TRACE METALS IN SOILS OF THE COEUR D'ALENE RIVER VALLEY AND THEIR POTENTIAL EFFECTS ON WATER QUALITY

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TRACE METALS IN SOILS OF THE COEUR D'ALENE RIVER VALLEY AND THEIR POTENTIAL EFFECTS ON WATER QUALITY

Abstract

Soils in the Coeur d'Alene River Valley(s) have become contaminated with trace metals. Studies presented here show that the degree of contamination in these soils is dependent on distance from the local mining industry's smelting complex in the South Fork Coeur d'Alene River Valley and on river deposited mine wastes in the Main Stem Coeur d'Alene River Valley. Controlled greenhouse studies of garden vegetables and crops grown in trace metal contaminated soils from this locale suggest that most species suffer adverse growth effects and that all species accumulate the trace metals.

A rapid decrease of trace metal concentrations in soils with increasing depth in the South Fork Coeur d'Alene River Valley indicates that these soils have become contaminated primarily as a result of atmospheric fallout/washout of smelter emissions. Under laboratory conditions the solubilization of these contaminants generally appears to have a linear relationship with time and rapidly reach equilibrium concentrations which are dependent on the pH of the soil solution and relative soil characteristics. Due to the high solubilities of the oxidation weathering products of the trace metal emissions and the river deposited mine wastes potentially high concentrations of trace metals can be rapidly leached from the contaminated soils by rainfall and high stage water tables.

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CHAPTER ONE

INTRODUCTION

Historical Background

The Coeur d'Alene River Valley (Fig. 1) of Idaho is the home of the world famous Coeur d'Alene Mining District. Mining in this region began approximately 100 years ago. A. J. Prichard discovered gold in the Murray-Eagle Mining District in 1882. Within two years, those gold deposits were found to be much less extensive than originally thought, and some miners pushed on to discover the first of the Coeur d'Alene ores about twenty miles (30 km) west of the Murray-Eagle district (Idaho Division of Tourism and Industrial Development, 1976).

The Coeur d'Alene Mining District is one of the major antimony, lead, silver, and zinc producing areas in the world (U. S. Bureau of Mines, 1969). Associated with the mining industry of the area has been the problem of trace metal pollution. For almost 100 years, mining and smelting operations along the South Fork of the Coeur d'Alene River have discharged wastes containing high levels of trace metals into the local environment.

Statement of the Problem

Trace metal contamination of the soils in the Coeur d'Alene River Valley has occurred due to mining and smelting. Direct exposure to those contaminated soils has been shown to be detrimental to human health (Yankel, Von Lindern, and Walter, 1977). Indications that indirect exposure to trace metals can occur via garden vegetables and

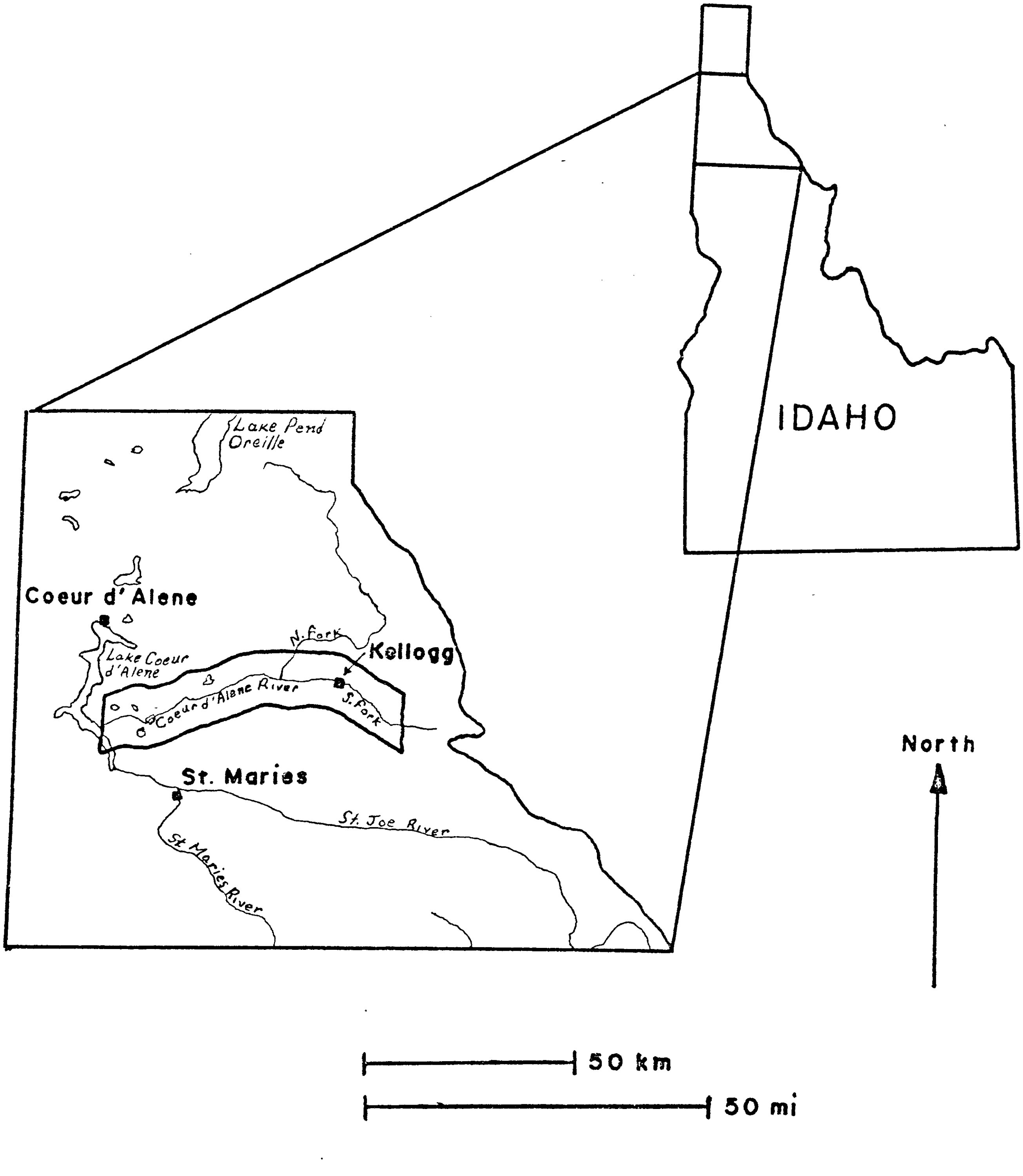

Figure 1. The Coeur d'Alene River Valley.

crops grown in contaminated soils has also been presented previously (Keely and others, 1976). Although trace metal contamination of natural waters by leaching of mine tailings has been demonstrated (Galbraith, 1971, and Reece, 1974), trace metal contamination of waters by solubilization of contaminated soils has not. The sources and effects of trace metal contaminants in the Coeur d'Alene River Valley must be assessed as the first step toward deriving solutions to this problem.

Previous Investigations

Mink and others (1971) evaluated the effect of industrial and domestic effluents on the water quality of the Coeur d'Alene River. Industrial effluents were found to have a direct influence on the concentrations of trace metals in the Coeur d'Alene River.

In the summer of 1971, a National Science Foundation Student Originated Studies group from the University of Idaho conducted an extensive study of the trace metal distribution in the sediments of the Coeur d'Alene River delta and its lake area vicinity, which is about 30 miles (50 km) downstream from the mining operations. The study revealed that a serious pollution problem exists in the sediments of the delta and of the southern part of the Coeur d'Alene Lake; the delta consists of mine tailings (Maxfield and others, 1974a, 1974b). In 1974, the Environmental Protection Agency (EPA) ordered the Bunker Hill Company, the largest mining company in the district, to limit their total solids waste dumping to 325 pounds (148 kg) of zinc and 80 pounds (36 kg) of lead per day into the river (The Daily Idahonian, August 28, 1974). However, the huge amounts of polluted sediments already present in the river continue to be a source of pollution to the environment. During the spring season, they are carried into the floodplains along the river (Reece and others, 1978).

Of considerable environmental significance is the number of abandoned tailings piles scattered throughout the district (Norbeck, 1974), the accumulation of mine waste discharges/tailings in the bed (Ellis, 1940) and delta (Maxfield and others, 1974a, 1974b) of the Coeur d'Alene River, and the acid mine drainage from operative mines in the district (Trexler and others, 1975). Lead levels in ambient air in the Coeur d'Alene Mining District are also higher than normal. At the time Ellsworth (1972) conducted his survey, air pollution was the major concern of Mining District residents. The Idaho Department of Health and Welfare and the Environmental Protection Agency were recently involved in a study of the distribution and effects of the Bunker Hill Company Smelter emissions for that reason (Johnson and others, 1977).

Emissions from the smelting complex have resulted in trace metal contamination of the surrounding soils. Although mandatory abatement regulations imposed by the U. S. Environmental Protection Agency have limited the trace metal and sulfur dioxide emissions of the smelting complex in recent years, environmentally significant levels of the trace metals are still emitted (Johnson and others, 1977). Additionally, the accumulations of prior year's emissions in the valley soils remain exposed and available for solubilization processes (e.g. aqueous contact through rainfall and high stage water tables).

There are indications that animals living around the Coeur d'Alene basin are affected by the levels of trace metals in this environment.

For example, tissue analyses from a number of waterfowl collected in the lower Coeur d'Alene River showed abnormally high concentrations of lead (Chupp, 1955). In another case, high lead concentrations were observed in the bone marrow of a horse whose death was attributed to lead poisoning (Galbraith, 1971). Sappington (1969) determined the acute toxicity of zinc to cutthroat trout to be at concentrations much below those normally found in the Coeur d'Alene River.

Purpose and Objectives

The purpose of this study is to add to the understanding of the distribution and effects of trace metal contaminants in the Coeur d'Alene River Valley. The general objectives necessary to accomplish that purpose are outlined as follows: (1) determine the trace metal contamination of soils in the Coeur d'Alene River Valley from previous studies and from additional field work; (2) determine the effect of contaminated soils on plant growth and trace metal concentration (uptake); and (3) determine the potential effect of contaminated soils on water quality by laboratory investigations.

The distribution of trace metal concentrations in soils of the Coeur d'Alene River Valley was determined by Keely and others (1976) during the summer of 1975. It was deemed necessary (by this author) to repeat select portions of that study during the summer of 1976 for verification/validation purposes. The data generated during the 1975 survey is presented in a new format here. The data generated by the 1976 survey is presented here as an original contribution.

Following the 1976 soil survey, it became desirable to estimate the effects that the contaminated soils had on parts of the environment which could result in human exposure to trace metal contaminants. Several common vegetables and farm crops were grown in contaminated soils under greenhouse conditions during 1976 and 1977. The growth rates and uptake of trace metals by the plants were determined, but because this author lacked proper biological/botanical training, no physiological effects were examined.

In 1978 and 1979 this author conducted solubilization experiments in an effort to determine potential water quality effects of the contaminated soils. These experiments entailed an examination of the following parameters: (1) the rate of solubilization and the equilibrium concentrations of solubilized trace metals; (2) the effects of agitated (stream simulation) and static (aquifer simulation) soil solutions on the solubilization process; (3) the effect of soil characteristics (e.g. organic content) on the solubilization process; and (4) the effect of oven drying the sediment-like Osburn and Cataldo soils on the solubilization process (a sample pre-treatment concern).

Despite the stated scope of this thesis it must be recognized that the data and interpretations given here cannot rigidly quantify specific relationships because numerous factors influence the mechanism by which trace metals are leached from soils. The mineral composition, surface oxidation, organic content, and physical aggregation of soil particles all affect the solubility of trace metals in soil solutions (Brady, 1974). Similarly, the chemical and hydrogeologic characteristics of the underlying media ultimately determine the mechanism and rate of transportation of dissolved species from the soil solution to aquifers below (Dominico, 1972). The mechanisms and rate of infiltration of hydrated ions in Coeur d'Alene River Valley soils are particularly difficult to assess because of the complex geology of the region and because of the effects mining operations have had on the local hydrosphere.

Geographic and Geologic Setting

The western portion of the study area, Kootenai County, (Fig. 2), has a land surface which gradually varies from wide, flat floodplains at the western end (Coeur d'Alene Lake) to a moderately steep valley at the east end. The valley floor at the boundary of Kootenai and Shoshone counties is roughly one mile (1.6 km) wide and appreciably narrows eastward into Shoshone County; narrowing to one-quarter mile (0.4 km) near Wallace, Idaho, at the east end of the study area. Kellogg, Idaho, the major mining/smelting town of the mining district, is located in the center of Shoshone County. The mountainsides of this valley are barren from Smelterville, Idaho to Osborn, Idaho due to the high sulfur dioxide smelter emissions in past years. Recent efforts to revegetate this area have proved fruitless because of the high acidity and trace metal content in these soils (Johnson and others, 1977).

Nearly all of the Coeur d'Alene Study Area lies within only a part of a very extensive area that is underlain by slightly metamorphosed, structurally complex sedimentary rocks. These rocks are part of the thick Belt Series of Precambrian age. They are mostly fine grained quartzites, impure quartzites, and siliceous argillites, which may contain in certain areas varying amount of calcium, magnesium, and iron carbonate. A group of small monzonite stocks intrude the sedimentary sequence at the far east end of the study area. Basalt flows bury part of the mountainous land surface near Coeur d'Alene Lake (Kopp, 1973).

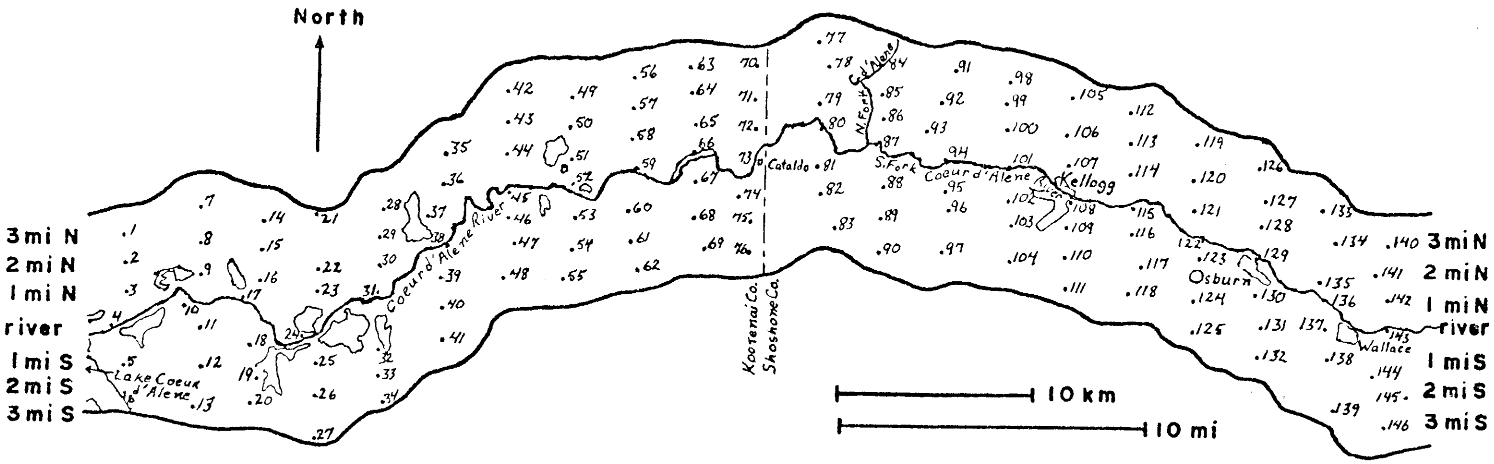

Figure 2. Study Area and Site Location Map for 1975 and 1976 Surveys of Trace Metal Contamination in Coeur d'Alene River Valley Soils (Sample Dots Were Numbered for Reference Purposes).

The bedded rocks have been displaced by extensive faulting and folding that has resulted in local overturning. The faults and associated fractures have been the principal loci for the development of the lead, zinc, and silver veins for which the Coeur d'Alene Mining District is world famous. Most of the productive veins of the district can be grouped in zones or belts. These belts are approximately located south of the South Fork of the Coeur d'Alene River from Kellogg to Wallace and north of the South Fork from Wallace eastward (Reid, 1961).

Anderson (1940) believes the structural features of Kootenai County are quite similar to those of Shoshone County, and notes that the ore bodies of Kootenai County are relatively small mineralized zones related to geologic structure. Hobbs (1961), described the Shoshone County ore bodies as having formed tabular ore shoots in steep-dipping veins and mineralized faults. The ore deposits are not of the disseminated kind where the ore metals are more or less uniformly distributed through the country rock.

Soils Background

The extent to which soils reflect the metal content values of the parent rock material depends on the degree of soil development. Well-developed soil profiles result from a combination of biological and chemical processes; these processes vertically distribute the metals in varying proportions. The uppermost humus layer and the soil below the leached horizon become enriched in certain metals (Hawkes and Webb, 1962 and Huff, 1952). Some soil studies indicate that metal content of bedrock is actually an insignificant influence on metal content of well developed soils (Chapman and Shacklette, 1960 and Vinogradov, 1959). The dispersion of elements and therefore their content in soils is actually affected by other factors, including clay content, organic content, acidity, potential of the ions, and stability of minerals to be decomposed.

In young or immature soils which are horizonless, biological and chemical processes have not had sufficient opportunity to operate. In this case metals in the weathered parent material seem to be distributed through the soil by simple mechanical dispersion processes such as sheetwash and creep. In the mountainous terrain of the Coeur d'Alene Study Area, the soils are usually poorly developed, apparently due to steady erosion of soil cover on the steep slopes. This is certainly true for parts of the study area where vegetation is sparse and erosion has left only a loose rubble of rock. At such locations the effect of biological and chemical processes would be at a minimum and the metal content of the bedrock would be a primary influence on the metal content of the soil. Because the Coeur d'Alene ores are not of the disseminated kind, a vein outcrop would be required to yield high trace metal concentrations in the absence of anthropogenic contamination. It has been noted that such outcrops are rare in the Coeur d'Alene Mining District (Reid, 1961).

Soil samples in a geochemical study of the Coeur d'Alene Mining District by Kennedy (1961) were taken by removing most of the surface cover and collecting soil from the first four inches (10 cm) below the surface. With this sampling procedure he successfully verified the location of known ore veins. Local background trace metal content in

CHAPTER TWO

THE DISTRIBUTION OF TRACE METAL CONTAMINANTS IN SOILS OF THE COEUR D'ALENE RIVER VALLEY

Methodologies

The 1975 mapping of the concentrations of trace metals in soils throughout the Coeur d'Alene Valley(s) was facilitated by arranging the sampling sites in traverses paralleling the course of the Coeur d'Alene River (Fig. 2). Five samples each, for averaging purposes, were taken from 117 of the 146 projected sampling sites. The remaining 29 sites were inaccessable. An additional 60 sites were located in and near the mining/smelting towns of Kellogg and Smelterville, Idaho (Fig. 3). The variations of trace metal concentrations as a function of depth (0-5 cm/1-2 in, 5-10 cm/2-4 in, 10-15 cm/4-6 in) were investigated at all sampling sites. The 1976 survey repeated the sampling of soils at the sample sites on the traverses which were one mile (1.6 km) north and one mile (1.6 km) south of the Coeur d'Alene River.

