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AN ASSESSMENT OF THE EFFECTS OF ZINC, LEAD, CADMIUM, AND ARSENIC IN SOIL, VEGETATION, AND WATER RESOURCES SURROUNDING A ZINC SMELTER

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AN ASSESSMENT OF THE EFFECTS OF ZINC, LEAD, CADMIUM, AND ARSENIC IN SOIL, VEGETATION, AND WATER RESOURCES SURROUNDING A ZINC SMELTER

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ABSTRACT

Atomic absorption spectrophotometry was used to determine the amounts of zinc, lead, cadmium, and arsenic in soil, vegetation, and water resources sampled within a seven mile radius of the zinc smelter in Blackwell, Oklahoma. Within a pasture adjacent to the smelter, decreased productivity, altered floristic composition, and lowered species diversity were found to be correlated with increased proximity to the smelter and levels of metals in both the soil and vegetation. Productivity of wheat (the major crop) during the fall was similarly affected by these metals; however, by harvest neither the quantity nor the quality of the wheat appeared to be affected. Varieties of crops commonly planted in this region were grown under controlled conditions in soils containing incremental amounts of these metals in order to establish tolerance and productivity differences - none of economic significance were found. Based on published toxic levels of these metals for livestock, forage and water collected from within the study area were found to contain sufficient amounts of these metals to be detrimental to livestock. Land use recommendations with regard to crop suitability and grazing potential for this area were made using these data. For crops like alfalfa, which have a low tolerance for arsenic, aluminum sulfate added to the soil along with lime provided a suitable soil treatment. Surface soil samples were collected from approximately 55 square miles of farmland and SYMAPS generated illustrating the horizontal distribution of these metals; while soil pits were dug to determine the distribution of these metals within the soil profile. To complete this study, flow models were built which predict rates of movement of zinc through the system during the next 1000 years and suggest what effects the closing of this smelter will have on the productivity and grazing potential of neighboring lands.

AN ASSESSMENT OF THE EFFECTS OF ZINC, LEAD, CADMIUM, AND ARSENIC IN SOIL, VEGETATION, AND WATER RESOURCES SURROUNDING A ZINC SMELTER

PART I

THE ACCUMULATION OF ZN, CD, PB, AND AS IN SOILS

INTRODUCTION

From 1849 to 1949 the Oklahoma-Kansas-Missouri Tri-State Mining District was a major source of zinc and lead ores (McReynolds, 1954). Smelter site selection was based primarily on proximity to these ores and the natural gas fields in this area. These smelters were of the horizontal retort type, and most remained operational only as long as the local supply of ore or gas lasted; however, the smelter in Blackwell, Oklahoma remained operational for 57 years. During these years, this smelter was the major contributor of heavy metals to the atmosphere in the Blackwell area.

Airborne Zn, Cd, Cu, and Pb have been shown to contaminate soil and vegetation surrounding zinc smelters (Greszta and Godzic, 1969; Buchauer, 1973). Zinc ores contain a spectrum of additional metals and these along with Zn, Cd, Cu, and Pb are usually part of the emissions from horizontal retort furnaces. This study involved the accumulation of Zn, Cd, Pb, and As in various components of the neighboring ecosystem. These elements were selected as they were thought to be of most significance to the productivity and grazing potential of the area.

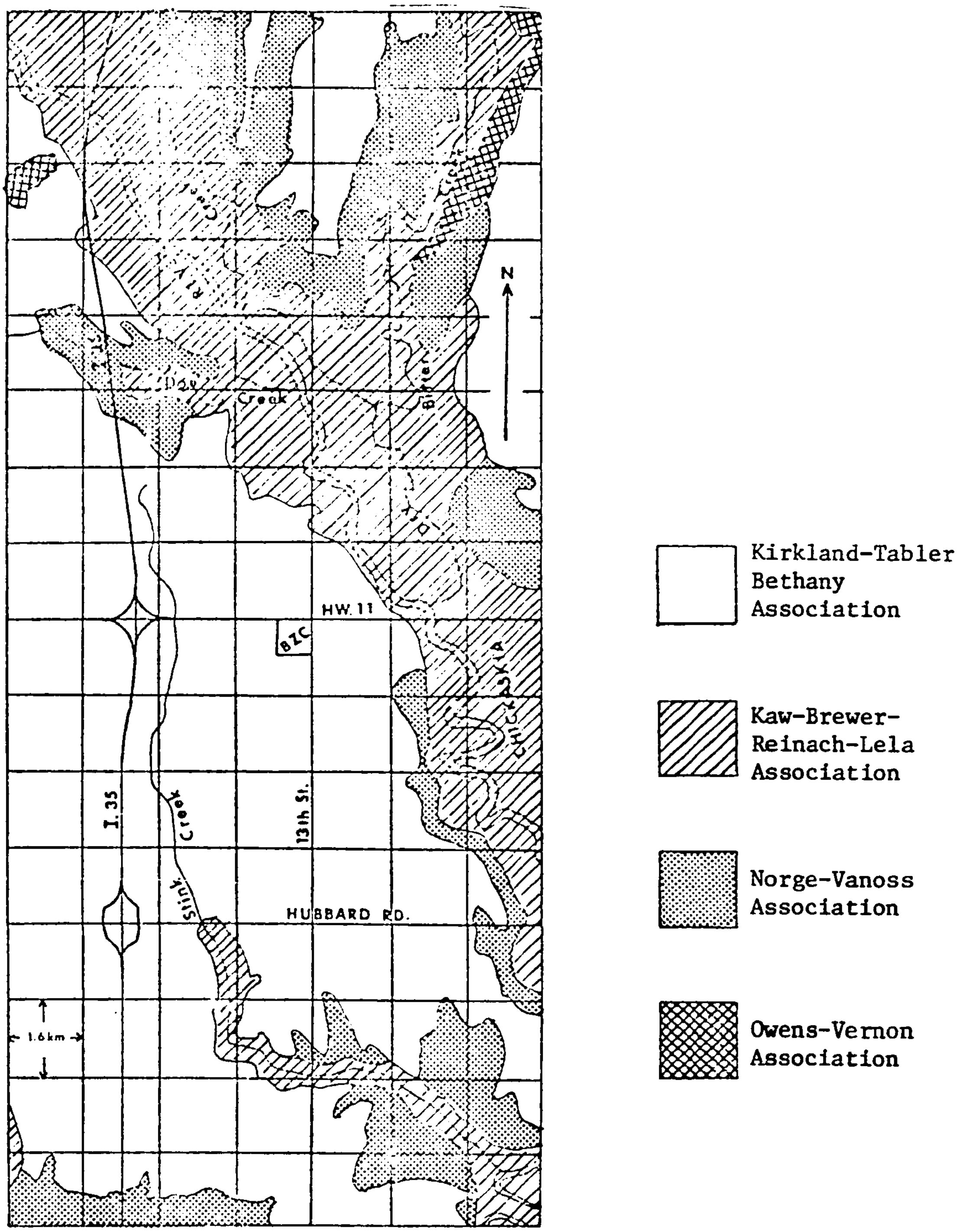
STUDY AREA

Blackwell is located in the western half of Kay County, which lies in the central part of the Redbed Plains of Oklahoma. The topography is level to gently undulating with terraces up to 4.8 km wide along the Chickaskia River. The climate of the area is temperate, subhumid (Trewartha, 1968). The mean annual temperature is 16°C and the mean annual precipitation is 72.80 cm, with a frost free season which averages 195 days. Prevailing winds (19 km/hr annual average) are southerly during most months; however, in January and February winds are predominately from the north.

Four soil associations are found within the study area. Kirkland-Tabler-Bethany Association soils are found in nearly level to moderately sloping areas away from floodplains; Kaw-Brewer-Reinach-Lela Association soils make up the nearly level 1.6 - 3.2 km wide bands along the Chickaskia and somewhat narrower bands along Stink Creek; and Norge-Vanoss Association soils are found within 3.2 km of the Chickaskia mainly on gently sloping uplands and in similar locations along Stink Creek where it enters the Chickaskia (Fig. 1).

The study area is treeless except along streams, on some uplands adjacent to streams, and where windbreaks have been planted.

Figure 1. Soil associations within the study area (after Soil Survey, Kay County, Oklahoma, 1967).



Winter wheat is the predominant crop; although other small grains, alfalfa, and field corn are commonly grown. There is also some ranching in the study area.

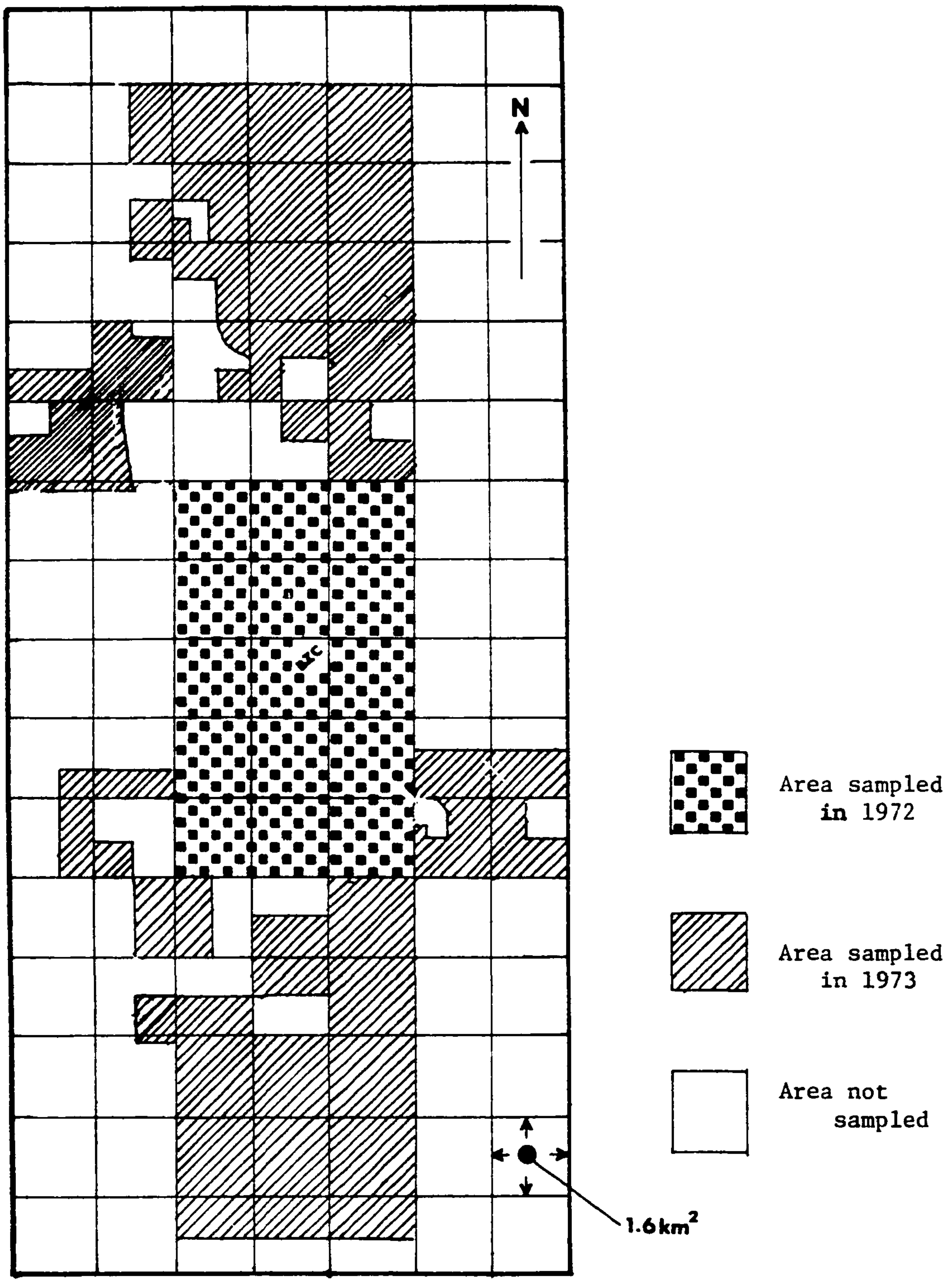
METHODS

Soil samples were taken to a depth of 15 cm using an incremental corer. Each sample was a composite of 20 cores randomly taken along a 0.2 km transect parallel to the smelter. During 1972, 38.8 km^2 around the smelter were sampled. A minimum of 8 composite samples were taken from each section. In 1973, an additional 103.6 km^2 were sampled. At least one composite sample was collected from each section sampled; however, some quarter sections were not sampled due to a pending litigation (Fig. 2).

Seven soil pits were dug to a depth of 90 cm and samples were taken at each 15 cm increment. All pits were located within 11.3 km of the smelter, and all were north of the smelter (Fig. 3). In addition to these pits, one set of samples was collected 1.6 km north of the smelter using an incremental corer. As in the pits, samples were taken at each 15 cm increment to a depth of 90 cm.

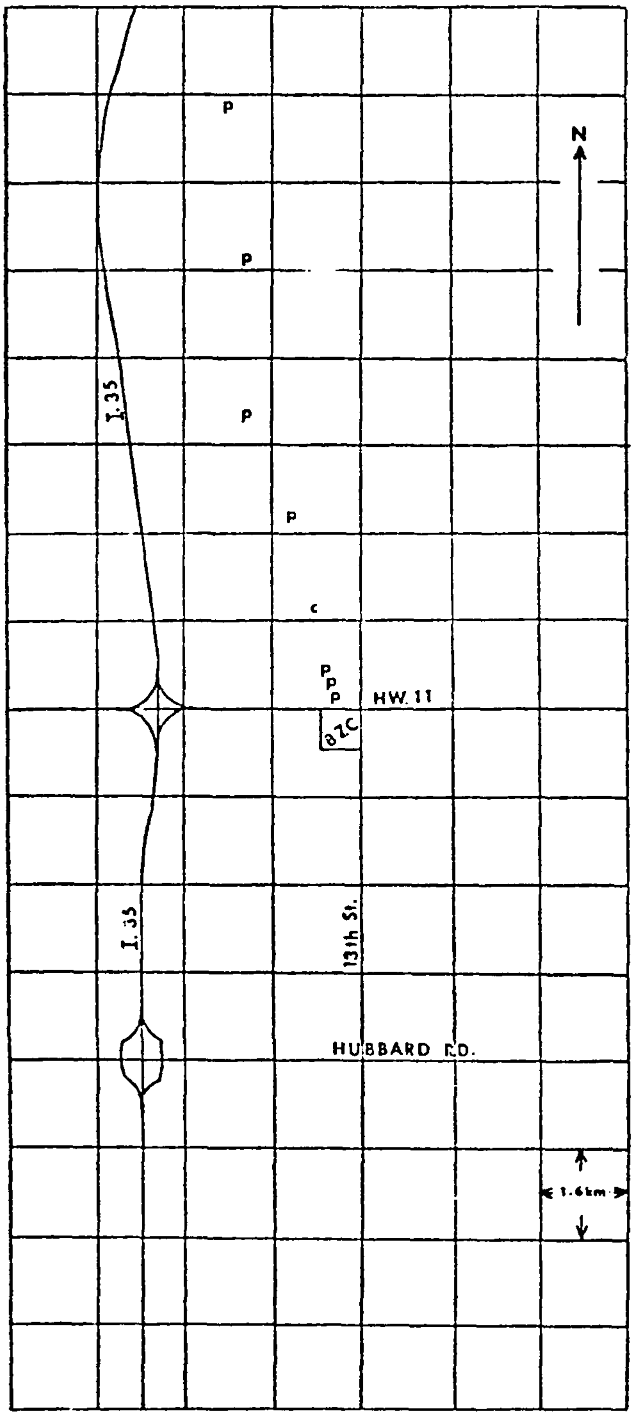
All soil samples were air dried, crushed, passed through a 4 mesh sieve, ground to pass through a 40 mesh screen in a stainless steel hammer mill, and then oven dried at 90°C. To minimize contamination, those samples collected farthest from the smelter were ground first, and the mill was cleaned between samples. Prior to oven drying, soil pH was determined using

Figure 2. Acreage from which soil samples were collected in 1972 and 1973.



BZC = Blackwell Zinc Company

Figure 3. Location of the seven soil pits and soil cores taken in 1973.



BZC = Blackwell Zinc Company

a 10:1 water to soil solution and a pH meter.

Total Zn, Cd, Pb, and As and extractable Zn were determined by the Blackwell Zinc Company Laboratory. Total Zn, Cd, and Pb and extractable Zn were determined using a Perkin Elmer Model 304 atomic absorption spectrophotometer. For total Zn, Cd, and Pb, soils were digested with nitric acid; while for extractable Zn, a diethylenetriamine pentaacetic acid - triethanolamine (DTPA-TEA) extraction (Lindsey and Norvell, 1967) was used. Due to the high concentrations of zinc in the soil, the amount of the DTPA-TEA extracting solution used (100 ml) was five times that used by Lindsey and Norvell (1967). A distillation isolation of total As, followed by photometric determination by the molybdenum blue method (Ernst, 1954) was used for measuring soil As. Twenty grams of soil were required for As determination.

Horizontal dispersion maps for total Zn, Cd, Pb, and As and extractable Zn contained in the top 15 cm of soil within the surveyed area were produced using version 5.15 of the SYMAP program (Reader, 1971). This program assumes continuous variation between known data point values, and interpolates between these values using an inverse distance function. Copies of each soil map were cut along isolines, and the pieces then sorted according to map symbol and measured with a Hayashi Denko AAM-5 photoelectric planimeter. By multiplying the percent of the total area for each concentration range and the total area surveyed (14,146.6 ha), the number of hectares containing specified ranges of these metals in the top 15 cm of soil was calculated.

RESULTS AND DISCUSSION

Horizontal Distribution

Due to predominately southerly winds, the highest concentrations of Zn, Cd, and Pb were found north of the smelter; while the lowest concentrations were found in an east-west direction (Figs. 4 - 8). Bowen (1966) reported an average of 50 ppm soil Zn (range of 10 to 300 ppm); while Shacklette et al. (1971) reported an average of 44 ppm soil Zn for surface material collected from 48 states. Within the lead belt of southeastern Missouri, 10 - 60 ppm Zn was found in the top 7.6 cm of soil (Wixon et al., 1972); and within 1 km of a zinc smelter in Pennsylvania, 50,000 - 80,000 ppm Zn was found in the A_1 horizon (Buchauer, 1973). Concentrations of total Zn in the top 15 cm of soil sampled within 1 km north of the Blackwell smelter were between 2,680 - 26,150 ppm. The sample containing 26,150 ppm Zn was collected about 300 m from the row of 12 furnaces. This high concentration is in part deposition of windblown dusts from residue piles located just north of the furnaces. Soil concentrations are below 400 ppm at distances greater than approximately 4.8 km north, 3.6 km south, and 2.4 km east and west, which constitutes about 57% of the study area (Fig. 4).

Figure 4. Acreage having various levels of total zinc in the top 15 cm of soil.

Map Symbol	Total Zinc (ppm)	Hectares	% Area
·····	<50	505	3.6
:::::	50-100	1972	13.9
-----	100-200	5616	39.7
>>>>>	200-400	3302	23.3
<<<<<	400-800	1371	9.7
xxxxx	800-1600	593	4.2
ccccc	1600-3200	312	2.2
33333	3200-6400	285	2.0
zzzzz	6400-12800	109	0.8
▮▮▮▮▮	>12800	88	0.6

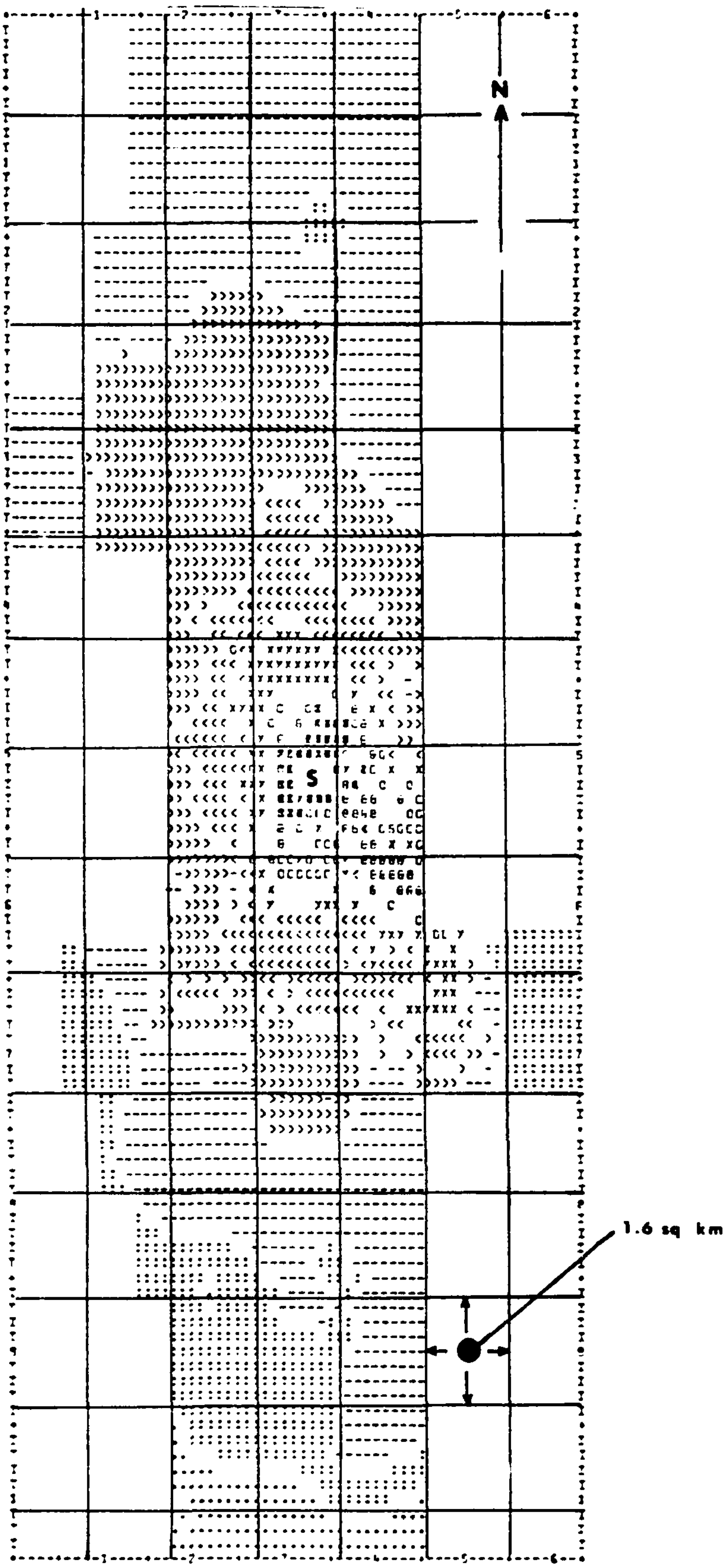
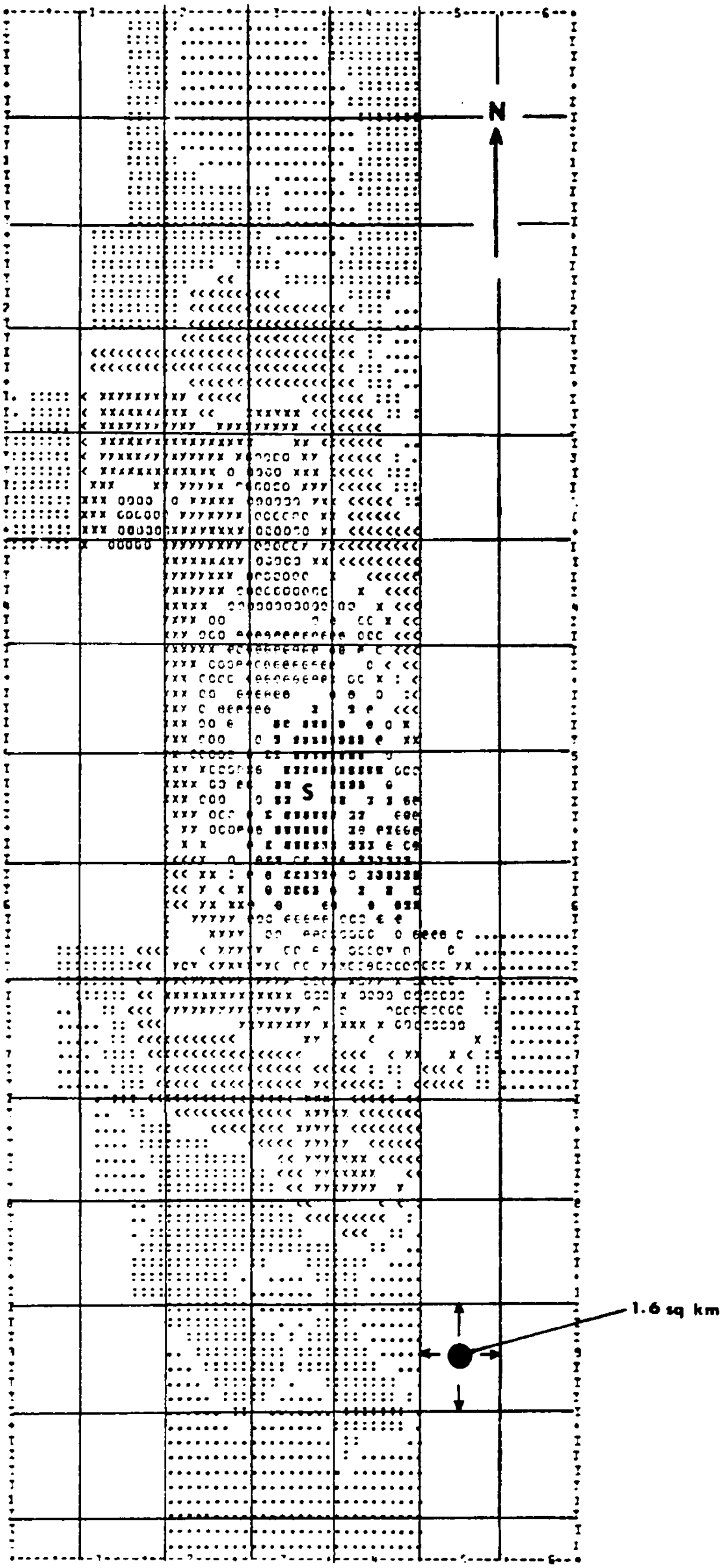

N
S
1.6 sq km

Figure 5. Acreage having various levels of extractable zinc in the top 15 cm of soil.

Map Symbol	Extractable Zinc (ppm)	Hectares	% Area
·	<25	3101	21.9
:	25-50	3894	27.5
<	50-100	2433	17.2
x	100-200	2080	14.7
c	200-400	1364	9.6
9	400-800	631	4.5
x	800-1600	364	2.6
▮	> 1600	289	2.0


N
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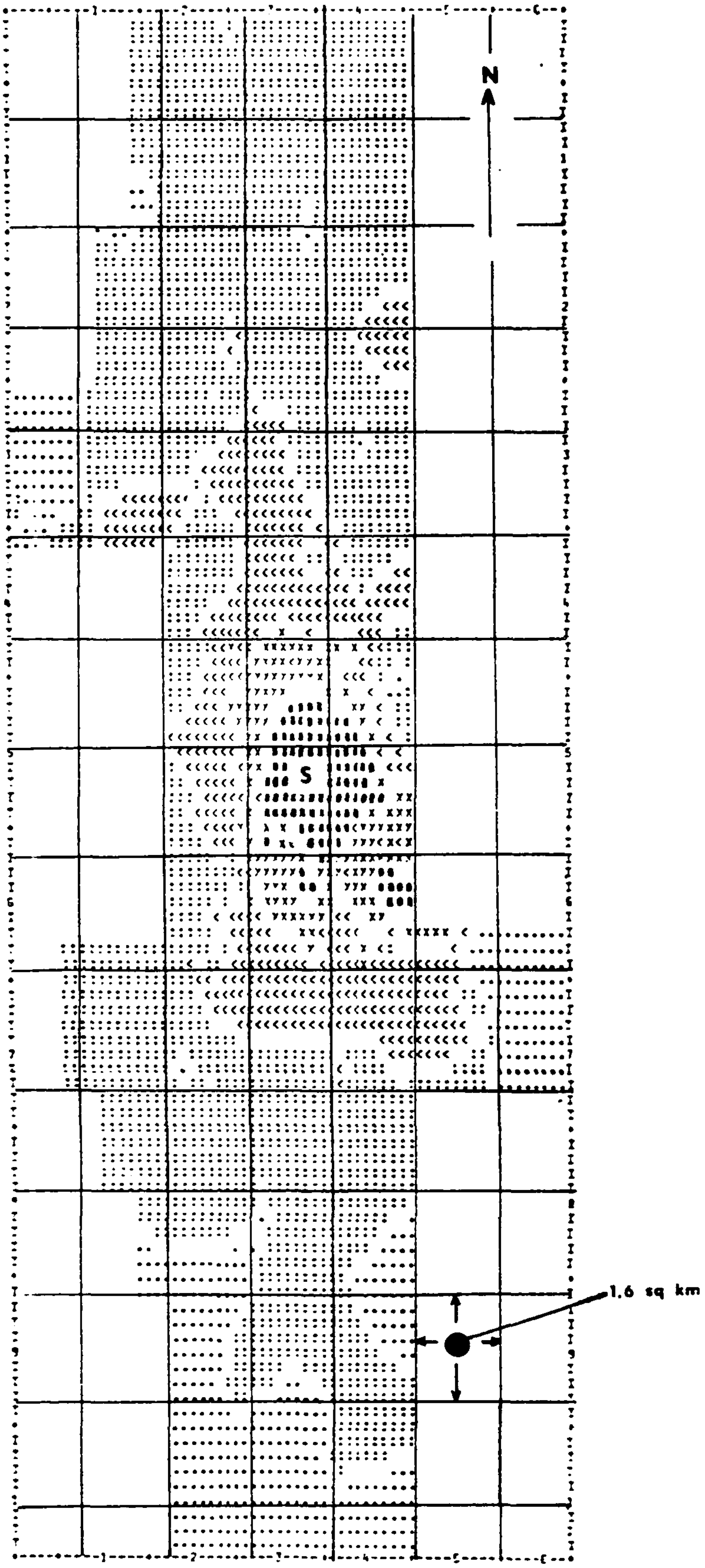
1.6 sq km

Figure 6. Acreage having various levels of total cadmium in the top 15 cm of soil.

Map Symbol	Total Cadmium (ppm)	Hectares	% Area
· · · · ·	<2	2387	16.9
: : : : :	2-4	8043	56.8
< < < < <	4-8	2468	17.4
x x x x x	8-16	759	5.4
▮▮▮▮▮	>16	496	3.5


N
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1.6 sq km

Figure 7. Acreage having various levels of total lead in the top 15 cm of soil.

Map Symbol	Total Lead (ppm)	Hectares	% Area
....	<21	3189	22.5
:::::::::	21-30	5316	37.6
<<<<<<<<<	30-50	3514	24.8
XXXXXXXXX	50-90	914	6.5
▨	90-170	688	4.9
▦	170-330	175	1.2
■	>330	357	2.5

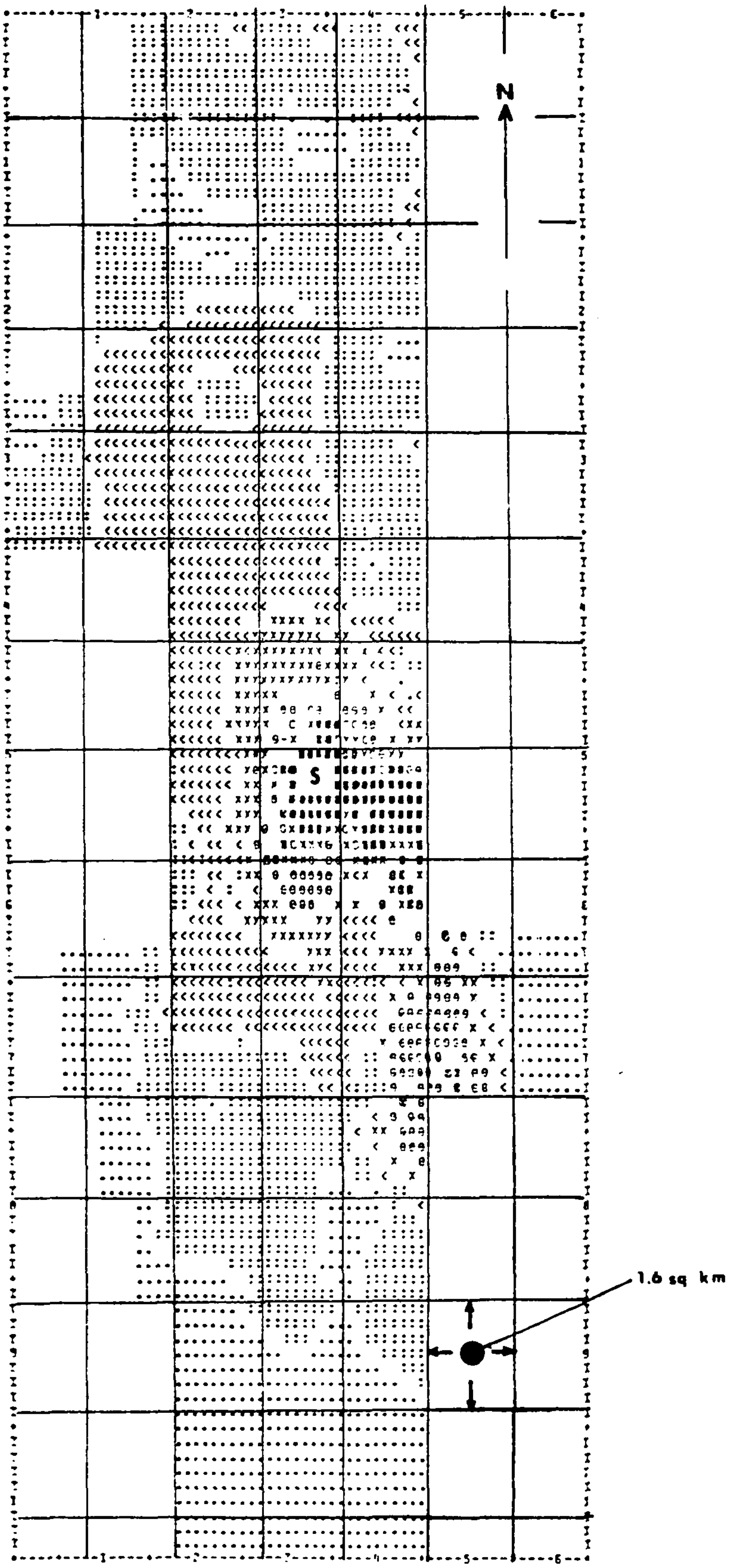
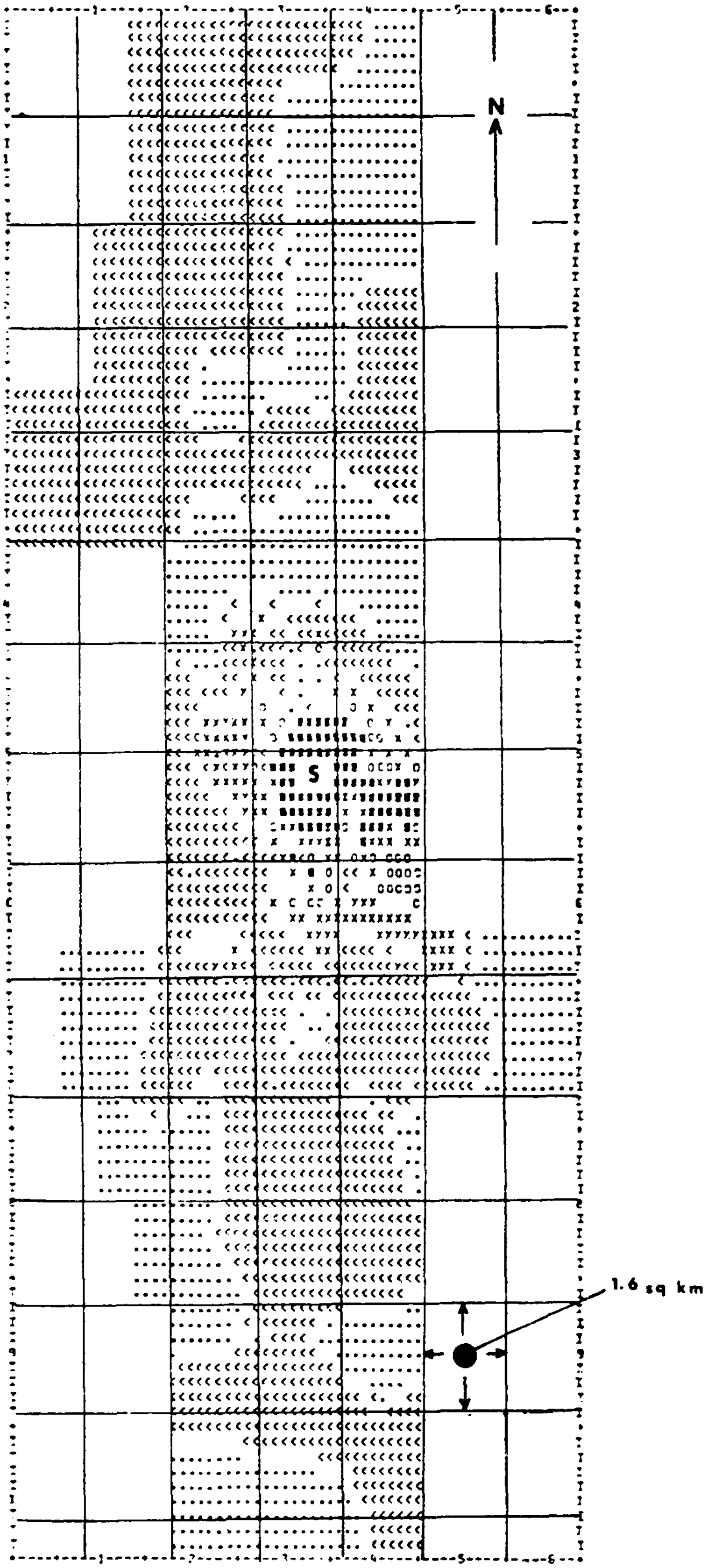

N
S
1.6 sq km
1
2
3
4
5
6

Figure 8. Acreage having various levels of total arsenic in the top 15 cm of soil.

