenum had already been stimulated by observations that cattle on so-called "teart" pastures were found to scour persistently and profusely owing to high molybdenum levels in the pasture. Research on molybdenum in animal nutrition has been focussed primarily on its interactions with copper and sulphate, particularly in ruminant nutrition. At least four significant interactions occur in the gastrointestional tract or in the tissues

(Nicholas and Egar, 1974):-

1. Interaction of molybdate and sulphate in the reduction of sulphate to sulphide by ruminal microorganisms.
2. Formation of copper sulphide in the gastrointestional tract, decreasing copper availability.
3. Interaction of molybdate with transport of copper across membranes, and
4. Interaction of sulphate on absorption, transport and excretion of molybdate.

A variety of factors other than dietary copper, molybdenum and sulphur interrelationships have been suggested (Christensen and Cochran, 1975) as factors in the incidence and severity of Cu deficiency. Dried forage was found to permit greater retention of liver copper than the same forage consumed fresh. Toxic levels of cadmium increased liver copper concentrations, manganese levels in forage of cattle also may be important.

Copper Levels in Forage

Work in Canada on the occurrence of copper deficiency (Henderson, 1957; Miltmore et al., 1964, 1971, 1973) confirms the existence of "conditioned copper deficiency" which Henderson attributed to the high molybdenum intake rather than an uncomplicated copper deficiency. Henderson (1957) described the deficiency as occurring in the Swan River area of Manitoba, mainly in summer months, especially in a year of high rainfall in cattle grazing lush pasture. Later work on soil parent material (Fletcher and Doyle, 1971) in West Central Manitoba reported a few small area of abnormally high molybdenum values related to weathering shales but found that the shales were usually marked by variable thickness of glacial drift material. Plant Mo levels were not related to total soil Mo levels.

Miltmore's studies (1964, 1971, 1973) looked at copper, molybdenum and sulphate contents of forage and suggested that ratios of copper to molybdenum of 2:1 and higher were considered safe but all feeds having ratios of 1.9:1 and lower were dangerous. Grass, sedge and oat forages tended to have lower ratios than legumes, corn silage, or cereal grains. As far as suphur content of forage were concerned, scouring occurred in cattle when forage sulphur was high (0.65%), but was found to be lower (0.26%) where scouring did not occur.

Current United States NRC (1971) beef and dairy cattle requirements for copper are in general agreement with these findings as "copper to molybdenum ratios in feeds may be of more importance than actual copper levels. Ratios of 1:1 or

2:1 may lead to copper deficiency, particularly at high (over 0.3% of sulphur in dry matter), Cu/Mo ratios of 4:1 and higher should not cause any problems."

Clark and Drysdale (1974) made a study of forage in the northwest region of Manitoba and suggested that the requirements for cattle from the copper-molybdenum standpoint are 10 ppm copper when molybdenum content is 1 ppm or less. When molybdenum is greater than 1 ppm the copper-molybdenum ratio should be at least 3:1 with a ratio of 4:1 preferred. In their survey of 66 locations, only 10 samples were found to be sufficient in copper for cattle production.

Copper Levels in Soils

Stewart (1969) carried out a survey of the levels of available soil copper in Saskatchewan soils and related it to production of cereal grains. This study showed that the level of copper in the soils was not limiting cereal yield and that there was a good correlation between the amount of copper extracted by a chelate such as EDTA or DTPA and the concentrations in the plant material. Plant copper concentration of 5 ug/g D.M. and greater was thought to be sufficient for normal plant growth. Later work by Heil and Follet (1972) is in agreement with this finding and that 0.2 ug/g DTPA extractable Cu or more in the soil would be sufficient for plant growth. Available sulphate levels in soil are currently run on all soil samples submitted to the Soil Testing Laboratory and information is available on the sulphur status of soils in many areas of Saskatchewan. Some information is also available on plant sulphate levels. A few studies have been reported in the literature on the interaction of Cu X S X Mo in soils and the effect of this interaction on forage composition (Gupta and McLeod, 1975).