The soil samples were dried for several hours at 105°C and then homogenized by grinding with a large porcelain mortar and pestle. The resulting material was sifted through a U. S. No. 80 stainless steel sieve. A one-gram sample of the sifted powder was digested with 5 ml concentrated nitric acid at 70°C (hot plate) to near dryness (0.5-1.0 ml), then diluted with 3 ml dilute nitric acid (3N) and removed for filtering. The digestates were filtered through No. 41 Whatman filter and diluted with 18 MΩ deionized water to a final volume of 25 ml. The solutions were analyzed for Cd, Cu, Pb, and Zn using a Perkin-Elmer

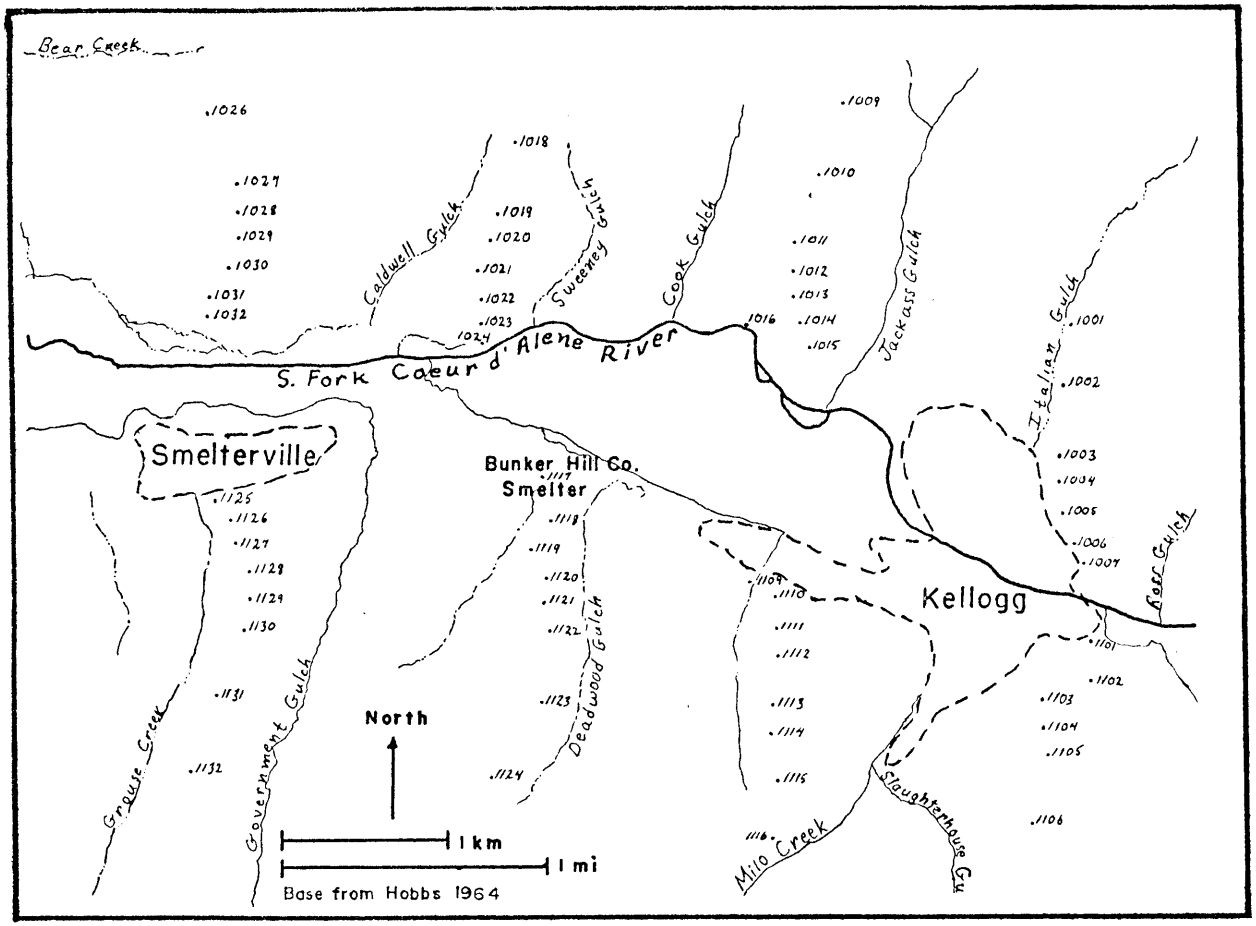

Figure 3. Study Area and Sample Site Location Map for 1975 Survey of Trace Metal Contamination in Kellogg and Smelterville Soils (Sample Site Dots Were Numbered for Reference Purposes).

Model 303 Atomic Absorption Spectrophotometer. These digestion and analysis procedures are similar to a U. S. Geological Survey method for the determination of silver in mineralized rocks (Huffman and others, 1966).

Data Discussion

Examination of Table 1 reveals two significant trends, as well as the fact that the average trace metal concentrations for Shoshone County soils exceed those for Kootenai County soils. The values for both counties are seen to decrease as a function of depth and as a function of distance from the Coeur d'Alene River. The decrease as a function of depth will be treated later in this discussion. A tabular summary of the ratios of trace metal concentrations in surface (top 5 cm/2 in) soils as a function of distance from the Coeur d'Alene River is given here:

Ratios of Table 1 Surface Soil Trace Metal Concentration
Means as a Function of Distance From the Coeur d'Alene River

	Shoshone County					Kootenai County				
Distance Ratios	Cd	Cu	Pb	Zn	Ave	Cd	Cu	Pb	Zn	Ave
1 mile/2 mile (1.6 km/3.2 km)	1.16	1.46	1.57	1.84	1.51	1.20	1.09	1.03	1.18	1.13
2 mile/3 mile (3.2 km/4.8 km)	2.02	1.02	1.43	0.93	1.35	1.19	0.84	1.33	1.28	1.16
1 mile/3 mile (1.6 km/4.8 km)	2.35	1.48	2.25	1.71	1.95	1.42	0.91	1.37	1.52	1.30

It is evident that there is a marked difference between the behavior of the trace metal concentrations of soils in the two counties. The trace metal concentrations in soils of Shoshone County decrease with increasing

TABLE 1a

TRACE METAL CONCENTRATIONS IN SOILS ON PARALLEL TRAVERSES OF THE COEUR D'ALENE RIVER
(Values in ug/g)

SHOSHONE COUNTY

		One Mile (1.6 km) Traverses			Two Mile (3.2 km) Traverses			Three Mile (4.8 km) Traverses		
Depth	(cm)	0-5	5-10	10-15	0-5	5-10	10-15	0-5	5-10	10-15
	(in)	0-2	2-4	4-6	0-2	2-4	4-6	0-2	2-4	4-6
Cd	Range	0.99- 17.46	0.66- 13.97	0.56- 12.57	0.99- 23.77	0.50- 13.24	0.47- 10.54	0.47- 5.68	0.53- 4.67	0.01- 15.28
	Mean	4.82	3.60	2.95	4.15	2.42	1.96	2.05	1.57	2.16
Cu	Range	11.70- 64.37	5.76- 77.82	2.53- 43.30	6.96- 41.32	6.04- 52.64	6.48- 47.08	8.44- 32.26	7.44- 31.14	8.04- 25.85
	Mean	25.60	23.40	17.20	17.53	18.74	17.53	17.24	16.78	15.06
Pb	Range	48.31- 1075.30	34.68- 884.57	12.24- 361.56	23.46- 1565.47	21.94- 1147.28	12.55- 698.76	17.55- 577.96	12.26- 406.97	12.51- 343.60
	Mean	338.23	205.38	127.92	215.05	175.28	121.16	150.56	112.07	95.03
Zn	Range	46.51- 865.44	46.08- 503.78	44.75- 475.02	42.55- 398.62	38.08- 539.09	39.59- 654.79	39.16- 483.06	34.78- 418.22	32.16- 425.49
	Mean	276.75	200.30	157.69	150.38	148.90	140.29	161.53	133.06	114.62
		number of samples = 18			number of samples = 15			number of samples = 16		

TABLE 1b

TRACE METAL CONCENTRATIONS IN SOILS ON PARALLEL TRAVERSES OF THE COEUR D'ALENE RIVER
(Values in ug/g)

KOOTENAI COUNTY

		One Mile (1.6 km) Traverses			Two Mile (3.2 km) Traverses			Three Mile (4.8 km) Traverses		
Depth	(cm)	0-5	5-10	10-15	0-5	5-10	10-15	0-5	5-10	10-15
	(in)	0-2	2-4	4-6	0-2	2-4	4-6	0-2	2-4	4-6
Cd	Range	0.24-4.71	0.26-2.55	0.25-1.78	0.72-3.80	0.69-2.41	0.24-1.77	0.48-3.21	0.56-1.80	0.43-1.26
	Mean	1.99	1.13	0.92	1.66	1.27	1.02	1.40	1.08	0.95
Cu	Range	7.96-17.64	7.79-17.72	0.26-18.52	7.71-17.31	7.39-15.40	7.96-15.93	6.05-22.83	7.34-23.08	6.88-24.52
	Mean	12.78	12.61	11.37	11.74	11.29	11.70	13.97	14.75	15.12
Pb	Range	30.34-231.81	9.98-211.17	9.90-113.40	19.90-474.20	10.78-284.38	4.98-278.22	14.52-135.72	11.26-92.53	6.70-85.13
	Mean	82.88	57.90	36.96	80.77	55.43	48.22	60.57	40.16	30.66
Zn	Range	34.03-206.37	36.05-195.08	33.86-126.86	24.13-215.29	22.94-141.71	23.30-157.58	28.31-148.40	35.61-335.03	38.69-125.92
	Mean	111.76	91.51	72.36	94.61	72.02	66.10	73.63	84.58	65.14
		number of samples = 16			number of samples = 14			number of samples = 18		

distance from Coeur d'Alene River at a greater rate than their counterparts in Kootenai County as indicated by the larger values for the ratios (a ratio equal to unity would indicate no difference in trace metal concentration between the surface soils at one mile and two or three miles from the river). The reason for this difference is that the Bunker Hill Company smelting complex, located between Kellogg and Smelterville, is less than one mile (1.6 km) from the Coeur d'Alene River and its emissums increase the soil trace metal contents there.

Table 2 lists the average trace metal concentrations for Shoshone County, Kootenai County, the Kellogg-Smelterville study area, and the Riverbank/Floodplains soils. The table shows that the trace metal concentrations of the Kellogg-Smelterville area initially decrease with depth much more rapidly than do those of the other study areas. The ratios for the soil trace metal concentration means at specified depths from the Table 2 data sets are:

Ratios of Table 2 Soil Trace Metal Concentrations Means by Depth

	Shoshone County					Kootenai County				
Depth Ratios	Cd	Cu	Pb	Zn	Ave	Cd	Cu	Pb	Zn	Ave
0-5 cm/5-10 cm (0-2 in/2-4 in)	1.43	1.02	1.45	1.24	1.29	1.45	0.99	1.46	1.11	1.25
5-10 cm/10-15 cm (2-4 in/4-6 in)	1.08	1.19	1.44	1.17	1.22	1.20	1.01	1.34	1.23	1.19
0-5 cm/10-15 cm (0-2 in/4-6 in)	1.55	1.23	2.08	1.45	1.58	1.74	1.00	1.96	1.36	1.52

TABLE 2+

TRACE METAL CONCENTRATIONS IN SOIL OF: (A) SHOSHONE COUNTY, (B) KOOTENAI COUNTY, (C) KELLOGG-SMELTERVILLE, AND (D) RIVERBANK/FLOODPLAINS

(Values in ug/g)

(A) SHOSHONE COUNTY*

Depth	(cm)	0-5	5-10	10-15
	(in)	0-2	2-4	4-6
Cd	Range	0.47-23.77	0.50-13.97	0.01-15.28
	Mean	3.73	2.60	2.41
Cu	Range	6.96-64.37	5.76-77.82	2.53-47.08
	Mean	20.50	19.88	16.65
Pb	Range	17.55-1565.47	12.26-1147.28	12.24-698.76
	Mean	241.22	166.49	115.78
Zn	Range	39.16-865.44	34.78-539.09	32.16-654.79
	Mean	201.97	163.36	139.18

number of samples = 49

(B) KOOTENAI COUNTY*

Depth	(cm)	0-5	5-10	10-15
	(in)	0-2	2-4	4-6
Cd	Range	0.24-4.71	0.26-2.55	0.24-1.78
	Mean	1.67	1.15	0.96
Cu	Range	6.05-22.83	7.34-23.08	0.26-24.52
	Mean	12.95	13.06	12.90
Pb	Range	14.52-474.20	9.98-284.38	4.98-278.22
	Mean	73.75	50.42	37.66
Zn	Range	24.13-215.29	22.94-335.03	23.30-157.58
	Mean	92.41	83.46	67.86

number of samples = 48

+Continued on following page.

TABLE 2 CONTINUED

TRACE METAL CONCENTRATIONS IN SOIL OF: (A) SHOSHONE COUNTY, (B) KOOTENAI COUNTY, (C) KELLOGG-SMELTERVILLE, AND (D) RIVERBANK/FLOODPLAINS

(Values in ug/g)

(C) KELLOGG-SMELTERVILLE

Depth (cm) (in)		0-5 0-2	5-10 2-4	10-15 4-6
Cd	Range	0.76- 74.45	0.50- 122.22	0.29- 28.85
	Mean	12.54	9.77	6.42
Cu	Range	10.15- 816.77	3.99- 229.98	3.70- 230.16
	Mean	70.46	27.85	25.73
Pb	Range	11.42 18992.98	9.62- 8567.51	0.86- 9739.20
	Mean	2452.35	737.56	566.44
Zn	Range	40.60- 3752.25	14.09- 4361.62	21.21- 3664.35
	Mean	703.63	382.55	328.20

number of samples = 58

(D) RIVERBANK/FLOODPLAINS

Depth (cm) (in)		0-5 0-2	5-10 2-4	10-15 4-6
Cd	Range	2.72- 44.77	2.04- 59.84	1.27- 68.77
	Mean	20.09	19.16	18.65
Cu	Range	10.87- 276.74	9.70- 272.80	8.83- 273.47
	Mean	101.31	99.43	100.99
Pb	Range	114.14- 8542.69	63.81- 9673.07	48.14- 10441.53
	Mean	3465.26	3413.20	3614.09
Zn	Range	92.15- 5771.50	81.68- 7937.67	62.58- 8372.74
	Mean	2451.73	2380.88	2477.19

number of samples = 20

*Note: These data are computed without the values for the riverbank/floodplains samples included. The riverbank/floodplains samples are located at sample sites 4, 17, 24, 31, 38, 45, 52, 59, 66, 67, 73, 80, 87, 94, 108, 115, 122, 129, 136, and 143 (Figure 2). The values for those sites are listed because they are not true soils, but are sediments, and because their high concentrations would overshadow the contaminated soil sites, making those sites appear disproportionately small.

Ratios of Table 2 Continued

	Kellogg-Smelterville					Riverbank/Floodplains				
Depth Ratios	Cd	Cu	Pb	Zn	Ave	Cd	Cu	Pb	Zn	Ave
0-5 cm/5-10 cm (0-2 in/2-4 in)	1.28	2.53	3.32	1.84	2.24	1.05	1.02	1.02	1.03	1.03
5-10 cm/10-15 cm (2-4 in/4-6 in)	1.52	1.08	1.30	1.17	1.27	1.03	0.98	0.94	0.96	0.98
0-5 cm/10-15 cm (0-2 in/4-6 in)	1.95	2.74	4.33	2.14	2.79	1.08	1.00	0.96	0.99	1.01

Within the Kellogg-Smelterville area, aerial fallout from the Bunker Hill Company smelter emissions accumulates sufficiently rapidly that the surface layer becomes enriched with high concentrations of trace metals. The barren hillsides in this locale preclude the possibility of a biogeochemical gradient as an explanation of those surface layer concentrations.

The steep, narrow South Fork (Shoshone County) Valley is prone to temperature inversions, trapping the smelter emissions. The Kellogg-Smelterville area is, in general, the most acutely affected by the trapped emissions because of the location of the smelting complex. However, prevailing northwesterly winds and the funneling action of the topography do have a long term influence on the distribution of the emissions, by displacing the air mass slightly eastward (Canney, 1959).

Figures 4 to 7 are plots of the trace metal concentrations of soils on traverses one, two, and three miles (1.6, 3.2, and 4.8 km) north and south of the Coeur d'Alene River. The displacement of the air mass is seen to have northernly and southernly components because of the deep gorges between the east-west aligned mountain peaks. It is readily

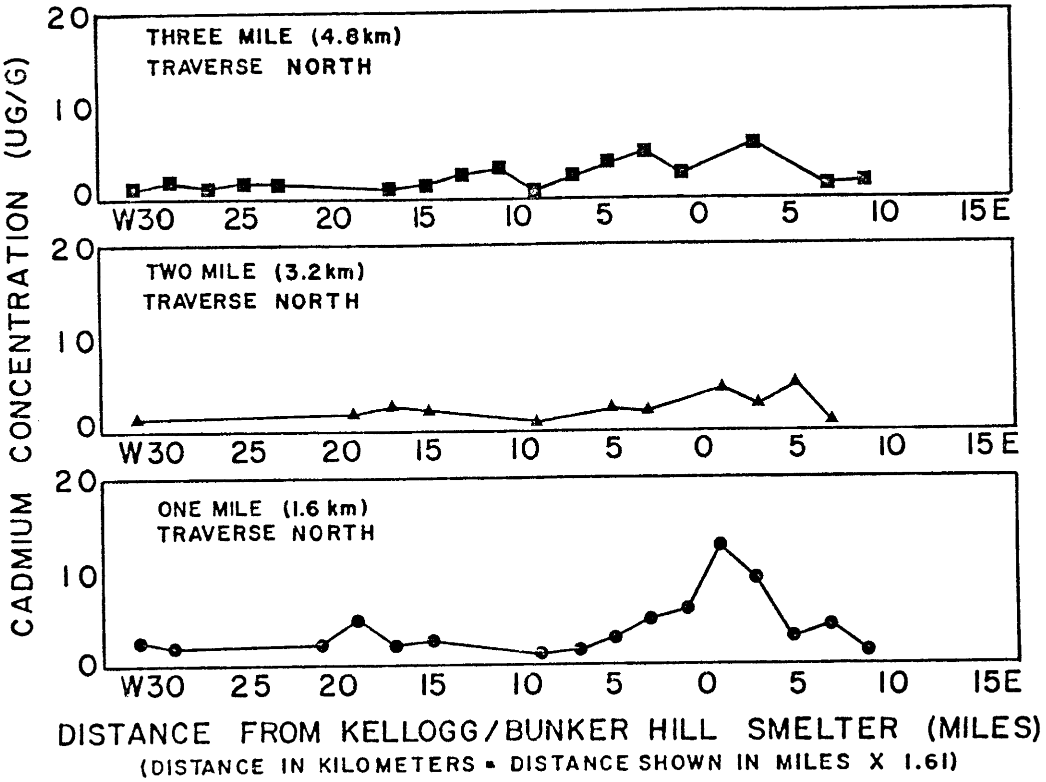

Figure 4 (a). Distribution of Cadmium in Soils Located on Traverses One, Two, and Three Miles (1.6, 3.2, and 4.8 km) North of Coeur d'Alene River.