Map Symbol	Total Arsenic (ppm)	Hectares	% Area
······	< 3	4421	31.2
<<<<<<	3-6	8305	58.7
xxxxxx	6-9	786	5.6
oooooo	9-12	269	1.9
▒	12-15	20	<0.1
▮	>15	351	2.5


N
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1.6 sq km
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Concentrations of DTPA-TEA extractable Zn within 1 km of the Blackwell smelter ranged from 992 - 3840 ppm. The greatest concentration, as before, was found just north of the furnaces. Eighty-one percent of the acreage sampled contained concentrations of extractable Zn below 200 ppm (Fig. 5), which included all but 12.4 km^2 around the smelter.

Bowen (1966) reported an average of 0.06 ppm soil Cd (range of 0.01 - 0.7 ppm). Fertilized fields in the Virgin Islands contained 3.38 ppm Cd; while unfertilized fields contained 0.15 ppm Cd (McCaull, 1971). Phosphate fertilizers might explain these differences. Superphosphate fertilizer (United States) was shown to contain 8.97 ppm Cd, and ground phosphate rock (Tennessee) was shown to contain 2.20 ppm Cd (Schroeder et al., 1967). Buchauer (1973) reported 900 - 1500 ppm Cd in the A_1 horizon within 1 km of a zinc smelter. Most Cd values found in the lead belt of southeastern Missouri were less than 0.5 ppm (top 7.6 cm of soil); a few samples contained up to 2 ppm (Wixon, 1972). Within 1 km north of the Blackwell smelter, the top 15 cm of soil contained from 21.6 - 145 ppm Cd. Levels of Cd comparable to fertilized fields in the Virgin Islands were found 6.4 km north, 4.8 km south, and 2.4 km east and west of the Blackwell smelter. About 74% of the study area contained less than 4 ppm Cd (Fig. 6).

John (1971) reported an average of 51.9 ppm total Pb in the top 20 cm of agricultural soils (standard deviation - 13.2 ppm); of this Pb, an average of 41.7 ppm (standard deviation -

8.0 ppm) was native. Anomalous values as high as 222 ppm Pb were recorded for the top 2.5 cm of soil near lead mines, a smelter, and roads on which ore concentrates were carried; while in other parts of this lead belt area, Pb was between 17 - 32 ppm for this increment (Wixon et al., 1972). Along heavily traveled Illinois Hwy 45 near Thomasboro, the Heavy Metal Task Force (1972) recorded from 340 ppm (adjacent to the highway) - 24 ppm Pb (a plowed field 10 m from the highway) in the top 17.8 cm of soil. Buchauer (1973) reported 200 - 1100 ppm Pb in the A_1 horizon within 1 km of a zinc smelter. Concentrations of Pb in the top 15 cm of soil sampled within 1 km north of the Blackwell smelter were between 160 and 1600 ppm. The sample containing 1600 ppm Pb was the same sample which contained the highest concentration of Zn and Cd. Generally, Pb concentrations decrease with distance from the smelter; however, high concentrations are also associated with the Blackwell Municipal Airport, Mauk Airpark, and green belts in the residential areas. Soil concentrations are below 50 ppm Pb 3.2 km north, 2.4 km south, 2.4 east, and 1.6 km west, which constitutes approximately 85% of the study area (Fig. 7). The residential and shopping areas of Blackwell are east of the smelter, which might explain the slightly higher concentrations of Pb to the east than to the west.

Workers in various states found an average of 165 ppm As (range of 1 - 2553 ppm As) in the top 15 cm of agricultural soils that were treated with arsenicals; whereas, those which were untreated contained an average of 13 ppm As (Woolson, Axley, and Kearney, 1971). Soils suspected of being contaminated by smelter fumes contained an average of 214 ppm As (range 114 - 315 ppm). Blackwell soils were found to contain from 0.4 - 98 ppm As in the top 15 cm of soil. Highest concentrations were found in close proximity to the smelter. For distances greater than 0.8 km north, south, and east and 0.4 km west, concentrations were less than 13 ppm (Fig. 8). A park area sampled 1.6 km east of the smelter contained a higher than expected As concentration (38.2 ppm) given its distance and direction from the smelter. With the exception of these anomalous areas, 59% of the soils in the study area contained from 3 - 6 ppm; and 31% contained less than 3 ppm As (Fig. 8). The highest concentration of As in the study area was located about 300 m west of the sample which contained the highest concentrations of Zn, Cd, and Pb.

Vertical Distribution

Zn, Cd, and Pb concentrations found along the profiles of the seven pits tended to decrease with depth and distance from the smelter (Figs. 9 - 11); however, As concentrations did not show this tendency (Fig. 12). The vertical distribution of Zn, Cd, and Pb within the soil cores taken 1.9 km north of the smelter appears to be atypical in comparison to that within the pits. It is difficult to explain higher concentrations of these metals 60 - 90 cm from the soil surface at 1.9 km north from the smelter, than at the surface, 0.1 km from the smelter. The only area found to contain as high a level of Zn and Pb as these cores was the quarter section on which the smelter is located, and no area

Figure 9. The vertical distribution of zinc in soil sampled to a depth of 90 cm and at various distances from the smelter.

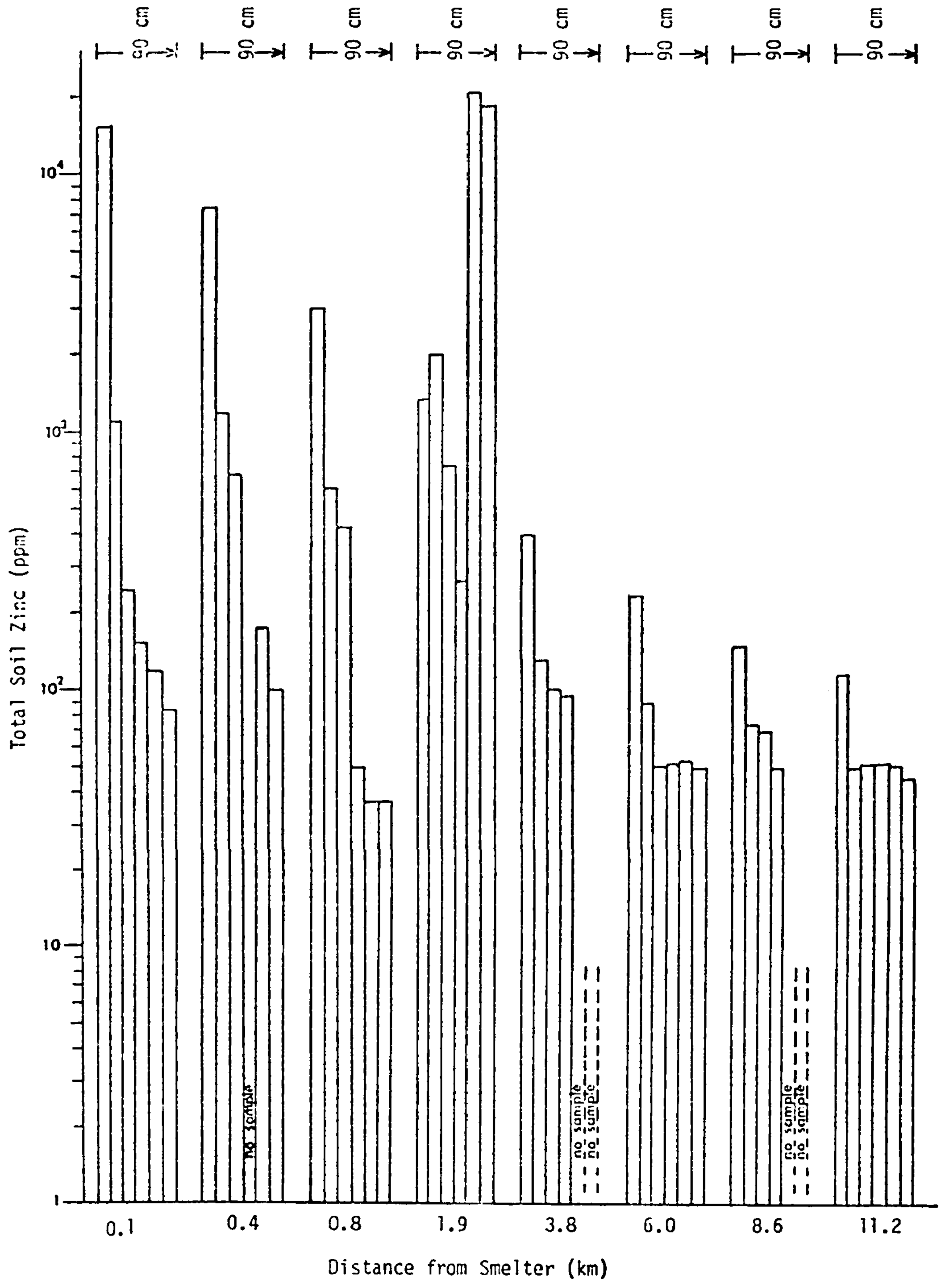


Figure 10. The vertical distribution of cadmium in soil sampled to a depth of 90 cm and at various distances from the smelter.

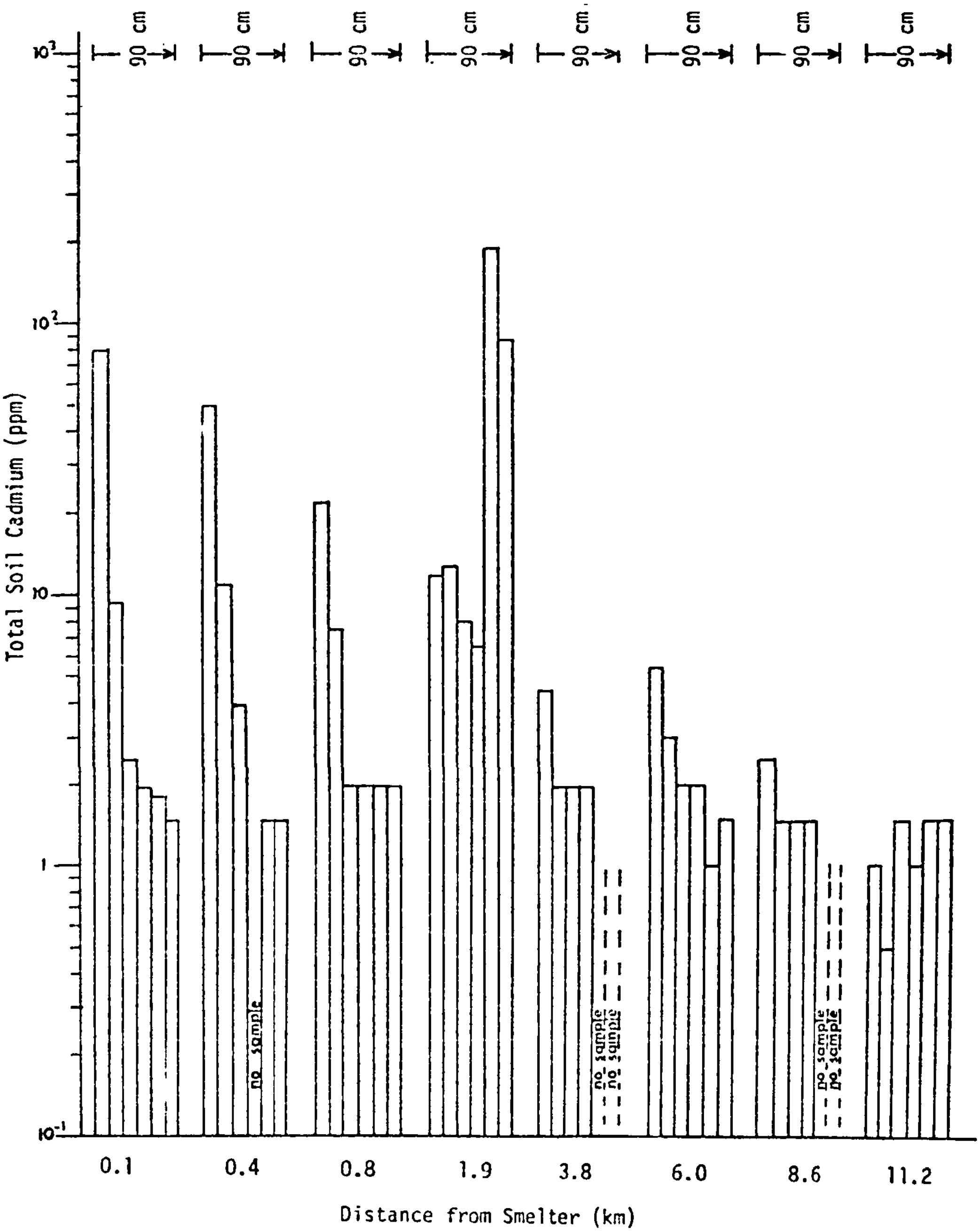


Figure 11. The vertical distribution of lead in soil sampled to a depth of 90 cm and at various distances from the smelter.

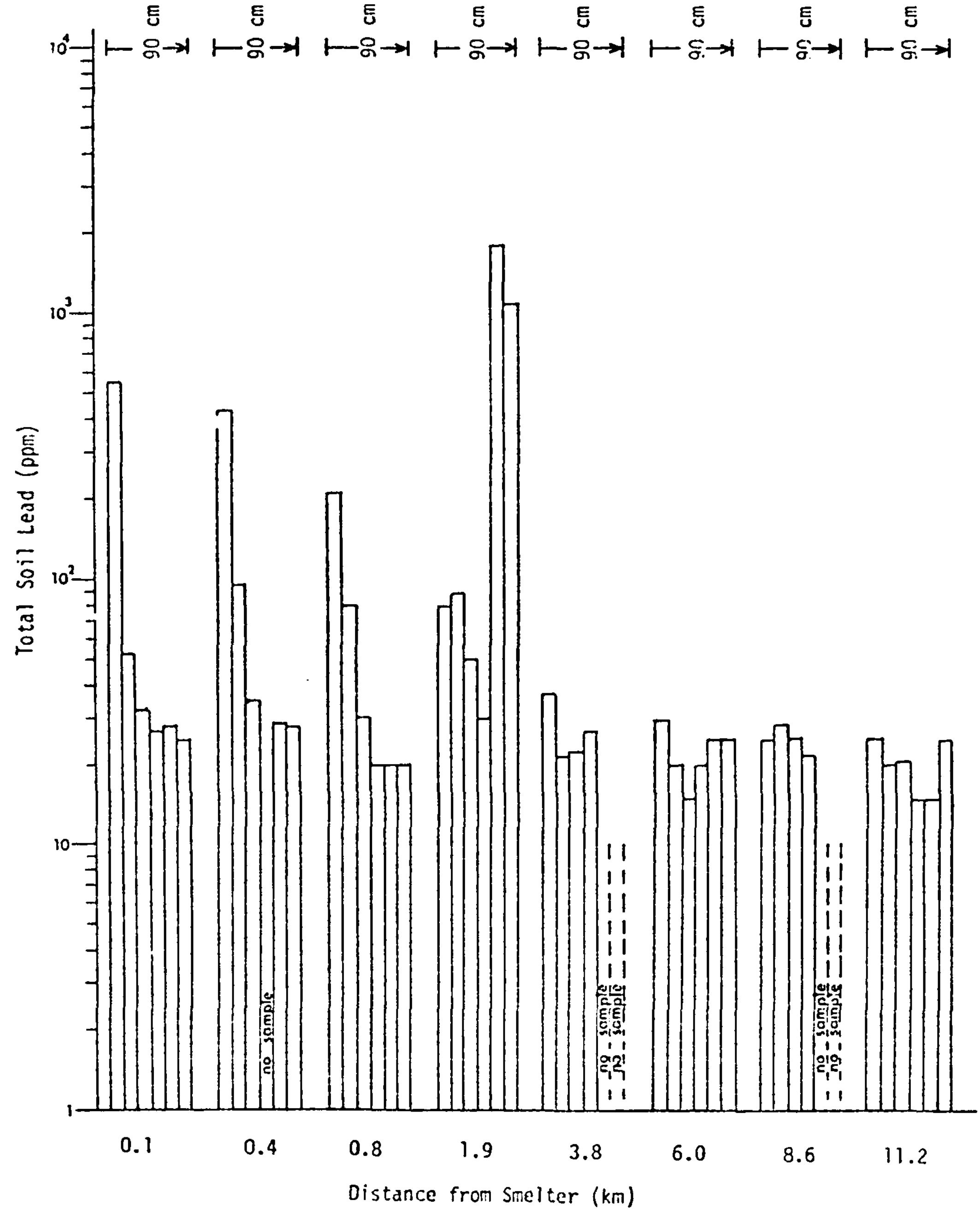
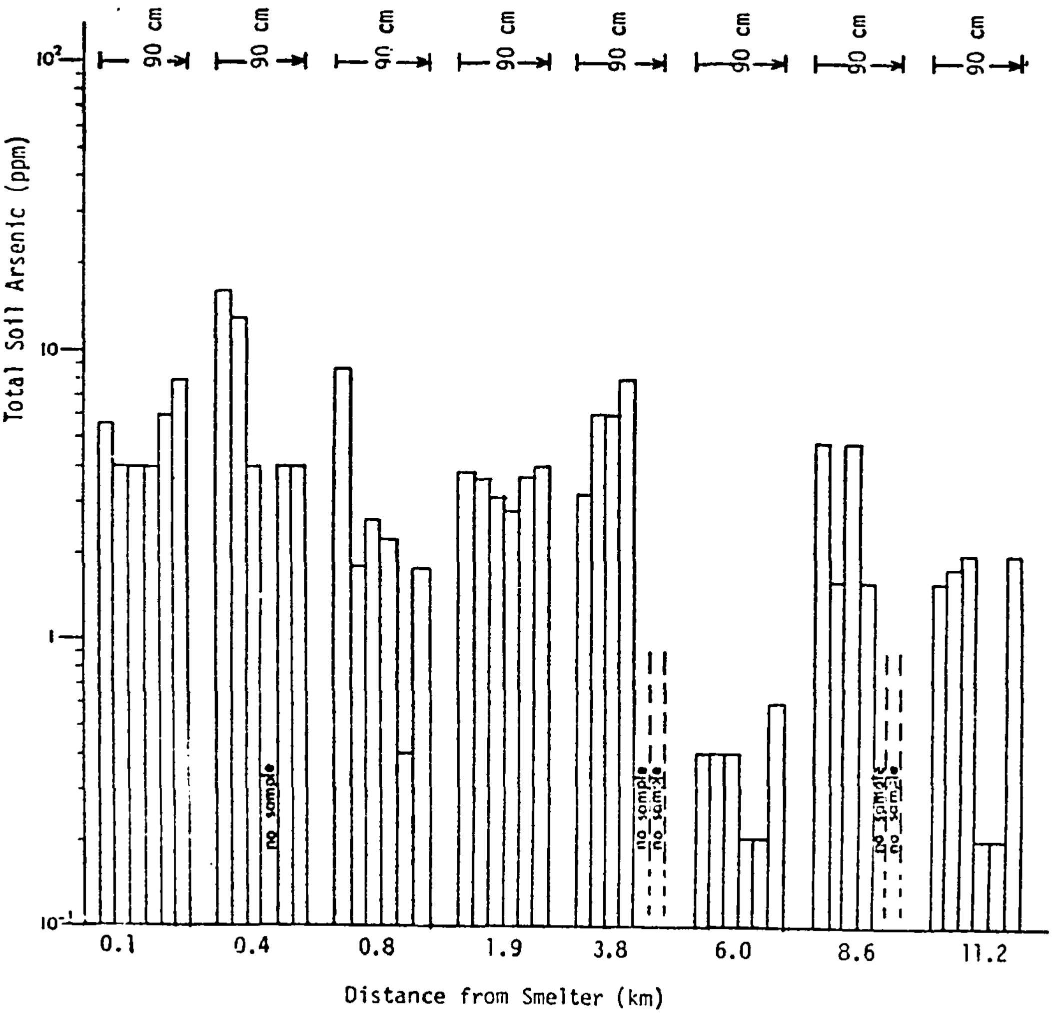


Figure 12. The vertical distribution of arsenic in soil sampled to a depth of 90 cm and at various distances from the smelter.



previously sampled had as high a level of Cd as in these atypical cores (195 ppm). With respect to the distribution of As, the profile in question was not noticeably different from any of the pits (Fig. 12). Average Zn, Cd, Pb, and As of the 7 pits tended to decrease with depth (Table 1); individually, pits showed this tendency for Zn, Cd, and Pb but not for As.

Buchauer (1973) estimated that in the area she studied, which was highly contaminated by zinc smelters, 85 - 95% of the total Zn content and 95% of the total Cd content were in the top 15 cm of the soil profile. The Heavy Metals Task Force (1972) found that 78% of the total lead in a soil profile sampled adjacent to Illinois Hwy 45 near Thomasboro was within the top 17.8 cm of soil. Comparable percent distributions for Zn, Cd, and Pb were found within 0.8 km of the Blackwell smelter; whereas, for arsenic, no general trend was apparent (Table 2).

Soil pH

Soils were grouped into the following pH ranges: <5.5, 5.6 - 5.9, 6.0 - 6.3, 6.4 - 6.7, and >6.8. Those soils that contained higher concentrations of total Zn, extractable Zn, or total Cd had a significantly ($\alpha=0.05$, df>40) higher pH (6.0 - 7.8) than soils containing lower concentrations of these metals (pH 4.3 - 5.9). Soil pH was not significantly associated with the concentration of soil Pb or As. Since these are agricultural soils, and since lime has been used not only to raise the pH of the soil but also to counteract the toxicity of Zn, this association between high Zn

Table 1. The average zinc, lead, cadmium, and arsenic concentrations for different increments within the soil pits.

Soil Depth (cm)	Average Zn (ppm)	Average Pb (ppm)	Average Cd (ppm)	Average As (ppm)
0-15	3820	187	23.8	5.7
15-30	462	45.6	5.0	4.2
30-45	231	25.8	2.2	3.4
45-60	75.4	21.6	1.8	2.7
60-75	88.7	23.2	1.5	2.2
75-90	63.1	24.6	1.6	3.2

Table 2. The percent zinc, lead, cadmium, and arsenic in the top fifteen cm of the soil at various distances north of the smelter.

Distances north of smelter (km)	Percent Zn	Percent Pb	Percent Cd	Percent As
0.1	98	94	96	7
0.4	93	89	91	59
0.8	92	84	86	80
3.8	71	37	56	-208
6.1	76	30	65	50
8.6	57	1	40	78
11.2	56	36	-20	22

content and higher pH might simply be the result of farming practices. Buchauer (1973) found the same relationship between total Zn and soil pH. She felt that if this relationship was real, it might be the result of the amphoteric properities of ZnO.

Based on expected pH range for the soil series comprising the associations within the study area, these soils should have a pH ranging from 5.6 - 8.4. All but one of the samples with a pH<5.6 were collected from Kirkland-Tabler-Bethany or Kaw-Brewer-Reinach-Lela Associations. These are heavily farmed soils, and this lower than expected pH range probably indicated insufficient lime additions to maintain optimal soil pH.

Even though selection of this smelter site was based on industrial economics, environmentally this site proved a good choice. Since Blackwell is located in the central plains, relatively flat topography and usually adequate winds allowed for unobstructed dispersion of emissions. In addition, most people live east of the smelter and thus very seldom complain of emissions. Lower concentrations of Zn, Cd, and Pb in the soils surrounding the Blackwell smelter than those reported surrounding smelters in Palmerton, Pennsylvania (Buchauer, 1973) may represent a more adequate dispersion in Blackwell, or may represent lower total emissions in Blackwell, and/or differences in sampling methods, sample preparation, or analytical procedures.

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AN ASSESSMENT OF THE EFFECTS OF ZINC, LEAD, CADMIUM, AND ARSENIC IN SOIL, VEGETATION, AND WATER RESOURCES SURROUNDING A ZINC SMELTER

PART II

VEGETATION AND GRAZING POTENTIAL

INTRODUCTION

From 1849 to 1949 the Oklahoma-Kansas-Missouri Tri-State Mining District was a major source of zinc and lead ores (McReynolds, 1954). Smelter site selection was based primarily on proximity to these ores and the natural gas fields in this area. These smelters were of the horizontal retort type, and most remained operational only as long as the local supply of ore or gas lasted; however, the smelter in Blackwell, Oklahoma remained operational for 57 years. During these years, this smelter was the major contributor of the heavy metals to the atmosphere in the Blackwell area.

Soil and vegetation near urban areas, industrialized areas, highways, mining areas, and smelters have been shown to contain higher amounts of Zn, Cd, Pb, and other heavy metals (John, 1971; Smith, 1973; Chow, 1970; Gish and Christensen, 1973;

Davies and Holmes, 1972; Wixon et al., 1972; Heavy Metals Task Force, 1972; Buchauer, 1973; and Hammond and Aronson, 1963). Chronic Pb poisoning of livestock related to the consumption of forage contaminated with Pb emitted from lead smelters has been documented by Schmitt et al. (1971), Hammond and Aronson (1963), and Knight and Burau (1973). Poisoning of livestock related to the consumption of forage contaminated with Zn emitted from a zinc smelter has yet to be documented. Farmers in the Blackwell area have reported poor cattle gains on both wheat and grass pasture systems close to the smelter. The purpose of this study was to measure the accumulation of Zn, Cd, Pb, and As in the ecosystem; to assess what effects this accumulation has had on the productivity and grazing potential of neighboring lands; to establish land use criteria for affected acreage; and to predict how the recent termination of smelter operations will influence the affected area.

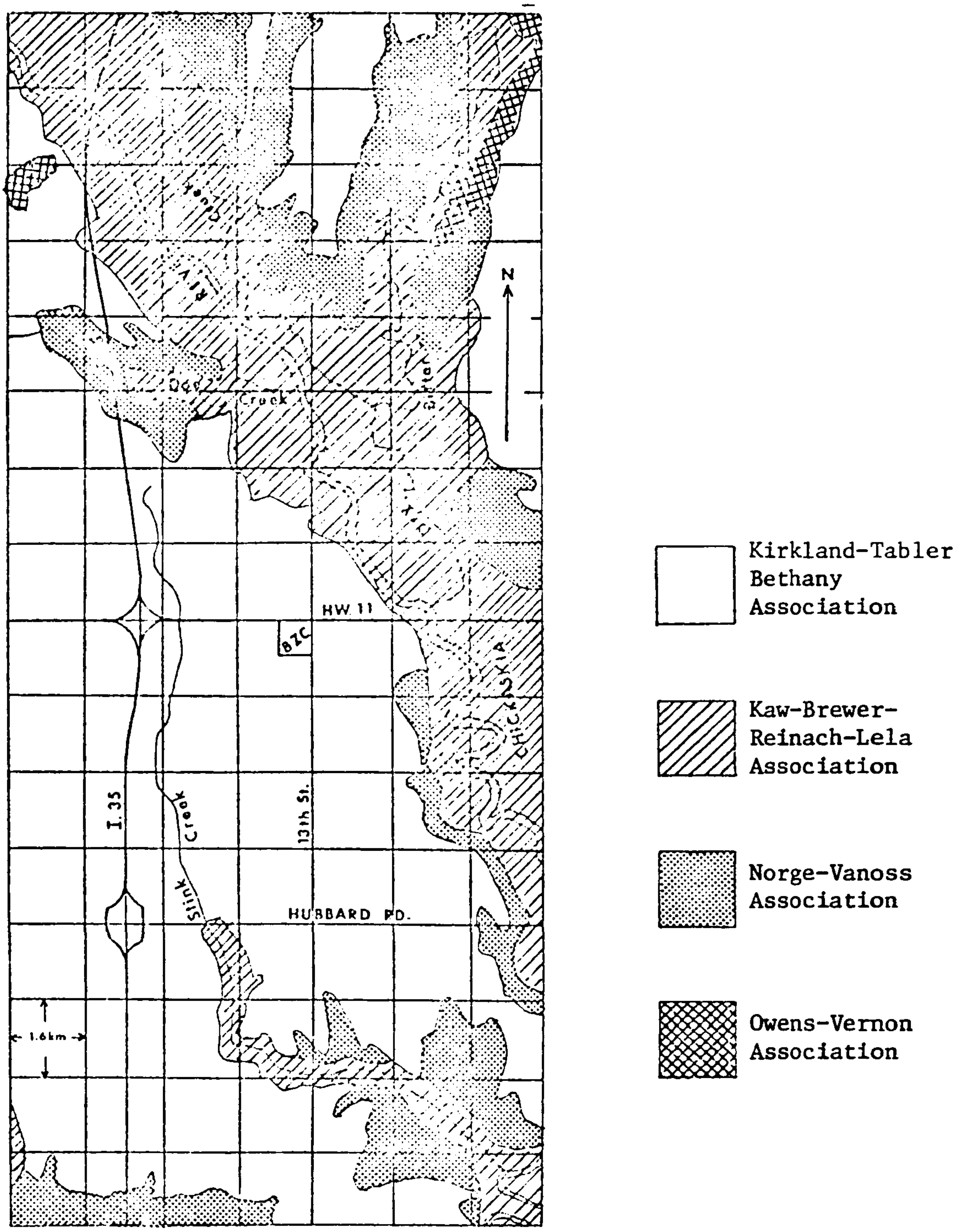
STUDY AREA

Blackwell is located in the western half of Kay County, which lies in the central part of the Redbed Plains of Oklahoma. The topography is level to gently undulating with terraces up to 4.8 km wide along the Chickaskia River. The climate of the area is temperate, subhumid (Trewartha, 1968). The mean annual temperature is 16°C and the mean annual precipitation is 72.80 cm with a frost free season which averages 195 days. Prevailing winds (19 km/hr annual average) are southerly during most months; however, in January and February winds are predominately from the north.

Four soil associations are found within the study area. Kirkland-Tabler-Bethany Association soils are found in nearly level to moderately sloping areas away from floodplains; Kaw-Brewer-Reinach-Lela Association soils make up the nearly level 1.6 - 3.2 km wide bands along the Chickaskia and somewhat narrower bands along Stink Creek; and Norge-Vanoss Association soils are found within 3.2 km of the Chickaskia mainly on gently sloping uplands and in similar locations along Stink Creek where it enters the Chickaskia (Fig. 1).

The study area is treeless except along streams, on some

Figure 1. Soil associations within the study area (after Soil Survey, Kay County, Oklahoma, 1967).



uplands adjacent to streams, and where windbreaks have been planted. Winter wheat is the predominant crop; although other small grains, alfalfa, and field corn are commonly grown. There is also some ranching in the study area.

METHODS

Wheat was collected throughout its growing season from various farms within the study area, using 0.5 m^2 quadrats designed by Kennedy (1972). Sampling within selected fields was at random intervals along straight rows of fairly equal density. Care was taken to sample fields that had been planted at approximately the same time. In this area winter wheat is grazed by cattle and harvested, therefore leafy shoots and heads were primarily analyzed. Fields were selected to maximize information as a function of distance from the smelter and were either north or south of the smelter. When possible, samples of other crops grown in the study area were collected.

The grassland just north of the smelter was sampled throughout most of the year; however, sampling was restricted to three 4 ha sites (0.1, 0.4, and 0.8 km north of the smelter). Randomly located 0.5 m^2 quadrats (Kennedy, 1972) were clipped within these sites; and the resampling of a previously clipped area was avoided. Again, emphasis was placed on that portion of the plant consumed by herbivores or harvested by man.