Preliminary Survey Program

A joint survey program was carried out in 1976 during which cattle hair, blood and where possible liver samples were analyzed from specific herds where Cu deficiency had been diagnosed and soil-plant-water samples were collected from the pastures grazed by the same cattle. Results on the cattle hair, blood and liver samples are recorded elsewhere (Brockman, 1976, 1977) and this report will deal with the results obtained to date from soil and plant analyses.

Material and Methods

Thirty-two pastures (locations shown on Fig. 1) were sampled in May 1976. Soil samples were taken in 15 cm intervals to 120 cm (48") depth in May; plant samples were taken at monthly intervals until September.

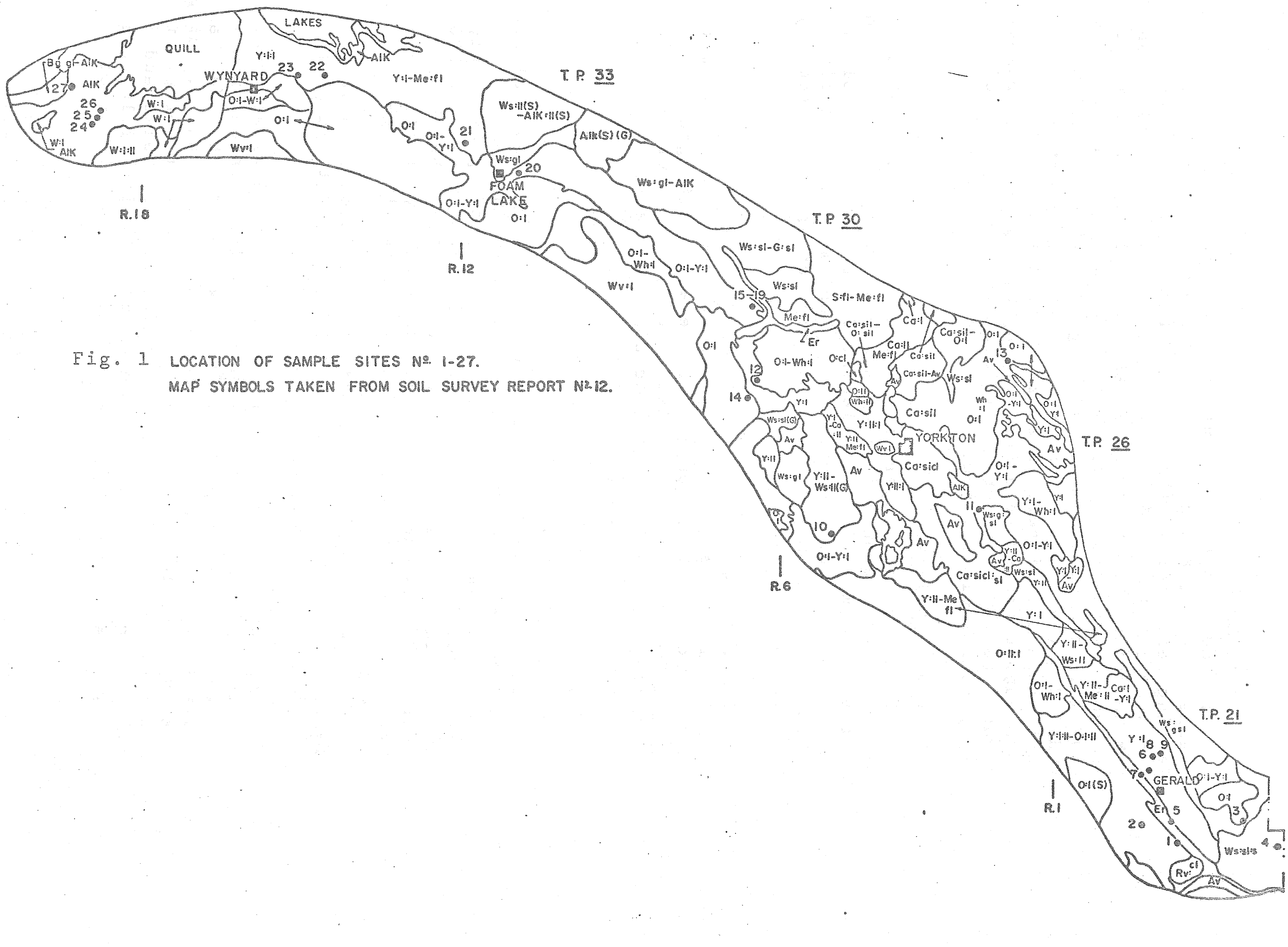

Fig. 1 LOCATION OF SAMPLE SITES № 1-27.
MAP SYMBOLS TAKEN FROM SOIL SURVEY REPORT № 12.