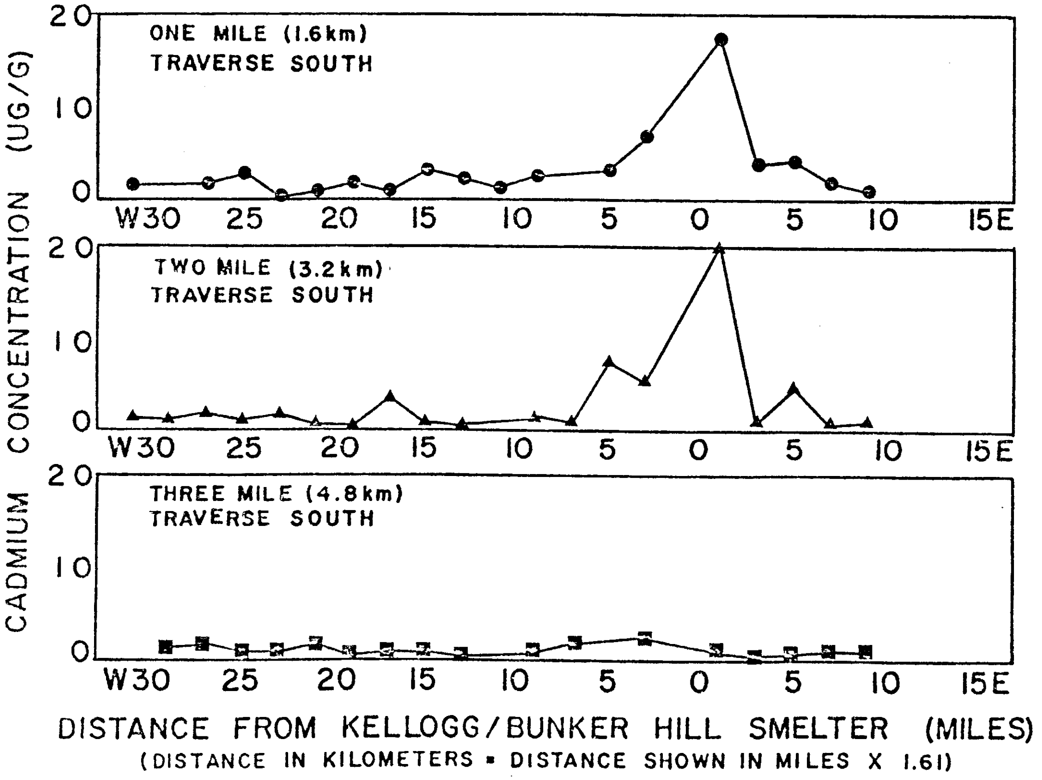

Figure 4 (b). Distribution of Cadmium in Soils Located on Traverses One, Two, and Three Miles (1.6, 3.2, and 4.8 km) South of Coeur d'Alene River.

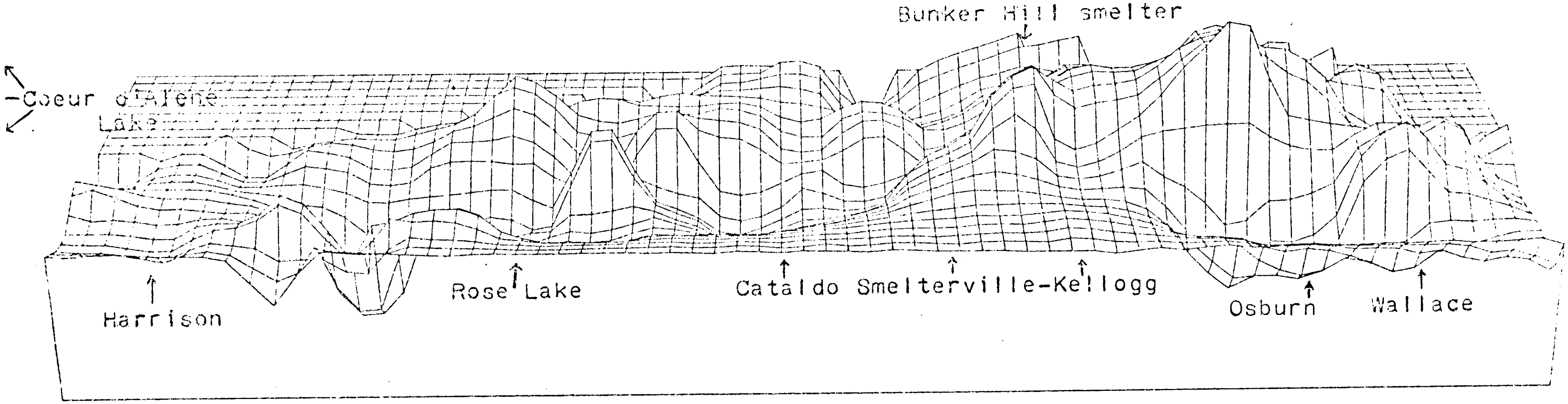

Figure 4 (c). Distribution of Cadmium in Coeur d'Alene River Valley Topsoils (Top 5 cm/2 in).

Note: The X-Y plane of the figure corresponds to the sample site location map, Figure 2. The Z axis peaks and valleys represent the logarithms of the cadmium concentrations in ppm. The table level is equal to the logarithmic mean, 1.9 ppm. The arithmetic mean is 2.7 ppm, the maximum value is 23.8 ppm, and the minimum value is 2.4 ppm. Riverbank/floodplains samples are not included.

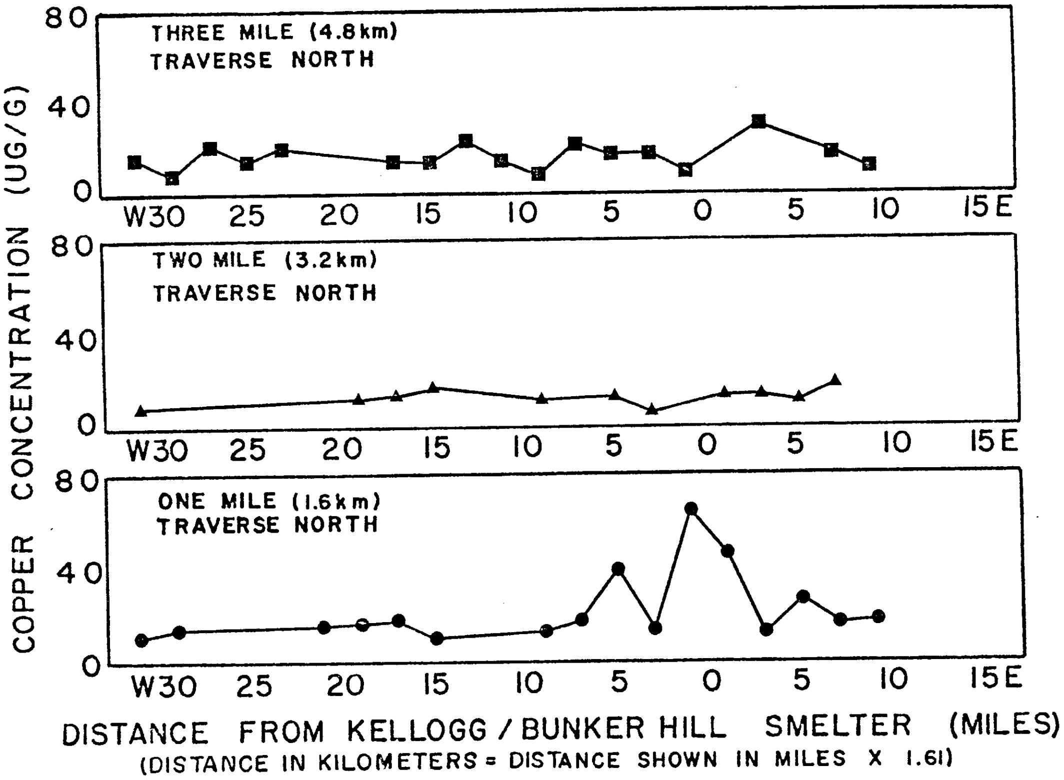

Figure 5 (a). Distribution of Copper in Soils Located on Traverses One, Two, and Three Miles (1.6, 3.2, and 4.8 km) North of Coeur d'Alene River.

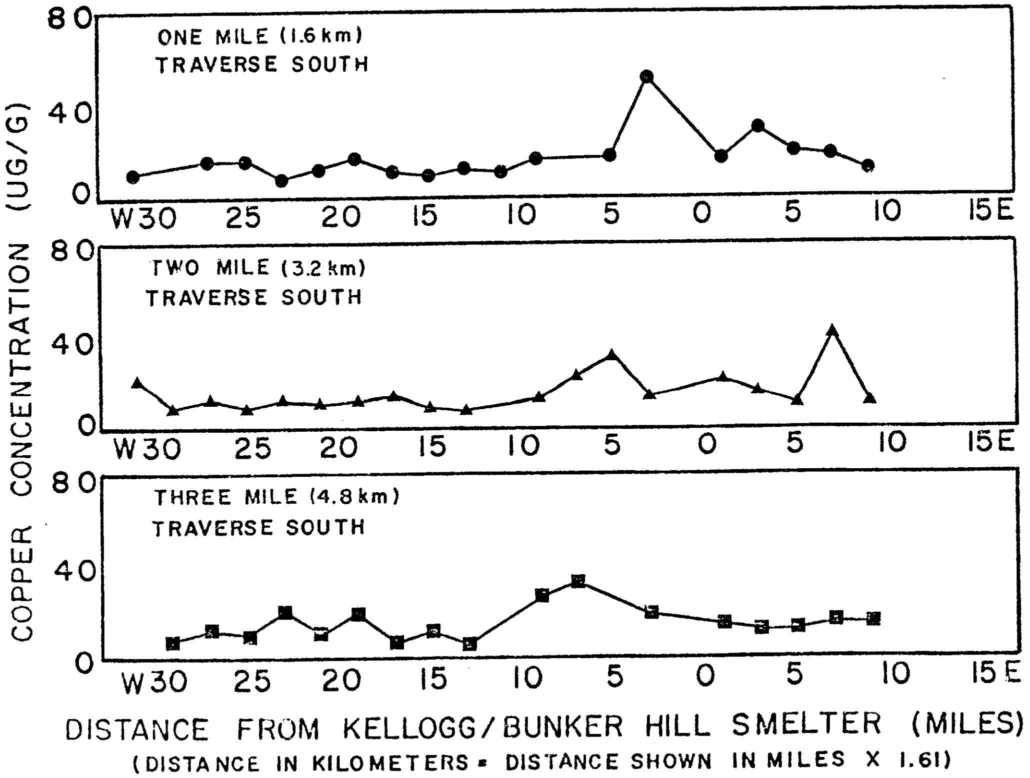

Figure 5 (b). Distribution of Copper in Soils Located on Traverses One, Two, and Three Miles (1.6, 3.2, and 4.8 km) South of Coeur d'Alene River.

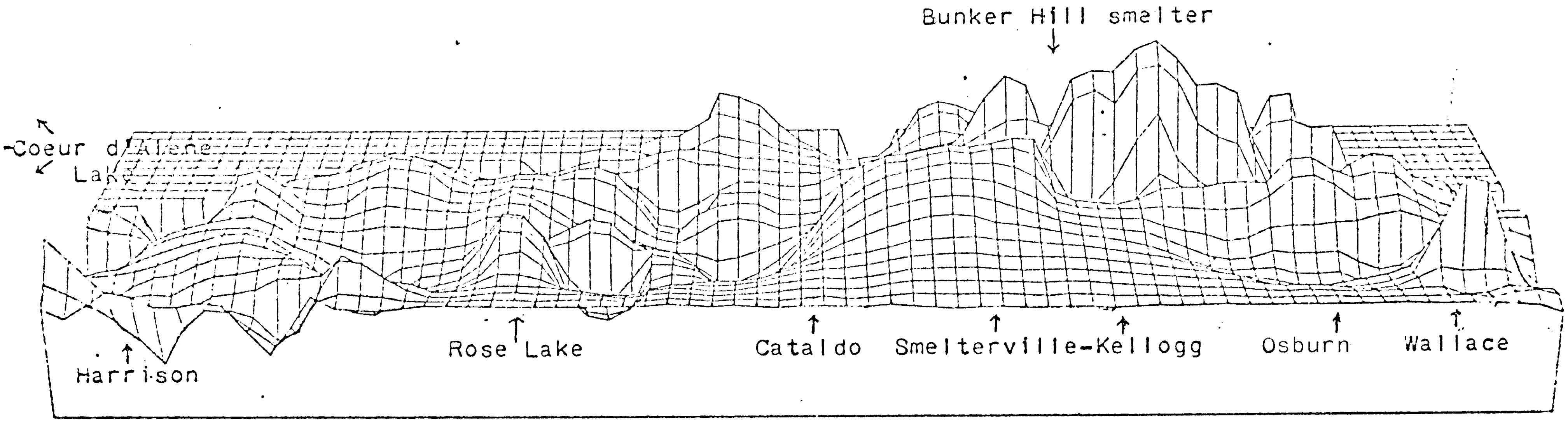

Figure 5 (c). Distribution of Copper in Coeur d'Alene River Valley Topsoils (Top 5 cm/2 in).

Note: The X-Y plane of the figure corresponds to the sample site location map, Figure 2. The Z axis peaks and valleys represent the logarithms of the copper concentrations in ppm. The table level is equal to the logarithmic mean, 14.9 ppm. The arithmetic mean is 16.6 ppm, the maximum value is 64.4 ppm, and the minimum value is 6.05 ppm. Riverbank/floodplains samples are not included.

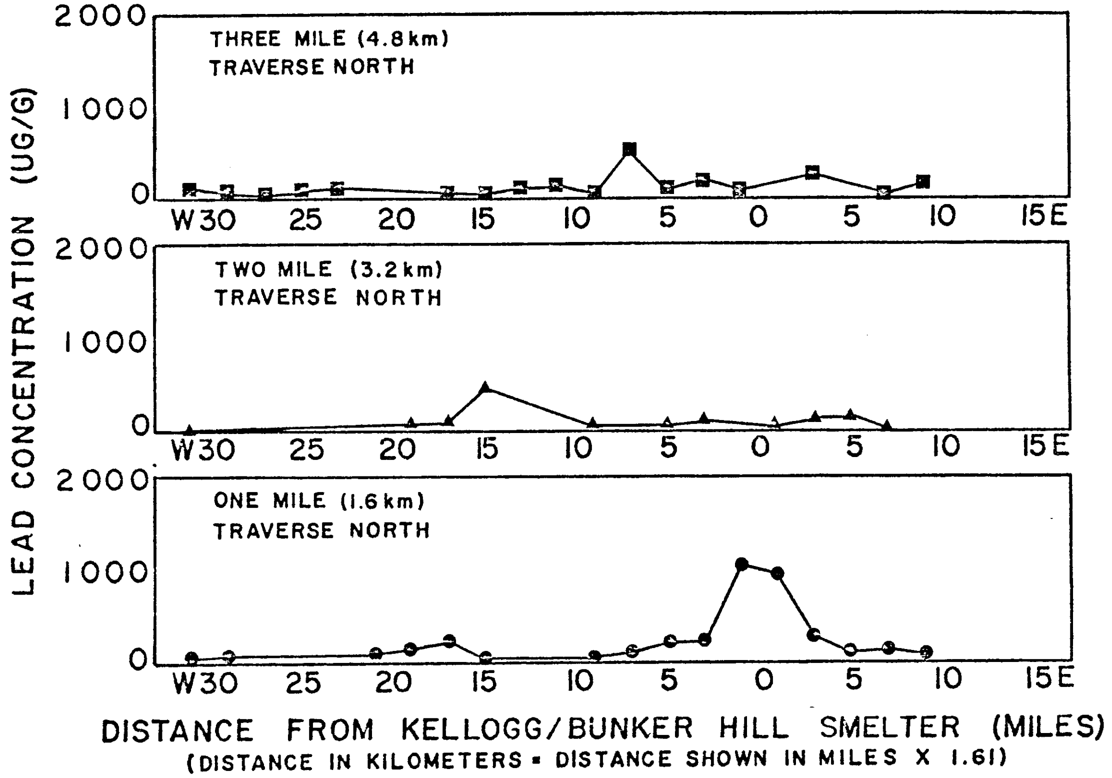

Figure 6 (a). Distribution of Lead in Soils Located on Traverses One, Two, and Three Miles (1.6, 3.2, and 4.8 km) North of Coeur d'Alene River.

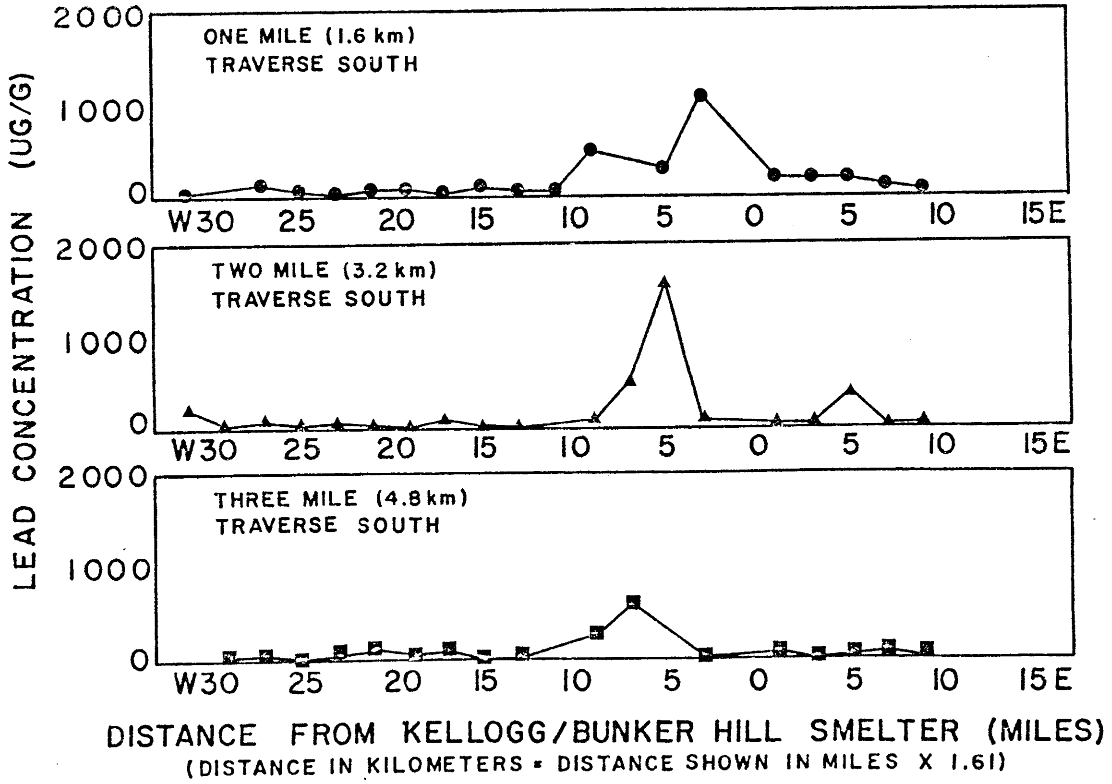

Figure 6 (b). Distribution of Lead in Soils Located on Traverses One, Two, and Three Miles (1.6, 3.2, and 4.8 km) South of Coeur d'Alene River.