Species composition and percent cover of plants growing in this grassland were determined along 2 parallel 0.8 km line transects perpendicular to the row of 12 smelter furnaces. Percent cover of each species was estimated under each 7.6 km segment of each transect.

Intact branches (leaves plus twigs) including previous years growth were collected from 7 deciduous tree species growing within 1.6 km north, 7.2 km north, and 181 km south (Norman, Oklahoma) of the smelter. Branches were taken from all sides of the lower to middle canopy - about 4 m above ground.

All vegetation samples were collected in polyethylene bags, and upon return to the laboratory stored in a cold room until sorted by plant part (leaf from petiole, petiole from new growth, new from previous years growth, heads from shoots, and grain from chaff). Grassland samples were sorted by species and on the basis of live or standing dead. Vegetation samples were oven dried 48 hr at 65°C, then ground in a Wiley mill through a 20 mesh screen.

Percent nitrogen content of wheat seed was determined using the Macro-Kjeldahl method (Bremner, 1965). Prior to digestion samples were reground to pass through a 100 mesh screen as suggested by Jackson (1958). Percent protein content of this seed was calculated by multiplying percent nitrogen by 5.7, while percent water content was based on the difference between fresh and oven dry weight.

Seven varieties of wheat, 4 varieties of alfalfa, Hairy vetch, and Midland bermuda grass were each grown in a growth chamber for approximately 3 - 5 mo under the following conditions: 1.61×10^4 lumen/m^2, a 16 hr photoperiod at 27°C, and an 8 hr dark period at 21°C. Potting soils were collected from the Blackwell area and mixed with incremental percents by weight of non-contaminated soil. After seedling emergence, pots (5 - 8/treatment) were thinned to contain an equal number of seedlings per pot, with the exception of bermuda, which formed a sod within each pot. Growth response (average leaf length, average number of leaves per plant, length of longest leaf, and the amount of aboveground and belowground biomass) was measured at 30 day intervals from the day of seedling emergence. Harvested plant materials were subjected to the same sample preparations as vegetation collected from Blackwell.

Samples of all soil blends were air dried, crushed, passed through a 4 mesh sieve, ground to pass through a 40 mesh screen in a hammer mill, and then oven dried at 90°C. To minimize contamination, those samples with the highest percent of non-contaminated soil were ground first, and the mill was cleaned between samples. Soil pH was determined using a 10:1 water to air dried soil solution and a pH meter.

Total Zn, Cd, Pb, and As for both soils and vegetation materials were determined by the Blackwell Zinc Company Laboratory. Plant and soil materials were digested with nitric acid, and total Zn, Cd, and Pb determined using a Perkin Elmer Model 304 atomic absorption spectrophotometer. A distillation isolation of total arsenic, followed by photometric determination by the molybdenum blue method (Ernst, 1954) was used for determining the concentration of As in plant and soil materials. For the experiment utilizing Triumph 64 variety wheat, extractable soil Zn was determined using a DTPA-TEA extraction (Lindsey and Norvell, 1967). Due to the high concentrations of zinc in the soil, the amount of the DTPA-TEA extracting solution used (100 ml) was five times that used by Lindsey and Norvell (1967).

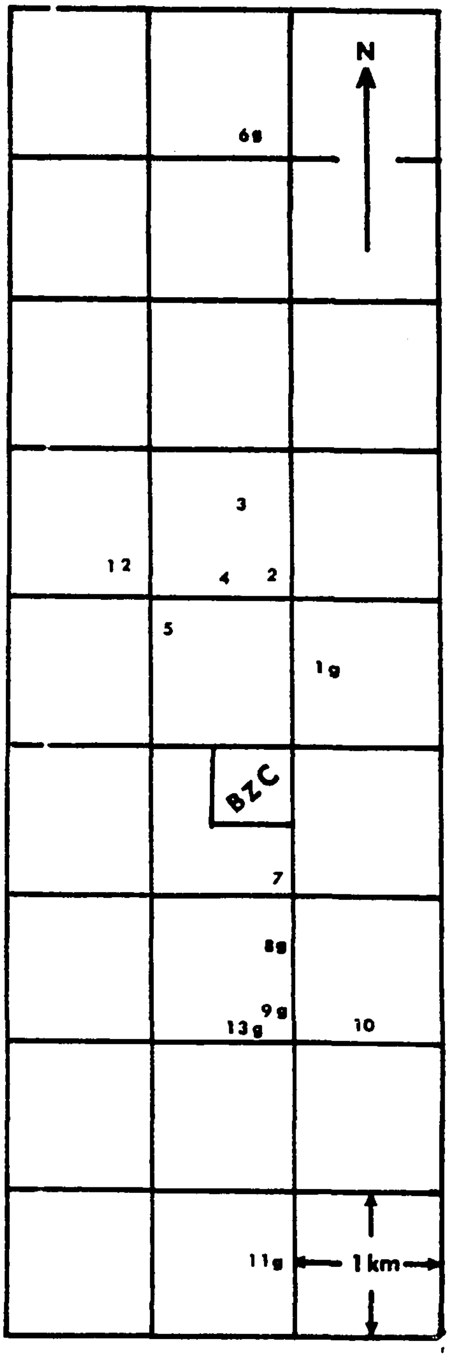
RESULTS AND DISCUSSION

Wheat

In the fall of 1971 clip quadrats were randomly sampled from 13 sites (Fig. 2) at 3 week intervals for 9 weeks after sowing. Both production of aboveground biomass (g/m^2), and production rate ($g/m^2/day$) tended to decrease with proximity to the smelter (Fig. 3). Some fields were grazed, but AUM/A are unknown. In addition, differences in soil, fertilizing, and/or variety of wheat planted may account for some of the variability within the data.

Just prior to the 1973 harvest, 9 fields were sampled to determine grain yield (g/m^2). To put these values into better perspective with regard to farm economics the weight of grain collected from each quadrat was converted to Bu/A assuming a 27 kg bushel. The average yield for each field was then compared to its distance from the smelter to ascertain any relationship between these two variables. Yield was not found to increase or decrease significantly as a function of distance from the smelter ($R<0.632, \alpha=0.05$) (Fig. 4). Mr. Harry Bathurst, a local farmer, provided yield data from the sections farmed by his family during the past 11 years. These data were averaged and compass direction and distance from the smelter determined for each section

Figure 2. Sampling sites for wheat biomass study.



BZC = Blackwell Zinc Company

g = grazed

Figure 3. Change in the fall wheat aboveground biomass (g/m^2) and production rate (g/m^2/day) for the 13 sites sampled in 1971.

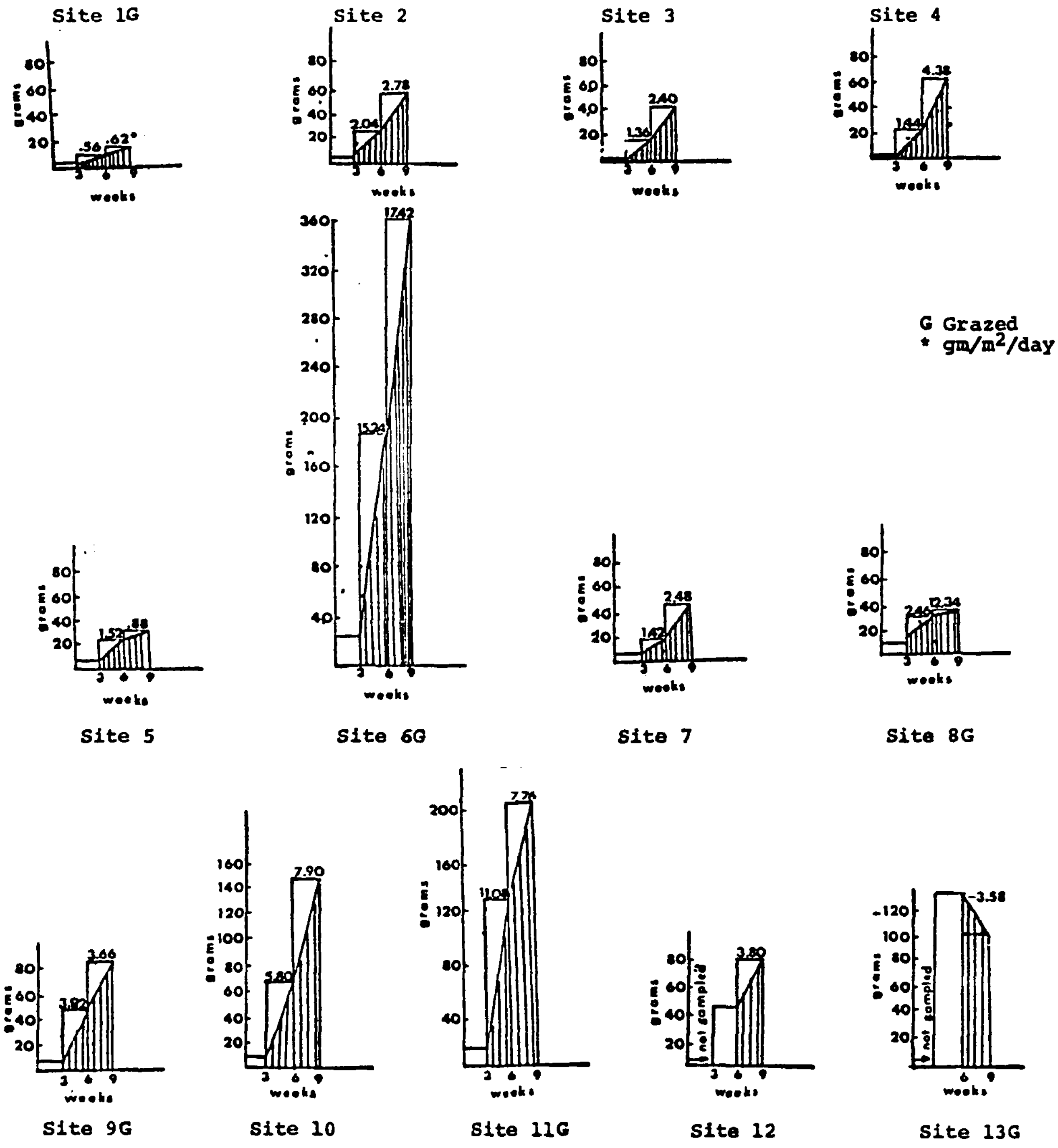
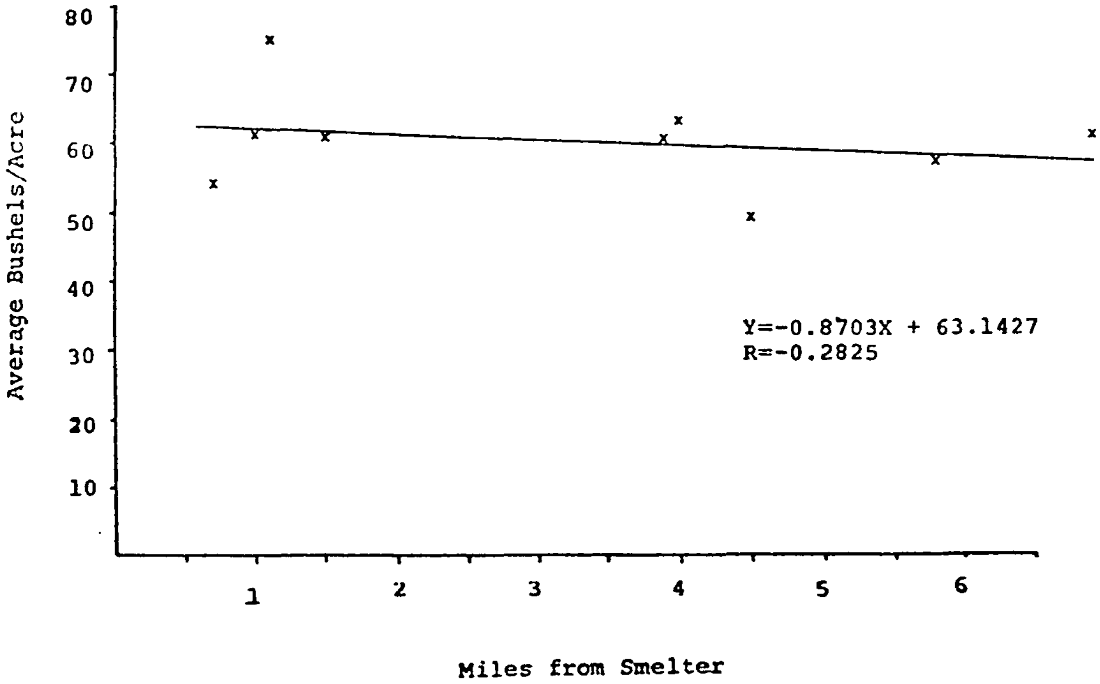


Figure 4. Average bushels of wheat per acre vs. distance collected from the smelter using quadrat data.



(Table 1). Yield per acre was not significantly correlated with distance from the smelter ($R<0.514, \alpha=0.05$); thus strengthening the previously drawn conclusion that yield is not related to smelter proximity. Average yields of the 9 fields sampled were also compared with Zn, Cd, Pb, and As contents of soil from these fields, and no associations were found ($R<0.632, \alpha=0.05$).

The average percent protein and average percent water content of wheat from these 9 fields were determined (Table 2) and compared with the distance of the fields from the smelter. As with yield and soil metal content, no correlation between either of these variables and distance was ascertained ($R<0.632, \alpha=0.05$). In addition, no correlation ($R<0.632, \alpha=0.05$) between either average percent protein content or average percent water content of this wheat seed and total soil Zn, Cd, Pb, or As was found.

Average Zn, Cd, and Pb content (ppm, dry weight) of this wheat were found to be inversely related ($R>0.632, \alpha=0.05$) with distance from the smelter and directly related ($R>0.632, \alpha=0.05$) with soil content of these metals (Figs. 5 - 10). By combining metal content and yield per acre, average kg/ha of each of these metals harvested were determined (Table 3). Arsenic content was below the detection limit of the photometric method for all but the three samples collected from field number 6 - located 1.6 km south of the smelter. Field number 6 had the highest soil arsenic content of the 9 fields sampled, suggesting a possible relationship between soil and grain content of this

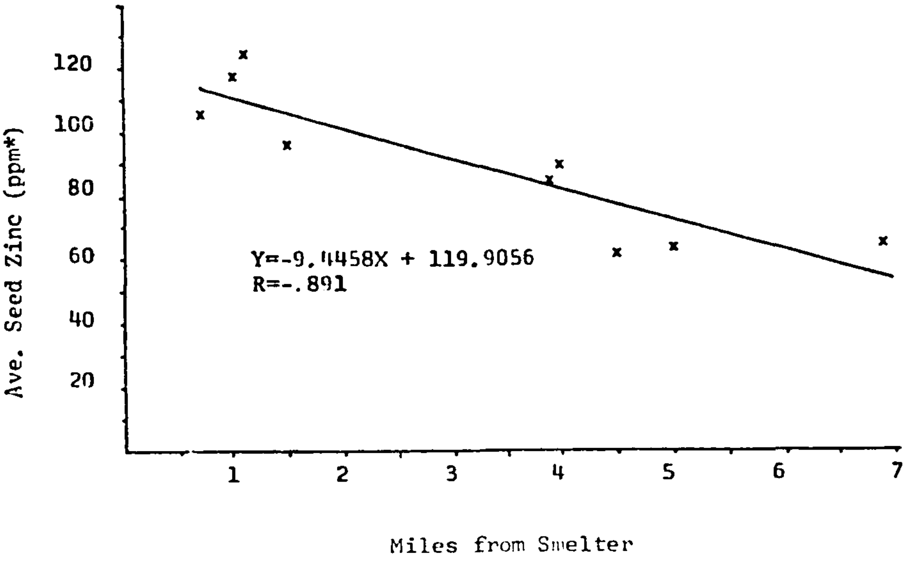
Table 1. A summary of the data provided by Mr. Harry Bathurst pertaining to wheat yields of sections farmed by his family during the past eleven years.

Legal Description	Number of Data Years	Average Number Acres Planted	Average Bushels per Acre	Distance and Direction from Smelter	Comments
SE¼-34-29-2W	11	119.4	34.0	17.0 km NW	
E½ of SW¼-34-29-2W	8	66.4	36.0	17.4 km NW	
NW¼-15-28-2W	3	104.9	32.6	21.1 km NW	Hailed out in 1972 (13.3 Bu/A ave.)
NE¼-27-28-2W	11	113.8	31.5	11.2 km NW	Tornado destroyed 40 acres - 1966
SE¼-27-28-2W	11	114.9	30.7	10.4 km NW	Tornado destroyed 40 acres - 1966
S½-26-28-2W	11	199.4	33.1	9.6 km NW	
SE¼-11-27-2W	11	105.0	36.7	7.2 km NWW	
NE¼-28-27-1W	10	98.2	33.1	1.8 km S	Hail loss 30% in 1964, Badly hailed, 1968
SE¼-9-27-1W	5	123.4	27.1	1.8 km N	
SW60 A of SW¼-10-27-1W	8	15.6	33.4	1.9 km N	
NW¼-15-27-1W	11	104.8	30.8	1.3 km NE	Badly hailed, 1969
SW¼-9-27-1W	11	94.0	35.2	2.4 km NNW	
NE¼-20-27-1W	11	113.4	39.6	1.6 km W	
SW½-16-27-1W	11	208.0	31.0	1.0 km NW	

Table 2. Metal content of the soil, average percent protein, and average percent water content of wheat from the nine fields sampled just prior to the 1973 harvest.

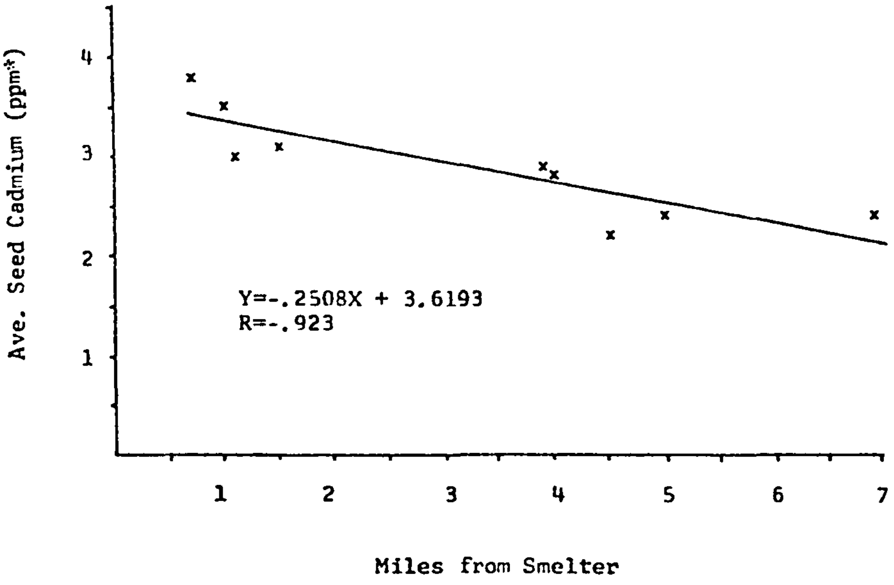
Field No.	Kilometers from the Smelter	Metal Content of Soil (ppm) Total Zn	Total Cd	Total Pb	Total As	Average % Protein	Average % Water
1	1.1	1650	12.9	134	7.0	14.0	6.6
2	7.2	280	4.0	40	4.4	11.6	6.4
3	11.0	118	2.5	25	4.0	10.8	6.2
4	6.2	295	3.0	40	4.2	13.0	6.6
5	1.8	1150	8.5	60	5.9	14.7	6.4
6	1.6	2150	19.0	105	14.2	15.0	6.6
7	2.4	450	5.0	43	5.6	12.4	6.8
8	6.4	190	2.0	25	5.0	14.4	6.7
9	8.0	60	1.5	15	4.4	15.0	6.7

Figure 5. Average Zn content of wheat seed vs. distance the wheat was collected from the smelter.



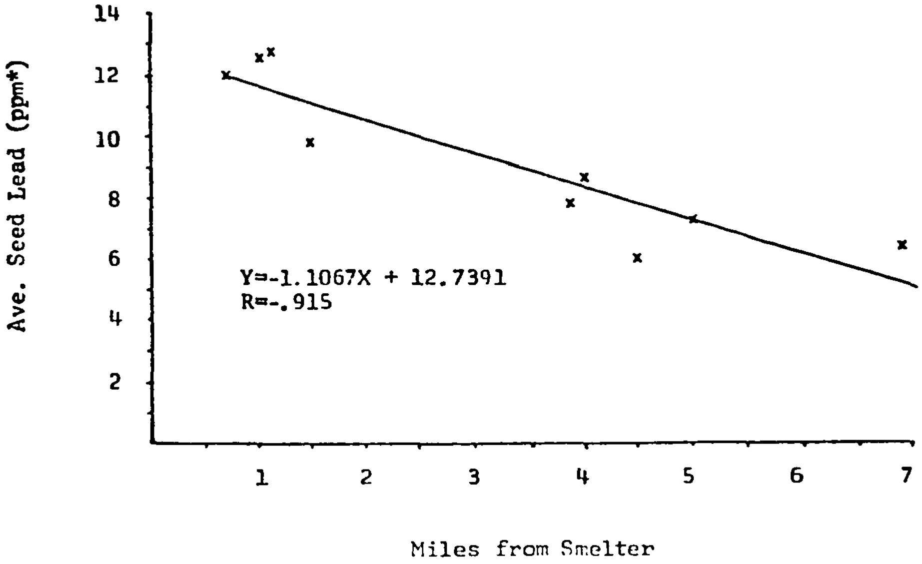
*Dry Weight

Figure 6. Average Cd content of wheat seed vs. distance the wheat was collected from the smelter.



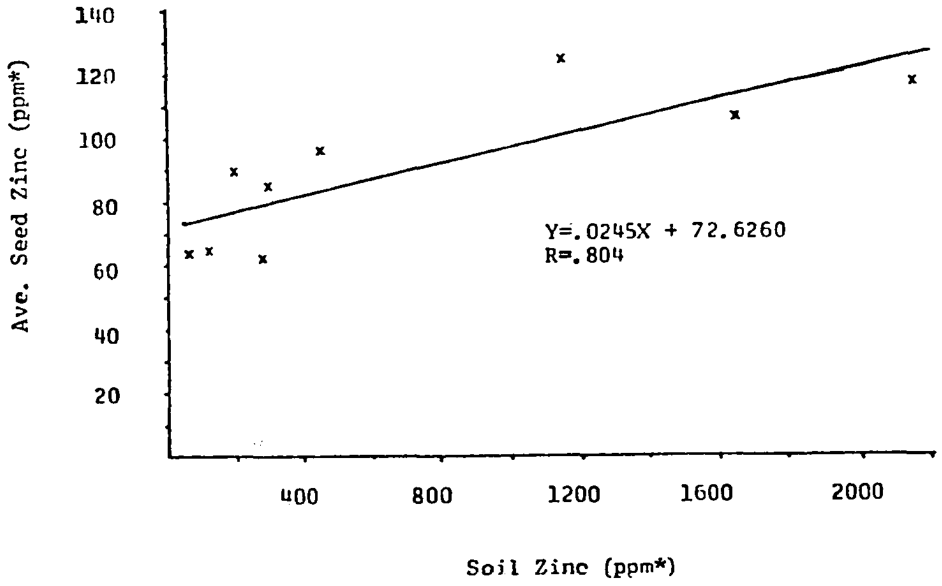
*Dry Weight

Figure 7. Average Pb content of wheat seed vs. distance the wheat was collected from the smelter.



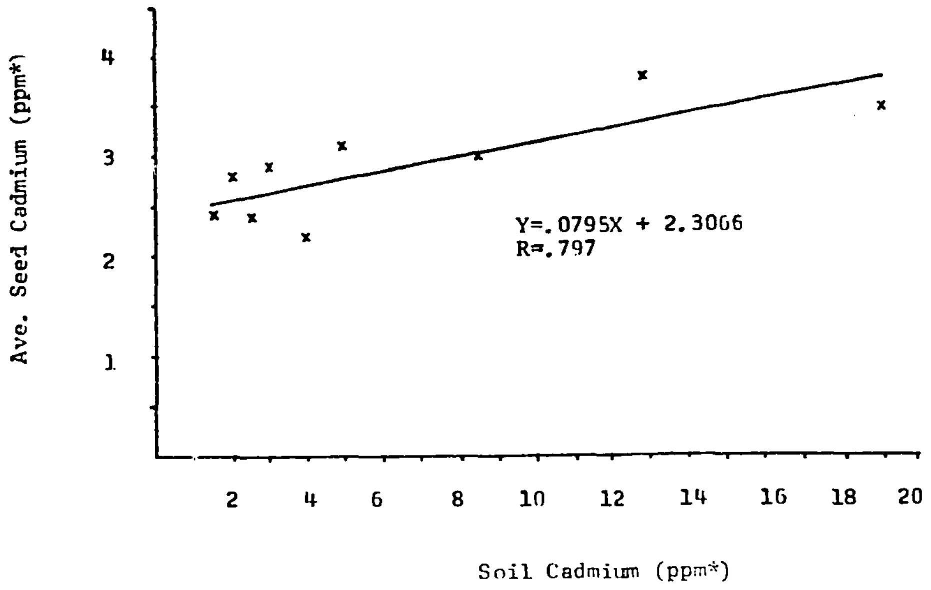
*Dry Weight

Figure 8. Average Zn content of wheat seed vs. ppm total soil Zn using quadrat data.



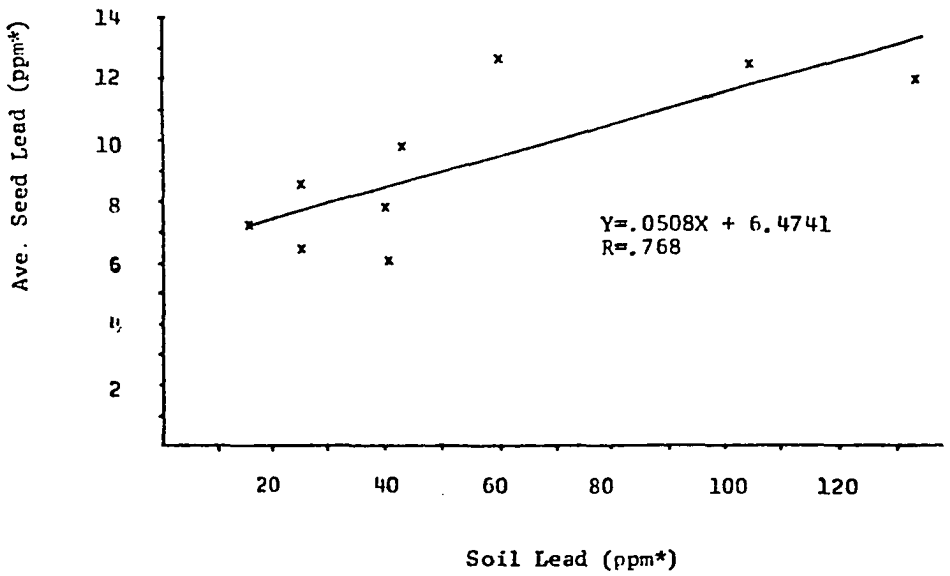
*Dry Weight

Figure 9. Average Cd content of wheat seed vs. ppm total soil Cd using quadrat data.



*Dry Weight

Figure 10. Average Pb content of wheat seed vs. ppm total soil Pb using quadrat data.



*Dry Weight

Table 3. Average kg/ha of metals removed by harvesting from the nine fields sampled just prior to the 1973 harvest.

Field No.	Kilometers from Smelter	Metals Removed by Harvesting (kg/ha)*		
		Zn	Cd	Pb
1	1.1	6.2×10^{-2}	2.2×10^{-3}	7.2×10^{-3}
2	7.2	3.3×10^{-2}	1.1×10^{-3}	3.3×10^{-3}
3	11.0	4.4×10^{-2}	1.3×10^{-3}	4.2×10^{-3}
4	6.2	5.7×10^{-2}	1.6×10^{-3}	5.2×10^{-3}
5	1.8	1.0×10^{-1}	2.6×10^{-3}	1.0×10^{-2}
6	1.6	7.9×10^{-2}	2.4×10^{-3}	8.5×10^{-3}
7	2.4	6.4×10^{-2}	2.0×10^{-3}	6.6×10^{-3}
8	6.4	6.2×10^{-2}	2.0×10^{-3}	5.9×10^{-3}
9	8.0	4.0×10^{-2}	1.5×10^{-3}	4.4×10^{-3}
Ave. for Region		6.0×10^{-2}	1.8×10^{-3}	6.1×10^{-3}

* Average of three samples per field.

metal.

The above results strongly suggest that neither wheat quantity nor protein and water content of the grain are affected by smelter proximity; however, these results might reflect good farming practices by the Bathursts, varietal differences, or edaphic factors within the sampled area. McCaull (1971) reported that whole-wheat bran free flour contains 18.3 - 19.4 ppm Zn and 0.28 ppm Cd; while refined flour contains 6.4 - 8.9 ppm Zn and 0.38 ppm Cd. The suitability of Blackwell wheat for human consumption is of undeterminable status for the following reasons:

the milling process decreases the amount of Zn and increases the amount of Cd available for absorption;

the level of Cd in wheat collected in Blackwell on the average was 11 times greater (range of 8 - 15) than normally found in whole wheat;

the level of Zn in this wheat was 5 times greater (range of 3 - 6) than normally found in whole wheat; and

wheat harvested in Blackwell is usually combined with wheat from other regions prior to milling.

It is suggested that Blackwell wheat not be locally ground unless blended with wheat harvested from farms distant from Blackwell.

Of the 13 sites sampled in November 1971, wheat above-ground biomass from sites 1,3,4,5,7,8, and 12 (all within 2.4 km of the smelter) contained levels of total Zn or Pb which equalled or exceeded potentially toxic daily intake for cattle (Tables 4 - 8). On 5 November 1972, 40 wheat samples were collected within a 3.2 km

Table 4. Average Zn, Cd, Pb, and As content of wheat aboveground biomass collected on 27 November 1971.

Site No.	Zn ppm*	Cd ppm*	Pb ppm*	As ppm*
1	1880	19.5	28.0	1.8
2	320	7.2	10.5	0.4
3	1358	11.9	18.5	1.8
4	1150	13.7	16.0	1.5
5	1430	16.8	16.8	1.5
6	195	5.9	9.5	0.7
7	980	16.2	19.5	1.6
8	1015	14.8	27.0	3.5
9	718	9.1	10.3	0.9
10	608	9.1	9.5	0.4
11	245	4.9	8.5	0.4
12	1258	11.1	12.5	0.3
13	418	6.8	9.7	< 0.2

* Dry Weight

Table 5. Potentially toxic Zn levels for livestock.

Test Animal	Daily Feed Intake (Dry Weight)	Author
Cattle:		
Hereford calves (steers and heifers)	900 ppm Zn as ZnO for 12 wk toxic	Ott, Smith, Harrington, and Beeson, 1966b
Jersey and Holstein lactating dairy cows	1,279 ppm Zn and ZnO for 6 wk not toxic	Miller, Clifton, Fowler, and Perkins, 1965
Swine:		
Duroc weanling pigs	2000-4000 ppm Zn as ZnO for 10 wk not toxic	Cox and Hale, 1962
Various breeds of weanling pigs	1000 ppm Zn as $ZnCo_3$ for 6 wk maximum amount tolerated	Brink, Becker, Terrill, and Jensen, 1959
Sheep:		
Western lambs	1500 ppm Zn as ZnO for 10 wk toxic	Ott, Smith, Harrington, and Beeson, 1966a
Horses:		
Mares	570 ppm Zn for 57 wk not toxic - nursing foals normal	Graham, Sampson, and Hester, 1940
Pinto and standard-bred type fillies	90 mg Zn/kg body wt/day for 30 wk toxic (equal to 3600 ppm Zn in feed)	Willoughby, Macdonald, McSherry, and Brown, 1972

Table 6. Potentially toxic Cd levels for livestock.

Test Animal	Daily Feed Intake (Dry Weight)	Author
Cattle:		
Holstein and Jersey heifer calves	160 ppm Cd as $CdCl_2$ for 5 days toxic	Powell, Miller, and Clifton, 1964
Holstein and Jersey bull calves	160 ppm Cd as $CdCl_2$ for 12 wk toxic	Powell, Miller, Morton and Clifton, 1964
Non pregnant lactating Holstein cows	250-300 ppm Cd as $CdCl_2$ for 2 wk toxic (didn't establish lowest toxic level)	Miller, Lamp, Powell, Salotti, and Blackmon, 1967
Swine:		
Yorkshire barrows	50 ppm Cd as $CdCl_2$ for 6 wk decreased weight gains	Cousins, Barber, and Trout, 1973
Yorkshire pigs	154 ppm Cd as $CdCl_2$ for 8 wk decreased weight gains (Zn offset Cd toxicity)	Pond, Chapman, and Walker, 1966
Swine	150 ppm Cd as CdO not toxic; while 300 ppm Cd as CdO toxic	Clarke and Clarke, 1967
Sheep:	- - - - none recorded - - - - - - - - - - - - - - - - -	
Horses:	- - - - none recorded - - - - - - - - - - - - - - - - -	

Table 7. Potentially toxic Pb levels for livestock.

Test Animal	Daily Feed Intake (Dry Weight)	Author
Cattle:	Forage contaminated with 25-46 ppm Pb toxic	Cited in Kradel, Adams, Guss, 1965
	6-7 mg Pb/kg body weight/day toxic (equal to 200-300 ppm Pb in forage)	Aronson, 1972; Hammond and Aronson, 1963
Swine:		
Hampshire pigs	66 mg Pb/kg body wt/day as lead acetate for 14 wk toxic	Link and Pensinger, 1966
Chester white pigs	10.4 ppm Pb as lead acetate or 79 ppm Pb as lead arsenate for 1 yr not toxic	Groves, McCullock, and St. John, 1946
Sheep:		
Lambs 2 to 10 wk old	herbage which contained 427 ppm Pb (ave) toxic	Abstract: Am. Vet. Med. Ass. J. 130:22
Ewes, cows, and calves	herbage which contained 427 ppm Pb (ave) not toxic	Abstract: Am. Vet. Med. Ass. J. 130:22
Lambs	261 to 914 ppm Pb in herbage toxic	Stewart and Allcroft, 1956

Table 7. Continued.