Soil Analyses

In addition to pH, texture, electrical conductivity, available N, P, K and S analyses carried out by the Soil Testing Laboratory, DTPA extractable Cu and Zn (Lindsay and Norvell, 1969), 1 N ammonium acetate extractable B and 1 M ammonium carbonate extractable Mo values were obtained. The ammonium carbonate test developed by Vleck and Lindsay (1976) is as follows:- Shake 25 g soil with 50 ml 1 M $(NH_4)_2CO_3$ (pH 9) for 12 hours on a rotary shaker. Centrifuge and filter. Analyze colorimetrically by the thiocyanate procedure after H_2O_2-H_2SO_4 digestion to remove organic matter. The critical level for alfalfa toxicity is approximately 1.7 ppm.

Plant Analyses

Boron, zinc, copper, molybdenum and sulphur analyses were carried out on the plant material using acid digestion of the plant material and element determination by colorimetric (boron, molybdenum and sulphur) methods utilizing a Technicon system and atomic absorption spectrophotometry (copper and zinc).

Water Analyses

Water samples were collected at each location from the main source of water supply for the animals (dugout, well, slough, creek). These samples were analyzed for electrical conductivity, B, Mo, Cu, Zn and SO_4-S content.

Results

Soil Analyses

The soil pH values ranged from 7.0 to 8.7 and salinity was determined by electrical conductivity increasing markedly in some lower soil depths and reaching extremely high values in the vicinity of Quill Lake. NO_3-N and HCO_3-P were low in all soils except where fertilizer had been applied. Potassium was in sufficient supply at all locations. Extractable sulphate was generally high >96 kg/ha in the top 60 cm except for very sandy soils in the vicinity of Theodore, Springside and Otthon. At Theodore a good yield response was obtained by other workers to sulphate fertilization of the same grassland site.

The extractable micronutrient fluctuated widely from site to site. For instance, DTPA Cu values ranged from 0.16 ug/g to 1.48 ug/g in the 0-15 cm soil depth. Heil and Follet (1972) suggest that any soil with less than 0.2 ug/g DTPA extractable Cu would not contain enough Cu for plant growth. Two top soils tested lower than this value and it could be argued that for a plant concentration of 10 ug/g the soil level should be higher. Extractable Mo levels varied from 0.10 to 0.61 in the top 0-15 cm soil depth. Lower depth in the soil (90-120 cm) tended to have more extractable Mo (range 0.05-0.77) but no consistent trend was observed nor did the level of extractable Mo reach levels known to produce toxic alfalfa >1.7 (Vleck, 1976). DTPA extractable zinc levels ranged from 0.36 to 5.40 ug/g in the top 0-15 cm. Lindsay and Norvell (1969) found that soils with extractable zinc levels of less than 0.5 were low in available zinc. Using this criteria (which was developed using maize as a test crop) four sites could be deficient in zinc.

Plant Analyses

Plant samples taken at each site in May, June, July, August and September were analyzed for total zinc, copper, molybdenum and sulphur. Table 1 presents a summary of the

Table 1. Mineral levels according to time sampled and type of forage (Yorkton forage samples, 1976).