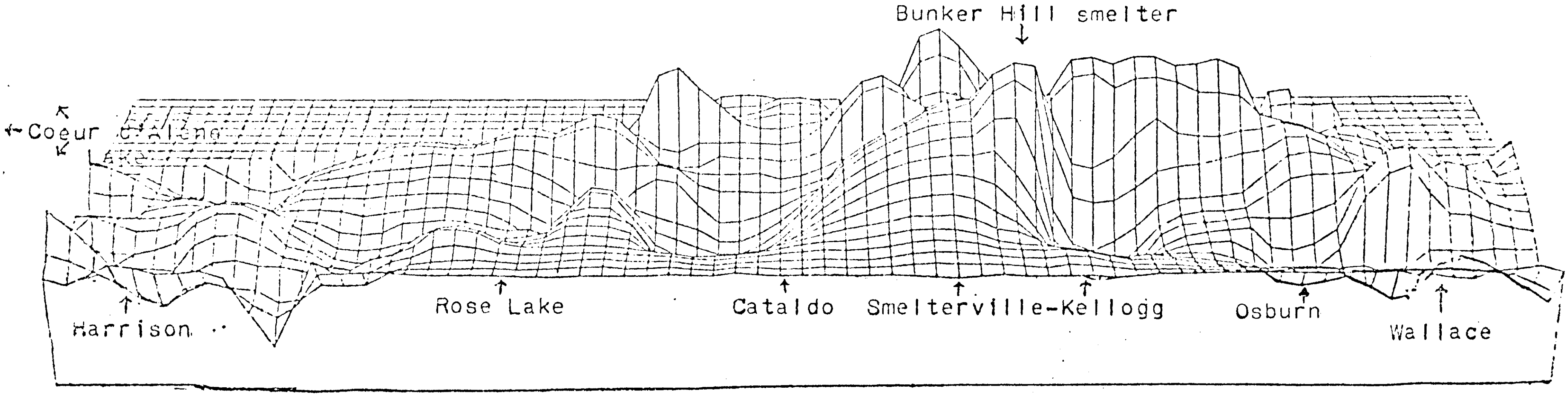

Figure 6 (c). Distribution of Lead in Coeur d'Alene River Valley Topsoils (Top 5 cm/2 in).

Note: The X-Y plane of the figure corresponds to the sample site location map, Figure 2. The Z axis peaks and valleys represent the logarithms of the lead concentrations in ppm. The table level is equal to the logarithmic mean, 85.7 ppm. The arithmetic mean is 156.6 ppm, the maximum value is 1,565.5 ppm, and the minimum value is 14.5 ppm. Riverbank/floodplains samples are not included.

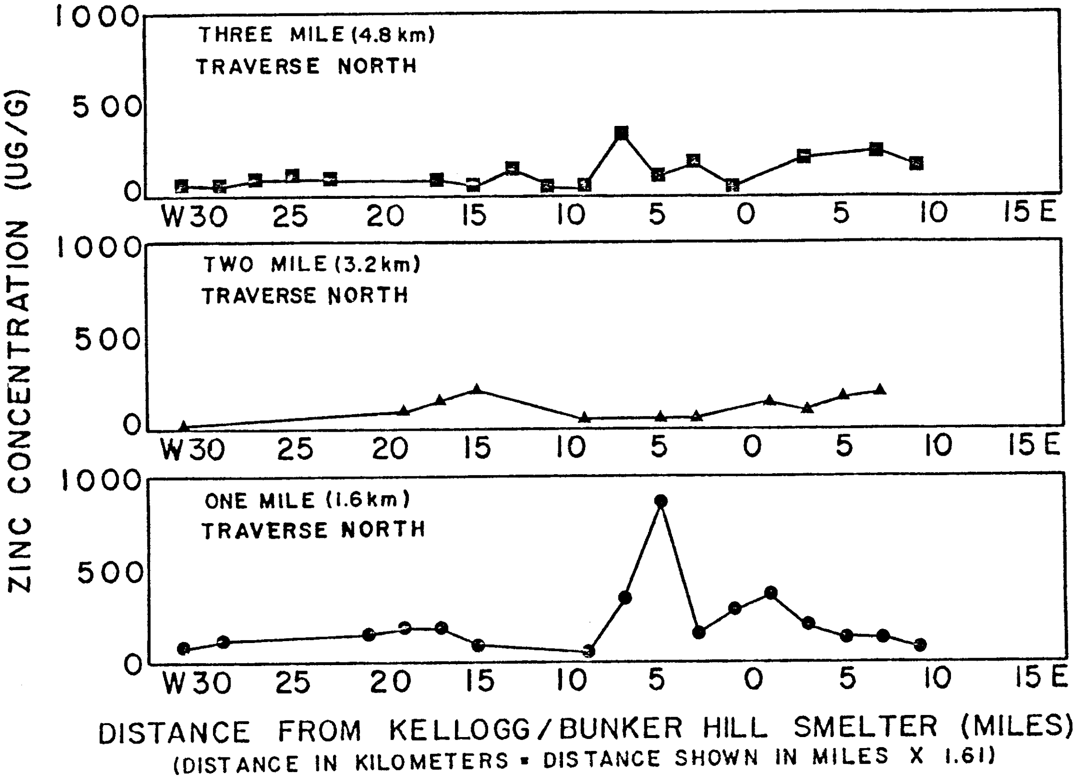

Figure 7 (a). Distribution of Zinc in Soils Located on Traverses One, Two, and Three Miles (1.6, 3.2, and 4.8 km) North of Coeur d'Alene River.

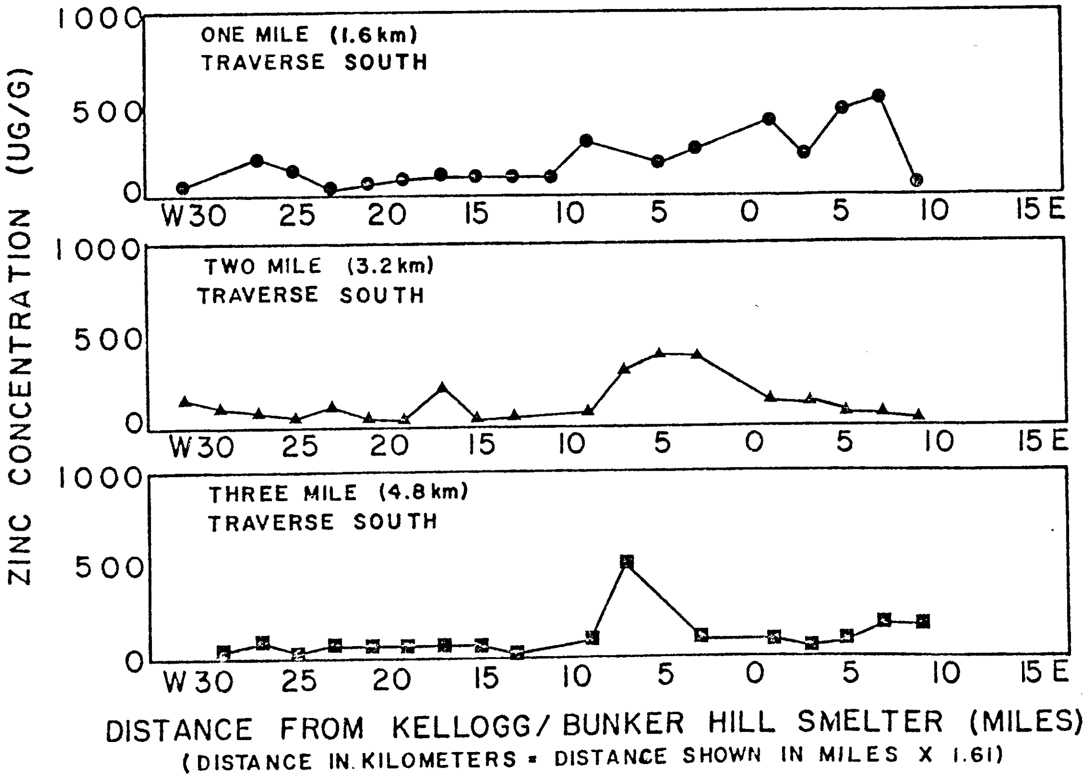

Figure 7 (b). Distribution of Zinc in Soils Located on Traverses One, Two, and Three Miles (1.6, 3.2, and 4.8 km) South of Coeur d'Alene River.

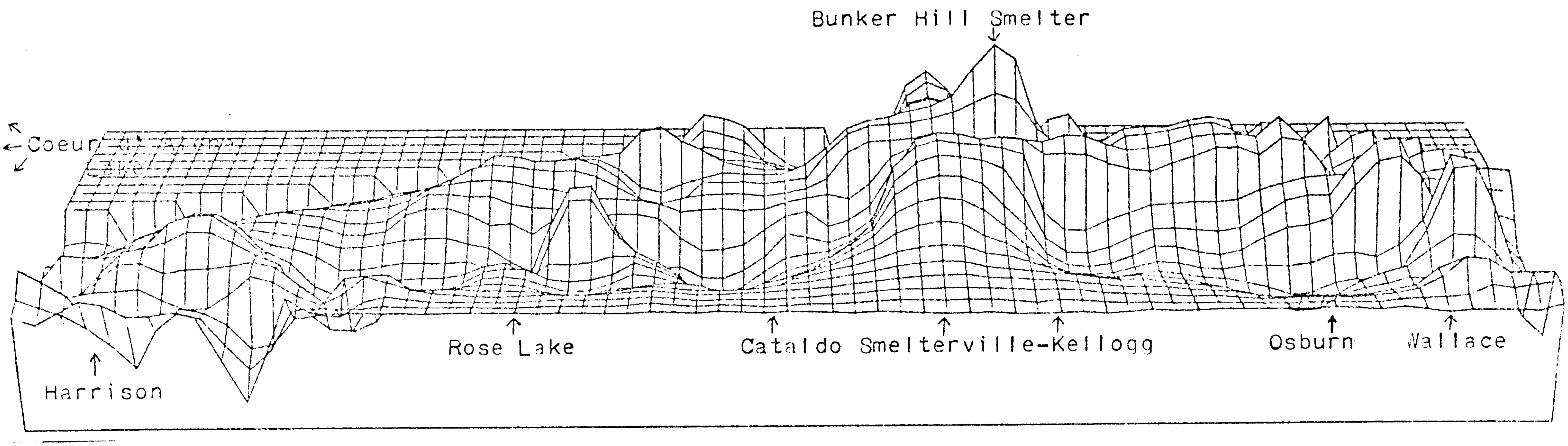

Figure 7 (c). Distribution of Zinc in Coeur d'Alene River Valley Topsoils (Top 5 cm/2 in).

Note: The X-Y plane of the figure corresponds to the sample site location map, Figure 2. The Z axis peaks and valleys represent the logarithms of the zinc concentrations in ppm. The table level is equal to the logarithmic mean, 112.3 ppm. The arithmetic mean is 147.7 ppm, the maximum value is 865.4 ppm, and the minimum value is 24.13 ppm. Riverbank/floodplains samples are not included.

apparent from these illustrations that trace metal concentrations decrease as a function of increasing distance away from the Bunker Hill Company smelting complex.

The data just discussed were collected during the summer months of 1975. This author conducted a follow-up study during the summer months of 1976 in order to verify these findings. The soils at the one mile (1.6 km) traverses were again collected and analyzed by the same methodologies as in the original study. Figures 8 to 11 are typical of comparisons between the 1975 and 1976 findings; they indicate that the 1976 data generally support the distribution of trace metals determined in the 1975 study.

Other studies have agreed with the interpretation of the decreasing trace metal concentrations with increasing soil depth as an indicator of aerial deposition (Ragaini and others, 1977 and Yankel, Von Lindern, and Walter, 1977). Ragaini and others (1977) point out that the largest active source of contamination is not wind blown tailings pile dusts but is actually the airborne emissions from the smelting complex. Aerosol enrichment factors above contributions from local resuspended soils were found to be 4100 for Cd, 110 for Pb, and 60 for Zn. The ratios of average surface soil concentrations at contaminated sites to average surface soil concentrations at background sites were found to be 5.6 for Cd, 9.4 for Pb, and 8.5 for Zn. However, the data presented by Ragaini and others are in slight disagreement with the distribution of contamination presented here. They list what this author believes are elevated background values because their control sites (Pinehurst and Osborn) are

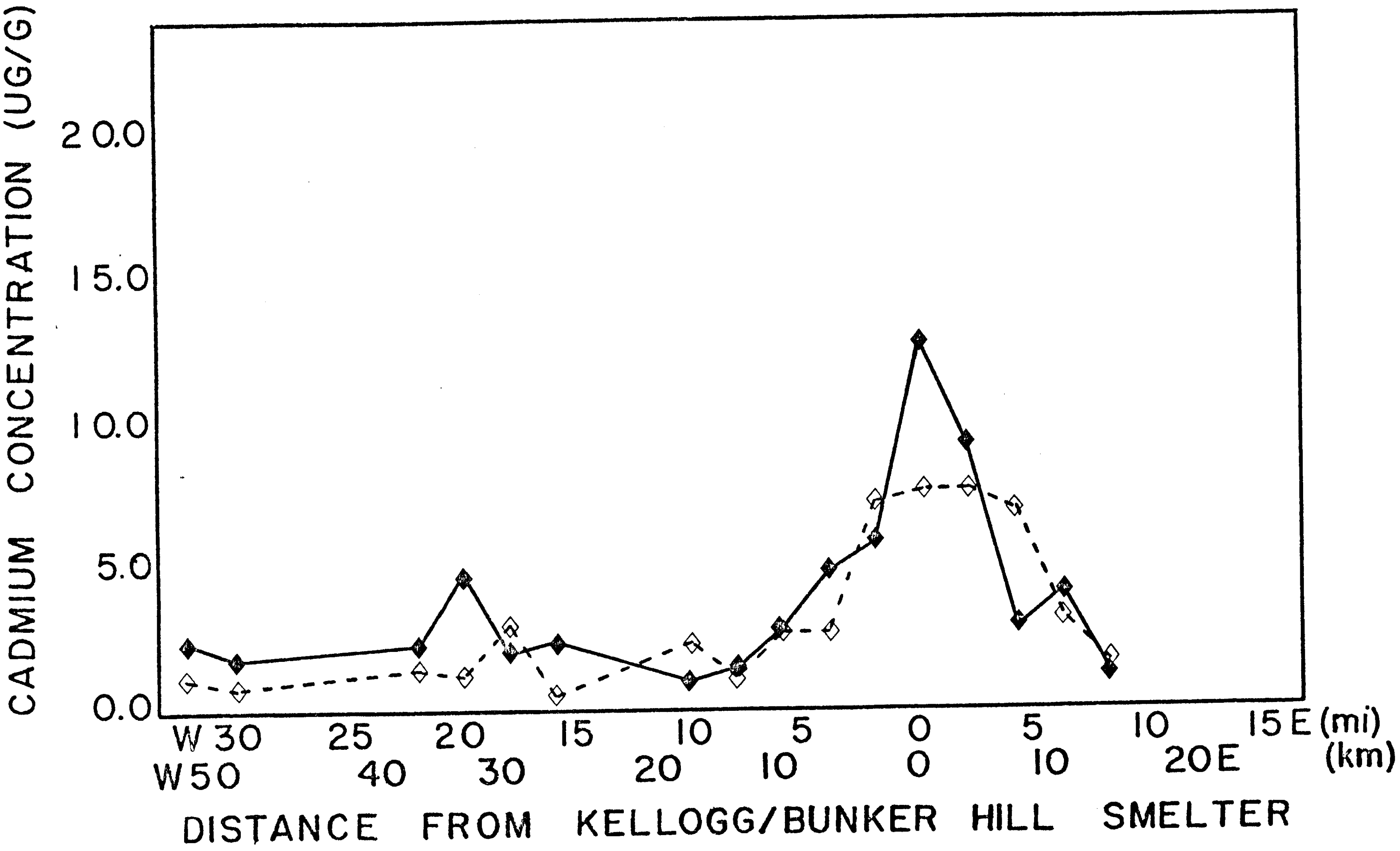

Figure 8. Cadmium in Surface Soils (Top 5 cm/2 in) at Sampling Sites Located One Mile (1.6 km) North of Coeur d'Alene River (Solid Line--1975, Dash Line--1976).

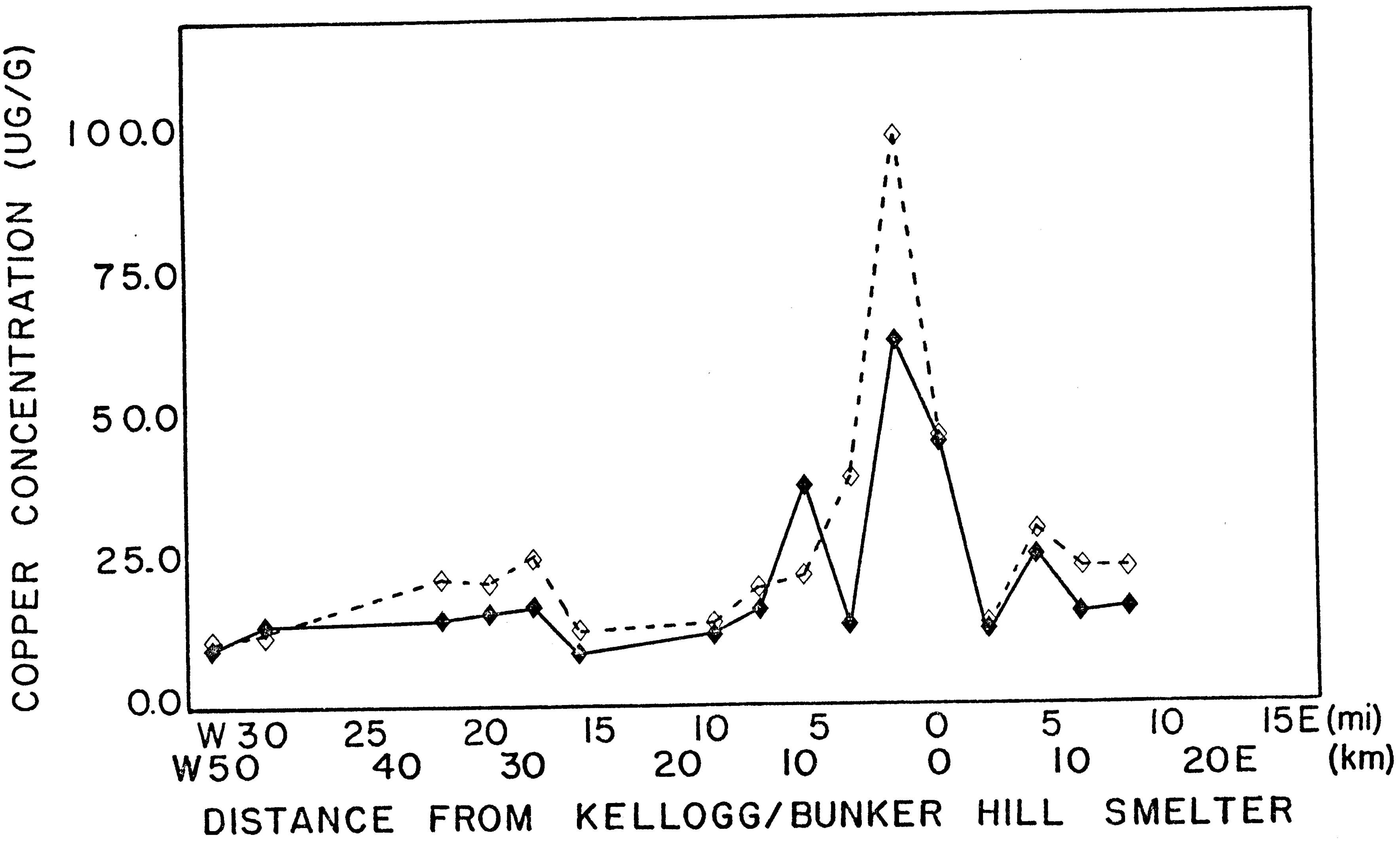

Figure 9. Copper in Surface Soils (Top 5 cm/2 in) at Sample Sites Located One Mile (1.6 km) North of the Coeur d'Alene River (Solid Line--1975, Dash Line--1976).