Test Animal	Daily Feed Intake (Dry Weight)	Author
Young lambs	162 to 764 ppm Pb in forage toxic (278 ppm ave)	Butler, Nisbet, and Robertson, 1957
Lambs	41.1 to 258 ppm Pb in forage toxic (158 ppm ave)	Innes and Shearer, 1940 (cited in Butler et al. 1957)
Lambs	37 to 215 ppm Pb in forage toxic (96.5 ppm ave)	Shearer, Innes, and McDougall, 1940 (cited in Butler, et al. 1957)
Lambs	6.0 to 91.1 ppm Pb in forage toxic (20.4 ppm ave)	Shearer and McDougall, 1944 (cited in Butler, et al. 1957)
Lambs	427 ppm Pb (ave) in forage toxic	Stewart and Allcroft, 1956
Ewes (pregnant)	50 ppm Pb as lead acetate equal to 1 mg Pb/kg body wt/day toxic	Allcroft and Blaxter, 1950
Ewes (not pregnant)	250 ppm Pb as lead acetate equal to 5 mg Pb/kg body wt/day can be tolerated for 1 yr	Allcroft and Blaxter, 1950
Ewes (not pregnant)	400 ppm Pb as lead acetate equal to 8 mg Pb/kg body wt/day for 220 days toxic	Allcroft and Blaxter, 1950

Table 7. Continued.

Test Animal	Daily Feed Intake (Dry Weight)	Author
Horses:		
Horses	1.7 mg Pb/kg/body wt/day toxic (about 80 ppm Pb in forage)	Aronson, 1972
Horses	2.4 mg Pb/kg/body wt/day toxic (about 113 ppm Pb in forage)	Hammond and Aronson, 1963
Pinto and standard-bred type fillies	3400 ppm Pb in diet for 30 wk toxic - 86 mg Pb/kg body wt/day	Willoughby, MacDonald, McSherry and Brown, 1972

Table 8. Potentially toxic As levels for livestock.

Test Animal	Daily Feed Intake (Dry Weight)	Author
Cattle:		
Holstein - type lactating cows	1.25 mg As/kg body wt daily as Arsenic acid for 8 wk not toxic (equal to about 60 ppm As in forage)	Peoples, 1963
Ontario - cattle	ingesta containing ave 35.7 ppm As toxic (range 2.3 to 104 ppm)	Hatch and Funnell, 1969
Swine:		
Chester white pigs	22 ppm As as arsenic trioxide or 19 ppm As as Lead arsenate for 1 yr not toxic	Groves, McCulloch, and St. John, 1946
Sheep:		
Western feeder lambs	690 ppm As as arsanilic acid for 8 wk toxic	Bucy, Garrigus, Forbes, Norton, and Moore, 1955
Lambs	82.8 ppm As as arsanilic acid not toxic	Bucy, Garrigus, Forbes, Norton, and James, 1954

Table 8. Continued.

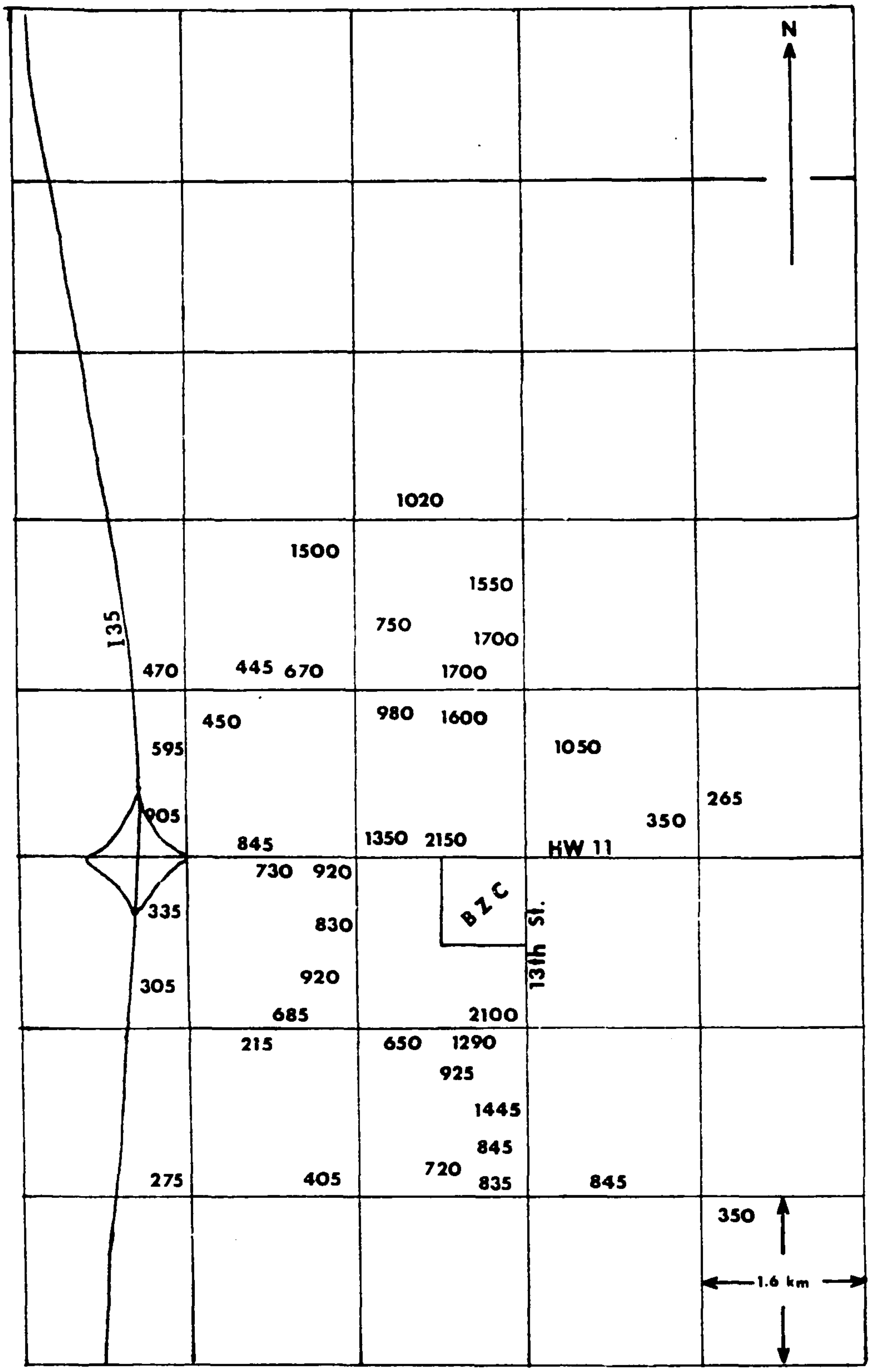
Test Animal	Daily Feed Intake (Dry Weight)	Author
Feeder lambs	on alfalfa pasture containing 62 ppm As for 36 hr in alfalfa toxic (wet weight)	Nelson, Crane, and Tomson, 1971
Horses:	1.3 to 1.9 grams As in diet daily not toxic (equal to 378 to 558 ppm As in forage of 500 lb horse)	Magill, Holden, Ackley, 1956

radius of the smelter in order to determine with more certainty the location and amount of wheat land that could be potentially toxic when used as a sole source of forage for cattle (Figs. 11 - 13). Based on published toxic levels of these metals in the diet of cattle, approximately 1012 ha of wheat land surrounding the smelter should not be grazed by cattle during the fall if used as a sole source of forage.

Additional wheat samples were collected 17 April 1973 within a 6.4 km radius of the smelter (Figs. 14 - 16). Compared with samples collected the previous fall, these samples contained an average of 66% less Zn, 46% less Cd, and 68% less Pb; while wheat straw collected in June 1971 from this area contained 53, 32, and 36% less of these metals than those collected the previous fall. Thus, the 1012 ha which were potentially toxic during the fall might safely be consumed even as a sole diet during the spring.

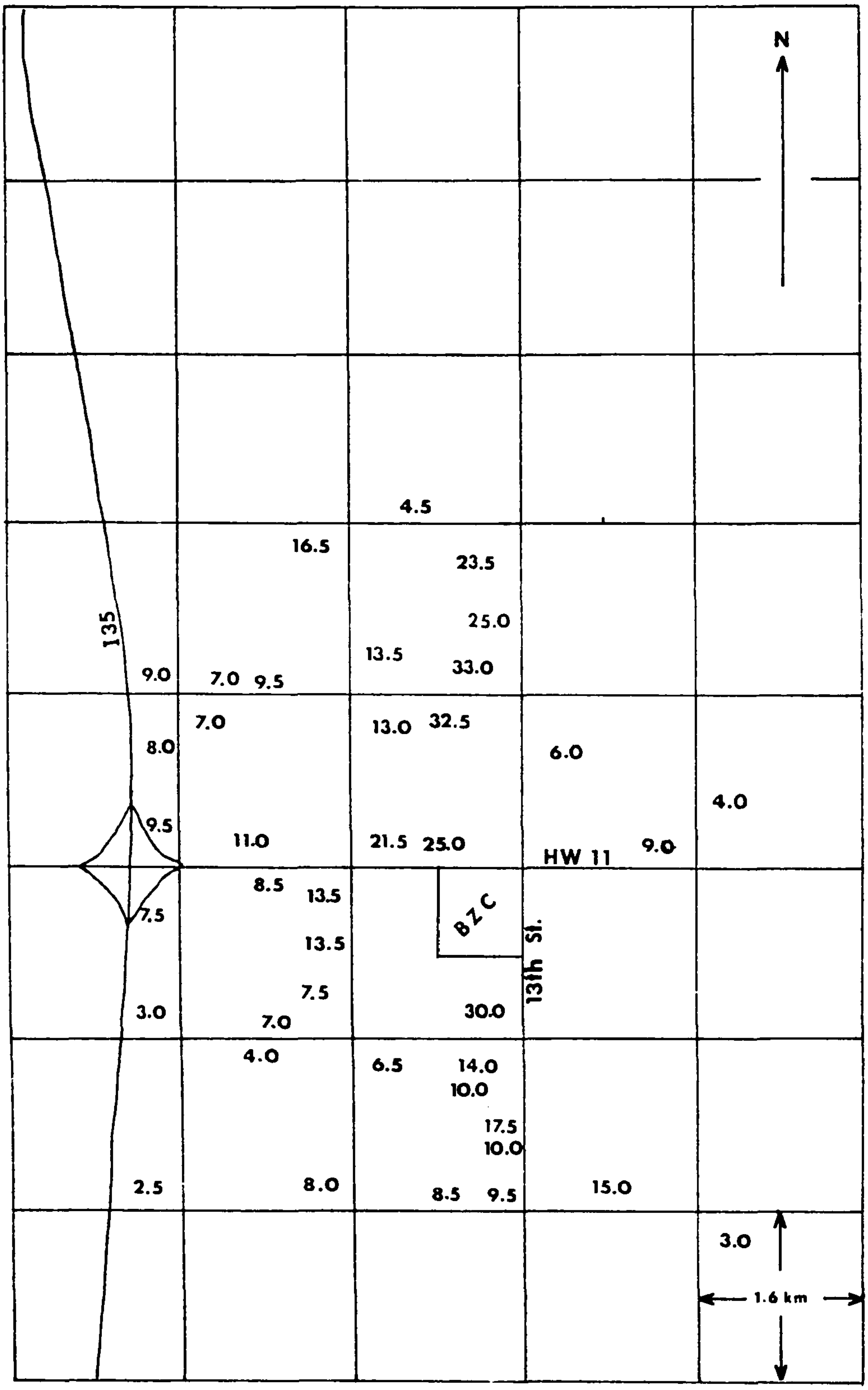
The following varieties of wheat are commonly grown in the Blackwell area: Triumph 64, Nicoma, Danne, Agent, and Centurk; while Apache and Scout 66 are commonly grown in southern Kansas. When grown in soils from Blackwell containing incremental amounts of Zn, Cd, Pb, and As, Centurk, followed by Nicoma had the highest percent germination, and Apache had the lowest (Table 9). After 5 mo growth in these soils, no economically significant differences in performance other than germination between these varieties were found (Table 10). Apache made comparable gains to the other 6 varieties after compensating for lower germination. In a subsequent experiment, Triumph 64 variety was used to determine growth response to a wider range of these metals. This variety

Figure 11. Zn content of aboveground biomass (ppm oven dry wt) collected on 5 November 1972.



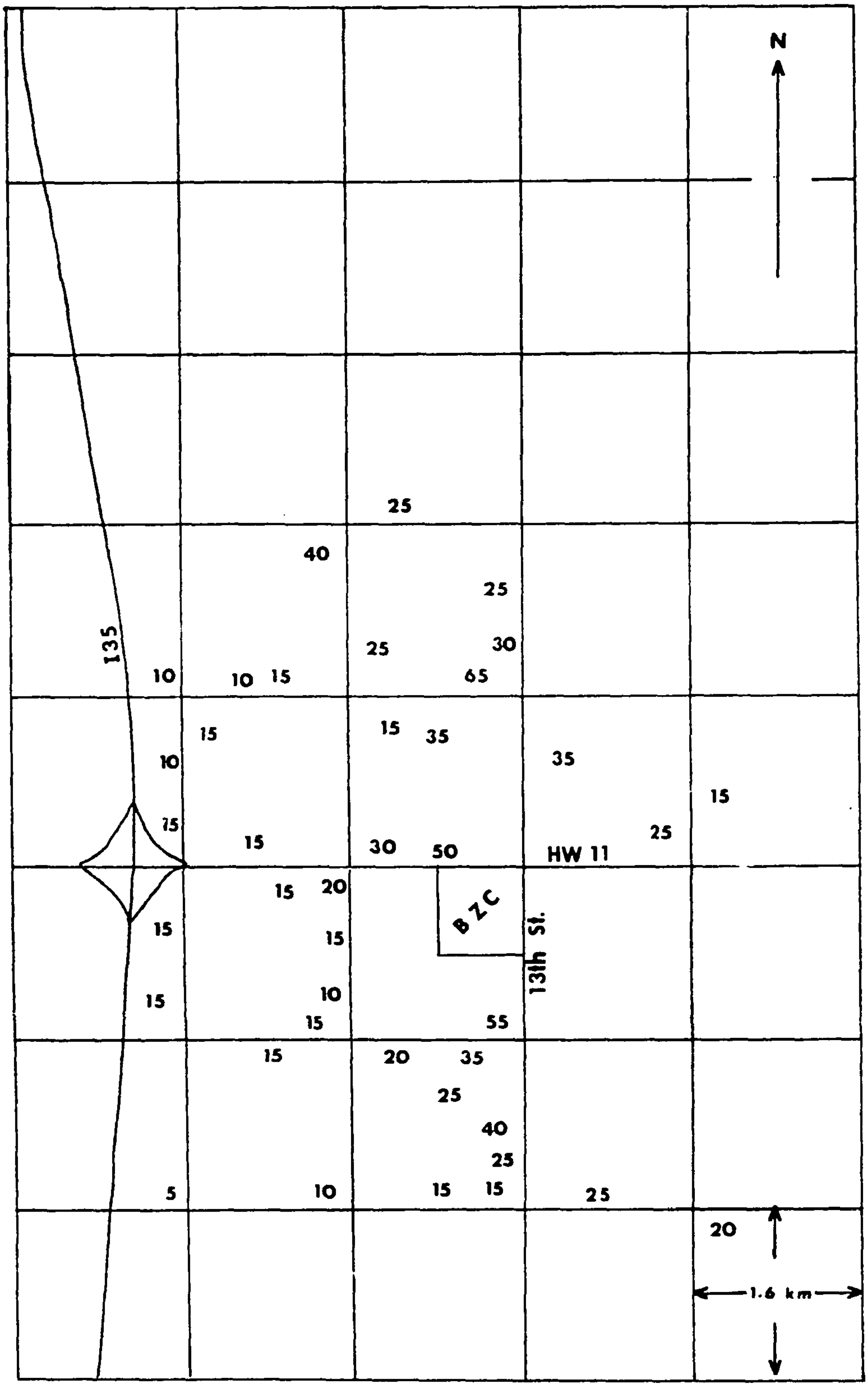
BZC = Blackwell Zinc Company

Figure 12. Cd content of aboveground biomass (ppm oven dry wt) collected on 5 November 1972.



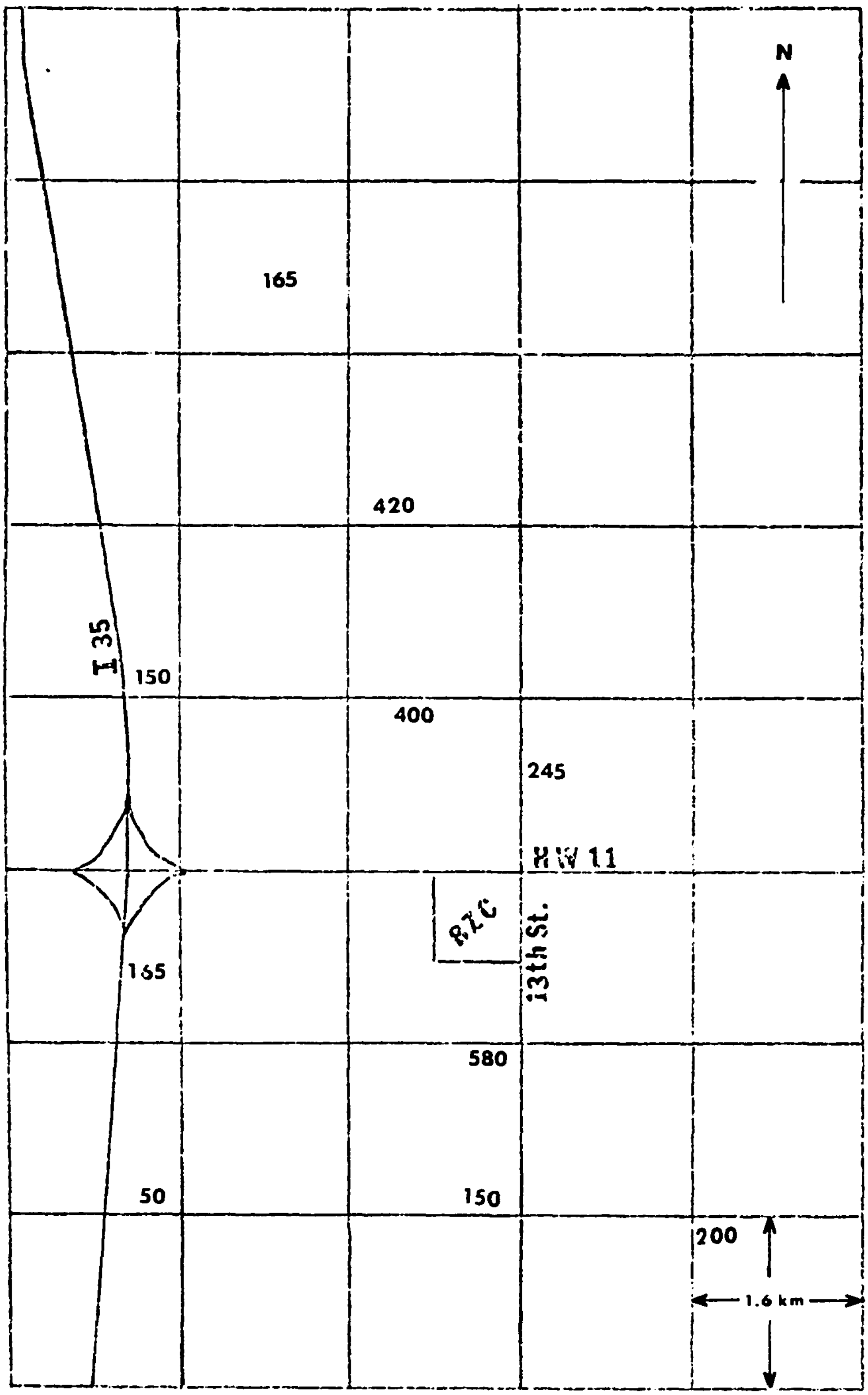
BZC = Blackwell Zinc Company

Figure 13. Pb content of aboveground biomass (ppm oven dry wt) collected on 5 November 1972.



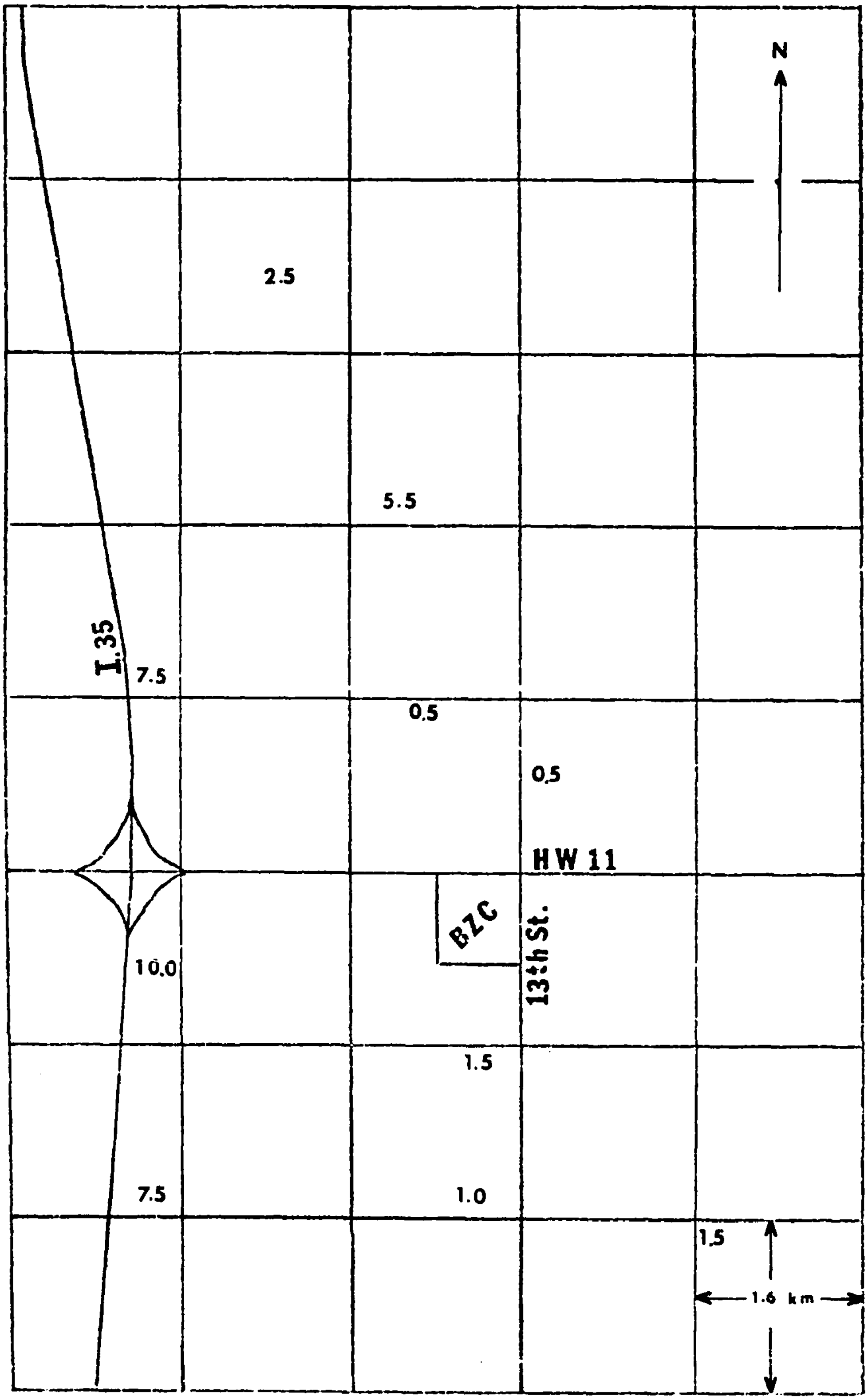
BZC = Blackwell Zinc Company

Figure 14. Zn content of aboveground biomass (ppm oven dry wt) collected on 17 April 1973.



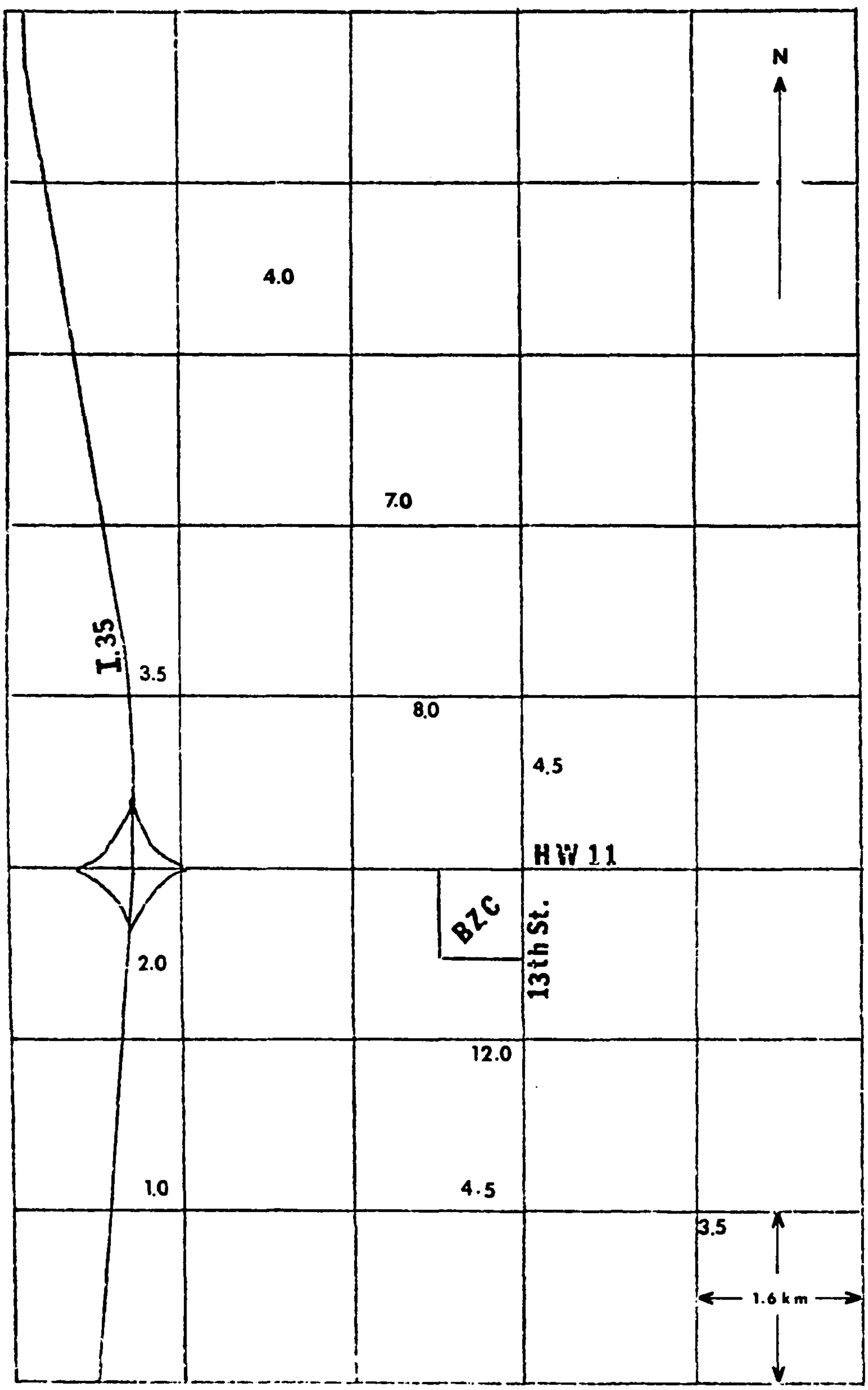
BZC = Blackwell Zinc Company

Figure 15. Cd content of aboveground biomass (ppm oven dry wt) collected on 17 April 1973.



BZC = Blackwell Zinc Company

Figure 16. Pb content of aboveground biomass (ppm oven dry wt) collected on 17 April 1973.



BZC = Blackwell Zinc Company

Table 9. Percent germination of the wheat varieties tested in incremental amounts of Zn, Cd, Pb, and As.

	Soil Metal Content (ppm)				Percent Germination						
Soil Contamination	Total Zn	Total Cd	Total Pb	Total As	Centurk	Nicoma	Danne	Triumph 64	Agent	Scout 66	Apache
Low	196	3.1	24	1.0	91	91	86	89	81	87	74
Medium	750	7.0	53	3.6	90	80	80	82	80	72	68
High	1650	12.9	116	7.0	94	87	82	76	85	81	63
				Avg	92	86	83	82	82	80	68

Table 10. Average aboveground biomass for 7 varieties of wheat tested in incremental amounts of Zn, Cd, Pb, and As.

Soil Contamination	Average Aboveground Biomass (g)*							
	Centurk	Nicoma	Danne	Triumph 64	Agent	Scout 66	Apache	Ave.
Low	2.74	3.34	3.03	2.88	2.73	3.03	2.78	2.93
Medium	2.41	2.57	2.55	2.48	2.58	2.32	2.79	2.53
High	1.13	0165	1.00	0.85	0.83	1.78	1.08	1.04

* dry wt, 5 pots/treatment, 15 plants/pot.

showed significantly ($\alpha=0.05$) decreased average leaf length, average number of leaves per plant, length of longest leaf, and the amount of aboveground and belowground biomass when grown in soils containing on the average: 612 ppm total Zn, 369 ppm DTPA-TEA extractable Zn, 7.6 ppm total Cd, and 8.6 ppm total As; while soil Pb did not appear to be associated with these decreases (Table 11).

The Zn and Cd content of aboveground biomass for this variety were directly related ($R>0.367, \alpha=0.05$) to total and extractable soil Zn and total soil Cd respectively (Figs. 17 - 19); while the Pb content of aboveground biomass was not correlated with soil Pb content ($R<0.367, \alpha=0.05$). Insufficient plant material was harvested from this experiment to determine As content. The average aboveground biomass content of Zn and Cd associated with the previously mentioned detrimental effects were interpolated from these graphs and thus found to be: 1140 ppm Zn and 10.3 ppm Cd. Boawn and Rasmussen (1971) reported that wheat with 909 ppm Zn in the tops showed a 45% decrease in yield; while wheat with 51 ppm showed no yield decrease. For Triumph 64, 909 ppm Zn in the tops would be approximately equivalent to 440 ppm total Zn in the soil. About 930 ha surrounding the smelter contain 1140 ppm or greater total soil Zn (Fig. 4, Part I). Presently, wheat is grown on approximately 1/2 this acreage, and yield decreases within this acreage have not been correlated with soil Zn content. During the past 40 years the Blackwell Zinc Company has subsidized the liming of farm lands within 2.5 km north and south of their smelter, and this practice has probably reduced the detrimental

Table 11. Soil Zn, Cd, and As content at which there were detrimental effects to Triumph 64 variety wheat.

Variable	Total Zn (ppm)	Extractable Zn (ppm)	Total Cd (ppm)	Total As (ppm)
Average Leaf Length	550	320	7.0	9.0
Length of Longest Leaf	600	350	7.5	8.0
Average Number of Leaves per Plant	760	475	9.0	9.0
Aboveground Biomass	550	300	7.0	9.0
Belowground Biomass	600	400	7.5	8.0

Figure 17. Total soil Zn vs. total wheat Zn.

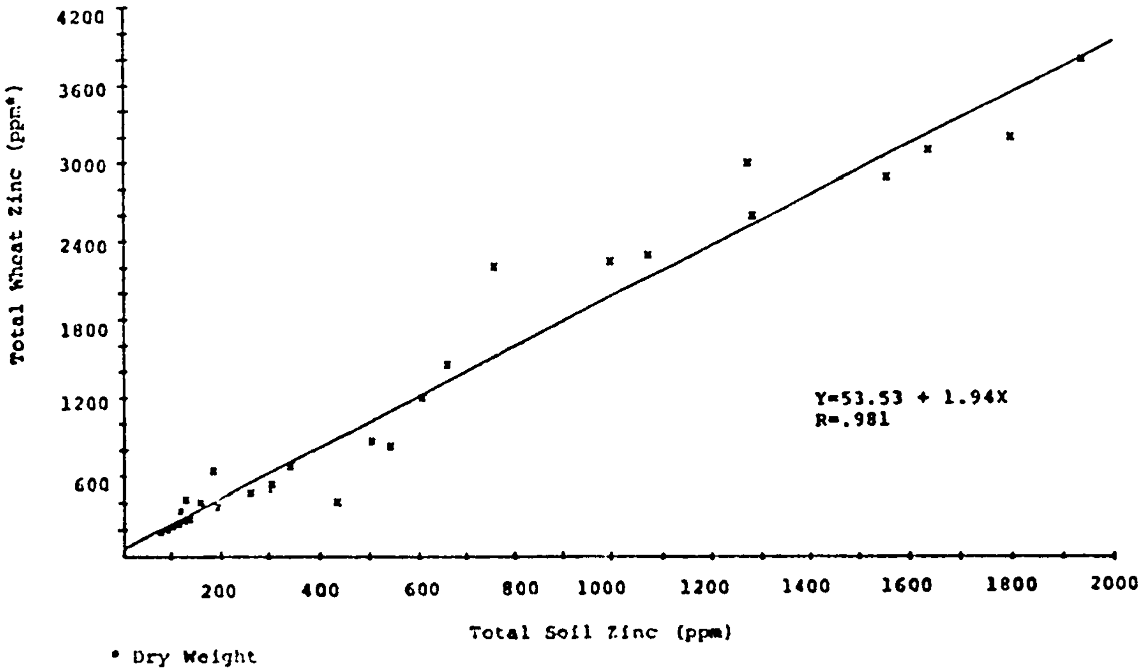


Figure 18. Extractable Zn in soil vs. total Zn in wheat.