	Cu	Mo	Ratio Cu:Mo
Group I (Definite Problems)			
Ave. of total sample* (14)	14.5	2.3	6.3
Ave. of cult. grass samples (9)	15.3	2.4	6.3
Ave. of native grass samples (2)	16.7	0.7	23.8
Ave. of total sample: May (14)	11.1	1.9	5.8
Ave. of cult. grass samples: May (9)	12.3	2.1	5.8
Ave. of native grass samples: May (2)	10.0	0.5	20
Ave. of total sample: July (14)	14.3	2.4	6.0
Ave. of cult. grass samples: July (9)	14.3	2.5	6.1
Ave. of native grass samples: July (2)	17.3	0.4	43.3
Group II (Possible Problems)			
Ave. of total sample* (16)	15.3	1.8	8.5
Ave. of cult. grass samples (10)	13.9	1.7	8.2
Ave. of native grass samples (5)	17.8	1.3	13.7
Ave. of total sample: May (16)	11.2	1.2	9.3
Ave. of cult. grass samples: May (10)	12.0	1.2	10
Ave. of native grass samples: May (5)	9.7	0.7	13.9
Ave. of total sample: July (16)	16.4	2.0	8.2
Ave. of cult. grass samples: July (10)	14.2	1.9	7.5
Ave. of native grass samples: July (5)	19.3	1.3	14.9

Table 1. Con't

	Cu	Mo	Ratio Cu:Mo
Group III (No Problems)			
Ave. of total sample* (2)	24.0	1.1	21.8
Ave. of May samples (2)	12.3	0.8	15.4
Ave. of July samples (2)	31.2	1.4	22.3

*Samples from each field in May, June, July, August and September.

( ) Denotes number of samples in each group.

copper and molybdenum data from all sites and compares the Cu:Mo ratios of forage from sites where copper deficiency had been diagnosed versus sites where copper deficiency was a possibility but not proven. Copper-molybdenum ratios were lower in the samples with definite Cu problems than in those with possible problems. Molybdenum uptake was greater with tame species (reflecting the greater uptake of Mo by alfalfa) than native species. Copper values were lower in the May samples than on later sampling dates. (Note - This may reflect the fact that dietary copper supplementation was practised by some herds).

A more detailed look at this data (Table 2) shows Cu and

Table 2. Forage copper and molybdenum samples taken from Maydel Farms, Theodore (sandy soils).

		Site 1	Site 2	Site 3	Site 5
pH		6.7	6.9	7.5	7.9
DTPA Cu		0.32	0.34	0.62	0.24
Ext. Mo		0.42	0.40	0.26	0.15
E.C.		0.5	0.2	0.4	0.2
Cu	May	19.2	8.1	9.6	6.3
Mo	May	1.6	1.0	2.1	2.8
Cu:Mo	May	12.3	8.0	4.7	2.3
Cu	July	13.0	13.1	9.7	7.8
Mo	July	0.7	1.8	1.5	2.7
Cu:Mo	July	15.8	7.1	6.4	2.8
Cu	Sept.	10.8	14.8	11.4	8.5
Mo	Sept.	2.1	1.9	2.4	3.6
Cu:Mo	Sept.	5.3	7.8	4.8	2.4

Site 1 and 2 are in the same location. Site 1 was fertilized N+S.

Mo levels from a sandy soil location at Theodore. Copper deficiency experiencedin cattle grazing than soils could be a straight Cu deficiency or a Cu X Mo reaction according to Clark's criteria. Similarly, data from the saline soil area south of Quill Lake (Table 3) exhibited low levels of

Table 3. Forage copper and molybdenum samples in saline soils.

		Alfalfa	Native	Native	Native
pH		7.6	8.0	8.4	8.1
DTPA Cu		0.34	0.40	1.24	1.12
Ext. Mo		0.14	0.47	0.14	0.38
E.C.		0.5	10.2	19.6	11.9
Cu	May	8.4	7.6	9.1	10.9
Mo	May	1.2	0.5	0.8	0.3
Cu:Mo	May	7.1	14.4	11.3	40.3
Cu	July	13.1	7.9	16.9	15.6
Mo	July	2.7	0.9	0.7	1.3
Cu:Mo	July	4.9	21.1	23.3	12.4

copper in the forage although Cu:Mo ratio were above deficient levels. The uptake of molybdenum appeared to be depressed by high salt content in the soil. In this and at other locations it also was observed that molybdenum uptake by alfalfa was greater than that from native grasses on the same soil. Table 4 shows data from sandy soil sites (Bucis)

Table 4. Forage samples.