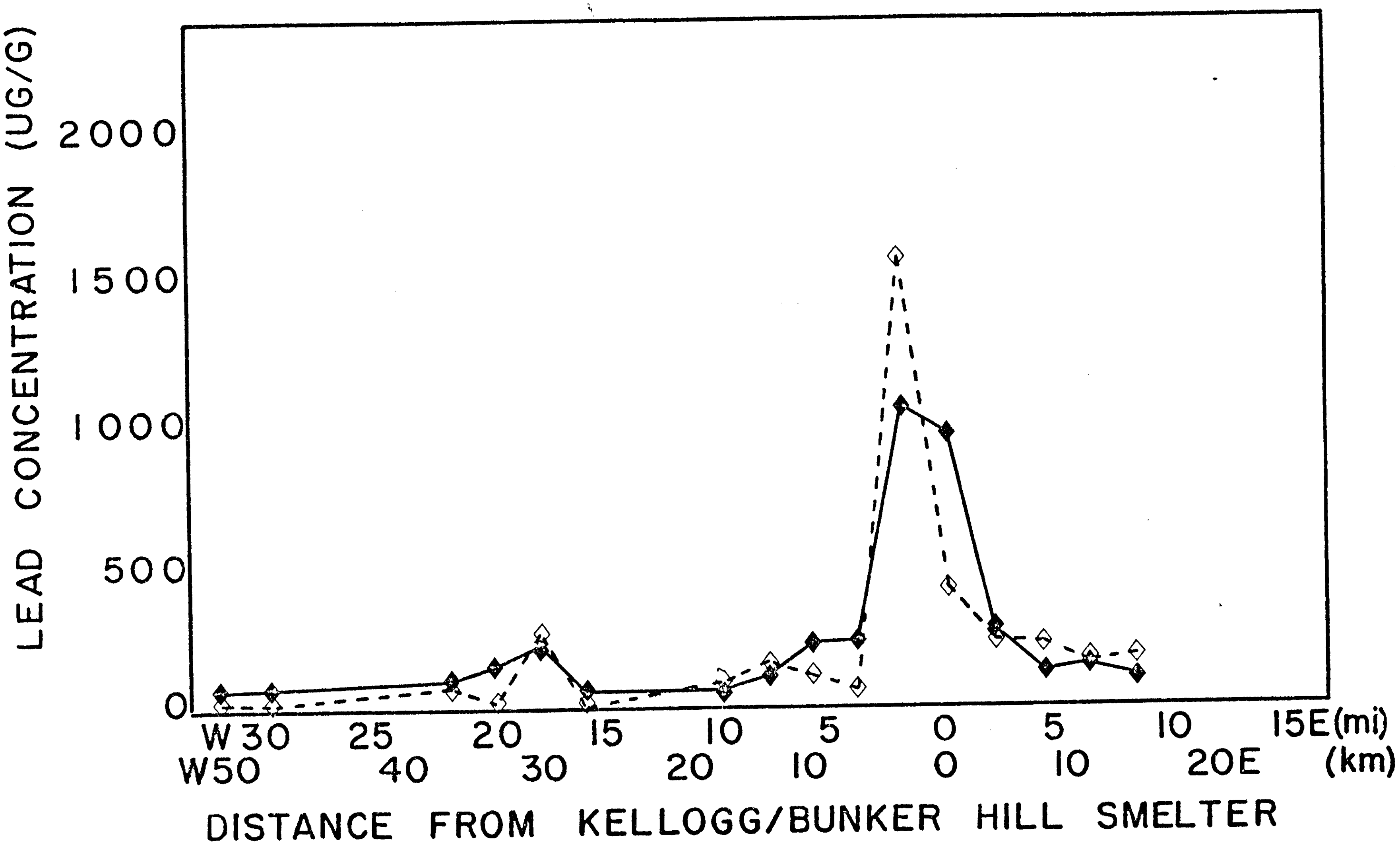

Figure 10. Lead in Surface Soils (Top 5 cm/2 in) at Sample Sites Located One Mile (1.6 km) North of Coeur d'Alene River (Solid Line--1975, Dash Line--1976).

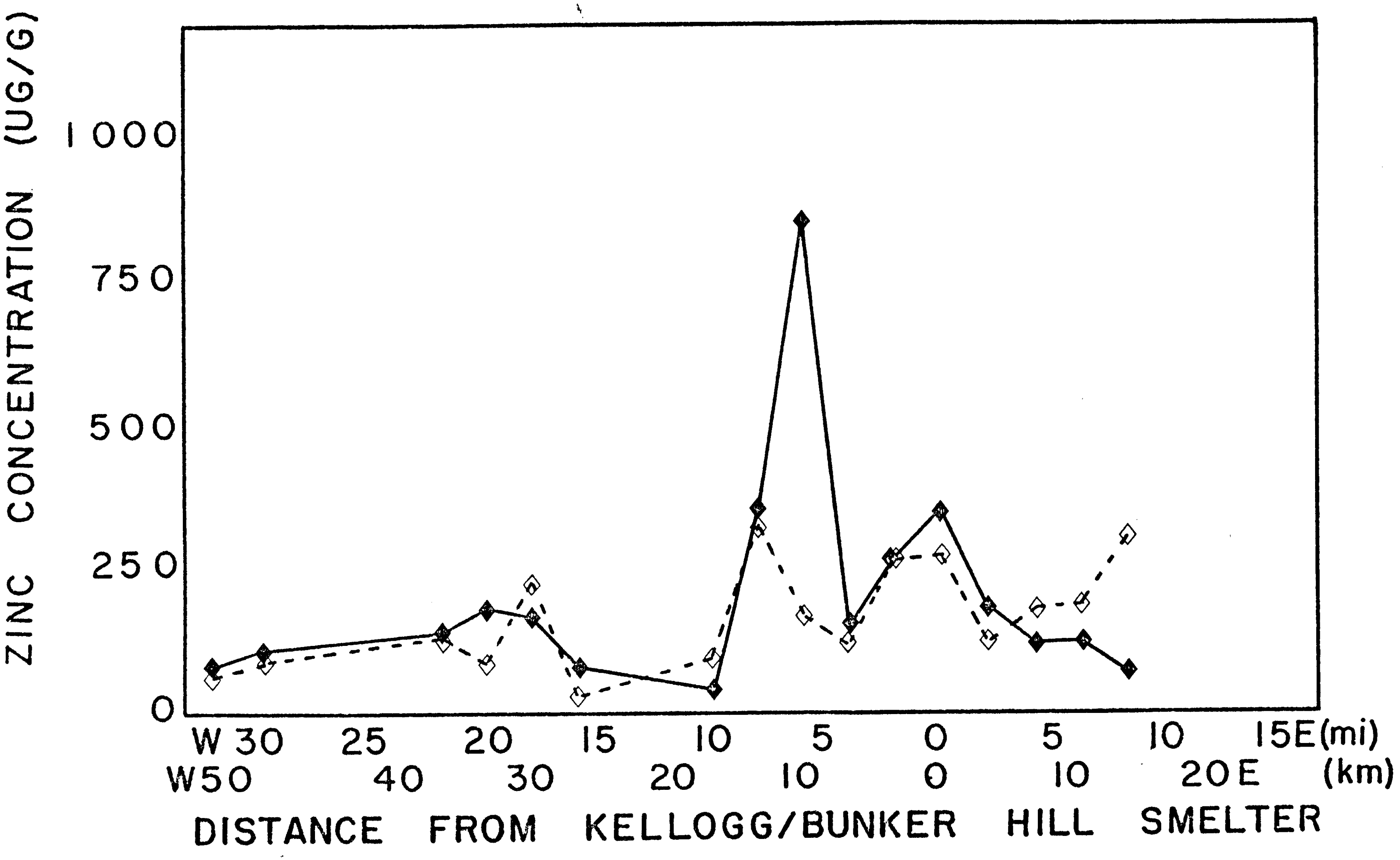

Figure 11. Zinc in Surface Soils (Top 5 cm/2 in) at Sample Sites Located One Mile (1.6 km) North of Coeur d'Alene River (Solid Line--1975, Dash Line--1976).

within the aerial fallout pattern of the smelting complex near Kellogg, Idaho, according to the data presented in this study.

This discussion should not be taken to imply that other trace metal contamination sources (point source-discharge sites, and non-point source--tailings and sediments) have not contributed significantly to the elevated trace metal concentrations in the soils, plants, and waters of the Coeur d'Alene Mining District and Coeur d'Alene River riverbed and floodplains. Simply put, the magnitude and distribution of the trace metal contamination from the smelter emissions are of more widespread effect. The smelter stacks are transitional point sources; that is, the smelter emissions start as point source discharges (primary atmospheric contaminants) but have secondary interactions (deposition by convective and diffusion transport) with the soils and waters of the local environment.

Such contaminated soils could result in human consumption of contaminated garden vegetables. Studies of garden vegetables, grasses, and grain grown under controlled greenhouse conditions in soils taken from the Coeur d'Alene Mining District sampling sites show the trace metal uptake and growth effects to vary from plant to plant (Tables 3 and 4). All of the plants grown in contaminated soils were found to have elevated trace metal concentrations, and differed only in the degree of trace metal uptake. Each species responds differently to the trace metals. Enrichment factors and growth are determined by the plants abilities to void specific metals and accumulate others. The interaction of contaminated soils with available vadose water apparently provides the opportunity for uptake of trace metals by the plants.

TABLE 3

UPTAKE OF TRACE METALS BY PLANTS GROWN IN KELLOGG, CATALDO, AND MOSCOW SOILS UNDER CONTROLLED GREENHOUSE ENVIRONMENT

(Values in ug/g)

	Cadmium	Copper	Lead	Zinc
Tomatoes				
Kellogg	20.6	34.1	25.8	544.0
Cataldo	0.4	11.5	10.3	271.0
Moscow	0.6	4.0	3.1	15.7
number of samples = 5 per soil				
Wheat				
Kellogg	5.5	36.8	5.8	123.0
Cataldo	2.5	6.7	4.9	118.0
Moscow	0.4	5.3	1.8	16.6
number of samples = 5 six-inch diameter pots per soil				
Soil*				
Kellogg	3.9	26.4	402.0	382.0
Cataldo	3.7	24.9	377.0	308.0
Moscow	1.2	14.8	14.8	19.4
number of samples = 5 per soil				

*Metal contents of the soils before the vegetables were planted. The soils were taken at a depth of 0-1.5 feet (0-0.45 meters) from the specified locations. The control soil sample was taken at the University of Idaho farms, Moscow, Idaho. Values represent the trace metal determinations made on the edible portions of the plants after digestion with HNO_3 and HBF_4, and on the -80 fraction of soil after HNO_3 digestion.

TABLE 4

AVERAGE MAXIMUM GROWTH OF SELECTED PLANTS GROWN IN OSBURN, KELLOGG, AND MOSCOW SOILS UNDER CONTROLLED GREENHOUSE ENVIRONMENT

(Heights in cm)

	Alfalfa	Spring Wheat	Peas
Osburn	4.5	28.0	36.0
Kellogg	12.0	25.0	32.0
Moscow	27.5	24.0	70.0

number of samples = 5 six-inch diameter pots per soil

Conclusions

The concentrations of trace metal contaminants in soils along the South Fork of the Coeur d'Alene River (Shoshone County, Idaho) decrease with increasing distance away from the Bunker Hill Company smelting complex near Kellogg, Idaho. The rapid decreases of trace metal concentrations with increasing depth in the Kellogg-Smelterville area soils indicate an accumulation of aerial fallout containing high concentrations of trace metals. Contamination in soils along the Main Stem of the Coeur d'Alene River appears to be limited to the riverbanks and floodplains, which are primarily contaminated with tailings-type sediments due to industrial waste discharges. The trace metal concentrations of these soils have been shown to have an adverse effect on the trace metal [illegible] concentrations and growth of selected vegetables and crops.

CHAPTER THREE

SOLUBILIZATION OF TRACE METALS FROM CONTAMINATED SOILS

The solubilization experiments will be discussed in the following manner: the methodologies, being identical for all four soils, will be presented in their entirety first. The data sets for each of the four soils will then be interpreted in turn. Finally, a summary of these four data sets will be given at the chapter closing.

Methodologies

These solubilization studies revolved around the investigation of four topics. The desired information was (1) the kinetics of solubilization and the equilibrium concentrations of solubilized trace metals, (2) the effects of agitated (stream simulation) and static (aquifer simulation) soil solutions on the solubilization process, (3) the effect of soil characteristics (e.g. organic content) on the solubilization process, and (4) the effect of oven drying the sediment-like Osburn and Cataldo soils on the solubilization process (a pre-treatment concern).

Figure 12 gives the methods of sample preparation and analysis. Figure 13 is a schematic of the apparatuses used for the solubilization experiments. As will be seen the overall design of the methods and the apparatuses emphasizes an analytically "clean" experimental process. A detailed discussion of this process follows.

Sample Collection

The samples were taken from four of the same sampling sites that were used for the 1975 and 1976 soil contamination surveys in the Coeur d'Alene River valley. Each of the soils had been collected in bulk on

FIGURE 12

METHODS OF SAMPLE PREPARATION AND ANALYSIS FOR SOLUBILIZATION STUDIES

FIELD

Collection-several lbs. (Kg) sample labelled and sealed in plastic bags for transport to the laboratory

LABORATORY

Dried-105°C for several hours
Homogenized-with a porcelain mortar and pestle
Sieved-to minus eighty mesh with U.S. No. 80 Standard Sieve
Weighed-to the nearest tenth of a milligram

1g Samples

Digested-with 10 ml concentrated HNO_3

Filtered-with Whatman No. 42 filters

Diluted-to 100 ml final volume with 5%HNO_3 solution
Stored-in acid cleaned 125 ml polyethylene sample bottles
Analyzed-by atomic absorption

100g Samples

Transferred-to 1000 ml reaction flasks for the solubilization experiments
Activated-by addition of 1000 ml $18M\Omega$ H_2O and 60 sec. stirring
Sampled-removed 10 ml aliquots at selected time intervals
Filtered-the 10 ml aliquots through 0.45 micron Millipore filters
Acidified-by filtration of the aliquots into 50 ml vacuum filtration flasks containing 10 ml 10% HNO_3
Stored-in acid cleaned 30 ml polyethylene sample bottles
Analyzed-by atomic absorption

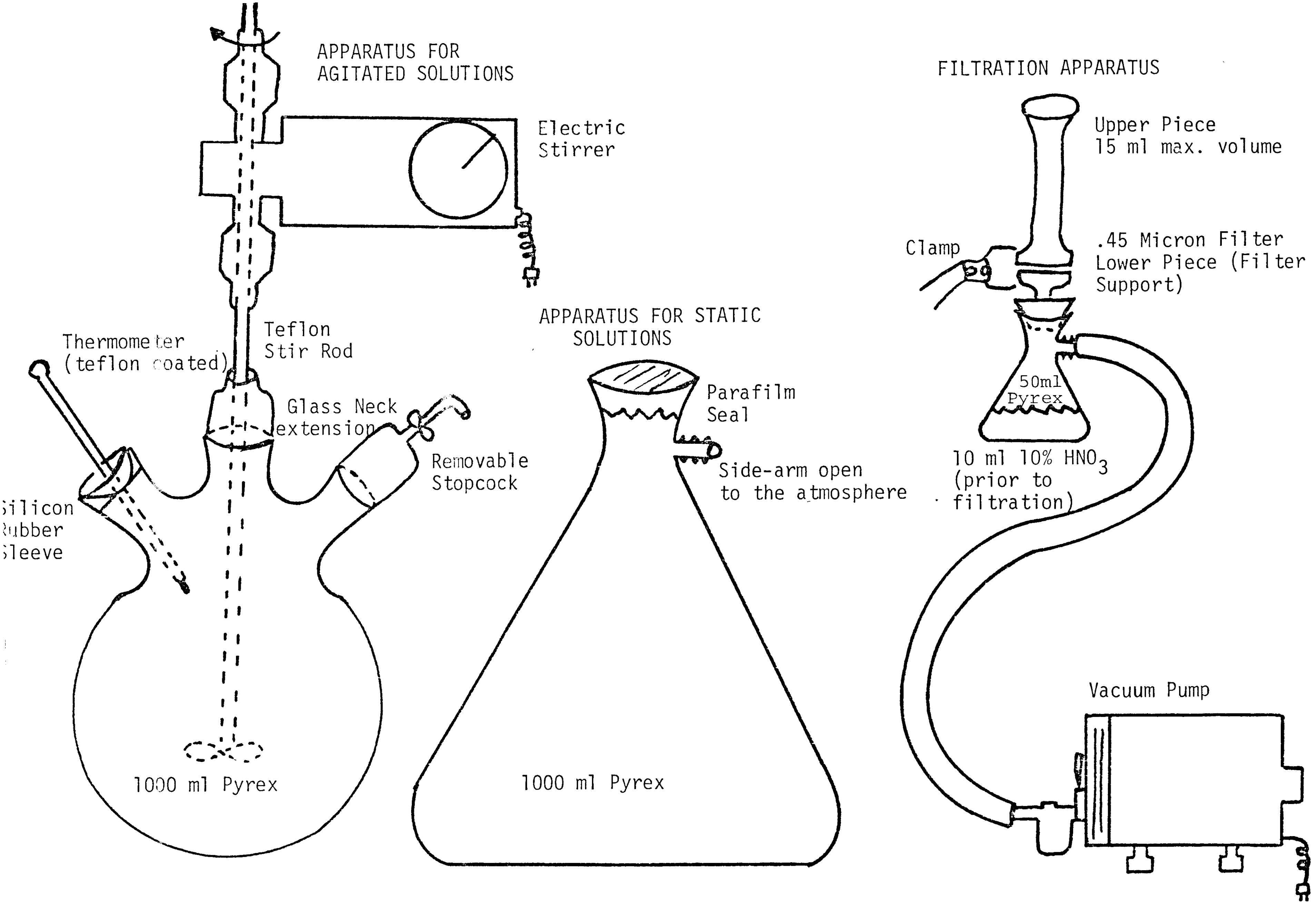

Figure 13. Schematics of Experimental Apparatuses for Solubilization Studies.

previous occasions for use in greenhouse experiments and digestion studies because each soil is representative of a general class of surface material in the Coeur d'Alene River Valley.

One of these samples was composed of topsoil from a private residence in Kellogg, Idaho (site 107, Fig. 2). That site is in a small neighborhood, Italian Gulch, approximately one and one-half miles (two kilometers) east of the Bunker Hill Co. smelter. The general quality of the soil was such that sparse grasses and small shrubs were growing in it and it appeared to have a minor amount of humus in it. Elemental analysis of the dried, sieved fraction of this soil which was used in the solubilization experiments yielded moderate carbon and nitrogen concentrations (Table 5), supporting the general classification of this soil as a humic soil. The overall texture was coarse and gravelly, but the weathered material was fine enough so that two-thirds of the soil by volume passed through an 80 mesh sieve.

A second topsoil sample came from a piece of frontage road right-of-way land just inside the west end of Smelterville, Idaho approximately one and one-half miles (two kilometers) west of the smelter (site 88, Fig. 2). The soil was supporting thick green grass and appeared to have a moderately heavy humic composition. Table 5 shows the dried, sieved fraction of this soil to have fair carbon and nitrogen concentrations, though less than those of the Kellogg soil. Approximately forty percent of this soil by volume passed an 80 mesh sieve.