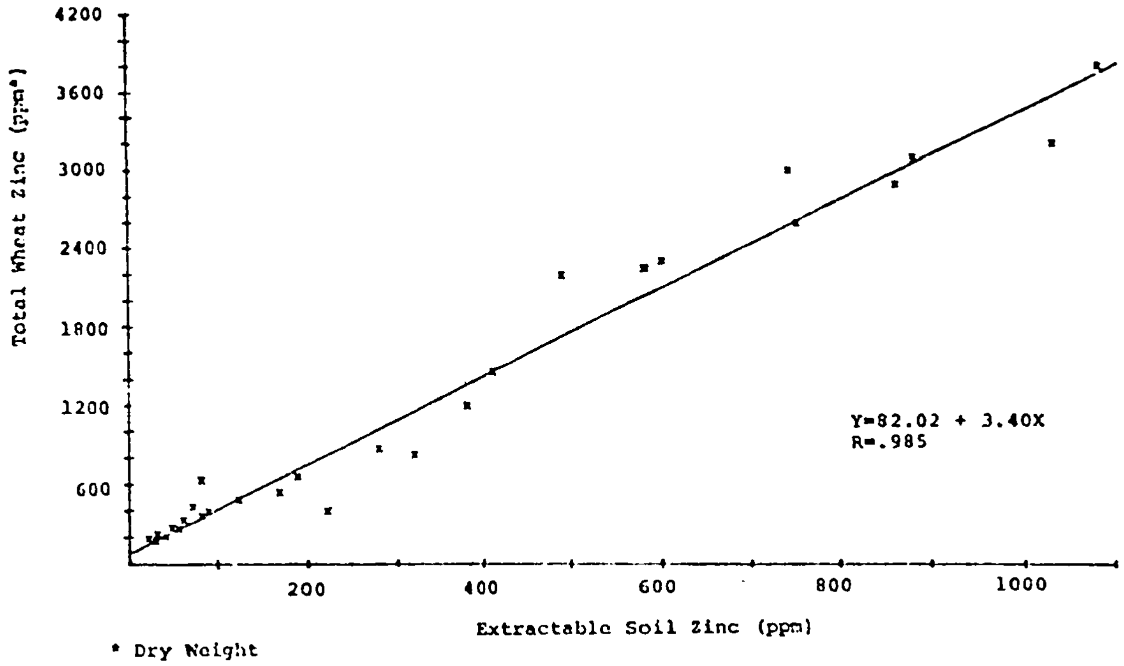
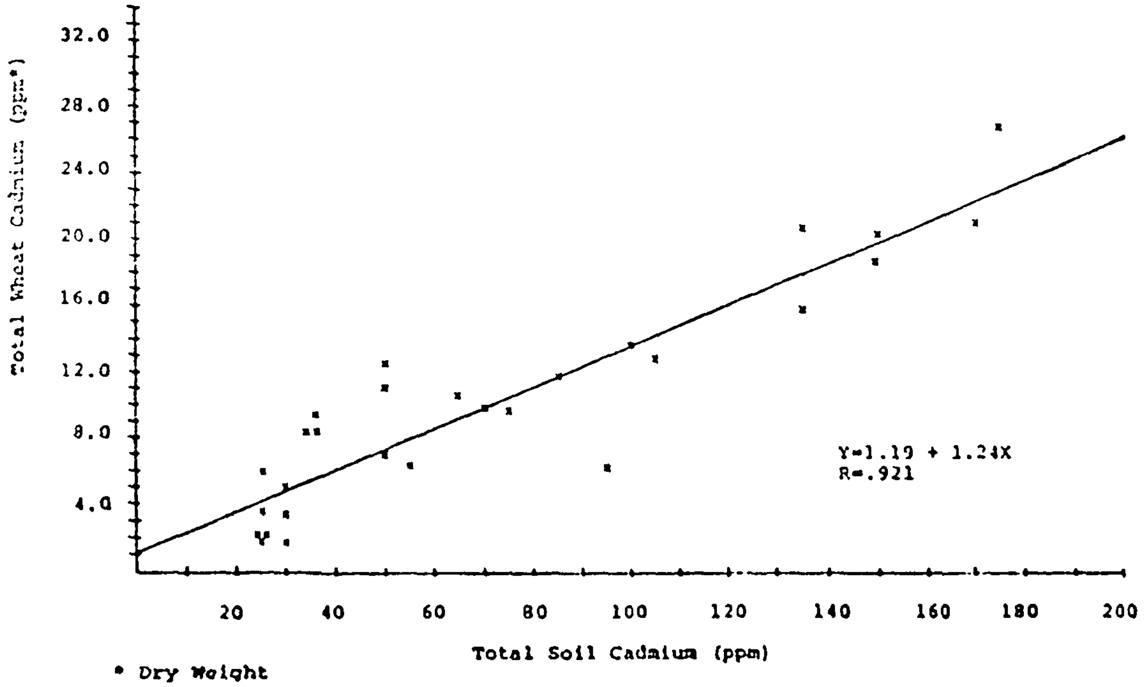


Figure 19. Total soil Cd vs. total wheat Cd.



effects of soil Zn on wheat. Kobayashi et al. (1961) found a 28% decrease in yield in soils containing 30 ppm total Cd. About 65 ha directly north of the smelter contain 30 ppm or greater soil Cd (Fig. 6, Part I). At present, though, wheat is not grown in this area.

Alfalfa

Common, Buffalo, Cody, and Dawson varieties of alfalfa which are commonly used in the north central part of Oklahoma were grown in incremental amounts of contaminated soil (Table 12). Some differences in the tolerance to these blends was shown by the four varieties, but these differences were economically insignificant (Tables 13 - 14). Zn and Cd content of alfalfa aboveground biomass harvested from these 4 varieties were directly correlated ($R>0.878, \alpha=0.05$) with the soil content of these metals; while the Pb content of the aboveground biomass was not significantly correlated ($R<0.878, \alpha=0.05$) with soil Pb content (Figs. 20 - 21). Insufficient plant material was harvested to determine As content. From the results of this experiment a 15 - 28% decrease in alfalfa growth would be predicted for a field containing average total Zn, Cd, and As levels similar to blend 2; while a 26 - 29%, a 38 - 69%, and a 100% decrease would be predicted in fields with levels similar to blends 3, 4, and 5 respectively (Table 12). Plant responses under growth chamber conditions may differ from those under field conditions in Blackwell even if both are exposed to equal concentrations of these metals. All 4 varieties showed increased mortality when

Table 12. Metal content of the soil blends utilized in the alfalfa varieties pot experiment.

Soil Blend Number	Total Metal Content (ppm)			
	Zn	Cd	Pb	As
1	52	3.0	15	2.0
2	835	9.5	50	1.8
3	1550	15.5	90	4.0
4	2650	20.0	125	5.8
5	3100	28.5	170	12.6

Table 13. Mean height of alfalfa varieties tested in incremental amounts of Zn, Cd, Pb, and As.

Soil Blend No.	Soil Metal Content (ppm)				Mean* Height (cm)**			
	Total Zn	Total Cd	Total Pb	Total As	Common	Cody	Dawson	Buffalo
1	52	3.0	15	2.0	18.4	18.1	16.6	16.0
2	835	9.5	50	1.8	13.2	15.4	12.6	12.8
3	1550	15.5	90	4.0	13.6	12.9	12.0	11.6
4	2650	20.0	125	5.8	6.7	7.1	5.2	10.0
5	3100	28.5	170	12.6	-	-	-	-

* Average 5 plants/pot, 8 pots/treatment

** 90 days after seedling emergence

\- Insufficient surviving plants

Table 14. Results of t-tests for pairs of varieties tested for significant differences in height after 90 days growth in each of the five soil blends. The variety listed in the table exhibited the superior growth in each pair-wise comparison.

Variety Pairs	Soil Blend Numbers 1	2	3	4	5
Common vs. Buffalo	Common	N.S.	N.S.	Buffalo	-
Common vs. Cody	N.S.	Cody	N.S.	N.S.	-
Common vs. Dawson	N.S.	N.S.	N.S.	N.S.	-
Buffalo vs. Cody	N.S.	Cody	N.S.	Buffalo	-
Buffalo vs. Dawson	N.S.	N.S.	N.S.	Buffalo	-
Cody vs. Dawson	N.S.	Cody	N.S.	Dawson	-

Note: N.S. = Not significant at .01 level

- = Insufficient surviving plants

Figure 20. Total Zn in soil blends vs. total Zn in alfalfa aboveground biomass.

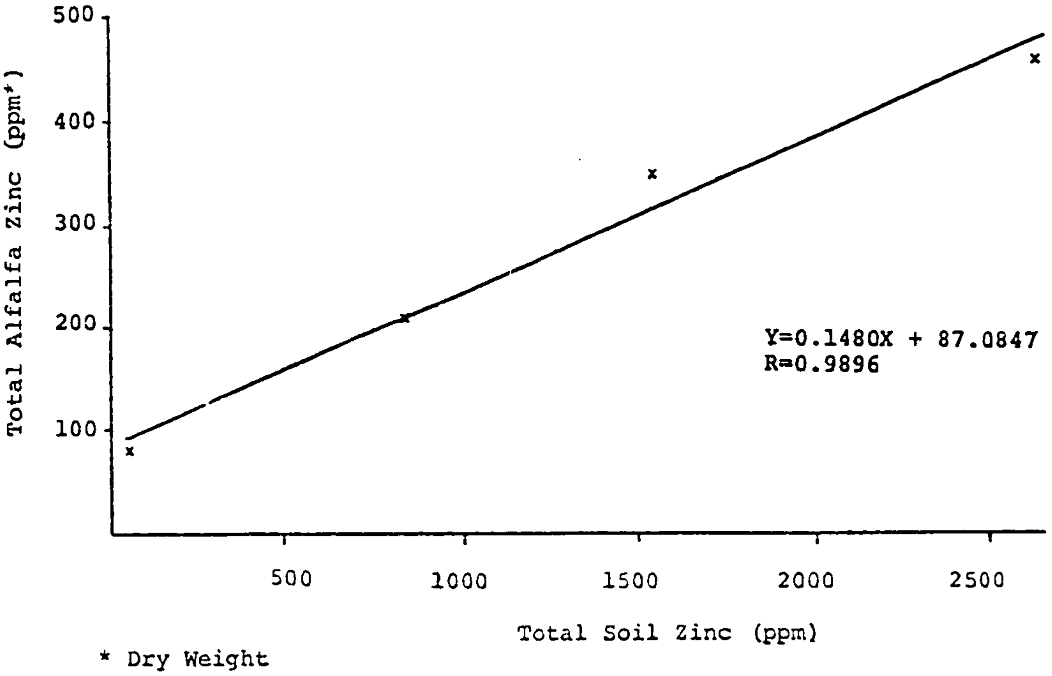
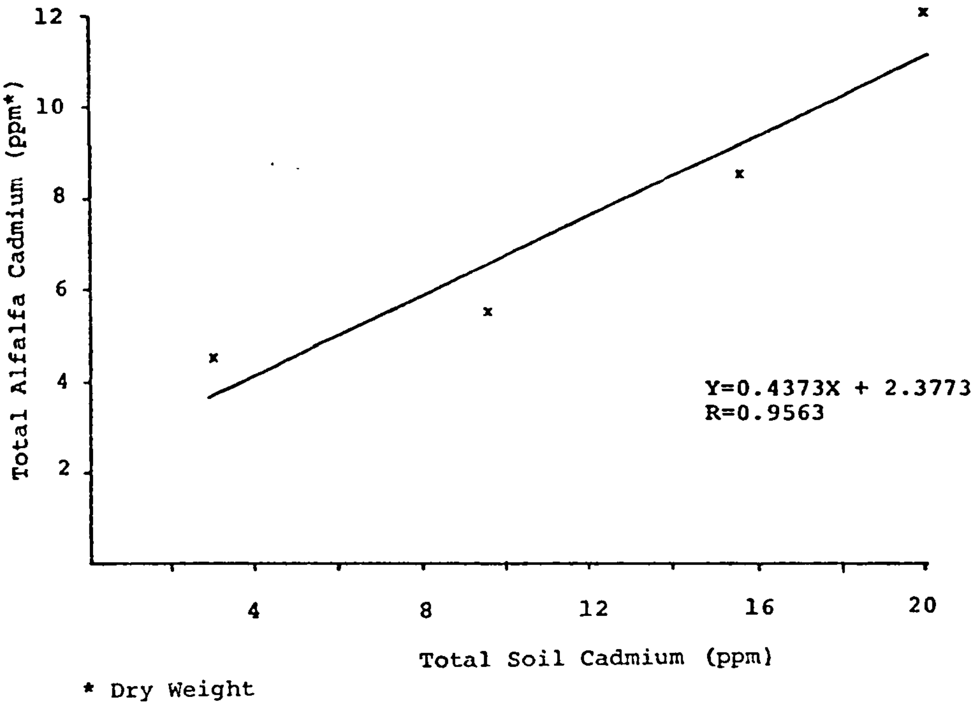


Figure 21. Total Cd in soil blends vs. total Cd in alfalfa aboveground biomass.



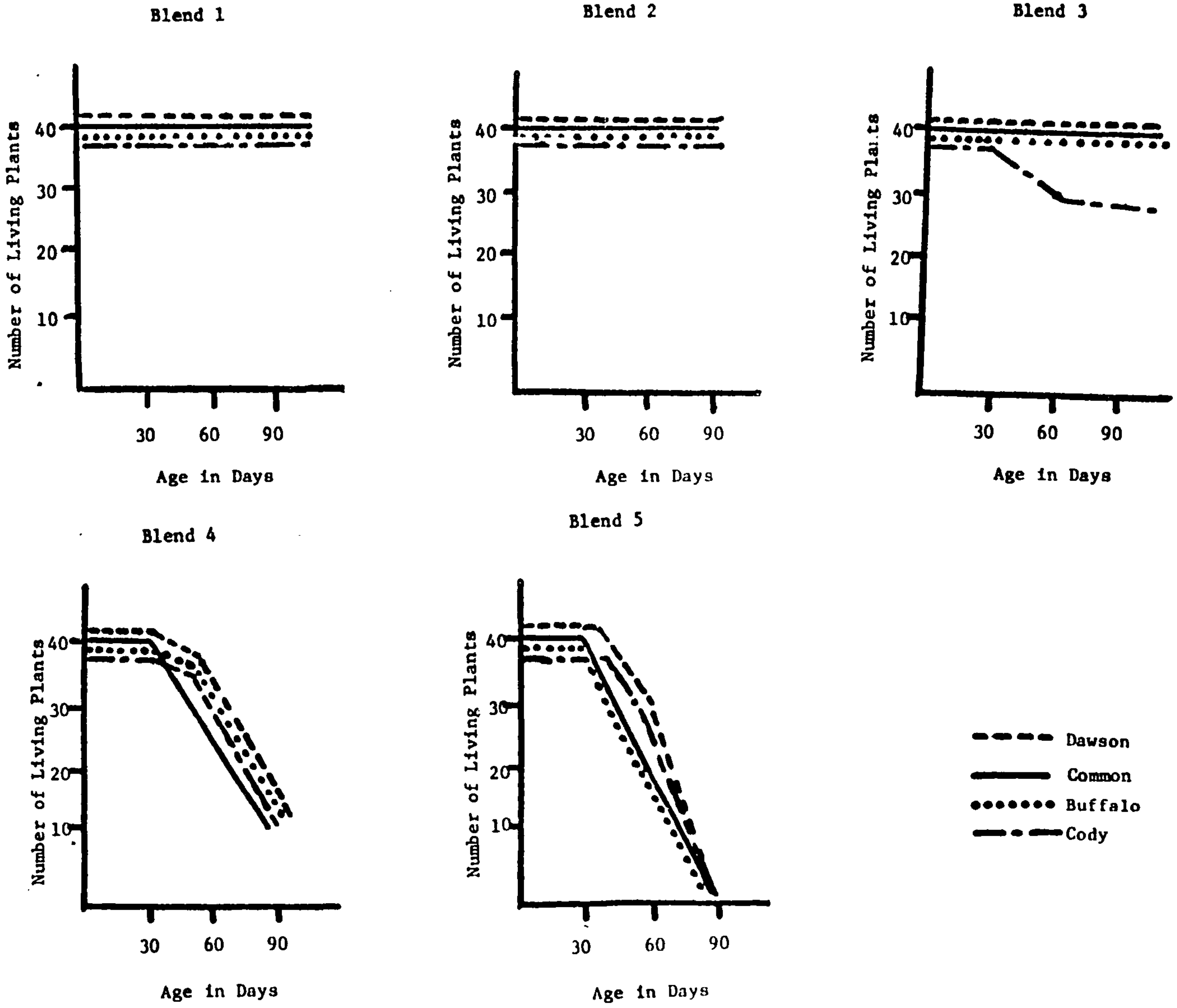
grown in blends 4 and 5 (Fig. 22). Vandecaveye, Horner, and Keaton (1936) reported 3.4 - 9.5 ppm soluble As in the soil to be toxic to alfalfa. Blends 4 and 5 contained 5.8 and 12.6 ppm total soil As. In a follow up experiment, growth of these 4 varieties was improved to equal that of the control by adding the equivalent of 1½ T/A aluminum sulfate and 3 T/A lime as $Ca(OH)_2$ - the soil treatment for arsenic toxicity (Chapman, 1966). About 1200 ha of farm land surrounding the smelter contain levels of these metals equal to or greater than blend 2 (Figs. 4, 6, 7, and 8, Part I).

Based on published potentially toxic Zn, Cd, and Pb levels for livestock (Tables 5 - 7), alfalfa produced on soils containing these experimental soil levels should be safe for livestock consumption. Alfalfa grown in these blends contained a maximum of 460 ppm Zn, 12 ppm Cd, and 10 ppm Pb.

Vetch

Hairy vetch was grown in 5 soil blends containing the same concentrations of total Zn, Cd, Pb, and As as the blends used for the alfalfa experiment. Significantly (α=0.05) more aboveground biomass (17%) was harvested from pots containing the lowest concentrations of these metals; while comparable amounts were harvested from the other 4 blends. If hairy vetch is planted in fields where the soil equals or exceeds 820 ppm total Zn, or 7.5 ppm total Cd; as predicted from these results a decrease of at least 17% production should be expected. Approximately 1200 ha of farm land surrounding the smelter contained these levels of Zn

Figure 22. Survival of alfalfa varieties in five different soil blends.



and/or Cd (Figs. 4 and 6, Part I); however, plant responses under growth chamber conditions may differ from those under field conditions in Blackwell even if both are exposed to equal concentrations of these metals. Zn and Cd content of aboveground biomass for this variety of vetch both increased ($R>0.811, \alpha=0.05$) as soil content of these metals increased (Figs. 23 - 25); Pb content was independent ($R>0.811, \alpha=0.05$) of soil Pb; and As content was not related ($R<0.811, \alpha=0.05$) to soil As.

Based on published potentially toxic Zn, Cd, Pb, and As levels for livestock (Tables 5 - 8), hairy vetch grown on soils containing these experimental soil levels should be safe for livestock consumption. The vetch grown in these blends contained a maximum of 580 ppm Zn, 28 ppm Cd, 2 ppm Pb, and 10 ppm As.

Forage Sorghum

Samples of forage sorghum were collected on 6 October 1972 from a quarter section (SE¼-17-27-1W) 1.6 km west-northwest of the smelter. The Zn content of this sorghum was potentially toxic to cattle and possibly weanling pigs (Tables 15 and 5); and the Pb content was potentially toxic to cattle and lambs (Tables 15 and 7). Sorghum heads alone were fit for animal consumption.

Field Corn

On 27 July 1973, samples of field corn were collected from a quarter section (SE¼-10-27-1W) 3 km northeast of the smelter. This corn contained on the average 265 ppm Zn, 12.5 ppm Cd, and

Figure 23. Total Zn in soil blends vs. total Zn in hairy vetch aboveground biomass.

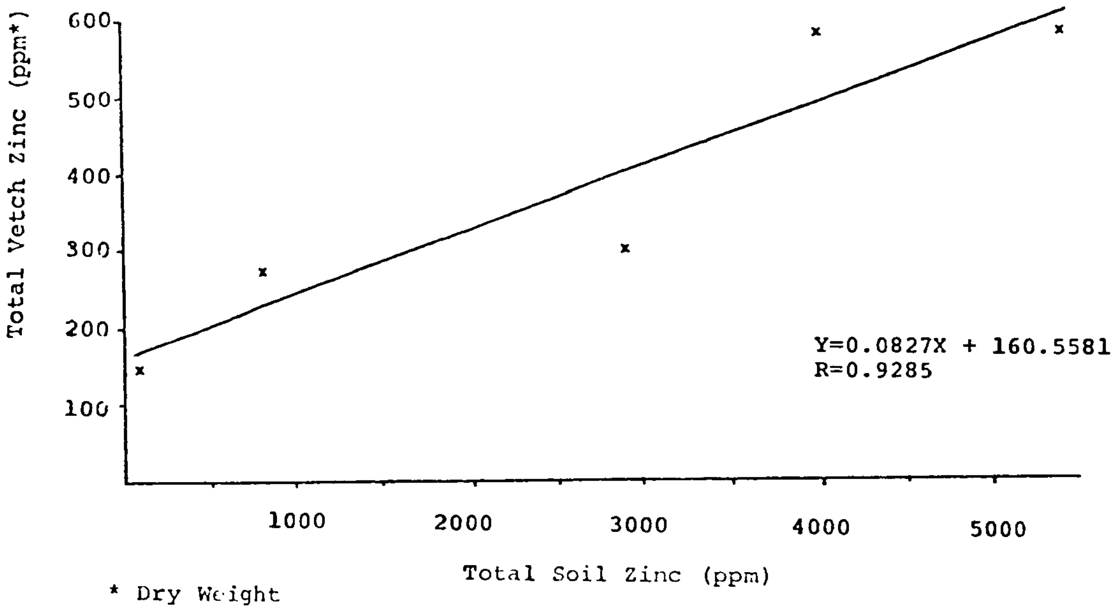


Figure 24. Total Cd in soil blends vs. total Cd in hairy vetch aboveground biomass.

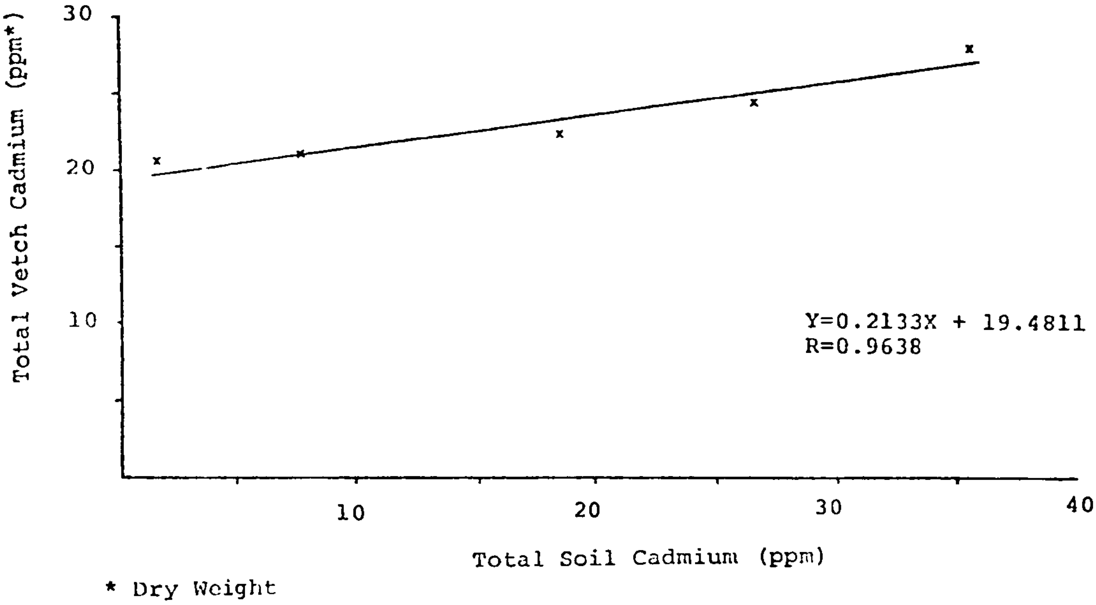


Figure 25. Total Pb in soil blends vs. total Pb in hairy vetch aboveground biomass.

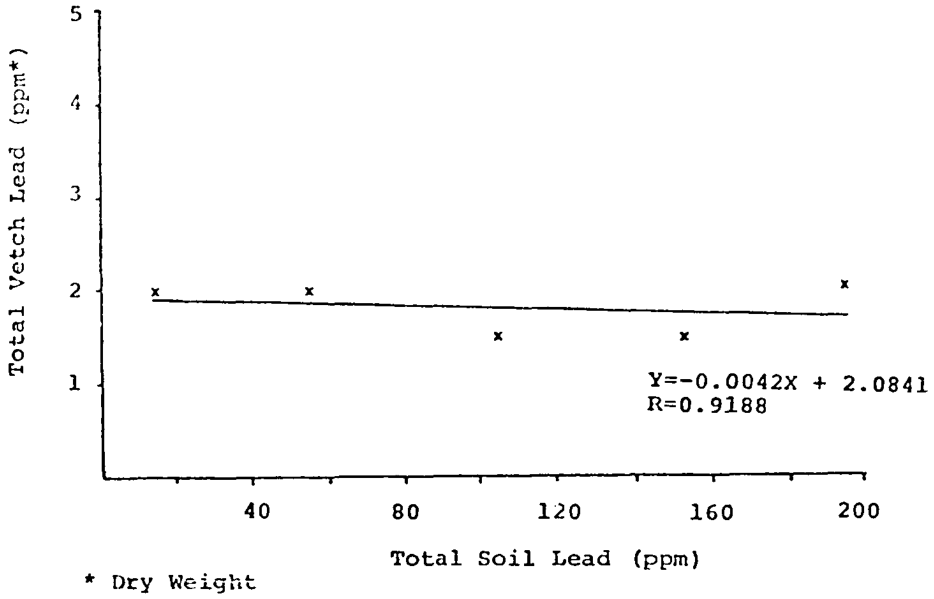


Table 15. Total Zn, Cd, and Pb content of forage sorghum collected on 6 October 1972.

Plant Part	Zn (ppm*)	Cd (ppm*)	Pb (ppm*)
Heads	370	20.0	20
Leaves	895	30.5	35
Shoots	1200	25.5	5
Standing Dead	2250	37.0	35

* Dry Weight

and 265 ppm Pb. The Pb content of this corn was potentially toxic to cattle, sheep, and horses if used as silage (Tables 5 - 7).

Grasses and Forbs

Midland variety bermuda grass was also grown in incremental amounts of Zn, Cd, Pb, and As (Table 16). Significantly ($\alpha=0.05$) more aboveground biomass was harvested from soil blends 1 and 2 than from the other 3 blends. From the results of this experiment, a 58% decrease in bermuda aboveground biomass would be predicted for fields or lawns with metal levels similar to blend 2; while 83 85, and 90% decreases would be predicted for fields or lawns with levels similar to blends 3, 4, and 5. The $\log_{10}$ of the amount of biomass harvested was inversely related ($R>0.878, \alpha=0.05$) to total soil Zn, Cd, and Pb content; while the Zn, Cd, and Pb content of the harvested bermuda was directly related ($R>0.878, \alpha=0.05$) to the soil content of these metals (Figs. 26 - 31). Since the Pb content of the harvested biomass ranged from 7.5 - 12 ppm, and the slope of the linear equation of this relationship is relatively flat, the Pb content of this variety of bermuda, as with the other crops tested, appears not to be influenced by soil Pb content. Mueller and Stanley (1970) concluded that the translocation of Pb from soil is less than 15 ppm (dry weight) of forage even in soils containing 3000 ppm total Pb. Approximately 1400 ha surrounding the smelter contain Zn and Cd levels equal to or greater than those of soil blend 2 (Figs. 4 and 6, Part I).

Bermuda grown in these blends contained a maximum of 1225

Table 16. Metal content of the soil blends used for the Bermuda grass experiment.

Soil Blend Number	Total Zn (ppm)	Total Cd (ppm)	Total Pb (ppm)
1	83	1.0	10
2	740	7.5	55
3	2500	18.0	105
4	2950	20.0	130
5	4150	30.0	180

Figure 26. Average bermuda grass aboveground biomass ($\log_{10}$) vs. total Zn content of the soil.

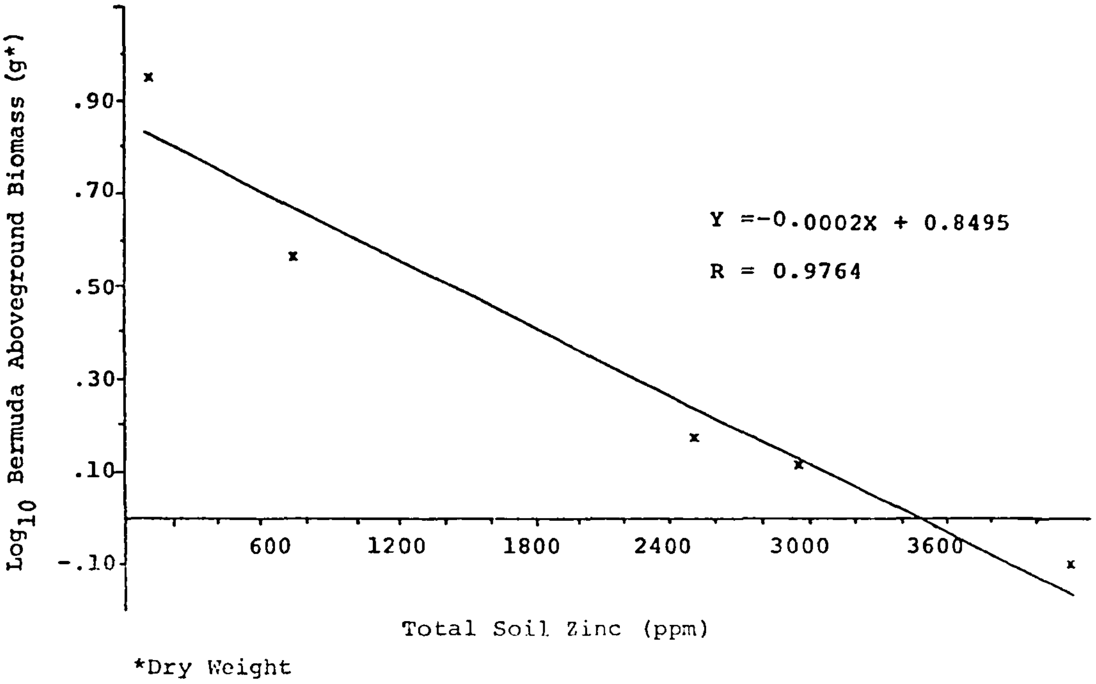


Figure 27. Average bermuda grass aboveground biomass ($\log_{10}$) vs. total Cd content of the soil.

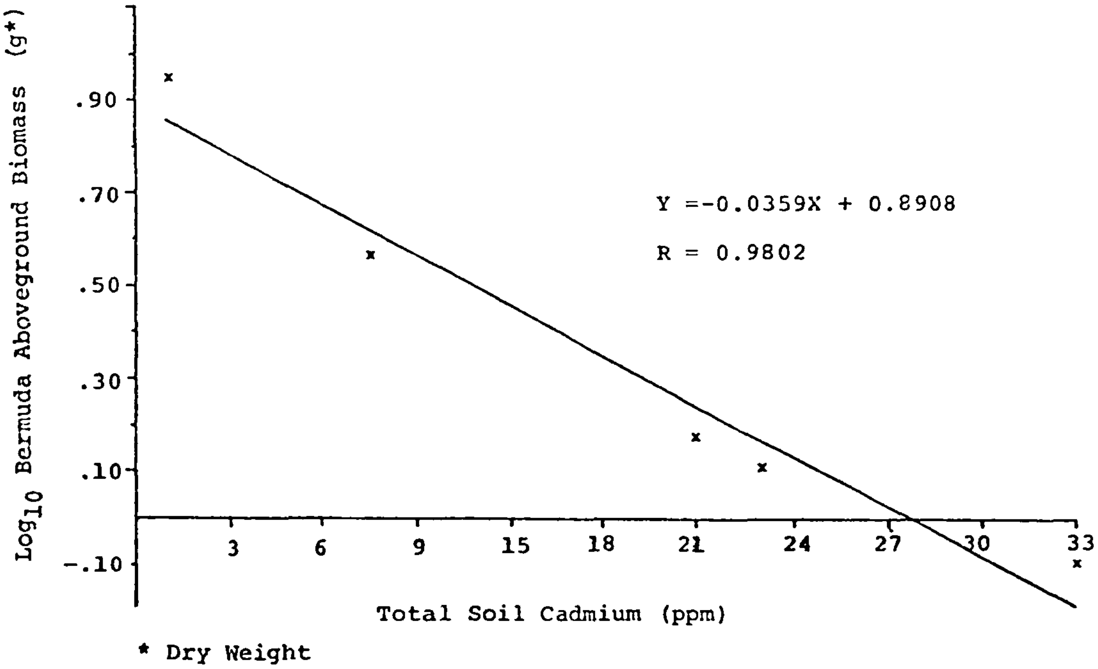


Figure 28. Average bermuda grass aboveground biomass ($\log_{10}$) vs. total Pb content of the soil.

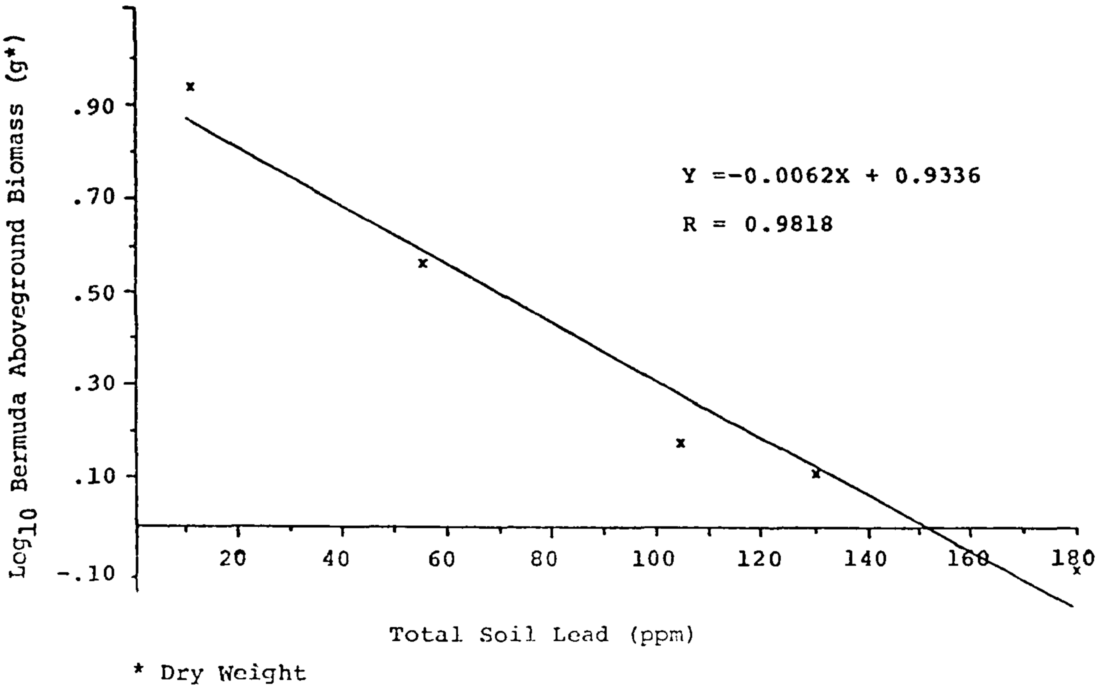


Figure 29. Total Zn content of the bermuda aboveground biomass vs. total Zn content of the soil.