		R. Bucis	B. Petracek	B. Petracek
		Native Pasture	Brome/Alfalfa	Native Grass
pH		8.2	8.0	7.6
E.C.		0.2	0.5	1.6
DTPA Cu*		0.16	0.54	1.20
DTPA Mo*		0.10	0.20	0.26
Cu	May	8.7	10.7	12.6
Mo	May	2.4	2.0	1.8
Cu:Mo	May	3.7	5.3	7.1
Cu	July	11.2	17.4	19.8
Mo	July	3.7	3.5	2.4
Cu:Mo	July	3.1	5.1	8.4
Cu	Sept.	21.1	11.7	24.1
Mo	Sept.	2.4	1.6	1.1
Cu:Mo	Sept.	8.9	7.4	22.9

*0-15 cm

where the level of soil available copper was low and forage copper reflected this assessment.

Soil Analyses

Soil copper values showed a reasonably good correlation with plant Cu values (Table 5) with the DTPA Cu from the 0-15 cm depth providing the best correlation with plant copper. Extractable soil molybdenum showed no correlation with plant levels and a better method of assessment will have to be found.

Table 5. Soil test correlations.

Extractable Cu	V	Plant Cu	
DTPA Cu (0-15 cm)	V	Plant Cu	June 0.51 **
	V	Plant Cu	July 0.62**
	V	Plant Cu	August 0.72***
	V	Plant Cu	Sept. 0.52**
	V	All Plant Cu	0.83***
Extractable Mo	V	Plant Mo	
(No significant correlation)			

Water Analyses

Water samples (Table 6) showed a wide range of salt

Table 6. Chemical assessment of water available for animals at 15 locations.

Location	Location No.	B	Mo	Cu	Zn	S	Cond.
S. Johnson	1	0.60	0.04	0	0.01	2	0.14
W. Johnson (unfiltered system)	2	0.20	0.05	0	0	216	0.52
W. Johnson (slough)	3	0.44	0.05	0	0	13	0.20
Clark (home ¼ dugout)	4	0.29	0.03	0	0.005	108	0.16
Salkald (creek)	6	0.25	0	0.005	0	60	0.60
Petracek (pressure system)	7	0.63	0.05	0.01	0.04	1134	2.59
Murphy (slough)	11	1.10	0.09	0.01	0.01	39	0.32

Table 6. Con't

Location	Location No.	B	Mo	Cu	Zn	S	Cond.
R. Bucis (dugout)	12	0.58	0.07	0	0	63	0.30
Stricker (slough)	13	1.72	0.20	0.02	0.01	567	1.33
Fould (creek)	14	0.21	0.03	0	0	81	0.18
M. Royal (Foam Lake creek)	23	0.46	0.03	0.01	0	297	0.66
Barber (lake)	25	1.14	0.11	0.005	0.01	729	1.60
Oliver #2 (dugout)	26	0.77	0.06	0.01	0.005	891	1.73
Lazy 8 (Dafoe slough)	28	0.37	0.03	0.01	0.01	432	0.90
Craven (slough)	32	0.78	0.05	0.01	0.02	810	1.65
Low		0.20	0	0	0	2	0.14
High		1.72	0.20	0.02	0.02	1134	2.59
Medium		0.64	0.06	0.01	0.01	363	0.86

content as shown by conductivity and sulphate values. Molybdenum, zinc and copper values were all low. Boron values varied with conductivity. The high sulphate content in some water samples could cause problems with copper uptake by animals at location No. 7, 13, 25, 26 and 32.

Sulphate levels in forage were not available for discussion at the time of this report. Comparison of Cu X Mo X S interactions will be completed at a later date.

Summary

A survey of soil and forage samples carried out during the summer of 1976 has shown that copper deficiency in animals could be caused by low copper herbage content in locations in Eastern Saskatchewan. Copper deficiency also could be the result of a copper X molybdenum interaction caused by low Cu:Mo ratios in pastures.

Potentially deficient Cu areas could be partially

diagnosed by extractable soil copper values. Extractable soil molybdenum values were not of use as they did not correlate with plant uptake--this may be due to higher uptake of molybdenum by tame species.

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