The other two soils cannot appropriately be called soils. One of the two was collected from an abandoned jig tailings pile between the railroad tracks and the channel of the South Fork Coeur d'Alene River,

TABLE 5: AVERAGE CARBON AND NITROGEN CONTENTS OF OSBURN, KELLOGG, SMELTERVILLE, AND CATALDO SOILS USED IN SOLUBILIZATION STUDIES

(Values in Percent)

Soil Sample	Carbon	Nitrogen	Classification
Kellogg (dried/sieved)	3.49	0.27	humic (mod.)
Smelterville (dried/sieved)	1.33	0.11	humic (fair)
Osburn (dried/sieved)	0.43	0.16	non-humic
Osburn (native)	0.36	0.11	non-humic
Cataldo (dried/sieved)	2.47	0.00	non-humic
Cataldo (native)	2.26	0.03	non-humic

TABLE 6: AVERAGE TERMINAL pH OF SOIL SOLUTIONS IN SOLUBILIZATION STUDIES

Soil Sample	Agitated pH	Static pH	Classification
Kellogg (dried/sieved)	4.03	4.56	very acidic
Smelterville (dried/sieved)	5.84	6.27	mildly acidic
Osburn (dried/sieved)	5.37	5.74	acidic
Osburn (native)	5.11	5.27	acidic
Cataldo (dried/sieved)	7.74	7.78	mildly alkaline
Cataldo (native)	7.39	7.18	mildly alkaline

about five miles (eight kilometers) east of the smelter (site 115, Fig. 2), just outside Osburn, Idaho. The tailings were removed from a spot roughly twenty-five feet (eight meters) from the edge of the river and several feet (one meter) above the high water mark so as to have remained dry and exposed under all but severe flood conditions. They did not appear to have been sedimented by stream action and were approximately five feet (one and one-half meters) thick where sampled. Their source is unknown. Elemental analysis of the dried, sieved (-80 mesh) fraction of these tailings and of the native tailings themselves showed them to contain minimal carbon and nitrogen concentrations, so that they were classified as non-humic soils. The grains were coarse but small enough that almost eighty percent by volume passed through the -80 mesh sieve.

The other tailing type material cannot properly be described as tailings per se. It was collected from the Cataldo Flats (site 66, Fig. 2), which are five to seven miles (eight to ten kilometers) west of the smelter. The materials of which the Cataldo Flats are composed were dredged from the South Fork Coeur d'Alene River in the late 1940's because mine waste discharges (tailings/millings) had severely restricted the channel. This particular sample was chosen so that it was not in contact with the stream waters. It was composed of extremely fine grains; an estimated ninety percent by volume passed an 80 mesh sieve. It appeared to have virtually zero humic content. Nitrogen was essentially absent from both the dried, sieved fraction and the native sediments themselves; therefore, the sediments could not be classified as humic soils. However, the carbon concentrations of the dried, sieved fraction and the native sediments were very high; this is attributed to an inorganic source of carbon in the sediments, such as calcite and dolomite.

Reece (1974) found concentrations of calcite in ores of the Bunker Hill Company mine to vary from extremely high to neglegible. The tailings and mine wastes from those ores are present in the sediments of the riverbed and floodplains of the Coeur d'Alene River as evidenced by their documented occurance in the river's delta sediments (Maxfield and others, 1974a, 1974b).

Sample Preparations

Several pounds (one pound = .45 kilograms) of each soil were transported to the laboratory and dried at 105°C for several hours. The dried soils were gently homogenized by grinding with a porcelain mortar and pestle. (The individual grains are not crushed by this method. Crushing the grains, such as with a ball mill, would expose fresh surfaces and influence the solubilization process.) They were then passed through a Tyler Equivalent U.S. Standard No. 80 Sieve. The drying of these soils at 105°C conflicts with the method of preparation of similar Coeur d'Alene samples, river sediments, by Reece and others (1974). They conducted leaching (solubilization) experiments on the unmodified wet sediments. Toth and Ott (1970) had previously shown that the proper method of preparation of bottom sediments differed from the oven dry method for soils because drying reduced the amounts of exchangeable iron and manganese. They note that bottom sediments are not simply a wet sample of soil because the conditions under which they were formed (reducing) differ from those which form soils (oxidizing).

Bower and others (1952, pp. 251-261) point out that for the determinations of soluble cations that the "Soil should not have been oven-dried, as heating at 105°C converts $CaSO_4 \cdot 2H_2O$ to $CaSO_4 \cdot \frac{1}{2}H_2O$. The latter hydrate has a higher solubility in water than ordinary gypsum for an indefinite period following its solution." However, Bower's soil preparation for determination of exchangeable cations employs the oven-dried soil: "Express the results in terms of milli-equivalents of cation per 100 g of oven-dry (105°C) soil." The reference method of exchangeable cation analysis (Black, 1964) routinely incorporates oven drying of soils at 105°C as part of the recommended sample preparation. Hence, it would appear that the advantages of oven drying soils outweigh the disadvantages for the soil types investigated in this thesis.

Drying of the soils at 105°C in this investigation was therefore deemed necessary for these reasons: (1) The natural condition of these soils <u>was</u> dry as opposed to the subsurface sediments used by Reece (1974), and it has been shown that it is preferable to dry such soils at 105°C, (2) Accurate weighing of these soils and the homogenization necessary to insure unbiased replicate aliquots made drying and sieving analytically mandatory, (3) Data presented here for dried and native versions of the two sediment-like soils (Osburn and Cataldo) are not significantly different, (4) The soil preparation procedures used in this investigation were the same procedures as were used to prepare the soils in the 1975 and 1976 soil contamination surveys. Therefore, the results of experiments on these soils would be directly applicable to the 1975 and 1976 soil survey samples on a dry weight basis.

Experimental

Four 100 gram aliquots and four one gram aliquots of each soil were weighed to the nearest tenth of a milligram on a Mettler Model H6T Digital Analytical Balance. Two of the 100 gram aliquots were duplicate "agitated" solubilization samples. The other two 100g aliquots were the duplicate "static" solubilization samples. The four one gram aliquots were replicates for the determination of the trace metal concentrations of each soil by wet chemical and atomic absorption spectrophotometric (AAS) methods. One of each set of replicates was spiked with a known concentration of the analyte species in order to estimate the accuracy of the analytical methods by the regression method (Massart and others, 1978). The determinations of the other three replicates of each set were to be used to estimate the precision of the method as the relative standard deviation (Huntsberger and Billingsley, 1977). The concentrations of trace metals determined on these soils are given in Tables 7 and 8. The precision and accuracy of these analyses are given in Tables 9 and 10 respectively.

Each of the two 100g agitated solubilization samples were transferred from their respective weighing beakers into separate acid cleaned one-liter [Pyrex three-neck, round-bottom] flasks by use of a Nalgene polyethylene funnel. The three-neck, round-bottomed flasks were fitted with a thermometer (through a silicon-rubber sleeve) in one side neck, a removable stopcock in the other side neck and an [Eberbach Model Power Stir-58] electric stirrer powered teflon stir rod in the main neck (Figure 13).

TABLE 7: TRACE METAL CONCENTRATIONS FOR KELLOGG AND SMELTERVILLE SOILS

	concentrations in ug/g						
Sample	Ag	Cd	Cu	Fe	Mn	Pb	Zn
Kellogg Original	7.00	8.00	70.0	$24.4\text{x}10^3$	577	$1.38\text{x}10^3$	328
Kellogg Duplicate I	5.96	7.95	68.6	$24.0\text{x}10^3$	600	$1.35\text{x}10^3$	339
Kellogg Duplicate II	4.96	7.93	70.4	$24.4\text{x}10^3$	580	$1.36\text{x}10^3$	342
Kellogg Average	5.97	7.96	69.7	$24.3\text{x}10^3$	586	$1.36\text{x}10^3$	336
Smelterville Original	1.00	4.00	25.0	$15.3\text{x}10^3$	260	226	197
Smelterville Duplicate I	1.00	3.99	25.0	$15.0\text{x}10^3$	266	231	197
Smelterville Duplicate II	0.99	3.98	25.9	$15.1\text{x}10^3$	261	237	201
Smelterville Average	1.00	3.99	25.3	$15.1\text{x}10^3$	262	231	198

TABLE 8: TRACE METAL CONCENTRATIONS FOR OSBURN AND CATALDO TAILINGS

concentrations in ug/g

Sample	Ag	Cd	Cu	Fe	Mn	Pb	Zn
Osburn Original	43.6	33.7	364	99.4×10^3	10.9×10^3	13.7×10^3	5.74×10^3
Osburn Duplicate I	41.9	33.9	346	98.7×10^3	10.9×10^3	13.6×10^3	5.66×10^3
Osburn Duplicate II	44.8	34.8	356	100×10^3	10.8×10^3	13.7×10^3	5.77×10^3
Osburn Average	43.4	34.1	355	99.5×10^3	10.9×10^3	13.7×10^3	5.72×10^3
Cataldo Original	19.0	32.9	149	130×10^3	14.3×10^3	4.77×10^3	3.66×10^3
Cataldo Duplicate I	18.4	32.4	151	128×10^3	14.1×10^3	4.78×10^3	3.61×10^3
Cataldo Duplicate II	18.0	32.9	148	128×10^3	14.4×10^3	4.82×10^3	3.75×10^3
Cataldo Average	18.5	32.7	149	129×10^3	14.3×10^3	4.79×10^3	3.67×10^3

TABLE 9

PRECISION OF ANALYSIS FOR THE NITRIC ACID DIGESTIONS OF SOLUBILIZATION STUDY SOILS

	Relative Standard Deviation (R.S.D.) in Percent						
Sample	Ag	Cd	Cu	Fe	Mn	Pb	Zn
Kellogg Soil	17.09	0.45	1.39	0.83	2.15	1.09	2.20
Smelterville Soil	0.58	0.25	2.03	1.07	1.17	2.56	1.20
Osburn Tailings	3.32	1.74	2.47	0.87	0.15	0.60	1.02
Cataldo Tailings	2.71	0.94	1.33	0.71	0.94	0.54	1.98
Average	5.93	0.85	1.81	0.87	1.10	1.20	1.60

TABLE 10

ACCURACY OF ANALYSIS* FOR THE NITRIC ACID DIGESTION OF SOLUBILIZATION STUDY SOILS

Parameter	Ag	Cd	Cu	Pb	Zn
Regression Slope, b	1.050	0.712	0.971	0.989	0.989
Regression Intercept, a	- .014	0.340	0.038	0.377	0.132
Proportional Error	105.05%	71.23%	97.13%	98.91%	98.94%
Constant Error	-5.05%	27.95%	1.44%	0.73%	0.51%
Total Accuracy	100.00%	99.18%	98.57%	99.64%	99.45%

*Note: These data were calculated by plotting the regression of the experimentally determined spiked digestate concentrations (Yi) of the four soils against the theoretically expected digestate concentrations (Xi); where:

$$\text{Total Accuracy} = \frac{\overline{Y}}{\overline{X}} = \frac{a}{\overline{X}} + b = \text{constant and proportional error.}$$

The other two 100g aliquots, the static samples, were added by polyethylene funnel to separate acid cleaned one-liter [Pyrex side arm erlenmyer] flasks equipped with a fresh roll of Parafilm to prevent contamination by sealing the open neck, thus limiting atmospheric contact to the small horizontal side arm opening (Figure 13).

To initiate the experiment, one liter of ultrapure 18MΩ reverse osmosis purified, deionized water (Millipore Corporation, Milli RO-20/ Milli Q System) was added to each of the four sample vessels. Each was vigorously stirred for 60 seconds to ensure full sample wetting. From that point on the open neck of the static sample flasks were sealed with Parafilm and not disturbed, except for removal of solution aliquots for trace metal determinations at select intervals. The two agitated sample solutions were stirred vigorously for four seconds of each minute by a [Glas-Col Model Minitrol PL-312 Laboratory Power Control Timer] controlled Eberback electric stirrer. The stirring cycles were only momentarily halted for removal of sample aliquots.

Removal of 10 ml aliquots from each of the agitated and static soil solutions was readily accomplished at elapsed experiment times of 1, 3, 5, 10, 15, 30, 50, 100, 150, and 300 to 325 hours by use of acid cleaned pipets. The aliquots so removed were filtered through 0.45 micron [Millipore HAWP-025] filters into acid cleaned 50 ml Kimax vacuum filtration flasks which contained 10 ml of 10 percent HNO_3 solution (Figure 13). The ten milliliters of 10 percent HNO_3 thus diluted the sample to twice its original volume to yield 20 ml of an analytically stable 5 percent HNO_3 sample solution. The filtration and acidification steps are in accord with E.P.A. recommended procedures for water analyses (1974). The sample solutions were swirled and emptied into acid cleaned 30 ml Nalgene screw-capped polyethylene bottles.

Analysis

The determinations of each of the desired elements were performed using a Perkin Elmer Model 603 Atomic Absorption Spectrophotometer equipped with a Perkin Elmer Model HGA-2100 Graphite Furnace, Deuterium Arc Background Corrector, Electrodless Discharge Lamp Power Supply, and digital concentration read-out. The instrument parameters employed in these determinations are given in Table 11. Each of the standard solutions used to create calibration curves during these determinations was prepared in a 5 percent HNO_3 solution to match the sample matrix.

At least three stable instrument readings were averaged to obtain the final results of each sample determination. These results (in ug/ml) were tabulated as "one-half of the solubilization concentration" (because of the 10 ml to 20 ml dilution with 10 percent HNO_3 during filtration). These values could have been multiplied by two to arrive at the true solubilization concentration, and then the two duplicates of each soil averaged; however, in actual practice, the two duplicate "one-half solubilization concentrations" for each soil solution were simply added together to compute the average solubilization concentration.

Data Discussion

The average solubilization concentration of each trace metal for each soil were plotted against the experimental elapsed time, and curves

TABLE 11

INSTRUMENTAL PARAMETERS FOR ATOMIC ABSORPTION DETERMINATIONS

(A) ACIDIFIED SOLUBILIZATION SOLUTIONS

	Ag	Cd	Cu	Fe	Mn	Pb	Zn
Wavelength (NM)	328.1	228.8	324.8	248.3	279.5	283.3	213.9
Slit (NM)	0.7	0.7	0.7	0.2	0.2	0.7	0.7
Spectral Source^1	HCL	EDL	HCL	HCL	HCL	EDL	EDL
Excitation Mode	Flame	Flame	Graphite	Flame	Both	Flame	Flame
Read-Out Mode^2	Cont.	Cont.	Peak Ht.	Cont.	Both	Cont.	Cont.
Flame Composition	Air-C_2H_2	Air-C_2H_2	N.A.	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2
Graphite Furnace Settings	N.A.	N.A.	----	N.A.	----	N.A.	N.A.
-Dry Cycle (40 sec.)	N.A.	N.A.	90°C	N.A.	90°C	N.A.	N.A.
-Char Cycle (20 sec.)	N.A.	N.A.	1000°C	N.A.	1000°C	N.A.	N.A.
-Atomize Cycle (10 sec.)	N.A.	N.A.	2500°C	N.A.	2600°C	N.A.	N.A.
Deuterium Arc Bkgd. Corr.	NO	NO	NO	NO	NO	NO	NO
Stable Detectibility							
-Flame (ug/ml)	±0.01	±0.01	N.A.	±0.01	±0.01	±0.01	±0.01
-Graphite (ng/ml)	N.A.	N.A.	±1.0	N.A.	±1.0	N.A.	N.A.
Standard Compound	$AgNO_3$	$Cd(NO_3)\cdot 4H_2O$	Cu	$FeCl_3$	$MnCl_2.4H_2O$	$Pb(NO_3)_2$	ZnO

TABLE 11

INSTRUMENTAL PARAMETERS FOR ATOMIC ABSORPTION DETERMINATIONS

(B) SOIL DIGESTATE SOLUTIONS

	Ag	Cd	Cu	Fe	Mn	Pb	Zn
Wavelength (NM)	328.1	228.8	324.8	248.3	279.5	283.3	213.9
Slit (NM)	0.7	0.7	0.7	0.2	0.2	0.7	0.7
Spectral Source[1]	HCL	EDL	HCL	HCL	HCL	EDL	EDL
Read-out Mode[2]	Cont.	Cont.	Cont.	Cont.	Cont.	Cont.	Cont.
Flame Composition	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2	Air-C_2H_2
Deuterium Arc Bkgd. Corr.	NO	YES	NO	YES	YES	NO	YES
Stable Detectibility (ug/ml)	±0.01	±0.01	±0.01	±1.0	±0.01	±0.01	±0.01
Standard Compound	$AgNO_3$	$Cd(NO_3)_2 \cdot 4H_2O$	Cu	$FeCl_3$	$MnCl_2 \cdot 4H_2O$	$Pb(NO_3)_2$	ZnO

[1] Note: HCL = Hollow Cathode Lamp. EDL = Electrodeless Discharge Lamp.

[2] Note: Continuous = Each reading is integrated over the selected Integration Time and, after an initial five second delay time (during which the sample solution travels from the capillary uptake origin to the flame), three stable readings are averaged by the operator to arrive at the reported value. Peak Height = This mode is used for graphite furnace measurements and is the maximum peak height measured during the operator selected Integration Time cycle, which is automatically activated just prior to the furnace Atomization Cycle. The reported values for graphite furnace determinations are the averages of three such measurements each.

[3] Note: Graphite furnace purge gas flow can be either continuous (Normal) or interrupted (Interrupt) during the Atomization Cycle. The Interrupt mode provides greater sensitivity for most elements.

visually fitted to the resulting plots (Figures 14 to 40). The estimated solubilization concentrations for one day ($C_{24\ hr.}$), two days ($C_{48\ hr.}$), and equilibrium (C_{∞}) were read from the fitted curves and tabulated (Tables 12 and 13). The pH's of the soil solutions at the end of the experiments are given in Table 6. Kinetic plots are given for only a few of the solubilization concentration vs. time data sets of each soil. Inclusion of kinetic plots for every solubilization plot would be too tedious and would not contribute much to the readers understanding of this thesis.

The parameters for the kinetic plots given here are derived from a general expression for the first order kinetic behavior of a chemical reaction such as

$$A + \text{other reactants} \rightarrow \text{products},$$

where

$$\frac{-d(A)}{dt} = k(A)$$

says that the disappearance of A with time is equal to a constant times the concentration of A at any given time. Upon rearranging and integrating, such as

$$\int_{0}^{\infty} \frac{d(A)}{(A)} = -k \int_{0}^{\infty} dt,$$

we have

$$\ln A = -kt + \text{an integration constant},$$

where it is clear that if $A = A_0$ at $t = 0$ (the starting time of the experiment) then a plot of $\ln \frac{A}{A_0}$ vs. time will yield a straight line with a slope = -k (the reaction rate). Conversely, a plot of $\frac{A}{A_0}$ vs. time yields an exponential (elbow-shaped) curve in accord with

$$(A) = (A_0)e^{-kt}$$

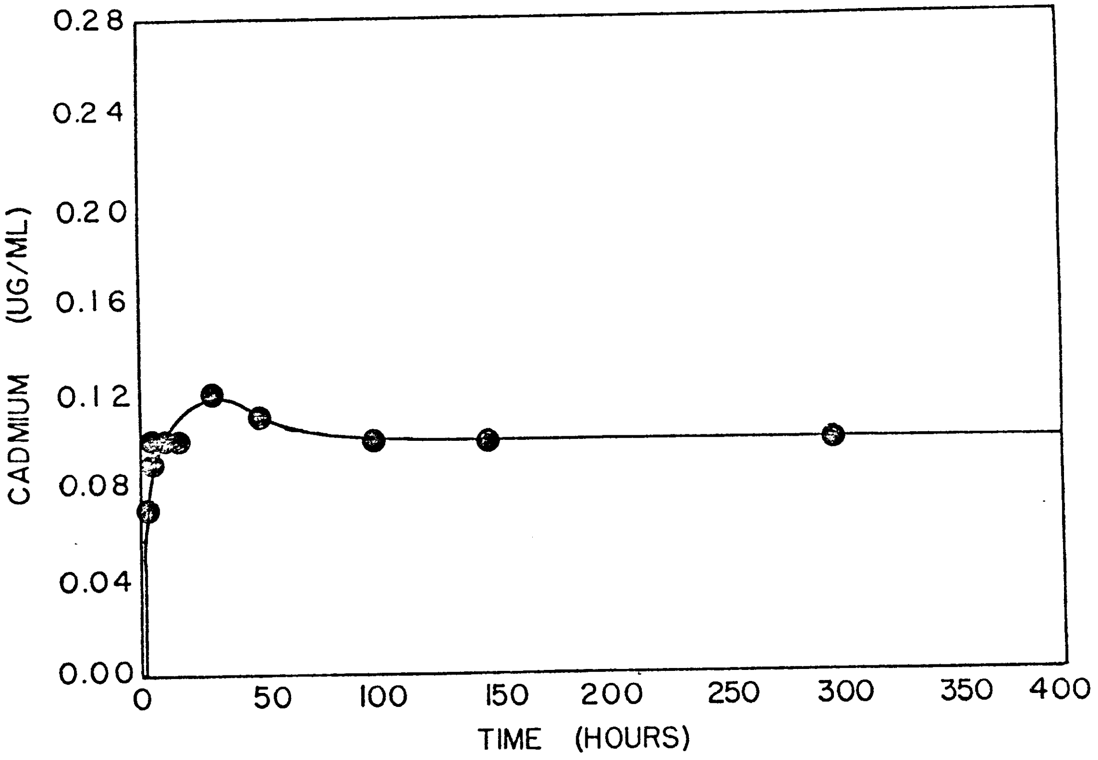

Figure 14 (a). Solubilized Cadmium in Agitated Kellogg Soil Solutions.