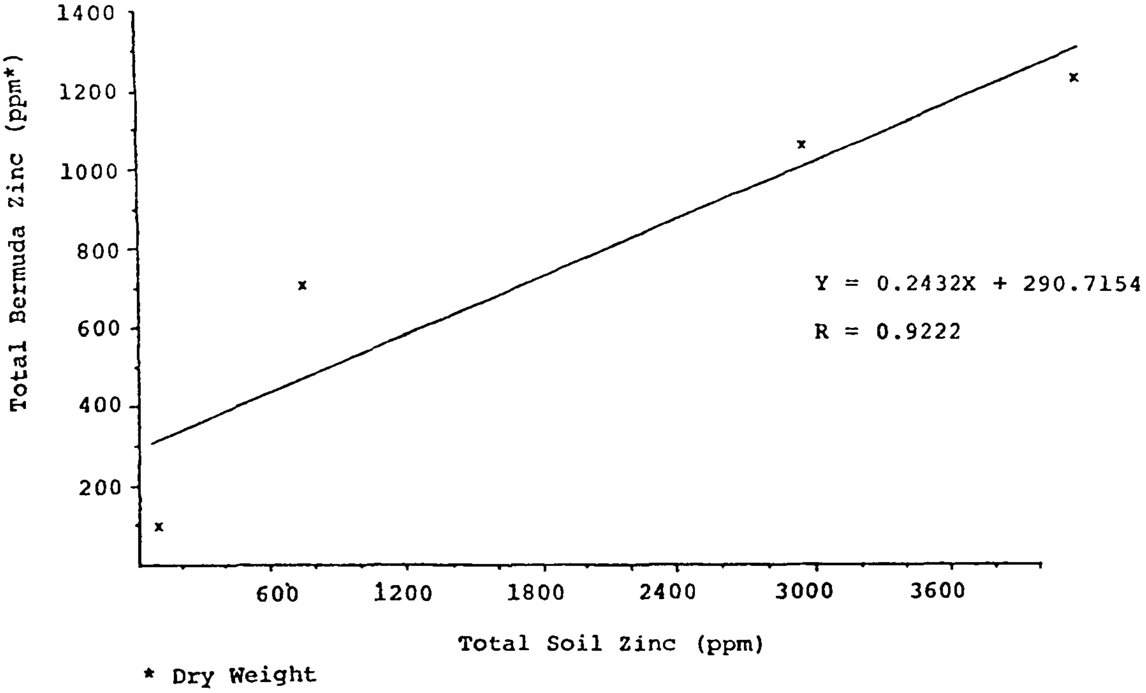


Figure 30. Total Cd content of the bermuda aboveground biomass vs. total Cd content of the soil.

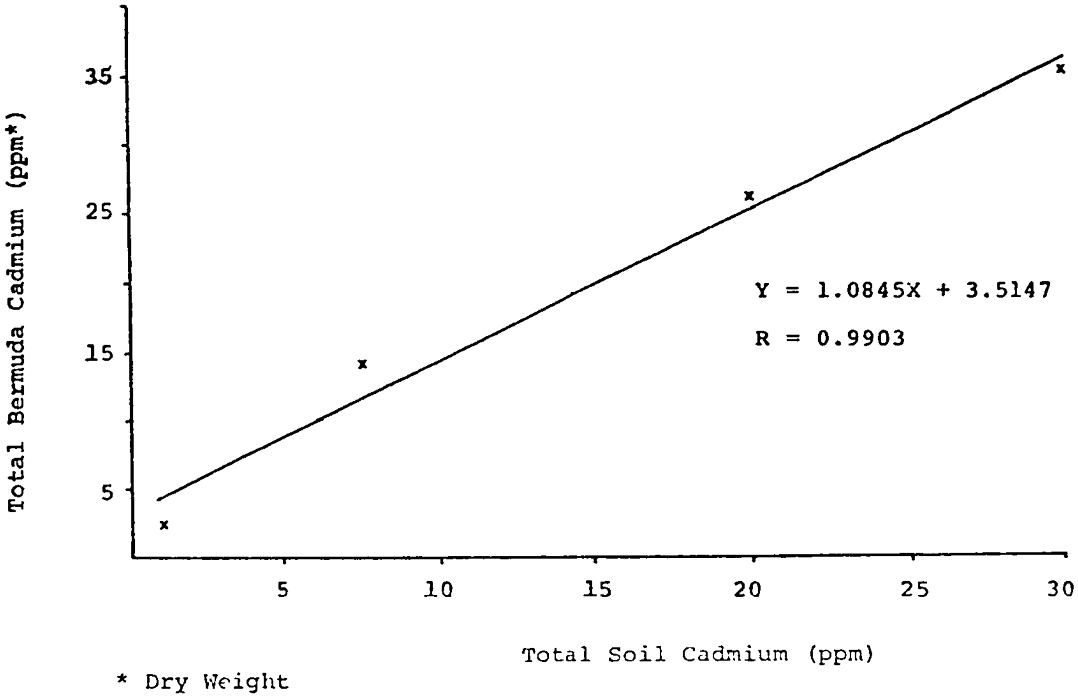
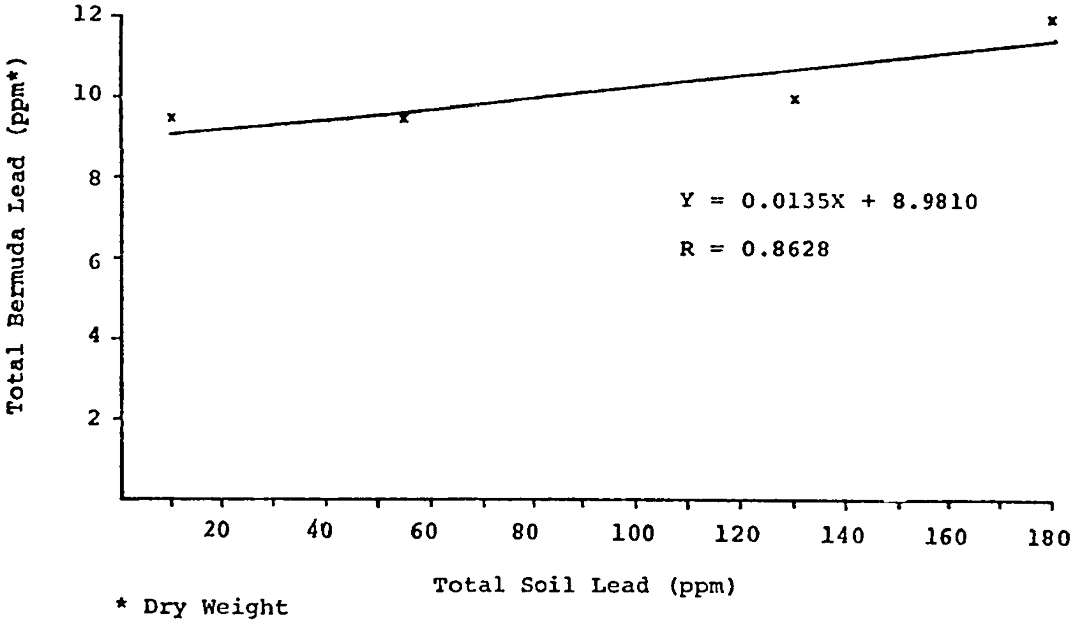


Figure 31. Total Pb content of the bermuda aboveground biomass vs. total Pb content of the soil.

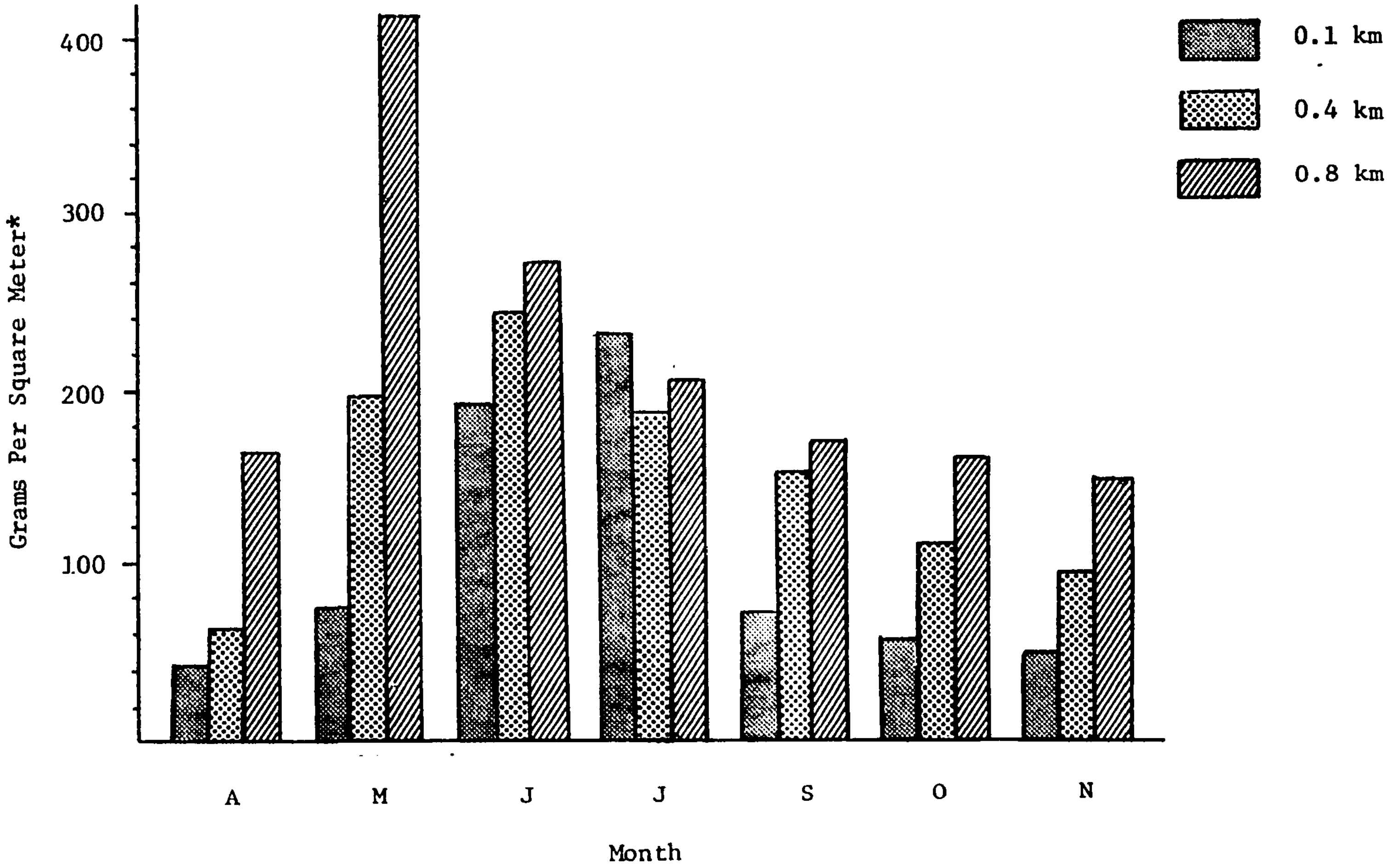


ppm Zn, 35 ppm Cd, and 12 ppm Pb. The Zn content of this bermuda is potentially toxic to cattle (Table 5) and soils in Blackwell supporting bermuda pasture that contain levels of Zn equal to or surpassing 2500 ppm should not be grazed by cattle (based on the linear equation of Fig. 29). Approximately 600 ha surrounding the Blackwell smelter contain 2500 or more ppm Zn in the soil (Fig. 4, Part I).

The effects of the smelter on the rate of bermuda grass production within 0.8 km north of the smelter was studied on a monthly basis. Important differences in standing crop were found within this quarter section. Bermuda collected 0.8 km north of the highway produced its maximum standing crop 2 months earlier than that collected 0.1 km north, and 1 month earlier than that at 0.4 km (Fig. 32). This time lag suggests that bermuda growing closer to the smelter (within this 0.8 km) has a slower production rate. Preceeding these peaks in standing crop, bermuda experienced a greater rate of increase at the 0.8 km sampling site (6.72 g/m^2/day); while at the 0.4 km and 0.1 km sites bermuda experienced lower rates of increase (3.70 and 3.29 g/m^2/day respectively). In addition, the average standing crop at 0.8 km was significantly ($\alpha=0.05$) greater than at the other 2 sites.

Bermuda grass forage production in Oklahoma ranges from 200 - 1270 g/m^2 (dry wt) depending on soil type, rainfall, and variety grown (Denman, Huffine, and Arnold, 1971), and with nitrogen fertilization, production can be as high as 1900 g/m^2 (Chiles, 1968). Production from this section for 1973 was as follows: at 0.1 km -

Figure 32. Changes in the standing crop (g/m^2) of bermuda grass with distance from the smelter and with time during the growing season.



* Dry Wt

233 g/m^2, at 0.4 km - 241 g/m^2, and at 0.8 km - 413 g/m^2. To put these values into better perspective with regard to farm economics, they were converted to lb/A (Table 17). Although yields within this section are comparable to the rest of Oklahoma, it is interesting to note that 1600 lb/A (294 kg/ha) more would have been harvested from that part of this quarter section 0.8 km from the smelter than from that part 0.1 km from the smelter. This production of bermuda was attained while the smelter was in full operation. With the termination of smelter operations, soil contamination should be the major source of these metals to the vegetation as entry of metal oxides through stomates and deposition of dusts on leaf surfaces should be reduced, and production should increase.

Within this pasture, the total number of grass species, the total number of forb species, the total number of plant species, and the Shannon-Weiner function of species diversity (McIntosh, 1967) all tended to increase ($R>0.468, \alpha=0.05$) with distance from the smelter (Fig. 33). Approximately 0.8 km north of the smelter species diversity was about that which would be expected for a moderately grazed pasture ($d=1.5 - 2.2$).

The Zn, Cd, and Pb contents of grasses and forbs collected from this quarter section were found to increase through the growing season and to decrease with distance from the smelter (Figs. 34 - 36). Schmitt et al. (1971) found the Pb content of forage near a lead smelter increased throughout the growing season and found the highest levels in overwintering vegetation. Within the quarter section just north of the smelter, forbs on the average contained the highest amounts of these metals while bermuda grass usually contained higher

Table 17. Conversion of production data to pounds per acre of oven dry forage.

Oklahoma Range	After 800 lb. Nitrogen per Acre	Study Site
Low 1,788 lb/A	16,960 lb/A	0.1 km - 2,080 lb/A
High 11,377 lb/A		0.4 km - 2,151 lb/A
		0.8 km - 3,688 lb/A

Figure 33. Average number of grasses, forbs, plant species and the Shannon-Weiner function vs. distance north of Highway 11.

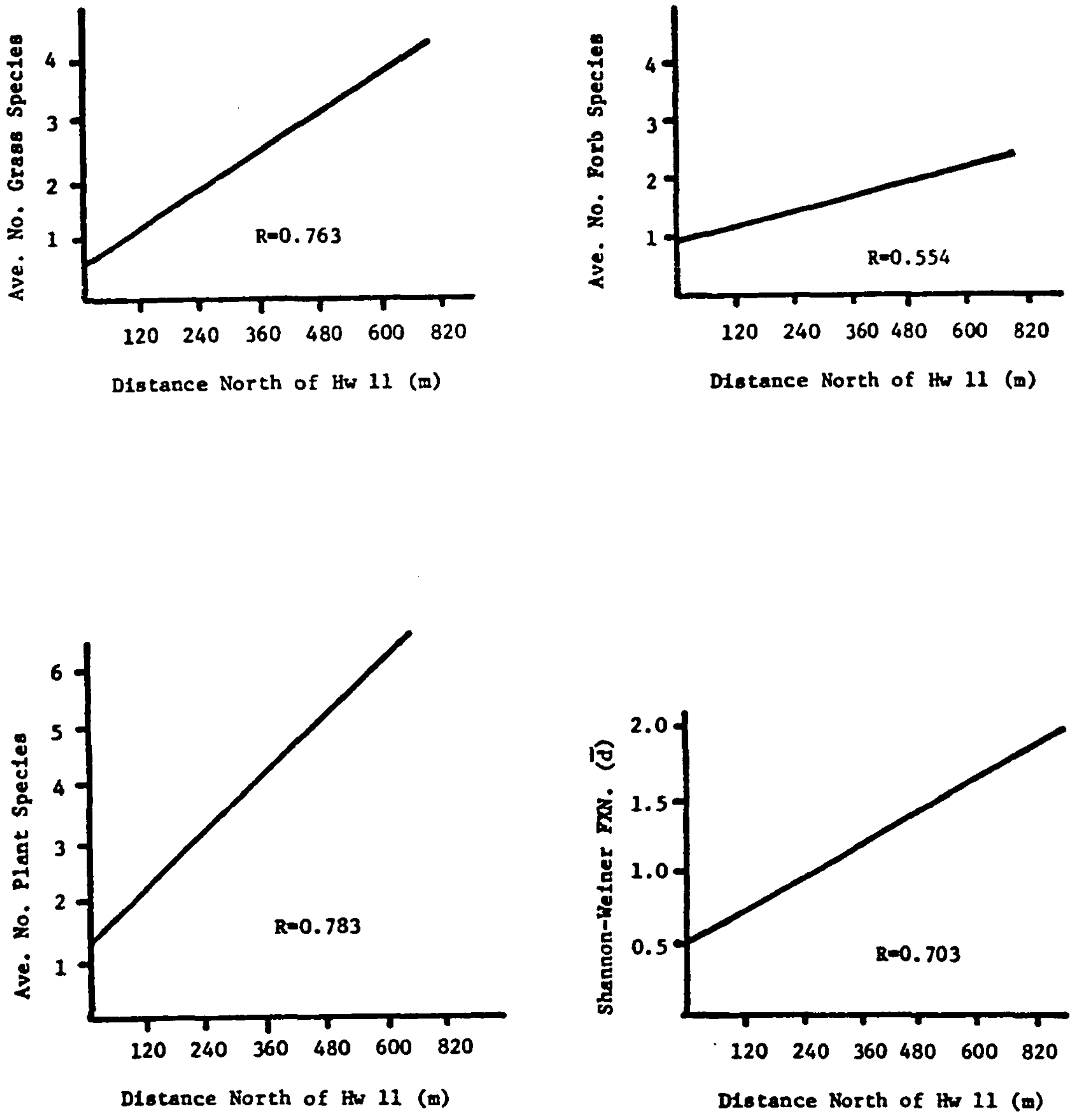
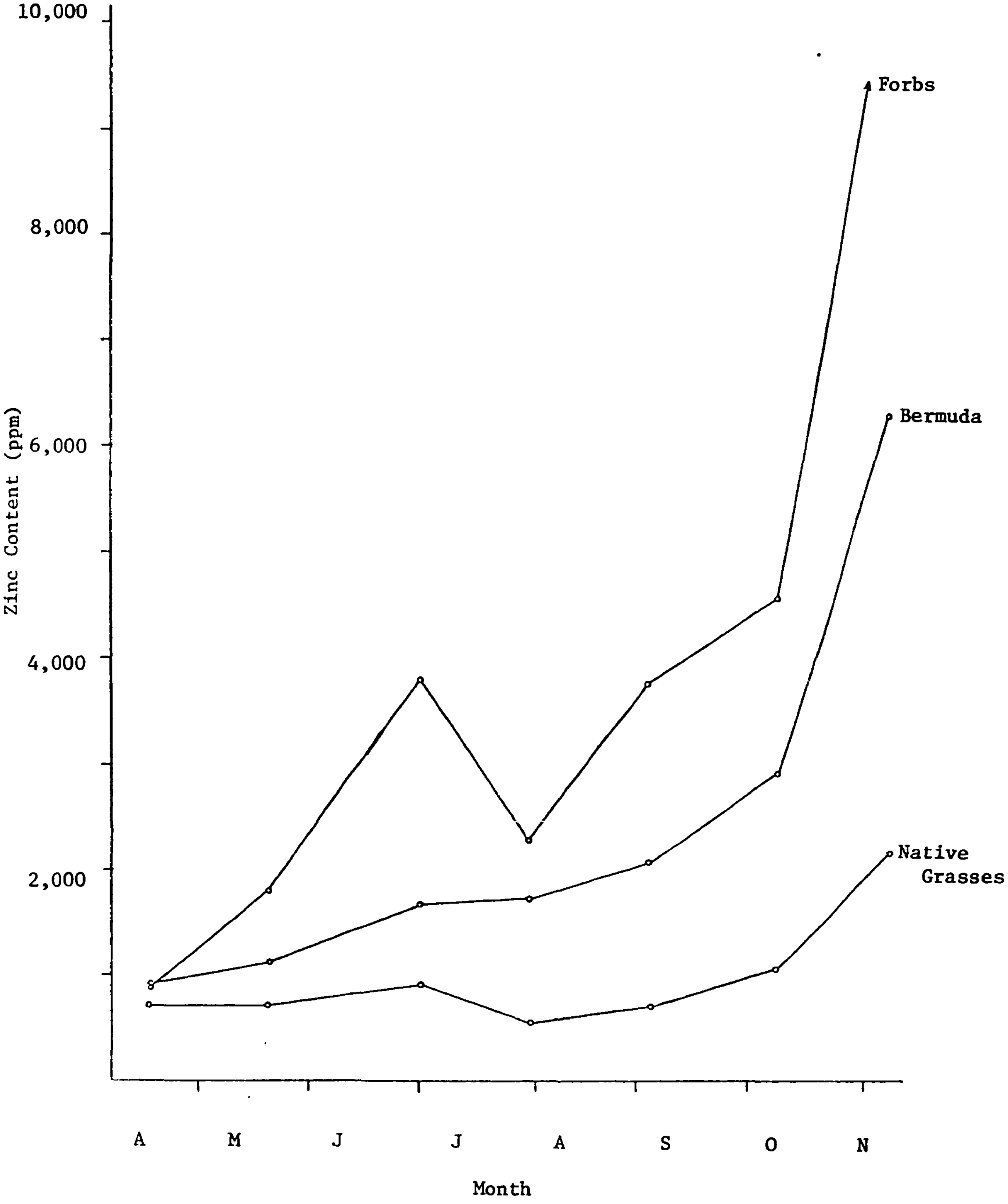
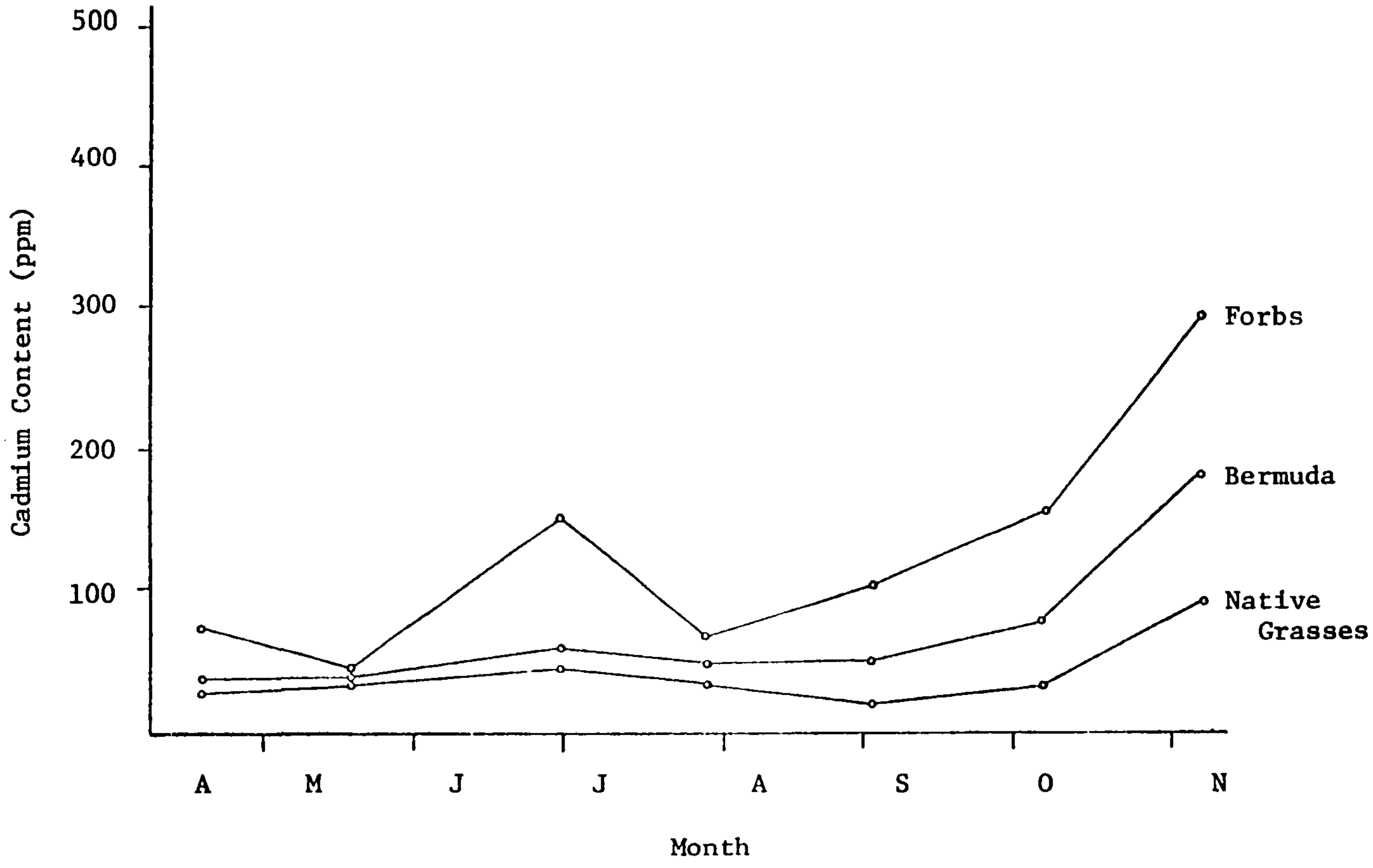


Figure 34. Seasonal variation in average Zn content of forbs, bermuda grass, and native grasses collected in the quarter section immediately north of the smelter.



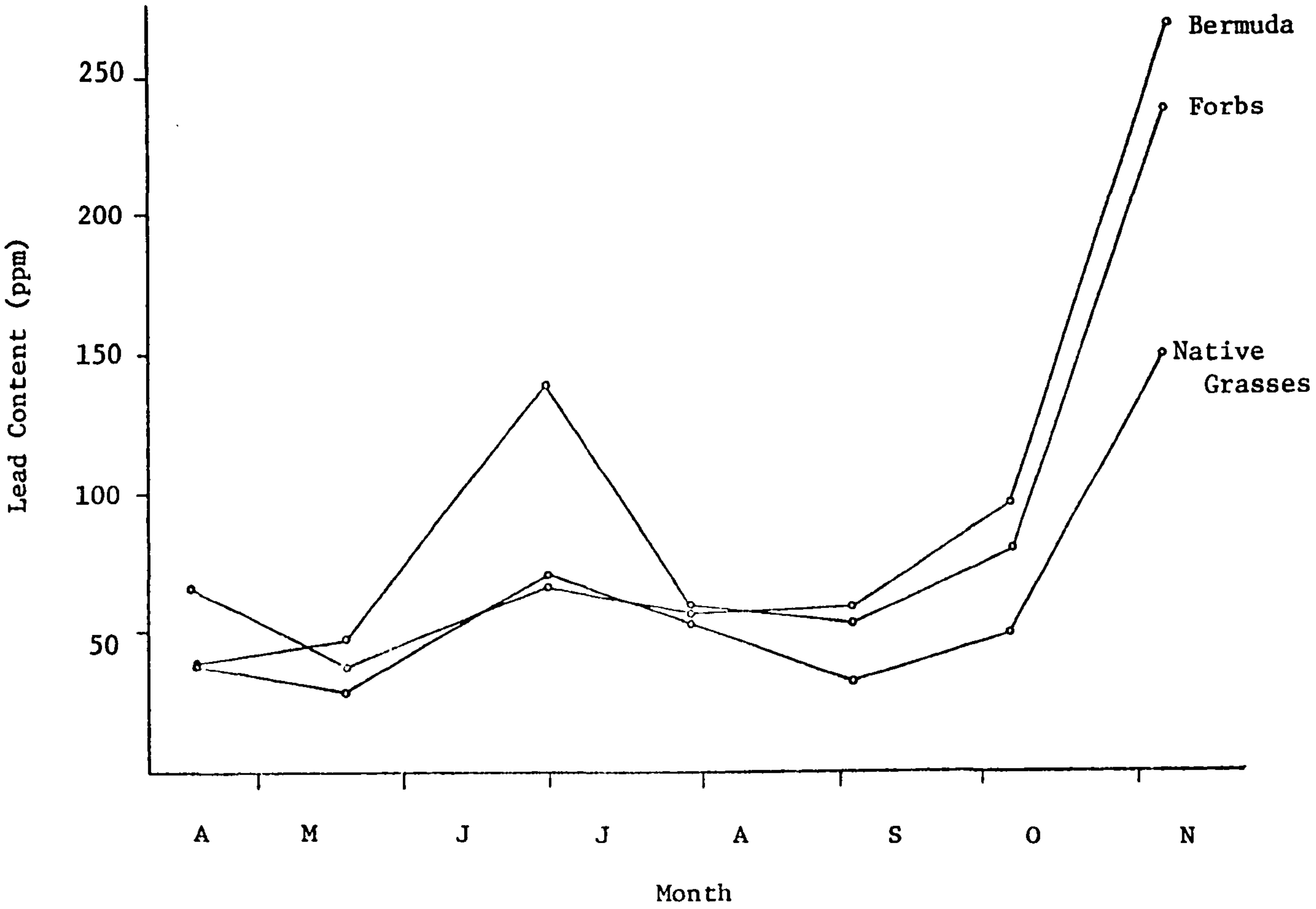
* Dry Wt

Figure 35. Seasonal variation in average Cd content of forbs, bermuda grass, and native grasses collected in the quarter section immediately north of the smelter.



* Dry Wt

Figure 36. Seasonal variation in average Pb content of forbs, bermuda grass, and native grasses collected in the quarter section immediately north of the smelter.



* Dry Wt

amounts of these metals than native grasses (Andropogon gerardii Vitman[1], Andropogon scoparius Michx., Panicum virgatum L., and Sorghastrum nutans (L.) Nash. For grasses collected in May, June, and July from this quarter section, standing dead grasses were found to contain on the average 5 - 16 times higher concentrations of Zn, Cd, and Pb than living grasses (Table 18). Standing dead grasses also contained higher concentrations of these metals than grasses collected the previous November. The potential grazing hazard of this forage is increased as a result of the concentrations of these metals in standing dead grasses. Native grasses appear a more desireable forage for cattle within highly contaminated areas close to the smelter and their use should be encouraged. During the fall sampling, the As content of plant materials was usually less than 0.5 ppm and as a result spring and summer samples were only spot checked (Table 19). In April, bermuda grass averaged 32 ppm As which is potentially toxic to livestock (Table 8). In conclusion, due to the potentially toxic amounts of Zn, Cd, Pb, and As in this pasture, this quarter section should not be grazed at this time. Forage may contain safe levels of these metals after termination of smelter operations since air contamination should decrease. The results of the bermuda pot experiment, though, suggest otherwise.

Trees

The following species of deciduous trees were sampled within

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[1] Nomenclature follows Waterfall, 1969.

Table 18. Comparison of live and standing dead grass Zn, Cd, and Pb content.

Date	Vegetation	Zn (ppm)*	Cd (ppm)*	Pb (ppm)*
24 May 74	Bermuda (SD)	8,480	166	573
	Native grasses (SD)	5,630	137	456
	Bermuda (L)	1,150	20	38
	Native grasses (L)	680	26	29
29 June 74	Bermuda (SD)	10,700	212	743
	Native grasses (SD)	3,730	10	393
	Bermuda (L)	1,700	28	27
	Native grasses (L)	807	20	27
29 July 75	Bermuda (SD)	6,970	144	640
	Native grasses (SD)	2,470	81	336
	Bermuda (L)	1,720	22	56
	Native grasses (L)	532	16	48
Average	Bermuda (SD)	8,700	174	652
	Native grasses (SD)	3,840	109	395
	Bermuda (L)	1,530	23	40
	Native grasses (L)	673	21	35

* Dry Weight

SD = Standing Dead

L = Live (green)

Table 19. Average arsenic content of different plant materials collected at various distances north of Highway 11 within the quarter section immediately north of the smelter.

Plant Material	April 17 As (ppm*)	May 24 As (ppm*)	June 29 As (ppm*)
Bermuda	32.0	1.8	3.8
Native Grasses	3.3	1.9	1.9
Forbs	2.9	1.6	2.1

* Dry Weight

1.6 km north of the smelter; within a picnic area near the Chickaskia River about 7.2 km north of the smelter; and on the campus at Oklahoma University, Norman: Black locust (Robinia pseudo-acacia L.), hackberry (Celtis occidentalis Pursh), catalpa (Catalpa speciosa Warder), sycamore (Platanus occidentalis L.), green ash (Fraxinus pennsylvanica Marsh.), American elm (Ulmus americana L.), and cottonwood (Populus deltoides Marsh.).

Average Zn and Cd content of leaves, petioles, springwood (green twigs), and twigs from previous years growth were found to decrease with distance from the smelter (Table 20). Pb and As content tended to be higher for trees within 1.6 km of the smelter; however, trees sampled in Norman had more As in their leaves and older twigs than the trees sampled in Blackwell. Trees sampled in Norman also contained higher than expected Pb levels. The levels of Pb and As in Norman probably reflect past use of arsenicals and possibly greater automobile emissions. Buchauer (1973) reported concentrations as great as 4500 ppm Zn and 70 ppm Cd in foliage of trees near a Pennsylvania zinc smelter; unwashed leaves contained 4 - 6 times more Zn and Cd than washed leaves. Catalpas sampled on the northern border of the smelter quarter section contained an average of 5990 ppm Zn and 72 ppm Cd in their leaves.

For trees sampled in Blackwell the highest concentrations of Zn, Cd, and Pb were associated with the leaves; while for trees sampled in Norman, the lowest concentrations of Zn and Pb and the highest concentration of Cd were associated with the leaves (Table 20). Since heavy metals either within or deposited on the leaves of woody plants may be recycled in short term, and since metals within or

Table 20. Average total metal content of various tree organs collected at three distances from the smelter.

Sample	Leaves (ppm*)				Petioles (ppm*)				Springwood (ppm*)				Older Twigs (ppm*)			
Location	Zn	Cd	Pb	As	Zn	Cd	Pb	As	Zn	Cd	Pb	As	Zn	Cd	Pb	As
1.6 km north	2380	32.9	98.6	7.4	113	13.2	48.0	N.D.	569	10.4	23.0	N.D.	865	23.0	61.0	0.5
7.2 km north	296	5.8	23.0	5.3	70	3.3	1.5	N.D.	131	4.3	12.0	N.D.	138	5.0	14.0	0.5
Norman, Okla.	34	1.1	13.6	8.1	42	0.8	19.0	N.D.	50	0.9	14.0	N.D.	50	0.6	12.8	1.9

* Dry Weight

N.D. - Not Determined

deposited on less deciduous organs may be stored for many years, Smith (1972) concluded that woody plants might act as both short and long term storages and thus be important in the cycling of heavy metals. Gish and Christensen (1973) reported the accumulation of Zn, Cd, and Pb in earthworms eating contaminated soils and speculated on the possible toxic effects to higher animals feeding on these worms. The consumption of leaves and twigs from these Blackwell trees by various herbivores and subsequent amplification through food chains is possible.