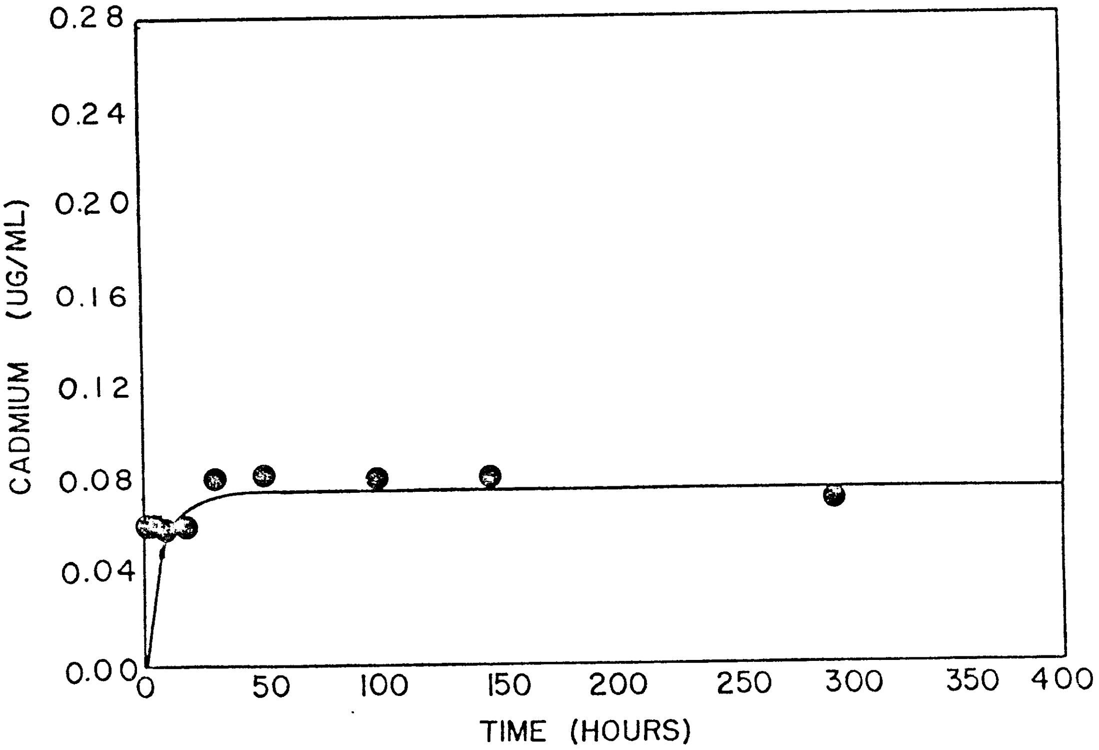

Figure 14 (b). Solubilized Cadmium in Static Kellogg Soil Solutions.

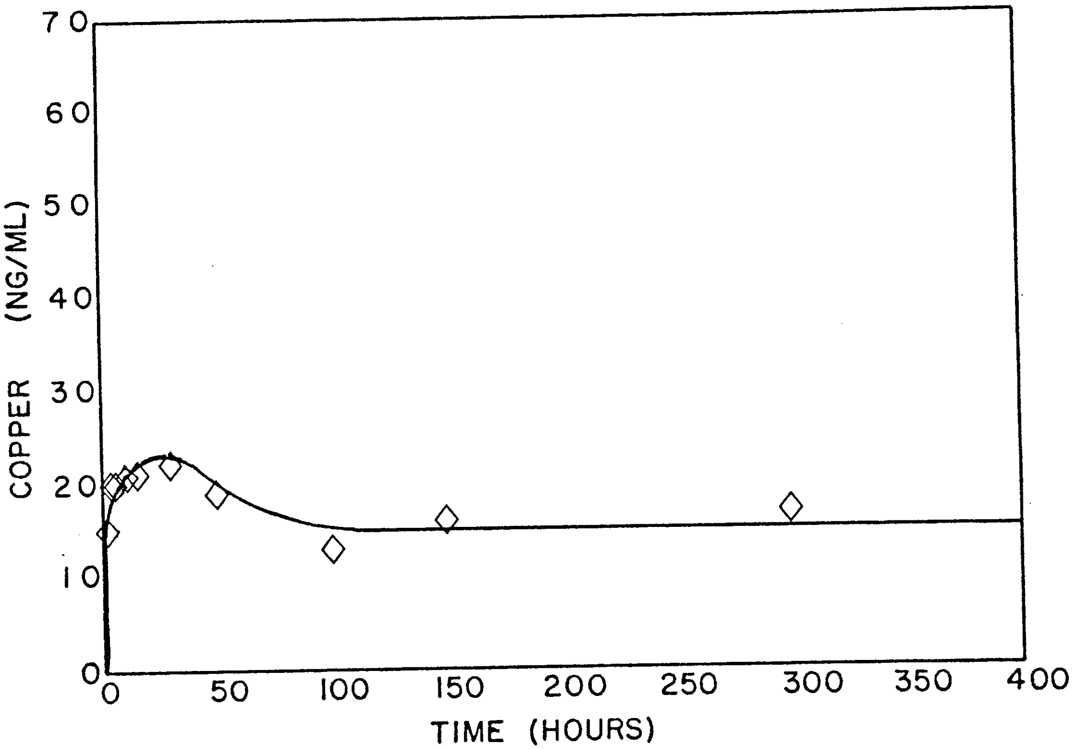

Figure 15 (a). Solubilized Copper in Agitated Kellogg Soil Solutions.

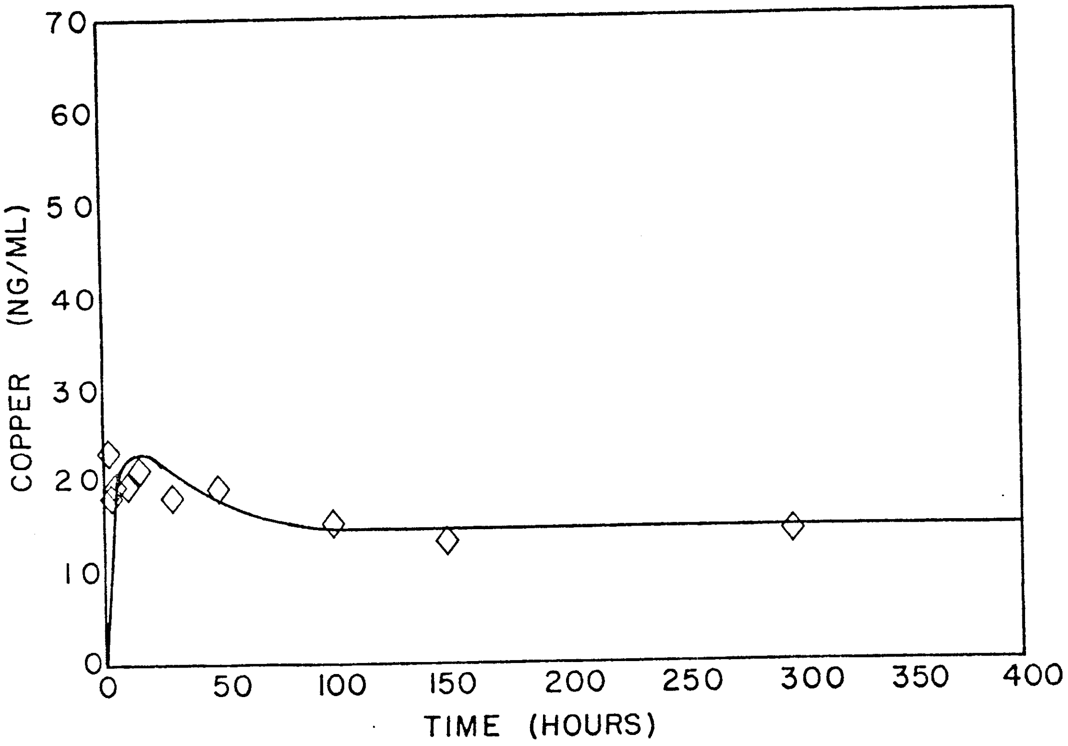

Figure 15 (b). Solubilized Copper in Static Kellogg Soil Solutions.

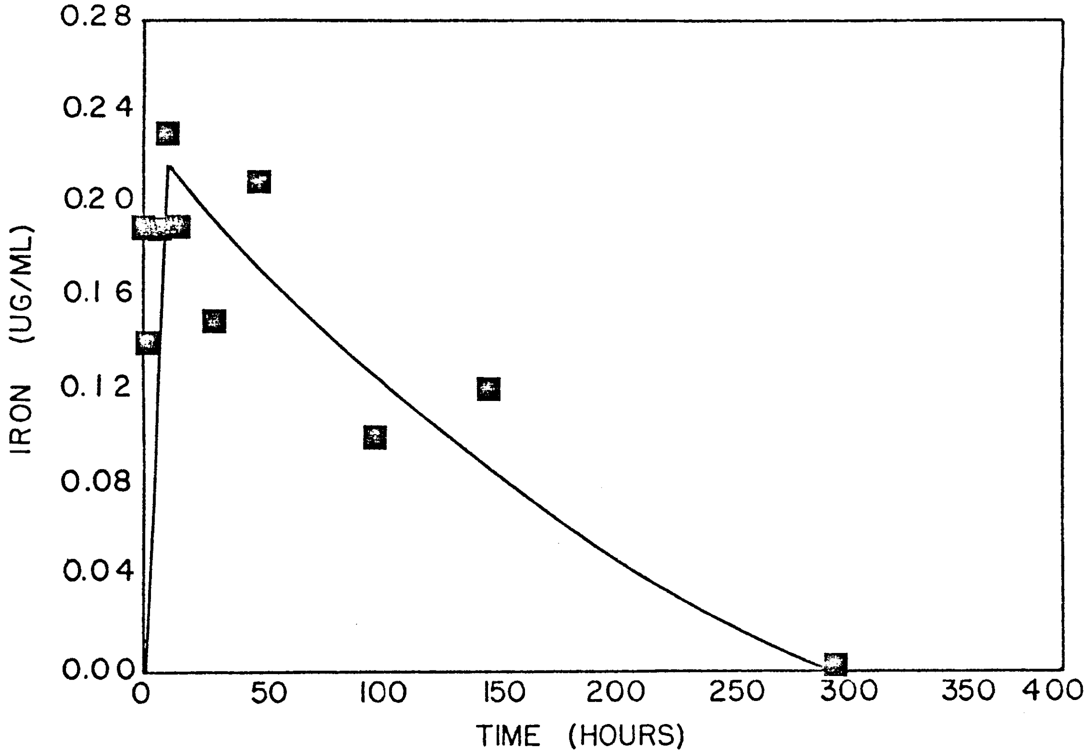

Figure 16 (a). Solubilized Iron in Agitated Kellogg Soil Solutions.

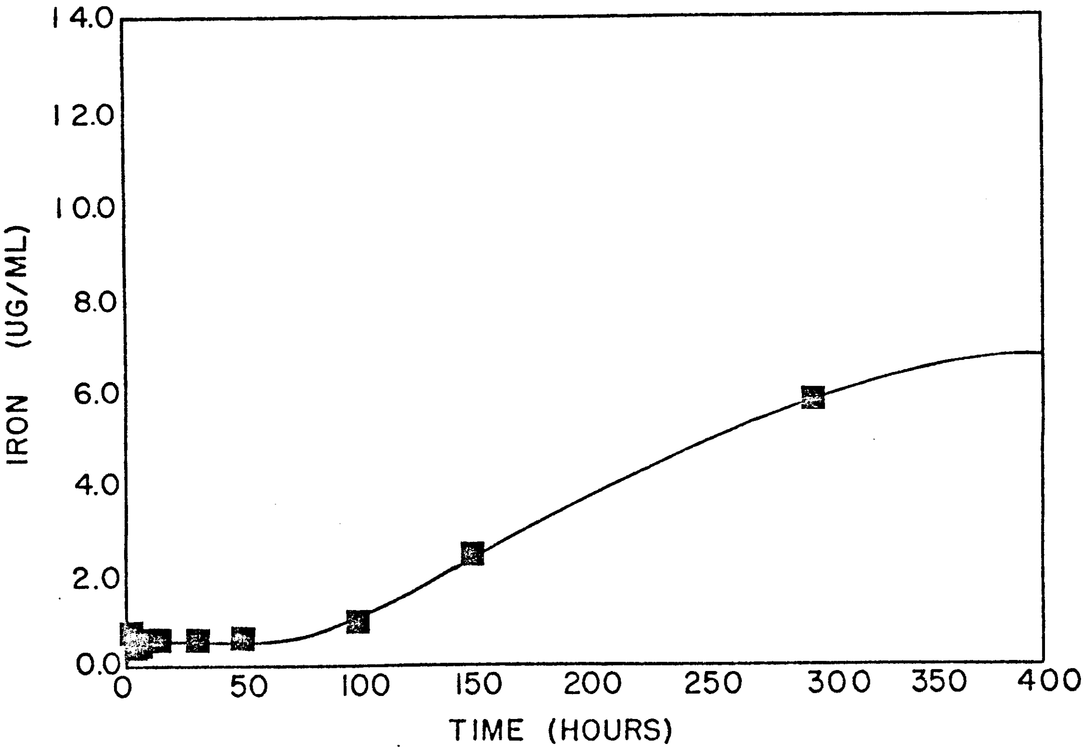

Figure 16 (b). Solubilized Iron in Static Kellogg Soil Solutions.

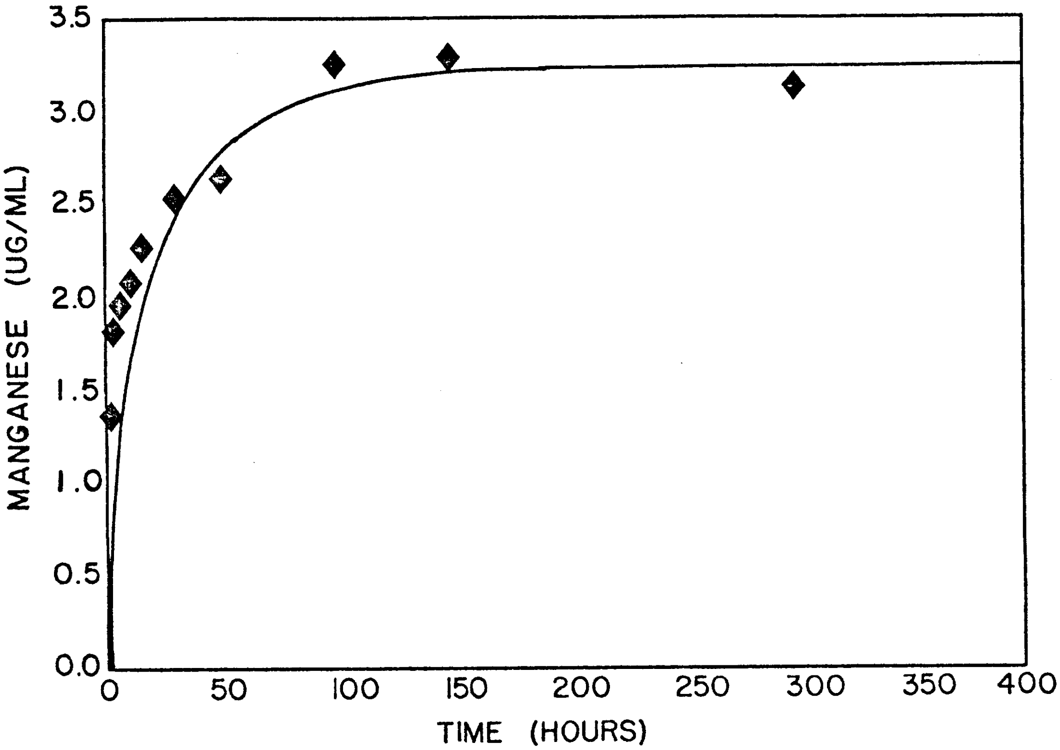

Figure 17 (a). Solubilized Manganese in Agitated Kellogg Soil Solutions.

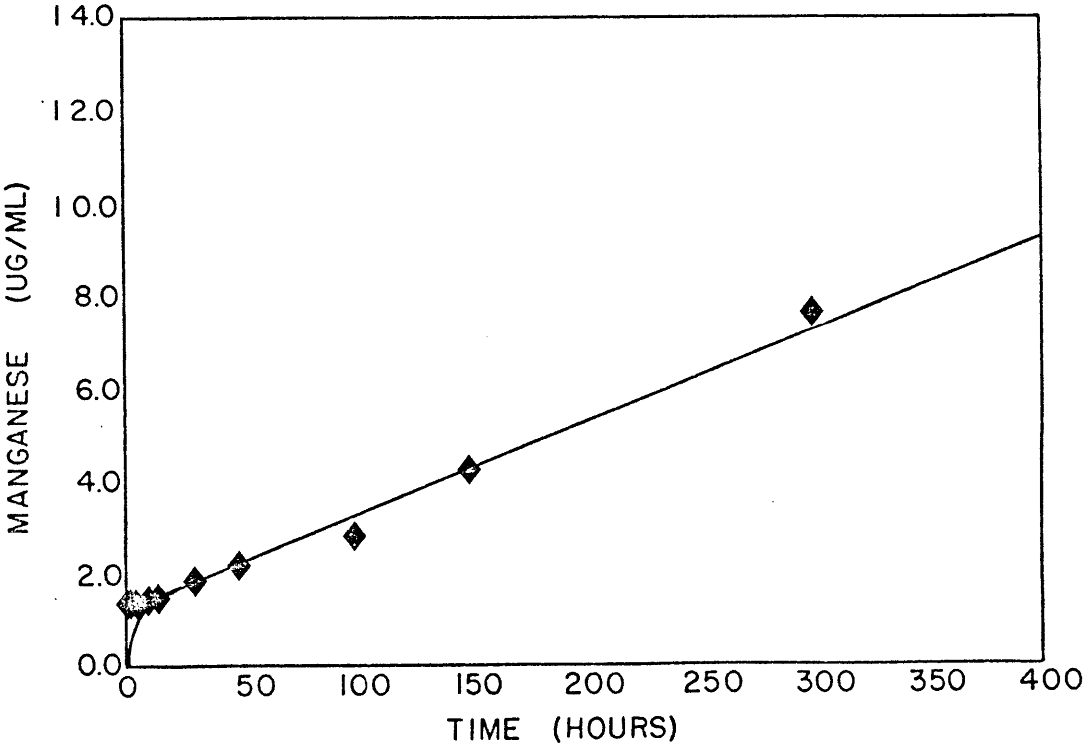

Figure 17 (b). Solubilized Manganese in Static Kellogg Soil Solutions.