In conclusion, grazing potential seems to be severely affected as forage collected within 4 km north, 1.6 km south, and 0.8 km east and west of the smelter contained sufficient levels of Zn, Cd, Pb, and As to be potentially toxic to cattle. Age, sex, exposure time, host stress, general health, physical condition, season, feed additives, digestive tract acidity, stage of pregnancy and lactation, species differences, and the source of the metals have all been shown to influence the toxic action of these metals. In addition, the following factors may also affect toxic action of these metals:

Cd and Pb are less toxic to animals that have simultaneously consumed high levels of Zn (Pond, et al., 1966; Powell, et al., 1964; Willoughby, et al., 1972).

Since animals (especially sheep) may be selective grazers and since the metal content of forage changes seasonally, the amounts of these metals consumed by an animal might not be equivalent to the reported average concentrations of these metals in a given field

(Allcroft and Blaxter, 1950).

Livestock have been shown to be more readily poisoned by contaminated vegetation than by feed supplemented with metals (Willoughby, et al., 1972; Kradel, et al., 1965).

Tables (5 - 8) can be used to determine whether silage or forage produced in the Blackwell area are potentially safe for consumption by cattle, sheep, swine, or horses; however, the previously mentioned factors (age, sex, feeding habits, etc.) might make a potentially safe diet unsafe or vice versa. The growth of vegetation and the grazing potential of this acreage should improve now that smelter operations have been terminated, and when residue piles north of the furnaces are either removed or stabilized. At present, deposition of dusts on vegetation is adding to the amounts of these metals available to herbivores; although it is probably less than when the furnaces were in production.

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AN ASSESSMENT OF THE EFFECTS OF ZINC, LEAD, CADMIUM, AND ARSENIC IN SOIL, VEGETATION, AND WATER RESOURCES SURROUNDING A ZINC SMELTER

PART III

WATER RESOURCES

INTRODUCTION

From 1849 to 1949 the Oklahoma-Kansas-Missouri Tri-State Mining District was a major source of zinc and lead ores (McReynolds, 1954). Smelter site selection was based primarily on proximity to these ores and the natural gas fields in this area. These smelters were of the horizontal retort type, and most remained operational only as long as the local supply of ore or gas lasted; however, the smelter in Blackwell, Oklahoma remained operational for 57 years. During these years, this smelter was the major contributor of the heavy metals to the atmosphere in the Blackwell area.

Ground water and surface water runoff from lead-zinc mining areas (Wixon et al., 1972; Galbraith, Williams, and Siems, 1972), highly urbanized areas (Heavy Metals Task Force, 1972, and areas where industrial processes discharge metal aerosols (Lazrus, Lorange, and Lodge, 1970; Friberg, Piscator, and Nordberg, 1971) contain on the average higher concentrations of heavy metals than other areas. Metals in rainfall and snowfall on the average are also higher in more urbanized areas (Lazrus et al., 1970; Kerin, 1973). An additional source of heavy metals in Blackwell, a predominately agricultural area, is the application of amendments - fertilizers, insecticides, herbicides - to the land. Superphosphates, for example, contain relatively large amounts of Cd (Friberg et al., 1971).

Since Zn, Pb, Cd, and As were found in high concentrations in soil and vegetation sampled in proximity to the smelter (Chapters 1 and 2), and since these metals are potentially toxic, and As is also a possible carcinogen (Heuper, 1960), the status of water resources in the Blackwell area is of utmost importance.

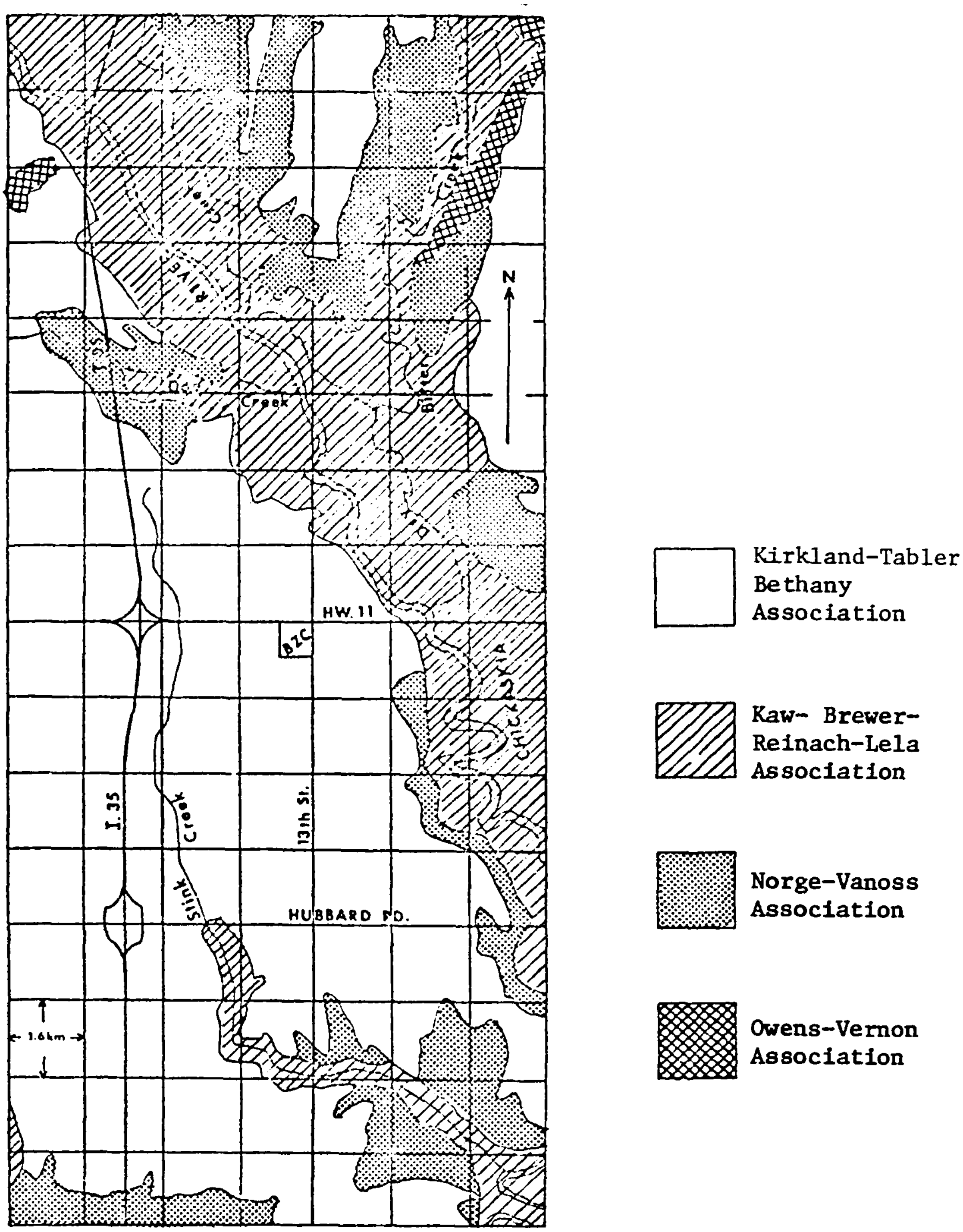
STUDY AREA

Blackwell is located in the western half of Kay County, which lies in the central part of the Redbed Plains of Oklahoma. The topography is level to gently undulating with terraces up to 4.8 km wide along the Chickaskia River. The climate of the area is temperate, subhumid (Trewartha, 1968). The mean annual temperature is 16°C and the mean annual precipitation is 72.80 cm, with a frost free season which averages 195 days. Prevailing winds (19 km/hr annual average) are southerly during most months; however, in January and February winds are predominately from the north.

Four soil associations are found within the study area. Kirkland-Tabler-Bethany Association soils are found in nearly level to moderately sloping areas away from floodplains; Kaw-Brewer-Reinach-Lela Association soils make up the nearly level 1.6 - 3.2 km wide bands along the Chickaskia and somewhat narrower bands along Stink Creek; and Norge-Vanoss Association soils are found within 3.2 km of the Chickaskia mainly on gently sloping uplands and in similar locations along Stink Creek where it enters the Chickaskia (Fig. 1).

Adequate ground water for farmstead use is usually found

Figure 1. Soil associations within the study area (after Soil Survey, Kay County, Oklahoma, 1967).



throughout the study area; while munincipal water is taken from the Chickaskia River. Average annual runoff from the study area is 12.7 cm and the Chickaskia River (stream gaging station 7-1520 located near the northeast edge of the city of Blackwell) has an average annual discharge of 4.13×10^8 m^3 (Oklahoma Water Resources Board, 1972). The Chickaskia and smaller streams also provide water for livestock; however, farm ponds and small reservoirs provide most of the water consumed by livestock.

The study area is treeless except along streams, on some uplands adjacent to streams, and where windbreaks have been planted. Winter wheat is the predominant crop; although other small grains, alfalfa, and field corn are commonly grown. There is also some ranching in the study area.

METHODS

Fifty-two water samples (W-1 to W-52) were collected in one liter polyvinyl plastic bottles from farm ponds, roadside ditches, creeks, stocktanks, public water supplies, and the Chickaskia River. Samples from ponds, creeks, and the Chickaskia were taken from along the shoreline so as to be representative of water available to livestock. Twenty of the samples (W-33 to W-52) were collected just after a rain of 2.41 cm had fallen in the Blackwell area.

All samples were fixed with nitric acid on the day of collection and refrigerated until analyzed by the Blackwell Zinc Company Laboratory. All 52 samples were analyzed for Zn, Cd, Pb, and Cu; in addition, the first 32 (W-1 to W-32) were also analyzed for As. Procedures given in Methods for Chemical Analysis of Water and Wastes (1971) were used for all determinations. Samples W-1 to W-32 were analyzed for dissolved metal content only; while the remaining samples (W-33 to W-52) were analyzed for both dissolved and total metal content.

Most of the samples were collected within 8 km of the smelter; however, some were collected as far as 44.8 km away. Sample locations were marked on field maps which were later used to determine the distance and direction each sample was from the smelter (Tables 1 - 4).

Table 1. Sample location and Zn, Pb, Cd, Cu, and As content of water samples collected from farm ponds.

Sample Number	Date Collected	Distance from Smelter (km)	Direction from Smelter (degrees)	Zn Total mg/l	Zn Dissolved mg/l	Pb Total mg/l	Pb Dissolved mg/l	Cd Total mg/l	Cd Dissolved mg/l	Cu Total mg/l	Cu Dissolved mg/l	As Dissolved mg/l
W-41*	4/15/72	1.76	12	2.45	0.91	0.06	<0.01	0.025	0.008	0.09	<0.01	N.D.
W-17	3/11/72	3.20	238	N.D.	0.35	N.D.	0.05	N.D.	<0.005	N.D.	0.03	<0.01
W-44	4/15/72	3.76	254	0.84	0.07	0.02	0.02	<0.005	<0.005	0.05	<0.01	N.D.
W-28	3/18/72	3.68	225	N.D.	0.37	N.D.	<0.05	N.D.	0.006	N.D.	0.04	<0.01
W-51*	3/15/72	4.40	89	0.21	0.03	0.05	<0.01	<0.005	<0.005	0.02	<0.01	N.D.
W-52*	3/15/72	3.84	83	0.86	0.04	0.09	0.03	0.008	<0.005	0.06	0.06	N.D.
W-15*	3/11/72	4.80	329	N.D.	0.73	N.D.	<0.12	N.D.	0.010	N.D.	0.02	<0.01
W-9	2/26/72	5.52	349	N.D.	0.06	N.D.	0.05	N.D.	<0.005	N.D.	<0.01	<0.01
W-11*	2/26/72	6.08	338	N.D.	0.32	N.D.	0.06	N.D.	0.010	N.D.	0.05	<0.01
W-23	3/18/72	25.60	173	N.D.	0.07	N.D.	<0.05	N.D.	<0.005	N.D.	<0.01	<0.01
W-22	3/18/72	44.80	185	N.D.	0.04	N.D.	<0.05	N.D.	<0.005	N.D.	<0.01	<0.01

N.D. - Not Determined

* - Ponds with concentrations of dissolved or total Pb and/or Cd equal to or greater than suggested maximums for animal consumption.

Table 2. Sample location and Zn, Pb, Cd, Cu, and As content of water samples collected from creeks.

				Zn		Pb		Cd		Cu		As
Sample Number	Date Collected	Distance from Smelter (km)	Direction from Smelter (degrees)	Total mg/l	Dissolved mg/l	Total mg/l	Dissolved mg/l	Total mg/l	Dissolved mg/l	Total mg/l	Dissolved mg/l	Dissolved mg/l
W-31*	3/18/72	1.36	78	N.D.	0.21	N.D.	0.06	N.D.	0.008	N.D.	0.01	<0.01
W-27*	3/18/72	1.44	73	N.D.	0.87	N.D.	0.09	N.D.	0.019	N.D.	0.08	<0.01
W-30	3/18/72	1.60	130	N.D.	0.60	N.D.	<0.05	N.D.	<0.005	N.D.	<0.01	<0.01
W-40*	4/15/72	1.68	170	3.80	3.45	0.02	<0.01	0.045	0.034	0.09	0.03	N.D.
W-42*	4/15/72	2.24	336	4.55	3.70	<0.01	<0.01	0.045	0.034	0.11	0.06	N.D.
W-16	3/11/72	2.88	248	N.D.	0.05	N.D.	<0.05	N.D.	<0.005	N.D.	<0.01	<0.01
W-3	2/19/72	3.44	360	N.D.	0.18	N.D.	<0.05	N.D.	0.007	N.D.	<0.01	<0.01
W-18	3/11/72	3.92	226	N.D.	0.03	N.D.	<0.05	N.D.	<0.005	N.D.	<0.01	<0.01
W-14	3/11/72	4.96	328	N.D.	0.07	N.D.	<0.05	N.D.	0.008	N.D.	<0.01	<0.01
W-36	4/15/72	4.96	134	0.26	0.04	<0.01	<0.01	0.005	<0.005	<0.01	<0.01	N.D.
W-50*	4/15/72	4.96	85	0.23	0.08	0.07	0.06	0.006	<0.005	0.02	0.02	N.D.
W-12	2/26/72	6.32	334	N.D.	0.04	N.D.	<0.05	N.D.	<0.005	N.D.	<0.01	<0.01
W-35	4/15/72	7.28	147	0.35	0.04	<0.01	<0.01	0.005	<0.005	<0.01	<0.01	N.D.
W-26*	3/18/72	10.48	85	N.D.	0.03	N.D.	0.05	N.D.	0.007	N.D.	<0.01	<0.01
W-25	3/18/72	28.00	85	N.D.	0.04	N.D.	<0.05	N.D.	0.006	N.D.	<0.01	<0.01

N.D. - Not Determined

* - Creeks with concentrations of dissolved or total Pb and/or Cd equal to or greater than suggested maximums for animal consumption.

Table 3. Sample location and Zn, Pb, Cd, Cu, and As content of water samples collected from roadside ditches.

Sample Number	Date Collected	Distance from Smelter (km)	Direction from Smelter (degrees)	Zn Total mg/l	Zn Dissolved mg/l	Pb Total mg/l	Pb Dissolved mg/l	Cd Total mg/l	Cd Dissolved mg/l	Cu Total mg/l	Cu Dissolved mg/l	As Dissolved mg/l
W-45*	4/15/72	1.60	230	1.93	0.70	0.02	0.02	0.010	0.010	0.08	0.04	N.D.
W-39*	4/15/72	1.92	165	6.55	6.00	0.02	<0.01	0.066	0.054	0.10	0.07	N.D.
W-6	2/19/72	2.08	12	N.D.	0.80	N.D.	<0.05	N.D.	0.006	N.D.	0.02	<0.01
W-46*	4/15/72	2.24	213	0.86	0.07	0.05	<0.01	<0.005	<0.005	0.04	<0.01	N.D.
W-38	4/15/72	2.48	140	1.03	0.48	<0.01	<0.01	<0.005	<0.005	0.04	0.02	N.D.
W-13	2/26/72	2.56	279	N.D.	0.06	N.D.	<0.05	N.D.	<0.005	N.D.	<0.01	<0.01
W-48*	4/15/72	2.88	171	2.34	1.96	<0.01	<0.01	0.037	0.020	0.07	0.06	N.D.
W-5	2/19/72	3.52	35	N.D.	0.26	N.D.	<0.05	N.D.	0.008	N.D.	0.03	<0.01
W-49*	4/15/72	3.52	145	0.77	0.17	0.02	<0.01	0.011	0.006	0.06	0.04	N.D.
W-2*	2/19/72	3.68	353	N.D.	2.15	N.D.	0.14	N.D.	0.012	N.D.	0.16	<0.01
W-37	4/15/72	3.68	135	0.50	0.13	0.03	<0.01	<0.005	<0.005	0.02	<0.01	N.D.
W-33	4/15/72	3.76	345	1.04	0.50	0.02	<0.01	0.005	0.005	0.07	0.04	N.D.
W-43*	4/15/72	3.76	254	1.47	0.13	0.04	0.04	0.011	<0.005	0.15	0.04	N.D.
W-47*	4/15/72	4.32	173	1.07	0.63	0.02	<0.01	0.011	0.010	0.04	0.02	N.D.

N.D. - Not Determined

* - Ditches with concentrations of dissolved or total Zn, Pb, and/or Cd equal to or greater than suggested maximums for animal consumption.

Table 4. Sample location and Zn, Pb, Cd, Cu, and As content of water samples collected from stock tanks and the Chickaskia River.

				Zn		Pb		Cd		Cu		As
Sample Number	Date Collected	Distance from Smelter (km)	Direction from Smelter (degrees)	Total mg/l	Dissolved mg/l	Total mg/l	Dissolved mg/l	Total mg/l	Dissolved mg/l	Total mg/l	Dissolved mg/l	Dissolved mg/l
Stock Tanks:												
W-34	4/15/72	4.16	26	0.30	0.06	0.03	0.03	<0.005	<0.005	<0.01	<0.01	N.D.
W-19	3/11/72	4.24	186	N.D.	0.41	N.D.	<0.05	N.D.	<0.005	N.D.	<0.01	<0.01
W-1	2/19/72	4.48	324	N.D.	0.30	N.D.	<0.05	N.D.	<0.005	N.D.	<0.01	<0.01
W-24	3/18/72	14.40	161	N.D.	0.81	N.D.	<0.05	N.D.	<0.005	N.D.	<0.01	<0.01
Chickaskia River:												
W-4	2/19/72	3.68	6	N.D.	0.04	N.D.	<0.05	N.D.	0.006	N.D.	<0.01	<0.01
W-10	2/26/72	8.80	348	N.D.	0.04	N.D.	<0.05	N.D.	<0.005	N.D.	<0.01	<0.01

N.D. - Not Determined

RESULTS AND DISCUSSION

Of the 11 ponds sampled, all contained concentrations below the suggested maximums for Zn, Cu, and As; while 5 had concentrations of Cd and/or Pb which equaled or exceeded the suggested maximum allowable concentrations of these metals for animal consumption set by the Federal Water Quality Criteria (1968) (Table 1). These 5 ponds were located within 6.4 km of the smelter; however, 4 other ponds within this area contained permissable levels of Cd and Pb when sampled. Thus, proximity alone does not appear to separate a safe water supply from one that is unsafe. Since 3 of the 5 unsafe farm ponds were sampled after a substantial rainfall (2.4 cm), it is probable that runoff from the drainage basin of the pond, along with associated mixing within the pond increased the amounts of suspended and/or dissolved metals. In addition, size and topography of the drainage basin, surrounding soil types, cover crop, and season of the year should all affect the amounts of metals in a pond.

Six of the 15 creeks sampled (Table 2) contained dissolved Cd and/or Pb concentrations which equaled or exceeded the suggested maximums set for animal consumption. Four of the 6 samples collected within 3.2 km of the smelter were unsafe for livestock consumption. The other 2 unsafe samples (W-50 and W-26) were collected close to State Highway 11, and the higher than expected Pb content was probably related to automobile emissions. Exceptionally high amounts of dissolved zinc (3.45 and 3.70 mg/l) were found in 2 of the 5 creeks sampled after the previously mentioned rainfall. These 2 creeks (W-40 and W-42) were within 3.2 km of the smelter; while the other 3 (W-35, W-36, and W-50) were all further from the smelter. In addition, differences in topography, in soil types along the drainage basin, in cover crops, and in sampling times may have influenced the amounts of these metals found. As in the ponds, the Zn, Cu, and As content of these creeks were below the suggested maximums when sampled.

Of the 14 roadside ditches sampled, 10 were collected after the rainfall. Seven of these 10 ditches contained levels of total or dissolved Zn, Cd, and/or Pb which equaled or surpassed suggested maximums for animal consumption (Table 3); while of the other 4 samples, only 1 contained exceeding amounts of dissolved Cd and Pb. In brief, ditches closer to the smelter tended to contain greater amounts of total and/or dissolved Zn, Cd, Pb, and Cu. Arsenic was not detected in any of the 4 samples analyzed. Since all ditches were samples within 4.8 km of the smelter and some of these ditches contained water safe for animal consumption, smelter proximity alone cannot be used to separate safe from unsafe water. Soil type, cover crop, season, topography, runoff rate, and proximity to roadways probably also influence the amount of these metals in runoff.

The galvanized stock tanks sampled (Table 4) contained levels of Zn, Cd, Pb, Cu, and As below suggested maximums for animal consumption. Only 1 farm pond (W-41) contained more dissolved zinc (0.81 mg/l) than the stock tank located 14.4 km south of the smelter; whereas, 3 stock tanks located within 4.8 km of the smelter contained an average of 0.26 mg/l zinc. Since the water source for these tanks is usually deep wells or munincipal water, no relation to smelter proximity was expected; however, the high value of Zn for the tank 14.4 km south might reflect something other than its galvanized steel construction.

The Chickaskia River was sampled at two locations (Table 4). Both samples contained levels of dissolved Zn, Cd, Pb, Cu, and As below suggested maximums for animal consumption. The sample collected 3.7 km north of the smelter contained much the same metal content as the sample collected 8.8 km north.

Seven samples of drinking water from public water supplies were analyzed for dissolved Zn, Cd, Pb, Cu, and As content. Concentrations of Cd, Pb, Cu, and As from all 5 samples collected in Blackwell were too small to be detectable. The level of Zn in Blackwell drinking water ranged from 0.07 - 0.12 mg/l (0.10 mg/l average). The State of Oklahoma Department of Public Health accepts 5.0 mg/l total Zn as permissable for drinking water (personal communication, Mark Coleman). Public water supplies usually have very small amounts of suspended material, and, as a result, dissolved and total metal content are virtually the same. Thus, drinking water in Blackwell appears to be fit for human consumption.

Based on these suggested maximums, runoff and standing water found in the vicinity of the smelter can be a potential hazard to livestock. Water which contains lower than these suggested maximums may also be potentially toxic expecially when forage also contains these metals. Cadmium and Pb have been shown to be less toxic to pigs, cattle, and horses that have simultaneously consumed high levels of Zn (Pond, Chapman, and Walker, 1966; Powell, Miller, Morton, and Clifton, 1964; Willoughby, MacDonald, McSherry, and Brown, 1972). For these animals, water supplies which contain toxic amounts of Cd and/or Pb may in actuality be non-toxic if they account for the total body burden of these metals. Jones (1964) reported that minnows were able to survive longer in an 8 mg/l Zn solution or a 0.2 mg/l Cu solution than in a mixture containing only 1 mg/l Zn and 0.025 mg/l Cu. Synergistic action between these two metals was thus shown. It is possible then that water deemed safe by today's standards may in the future be ruled unfit as more information is collected on synergistic action. Therefore, interactions between these metals make suggested maximum allowable concentrations based on single element studies of questionable value in determining the relative safety of these water resources.

Another shortcoming of these suggested maximums is that the Federal Water Quality Criteria (1968) does not specify whether these standards are based on total or dissolved metal content. Friberg, et al. (1971) in their review reported that water from cadmium polluted rivers usually contained undetectable dissolved cadmium; while suspended particles and sediments from these rivers usually contained high levels of Cd. Since farm ponds, creeks, ditches, and rivers in this part of Oklahoma are high in the amounts of suspended particles, total metal content of a given water supply is probably a better gauge of its fitness for animal consumption.

In conclusion, since 44% of the samples collected within 6.4 km of the smelter contained levels of dissolved or total Zn, Cd, and/or Pb which equaled or exceeded suggested maximums for animal consumption, farm animals within this area should be provided with deep well water or munincipal water and when possible be prevented from consuming runoff or standing water. Since not all samples collected within this area were potentially toxic, specific sources should be periodically checked by the farmer to determine any change in their status. If levels are below the suggested maximums, then the water may be used. As previously reported, public water supplies appear safe for human and animal consumption.

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AN ASSESSMENT OF THE EFFECTS OF ZINC, LEAD, CADMIUM, AND ARSENIC IN SOIL, VEGETATION, AND WATER RESOURCES SURROUNDING A ZINC SMELTER

PART IV

PREDICTIVE MODELS FOR WHEAT AND BERMUDA PASTURE SYSTEMS AND RELATED GRAZING POTENTIAL

INTRODUCTION

Heavy metal contamination of the environment is no longer restricted to localized areas. Emissions tend to be widely dispersed and both the flora and fauna are noticeably affected close to sources such as smelters, foundaries, and highways. Transport of Pb through an urbanized watershed in Champaign, Illinois, cottonweed trees, and the human body have been modeled by the Heavy Metals Task Force (1972). A model for Pb translocation between air, water, soil, vegetation, and cattle was developed for a test farm located within 0.8 km of a Pb smelter and compared to a similar model developed for an uncontaminated farm within the same geographical area (Missouri University, 1972).

Some farmers have reported poor gains for livestock on wheat and bermuda pastures near the Blackwell Zinc Company

Smelter in Blackwell, Oklahoma. Vegetation and water samples collected in areas close to this smelter have been found to contain toxic levels of Zn and Pb. Since Willoughby, MacDonald, McSherry, and Brown (1972) reported that Zn alone is more toxic than simultaneous poisoning by Zn and Pb (for horses), and since Zn was the most prevalent contaminant of those metals studied (Zn, Cd, Pb, and As), Zn was chosen as the driving variable for the models. Bermuda and wheat pasture models were built which predict rates of movement of Zn through the system during the next 1000 years and suggest what effects the closing of this smelter will have on the productivity and grazing potential of neighboring lands.

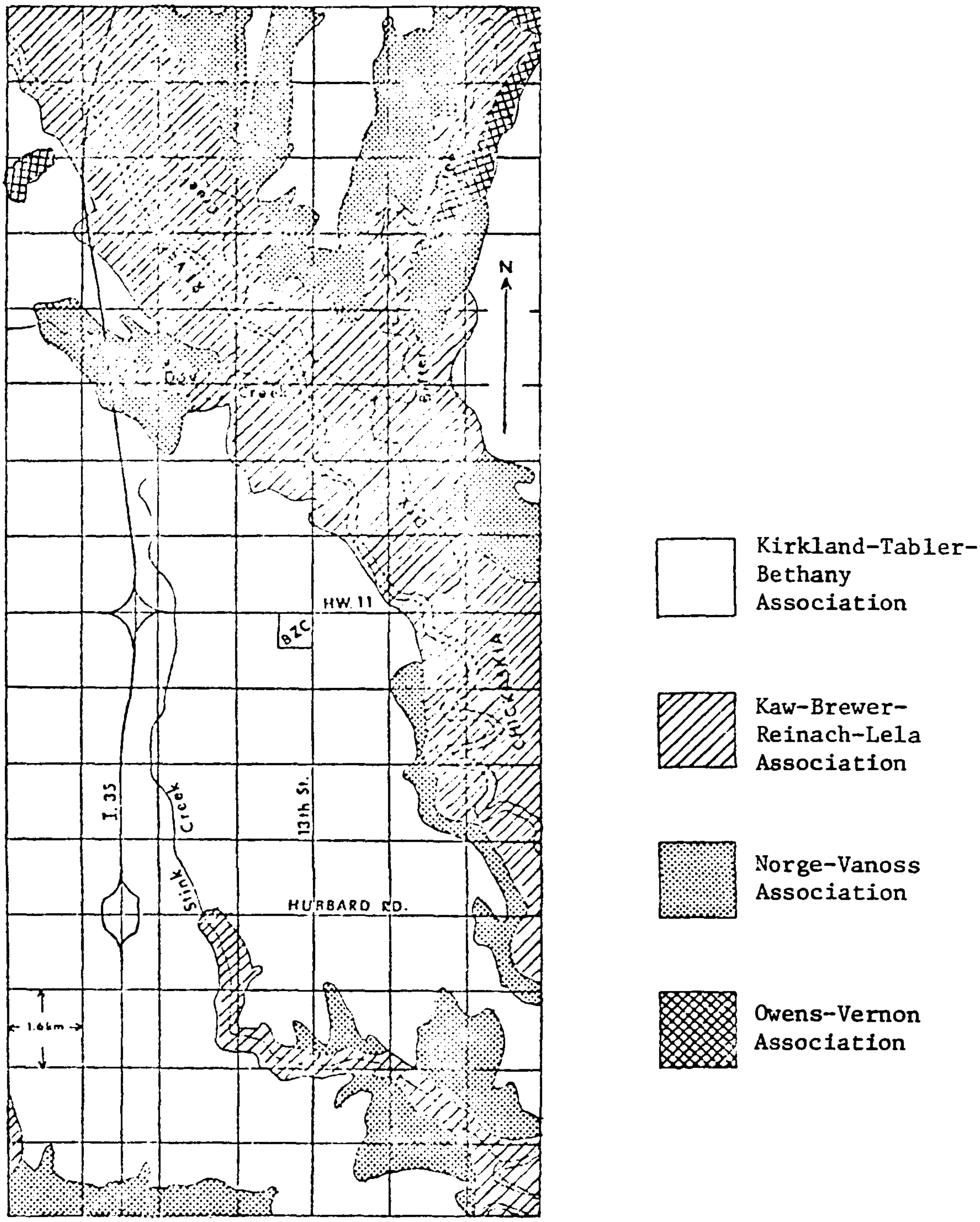
STUDY AREA

Blackwell is located in the western half of Kay County, which lies in the central part of the Redbed Plains of Oklahoma. The topography is level to gently undulating with terraces up to 4.8 km wide along the Chickaskia River. The climate of the area is temperate, subhumid (Trewartha, 1968). The area has a mean annual temperature of 16°C and a mean annual precipitation of 72.80 cm, with a frost free season which averages 195 days. Prevailing winds (19 km/hr annual average) are southerly during most months; however, in January and February winds are predominately from the north.

Four soil associations are found within the study area. Kirkland-Tabler-Bethany Association soils are found in nearly level to moderately sloping areas away from floodplains; Kaw-Brewer-Reinach-Lela Association soils make up the nearly level 1.6 - 3.2 km wide bands along the Chickaskia and somewhat narrower bands along Stink Creek; and Norge-Vanoss Association soils are found within 3.2 km of the Chickaskia mainly on gently sloping uplands and in similar locations along Stink Creek where it enters the Chickaskia (Fig. 1).

Adequate ground water for domestic use is usually found throughout the study area; while munincipal water is taken from

Figure 1. Soil associations within the study area (after Soil Survey, Kay County, Oklahoma, 1967).



the Chickaskia River. Average annual runoff from the study area is 12.7 cm, and the Chickaskia River (stream gaging station 7-1520 located near the northeast edge of the city of Blackwell) has an average annual discharge of 4.13×10^8 m^3 (Oklahoma Water Resources Board, 1972). The Chickaskia and smaller streams also provide water for livestock; however, farm ponds and small reservoirs provide most of the water consumed by livestock.

The study area is treeless except along streams, on some uplands adjacent to streams, and where windbreaks have been planted. Winter wheat is the predominant crop grown in the study area; although other small grains, alfalfa, and field corn are commonly grown. There is also some ranching in the study area.

METHODS

Triumph 64 wheat and Midland bermuda grass were grown in a growth chamber for 4 mo under the following conditions: 1.6×10^4 lm/m^2, a 16 hr photoperiod at 27°C, and an 8 hr dark period at 21°C Potting soils were collected from the Blackwell area and mixed with incremental percents by weight of non-contaminated soil. After wheat seedling emergence, pots (8/treatment) were thinned to 5 seedlings/pot; whereas, bermuda formed a sod within each pot (8/treatment).

Wheat aboveground biomass (g/m^2) was determined using data collected on 6 October 1972 from 13 wheat fields in the vicinity of Blackwell. At the time of collection the smelter was in full production. Wheat fields were selected to maximize information as a function of distance from the smelter and were either north or south of the smelter. Sampling was at random intervals along straight rows of fairly even density and was carried out using 0.5 m^2 quadrats designed by Kennedy (1972). All fields were examined for signs of grazing and only data from ungrazed fields were used. Prior to the 1973 harvest, wheat grain was collected using 0.5 m^2 quadrats from 9 fields located north and south of the smelter. The ppm Zn content of this grain was determined and converted from g Zn/m^2 to lb Zn/A. To put these models into better perspective with regard to farm economics lb/A was used instead of kg/ha.

Bermuda grass aboveground biomass (g/m^2) was determined on a per pot basis and related to soil Zn content; however, bermuda (g/m^2) collected using 0.5 m^2 quadrats on 5 November 1972 at approximately 0.8 km north of the smelter exceeded that attained in pots containing comparable levels of soil Zn (8300 lb/A). Field results were used as the baseline, and production in pots relativized accordingly.

Twenty-six 15 cm soil samples, each a composite of 20 cores randomly taken along 0.2 km transects perpendicular to the smelter, were collected from the fields sampled. Three soil pits were dug to a depth of 90 cm and samples were taken at each 15 cm increment. These pits were located 0.1 km, 0.4 km, and 0.8 km north of the smelter. The leaching rate of Zn was determined based on the past movement of this metal through these profiles.

All soil samples were air dried, crushed, passed through a 40 mesh screen in a hammer mill, and then oven dried at 90°C. To minimize contamination, samples with the highest percent of non-contaminated soil and samples collected furthest from the smelter were ground first. Harvested materials were oven dried 48 hr at 65°C, then ground through a 20 mesh screen in a Wiley mill. Total Zn content of both soils and vegetation were determined by the Blackwell Zinc Company Laboratory. Plant and soil materials were digested with nitric acid, and total Zn determined using a Perkin Elmer Model 304 atomic absorption spectrophotometer.

Literature citations were used for: recommended stocking levels and gains expected, average forage consumed, percent Zn absorption and excretion by cattle, expected bermuda grass production, and reported tolerable daily Zn intake for cattle. Two deterministic models were built, one for a bermuda grass pasture system, the other for a wheat pasture system. These models combine multiple regression equations, concentration varying coefficients, and built-in constants (Table 1).

The models were written in PL1 (Appendix A) and run at Merrick Computer Center, University of Oklahoma on an IBM 370/158. The models predict various Zn fluxes through these systems during the next 1000 years, with each iteration equal to one year. Data was printed for 20 year increments, and the accumulation of Zn in various compartments and exports during these 1000 years summed. These summations were used to determine average rates (lb/A/yr) of flow (arrows) between compartments (boxes) and average rates (lb/A/yr) of export out of the system (area enclosed by the dashed line) as leachate, runoff, harvested grain, and beef products (Figs. 2 - 3). The valve symbol represents whether grazing will be permitted or not, which depends on the Zn content (ppm dry weight) of the forage.

Table 1. Built-in constants for both models.

Title	Value	Reference
Forage consumption	22.5 g forage (dry wt)/kg body wt/day	Aronson, 1972
Bermuda system stocking level	160 A (65 ha) can support 27 heifer and 26 steer calves for 180 days	Chiles, 1968
Gains on Bermuda	250 lb (114 kg)/calf	Maynard and Walker, 1969
Bermuda forage production with some management	10,000 lb/A/yr (1838 kg/ha/yr)	Chiles, 1968
Wheat fall grazing stocking level	2.42 AUM (2.42 calves/A for 1 month)	Maynard and Hummer, 1970
Excretion of Zn	81.9% of ingested Zn	Miller, Blackmon, Gentry, and Pate, 1970
Retention of Zn in tissues	18.1% of ingested Zn	Ibid.
Toxic Zn concentration to steer and heifer calves	900 ppm Zn (dry wt) or greater	Ott, Smith, Harrington, and Beeson, 1966
Runoff	5 in/A/yr	Oklahoma Water Resources Board, 1972

Figure 2. Average lb/A/yr Zn flux during the next 1000 years for a bermuda pasture system.

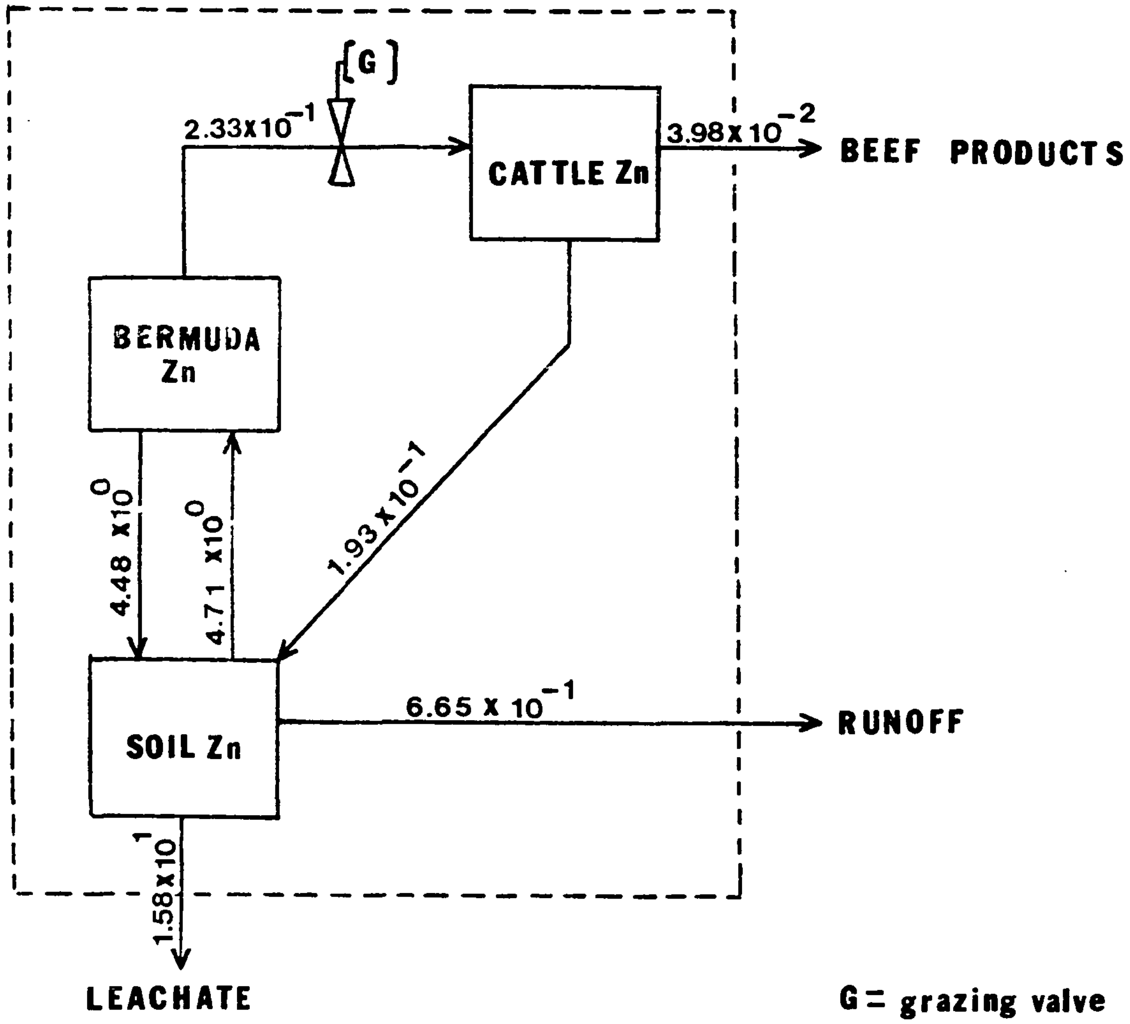
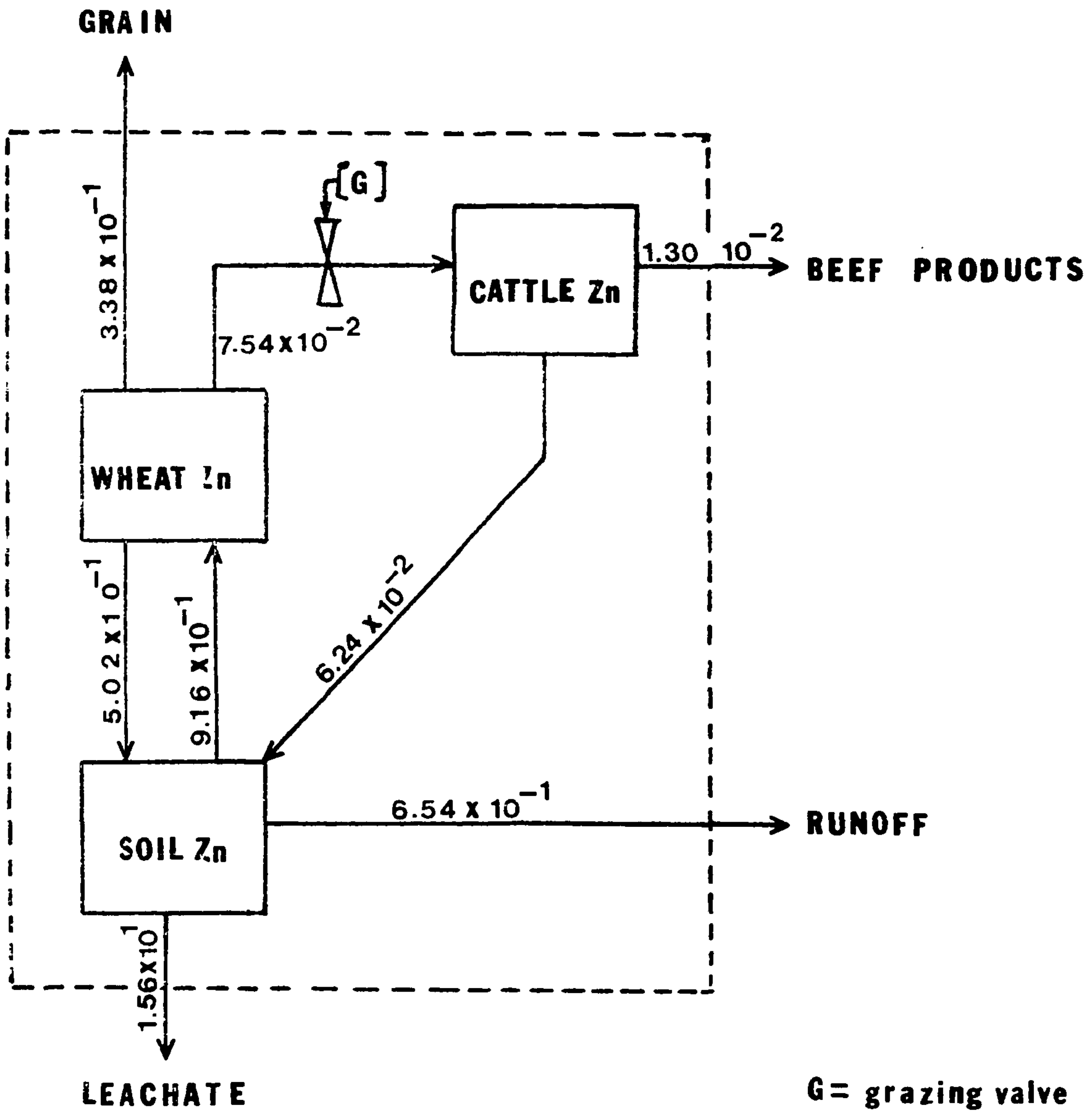


Figure 3. Average lb/A/yr Zn flux during the next 1000 years for a wheat pasture system.



RESULTS AND DISCUSSION

The following assumptions were built into either or both of the models:

For the bermuda pasture system, 149.6 lb beef/A/yr would be produced, and 765.9 lb forage/A/yr would be consumed; while for the wheat pasture system, 101.64 lb beef/A/yr would be produced, and 752.28 lb wheat/A/yr would be consumed.

Bermuda or wheat grown under growth chamber conditions in soil blends containing incremental amounts of Zn and other heavy metals will contain similar amounts of Zn as bermuda or wheat grown in Blackwell after termination of smelter operations.

Wheat grain sampled in 1973 from fields that contained an average of 1400 lb/A total Zn in the top 15 cm of soil contained an average of 0.33 lb/A Zn. The amount of Zn in grain would be directly proportional to the amount in the soil.

An average content of 2.12 mg/l Zn was found in water collected from drainage ditches within 3.2 km of the smelter. Runoff would then carry off 2.41 lb Zn/A/yr; while the amount of Zn in runoff would be directly proportional to the amount of Zn in the soil.

Soil pit data indicated that since the smelter began operation, an average of 57 lb Zn/A/yr has been leached from the top 15 cm of soil which contained an average of 17,000 lb/A total Zn in 1973. The amount of Zn leached each year would be proportional to the amount of Zn in the soil.

Runoff and leaching rates were assumed to be affected by neither cover crop nor duration and amount of rainfall.

Since a simulation time span of 1000 years was utilized, the recycling of Zn via decomposition of litter, dead root materials, and animal wastes should not influence the resolution of the models. One hundred percent of the Zn from these compartments was recycled each year.

Regression equations fit the data at the 0.01 level; however, major limitations to these equations and concentration coefficients are that data that were collected while the smelter was in full production had to be incorporated and that some of the assumptions made over simplify the natural system. In light of these limitations, the models predict that bermuda and fall wheat production (lb/A) will increase with time and will increase as the soil content decreases (Figs. 4 - 5). Total exports for 1000 years in order of magnitude from the wheat model system were predicted as follows: 15,550 lb Zn as leachate, 654 lb Zn as runoff, 338 lb Zn as grain, and 13 lb Zn as beef products; while for the bermuda system: 15,792 lb Zn as leachate, 665 lb Zn as runoff, and 40 lb Zn as beef products were predicted. Both models were given the same initial condition of 17,000 lb/A total Zn in the top 15 cm of soil. Even though the exports were somewhat

Figure 4. Predicted soil Zn and bermuda aboveground biomass during the next 1000 years.

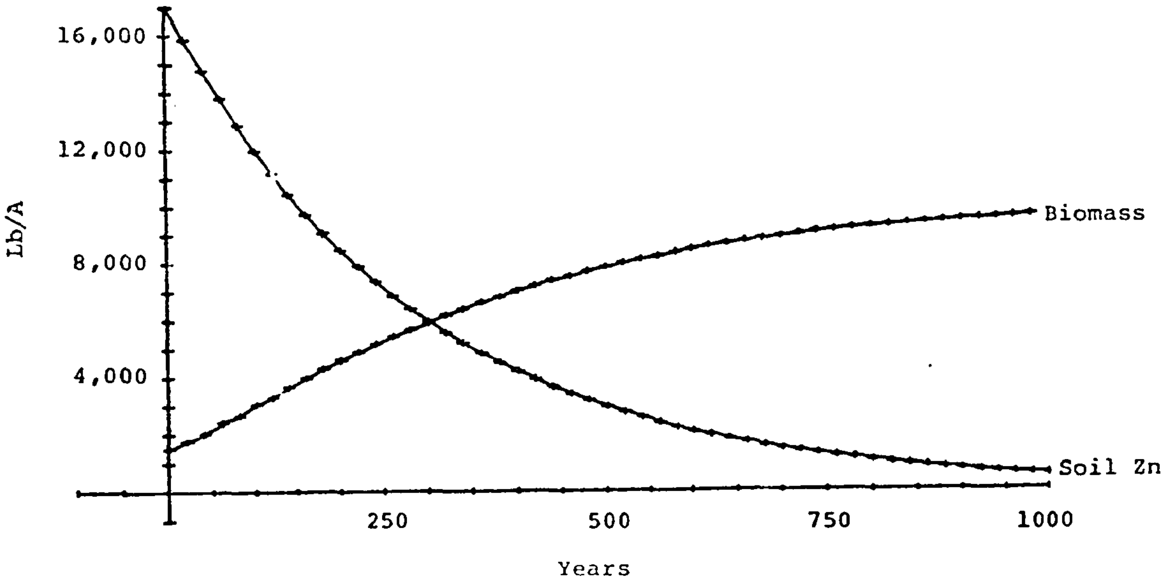
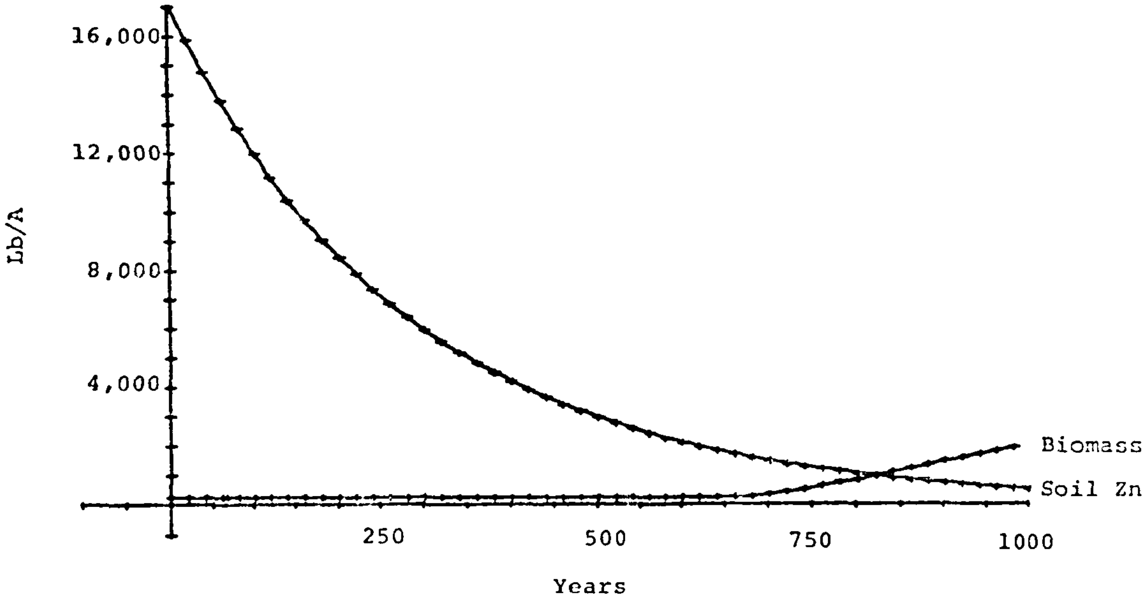


Figure 5. Predicted soil Zn and wheat aboveground biomass during the next 1000 years.



different for each model, the final soil Zn level predicted was only 59 lb/A greater for the wheat model. This probably reflects the assumption that leaching and runoff rates were independent of cover crop. Russell and Russell (1961) reported the average runoff under a permanent pasture as 4.3% of the total rainfall; while under wheat as 24.8% of the total rainfall. Since evapotranspiration will also differ for these two crops, the amount of water available for percolation through the soil will also differ.

The models also predict grazing potential. The control valve in both models allows the flow of Zn into the cattle compartment only when forage contains 900 ppm Zn or less (Figs. 2 - 3). The models were used to predict the number of years that must pass before potentially safe forage would be produced under the initial conditions of the model (Figs. 6 - 7). Time predictions were also made for soils containing less than 17,000 lb/A total Zn to produce potentially safe forage (Table 2). These results reflect the multiple regression equation for Zn uptake by bermuda aboveground biomass ($Y=0.23X - 1.29X^2 * 10^{-4} + 188.87$; where Y equals the ppm Zn in bermuda, and X equals the lb/A total soil Zn) which predicts less translocation than the multiple regression equation for Zn uptake by wheat aboveground biomass ($Y=1.36X - 1.10X^2 * 10^{-4} - 107.06$; where Y equals ppm Zn in wheat, and X equals lb/A total soil Zn). Predictions appear realistic, as reports of poor gains for cattle have been on bermuda pasture containing more than 3000 lb Zn/A in the soil. Soil containing more than 1600 lb/A Zn appears to retard fall wheat aboveground biomass to

Figure 6. Predicted Zn content (ppm dry weight) of bermuda aboveground biomass during the next 1000 years.

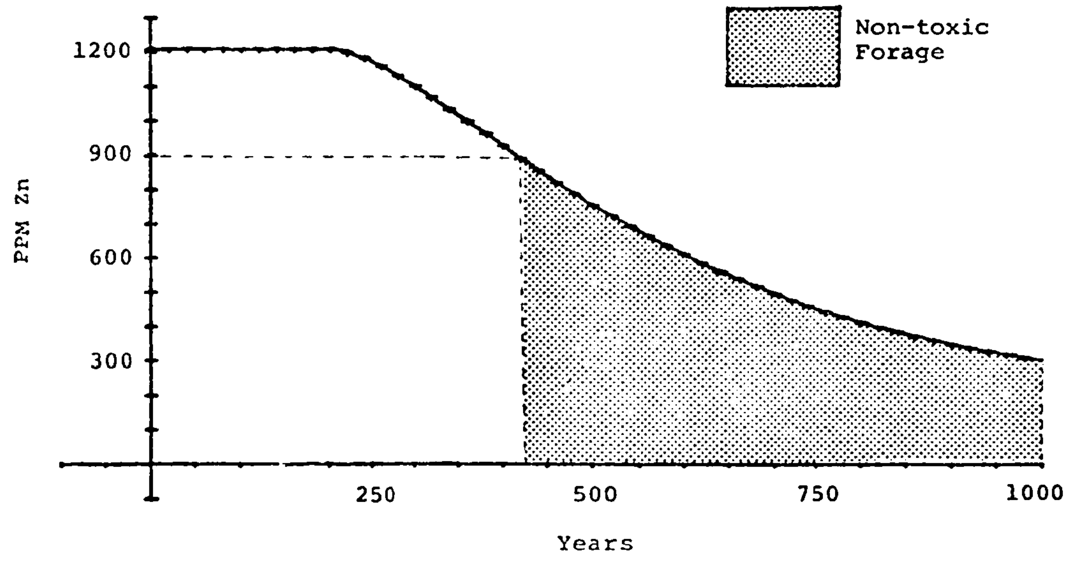


Figure 7. Predicted Zn content (ppm dry weight) of fall wheat aboveground biomass during the next 1000 years.

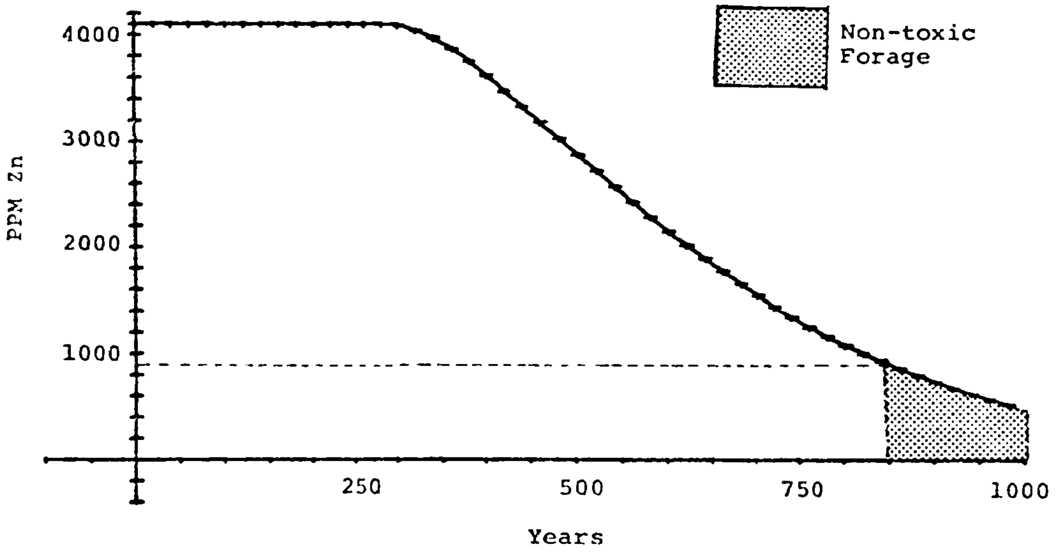


Table 2. Predicted times required for soil containing various amounts of Zn to produce forage non-toxic to calves.

Zn in Soil (lb/A)	Bermuda Forage (years)	Wheat Forage (years)
12,000	300	750
9,000	220	670
6,000	100	560
3,000	---	370
2,000	---	250
1,000	---	70

an extent that these areas cannot be economically grazed; while areas with less soil Zn are grazed, and poor gains have not been reported from these areas.

These models, although tentative, suggest future work that should be done in the Blackwell area (i.e., resampling vegetation not exposed to smelter stack and furnace emissions). Soil, vegetation, and water samples collected within the next 10 - 20 years, if compared to the model's predictions, could be used to improve the long term predictions of these "first generation models".

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APPENDIX A

ZINC FLOW MODELS

Symbol Key:

PERC(I) = Lb/A Zn in leachate each year
TPERC(I)= Lb/A Zn in leachate for 1000 years
RUN(I) = Lb/A Zn in runoff each year
TRUN(I) = Lb/A Zn in runoff for 1000 years
MEAT(I) = Lb/A Zn retained in calf body tissues each year
TMEAT(I)= Lb/A Zn retained in calf body tissues for 1000 years
COW(I) = Lb/A Zn ingested by calves each year
TCOW(I) = Lb/A Zn ingested by calves for 1000 years
SOIL(I) = Lb/A Zn in soil each year
BIOM(I) = Lb/A aboveground biomass each year
PPM(I) = ppm Zn in aboveground biomass each year
PLANT(I)= Lb/A Zn in aboveground biomass each year
TUPT(I) = Lb/A Zn in aboveground biomass for 1000 years
TRET(I) = Lb/A Zn in aboveground biomass returned to the soil for 1000 years
RBIO(I) = Lb/A Zn in biomass each year/ Lb/A Zn in soil each year
NSOIL(I)= Lb/A Zn in soil each year/100
SEED(I) = Lb/A Zn in wheat grain harvested each year
TSEED(I)= Lb/A Zn in wheat grain harvested for 1000 years

PL1 Program for Bermuda Model:

```
FEB14:PROCEDURE OPTIONS(MAIN);
DECLARE (TPERC,TRUN,TMEAT,SOIL(1001),PERC(1000)) FIXED (8,2);
DECLARE (NSOIL(1001)) FIXED (10,2);
DECLARE (BIOM(1000),PPM(1000),PLANT(1000)) FIXED(7,2);
DECLARE (MEAT(1000),RUN(1000)) FIXED (7,2);
DECLARE (TCOW, TRET, TUPT) FIXED (8,2);
DECLARE (COWS(1000)) FIXED (7,2);
DECLARE (RBIO(1000)) FIXED(3,2);
DECLARE (I,J) FIXED(4);
SOIL(1)=17000.00;
TPERC=0;
TRUN=0;
TMEAT=0;
TRET=0;
TUPT=0;
```

```
TCOW=0;
I=1;
AA:NSOIL(I)=SOIL(I)/100;
IF SOIL(I)>=8300.00 THEN PPM(I)=1209.00;
ELSE PPM(I)=188.87+23*SOIL(I)-1.29*(NSOIL(I)**2)/10;
RBIO(I)=.79-((1.67*SOIL(I))/100000);
BIOM(I)=10000.00-(RBIO(I)*SOIL(I));
PLANT(I)=BIOM(I)*PPM(I)/1000000;
TUPT=TUPT+PLANT(I);
PERC(I)=(3.35*SOIL(I))/1000;
TPERC=TPERC+PERC(I);
RUN(I)=(1.42*SOIL(I))/10000;
TRUN=TRUN+RUN(I);
IF PPM(I)>900.00 THEN GO TO AB;
ELSE GO TO AC;
AB:MEAT(I)=0.00;
TRET=TRET+PLANT(I);
SOIL(I+1)=SOIL(I)-PERC(I)-RUN(I);
I=I+1;
IF (SOIL(I)<100.00) | (I=1001) THEN GO TO AD;
ELSE GO TO AA;
AC:MEAT(I)=(138.65*PPM(I))/1000000;
TMEAT=TMEAT+MEAT(I);
COWS(I)=(766.02*PPM(I))/1000000;
TCOW=TCOW+COWS(I);
TRET=TRET+PLANT(I)-COWS(I);
SOIL(I+1)=SOIL(I)-PERC(I)-RUN(I)-MEAT(I);
I=I+1;
IF (SOIL(I)<100.00) | (I=1001) THEN GO TO AD;
ELSE GO TO AA;
AD:DO J=1 TO I-1 BY 20;
PUT EDIT ('LB PER ACRE ZN IN SOIL IN YEAR',J,'EQUALS',SOIL(J))
(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
END;
DO J=1 TO I-1 BY 20;
PUT EDIT ('LB PER ACRE ZN IN FORAGE IN YEAR',J,'EQUALS',PLANT (J))
(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(7,2));
END;
DO J=1 TO I-1 BY 20;
PUT EDIT ('LB PER ACRE BIOMASS IN YEAR',J,'EQUALS',BIOM(J))
(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(7,2));
END;
DO J=1 TO I-1 BY 20;
PUT EDIT ('LB PER ACRE ZN IN LEACHATE IN YEAR',J,'EQUALS',PERC(J))
(SKIP(2),A,X(2),F(4),X(2),A,X,(2),F(8,2));
END;
DO J=1 TO I-1 BY 20;
PUT EDIT ('LB PER ACRE ZN IN RUNOFF IN YEAR',J,'EQUALS',RUN(J))
(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(7,2));
END;
DO J=1 TO I-1 BY 20;
```

```
PUT EDIT ('LB PER ACRE ZN IN BEEF IN YEAR',J,'EQUALS',MEAT(J))
(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(7,2));
END;
DO J=1 TO I-1 BY 20;
PUT EDIT ('PPM ZN IN FORAGE IN YEAR',J,'EQUALS',PPM(J))
(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(7,2));
END;
DO J=1 TO I-1 BY 20;
PUT EDIT ('BIOMASS YEARLY RATE',J,'EQUALS',RBIO(J))
(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(3,2));
END;
PUT EDIT ('THE TOTAL LB PER ACRE ZN IN LEACHATE FOR',I,'YEARS EQUALS',
TPERC)(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
PUT EDIT ('THE TOTAL LB PER ACRE ZN IN RUNOFF FOR',I,'YEARS EQUALS',
TRUN) (SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
PUT EDIT ('THE TOTAL LB PER ACRE ZINC IN BEEF FOR',I,'YEARS EQUALS',
TMEAT)(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
PUT EDIT ('THE TOTAL LB PER ACRE ZINC IN COWS FOR',I,'YEARS EQUALS',
TCOW) (SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
PUT EDIT ('THE TOTAL LB PER ACRE ZINC IN TUPT FOR',I,'YEARS EQUALS',
TUPT) (SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
PUT EDIT ('THE TOTAL LB PER ACRE ZINC IN TRET FOR',I,'YEARS EQUALS',
TRET) (SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
PUT EDIT ('LB PER ACRE ZN IN SOIL IN YEAR  1000 EQUALS',SOIL(1000))
(SKIP(2),A,X(2),F(8,2));
END FEB14;
```

PL1 Program for Wheat Model:

```
FEB14:PROCEDURE OPTIONS(MAIN);
DECLARE (TPERC,TRUN,TMEAT,SOIL(1001),PERC(1000)) FIXED (8,2);
DECLARE (NSOIL(1001)) FIXED (10,2);
DECLARE (BIOM(1000),PPM(1000),PLANT(1000)) FIXED (7,2);
DECLARE (MEAT(1000),RUN(1000)) FIXED (7,2);
DECLARE (SEED(1000)) FIXED (7,2);
DECLARE (TCOW,TSEED,TRET,TUPT) FIXED (8,2);
DECLARE (COWS(1000)) FIXED (7,2);
DECLARE (I,J) FIXED(4);
SOIL(1)=17000.00;
TPERC=0;
TRUN=0;
TMEAT=0;
TSEED=0;
TRET=0;
TUPT=0;
TCOW=0;
I=1;
AA:NSOIL(I)=SOIL(I)/100;
IF SOIL(I)>=6385.00 THEN PPM(I)=4100.00;
ELSE PPM(I)=1.36*SOIL(I)-1.10*(NSOIL(I)**2)-107.06;
IF SOIL(I)>=1814.00 THEN BIOM(I)=246.00;
ELSE BIOM(I)=3746.16-3.88*SOIL(I)+10.73*(NSOIL(I)**2);
```

```
IF SOIL(I)>2150.00 THEN SEED(I)=.43;
ELSE SEED(I)=(2.00*SOIL(I))/10000;
TSEED=TSEED+SEED(I);
PLANT(I)=BIOM(I)*PPM(I)/1000000;
TUPT=TUPT+PLANT(I);
PERC(I)=(3.35*SOIL(I))/1000;
TPERC=TPERC+PERC(I);
RUN(I)=(1.42*SOIL(I))/10000;
TRUN=TRUN+RUN(I);
IF PPM(I)> 900.00 | BIOM(I)<1000.00 THEN GO TO AB;
ELSE GO TO AC;
AB:MEAT(I)=0.00;
TRET=TRET+PLANT(I)-SEED(I);
SOIL(I+1)=SOIL(I)-PERC(I)-RUN(I)-SEED(I);
I=I+1;
IF (SOIL(I)<100.0) | (I=1001) THEN GO TO AD;
ELSE GO TO AA;
AC:MEAT(I)=(136.16*PPM(I))/1000000;
TMEAT=TMEAT+MEAT(I);
COWS(I)=(752.28*PPM(I))/1000000;
TCOW=TCOW+COWS(I);
TRET=TRET+PLANT(I)-SEED(I)-COWS(I);
SOIL(I+1)=SOIL(I)-PERC(I)-RUN(I)-MEAT(I)-SEED(I);
I=I+1;
IF (SOIL(I)<100.00) | (I=1001) THEN GO TO AD;
ELSE GO TO AA;
AD:DO J=1 TO I-1 BY 20;
PUT EDIT ('LB PER ACRE ZN IN SOIL IN YEAR',J,'EQUALS',SOIL(J))
(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
END;
DO J=1 TO I-1 BY 20;
PUT EDIT ('LB PER ACRE ZN IN FORAGE IN YEAR',J,'EQUALS',PLANT(J))
(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(7,2));
END;
DO J=1 TO I-1 BY 20;
PUT EDIT ('LB PER ACRE BIOMASS IN YEAR',J,'EQUALS',BIOM(J))
(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(7,2));
END;
DO J=1 TO I-1 BY 20;
PUT EDIT ('LB PER ACRE ZN IN LEACHATE IN YEAR',J,'EQUALS',PERC(J))
(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
END;
DO J=1 TO I-1 BY 20;
PUT EDIT ('LB PER ACRE ZN IN RUNOFF IN YEAR',J,'EQUALS',RUN(J))
(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(7,2);
END;
DO J=1 TO I-1 BY 20;
PUT EDIT ('LB PER ACRE ZN IN SEED IN YEAR',J,'EQUALS',SEED(J))
(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(7,2));
END;
DO J=1 TO I-1 BY 20;
```

```
PUT EDIT ('LB PER ACRE ZN IN BEEF IN YEAR',J,'EQUALS',MEAT(J))
(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(7,2));
END;
DO J=1 TO I-1 BY 20;
PUT EDIT ('PPM ZN IN FORAGE IN YEAR',J,'EQUALS',PPM(J))
(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(7,2));
END;
PUT EDIT ('THE TOTAL LB PER ACRE ZN IN LEACHATE FOR',I,'YEARS EQUALS',
TPERC)(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
PUT EDIT ('THE TOTAL LB PER ACRE ZN IN RUNOFF FOR',I,'YEARS EQUALS',
TRUN) (SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
PUT EDIT ('THE TOTAL LB PER ACRE ZINC IN BEEF FOR',I,'YEARS EQUALS',
TMEAT)(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
PUT EDIT ('THE TOTAL LB PER ACRE ZINC IN SEED FOR',I,'YEARS EQUALS',
TSEED)(SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
PUT EDIT ('THE TOTAL LB PER ACRE ZINC IN COWS FOR',I,'YEARS EQUALS',
TCOW) (SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
PUT EDIT ('THE TOTAL LB PER ACRE ZINC IN TUPT FOR',I,'YEARS EQUALS',
TUPT) (SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
PUT EDIT ('THE TOTAL LB PER ACRE ZINC IN TRET FOR',I,'YEARS EQUALS',
TRET) (SKIP(2),A,X(2),F(4),X(2),A,X(2),F(8,2));
PUT EDIT ('LB PER ACRE ZN IN SOIL IN YEAR  1000 EQUALS',SOIL(1000))
(SKIP(2),A,X(2),F(8,2));
END FEB14;
```