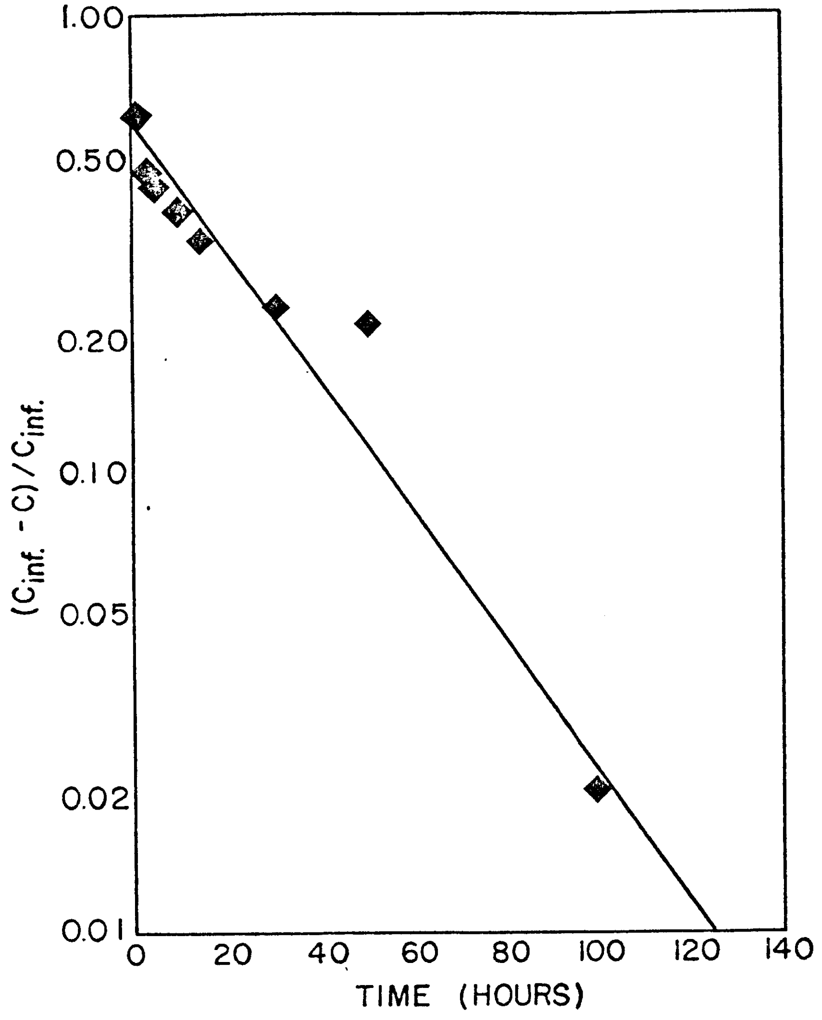

Figure 17-2a. Kinetic Plot for Solubilized Manganese in Agitated Kellogg Soil Solutions.

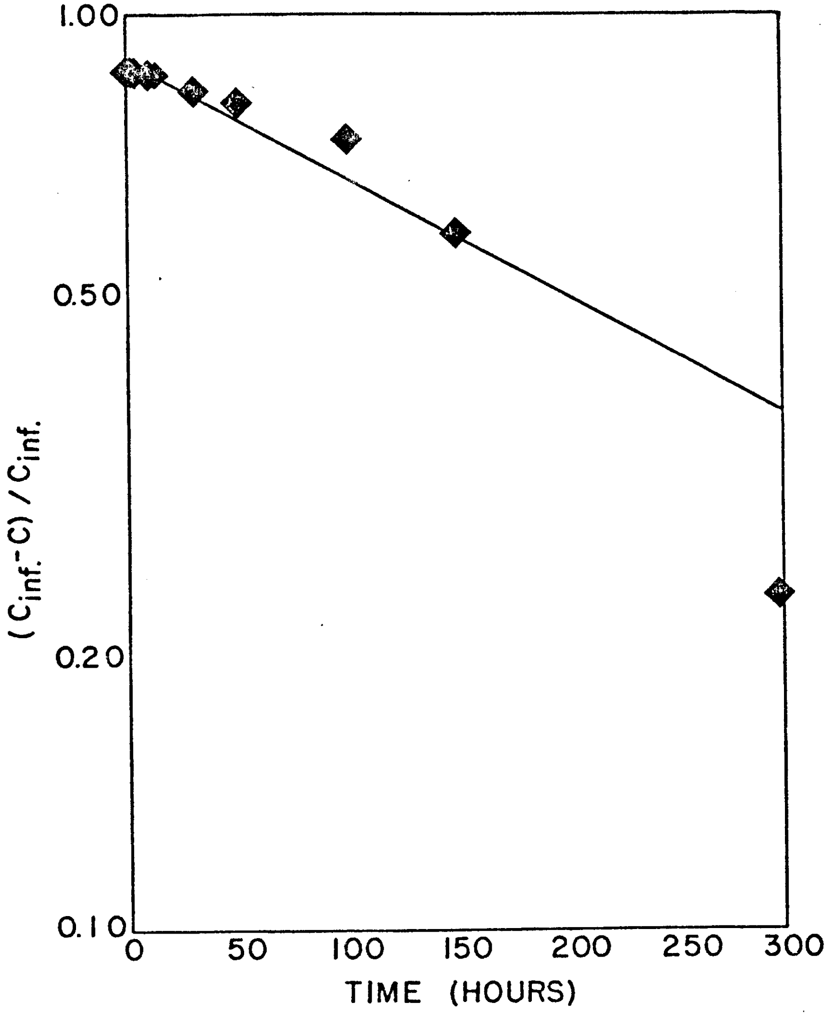

Figure 17-2b. Kinetic Plot for Solubilized Manganese in Static Kellogg Soil Solutions.

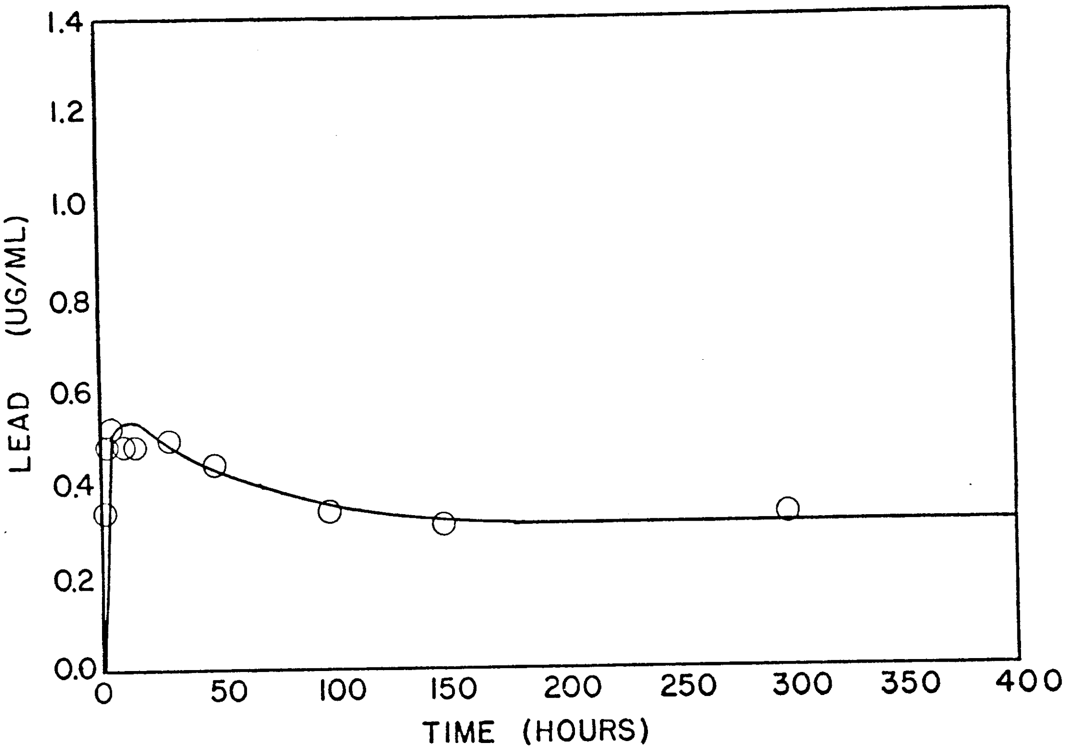

Figure 18 (a). Solubilized Lead in Agitated Kellogg Soil Solutions.

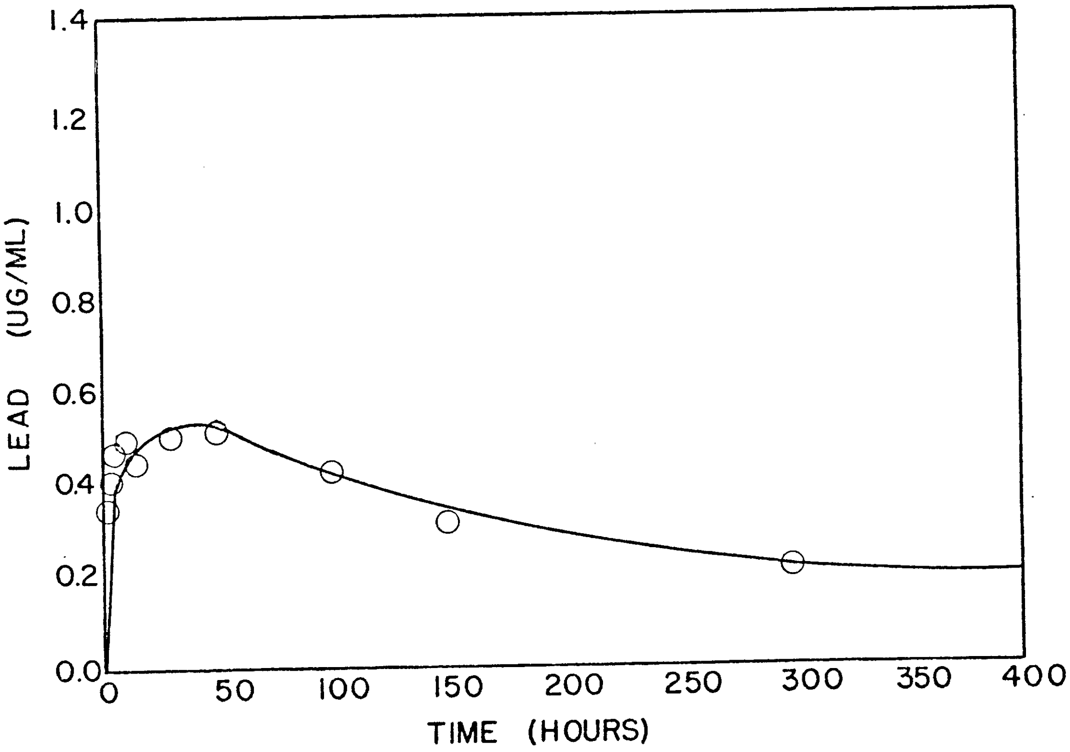

Figure 18 (b). Solubilized Lead in Static Kellogg Soil Solutions.

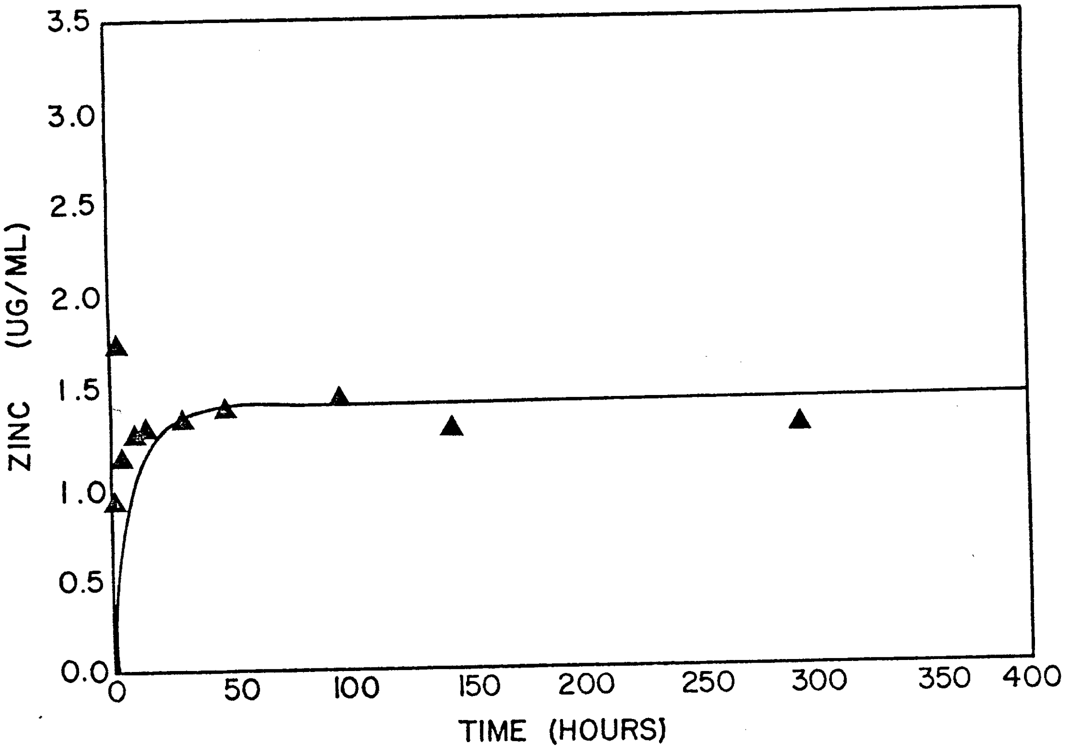

Figure 19 (a). Solubilized Zinc in Agitated Kellogg Soil Solutions.

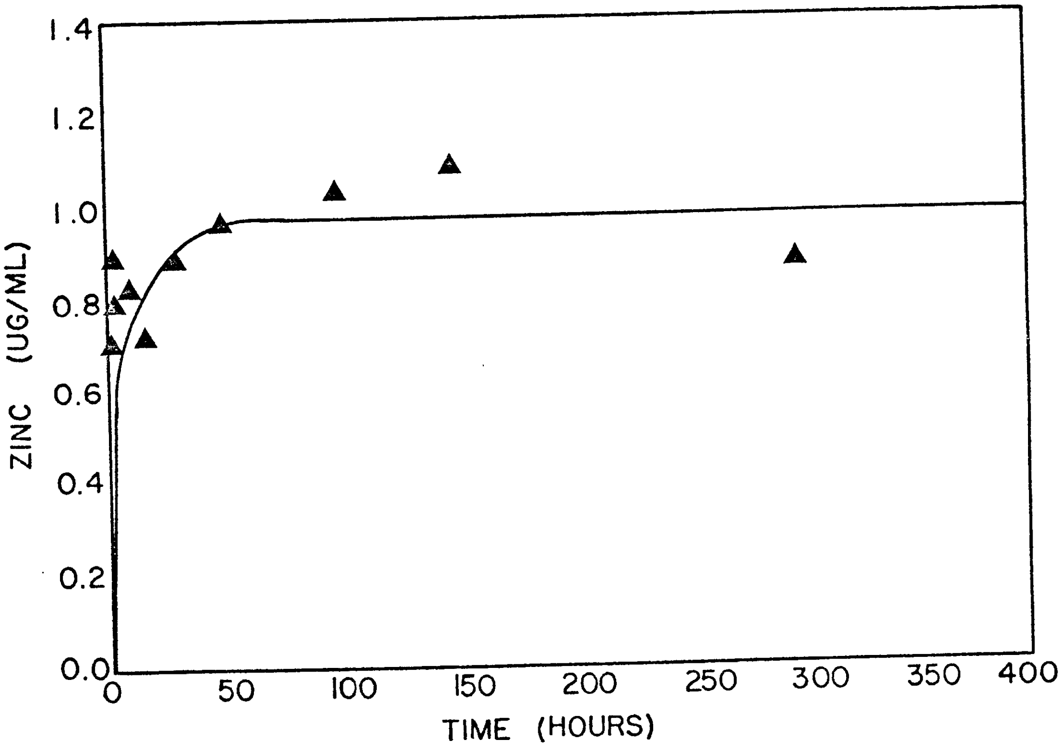

Figure 19 (b). Solubilized Zinc in Static Kellogg Soil Solutions.

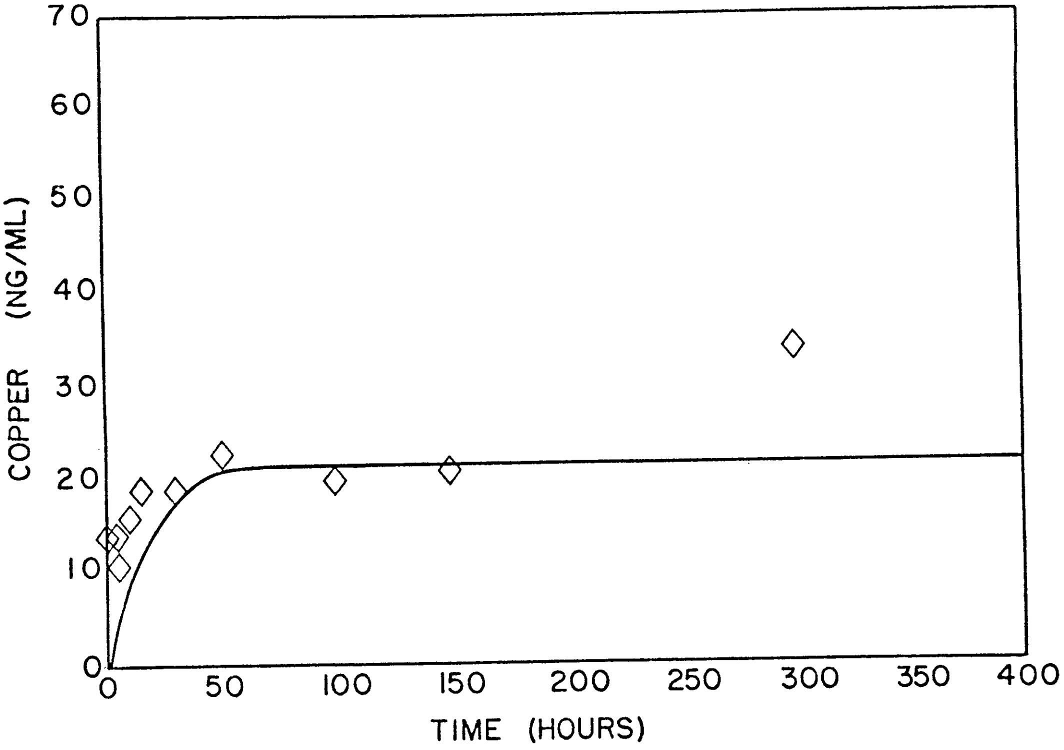

Figure 20 (a). Solubilized Copper in Agitated Smelterville Soil Solutions.

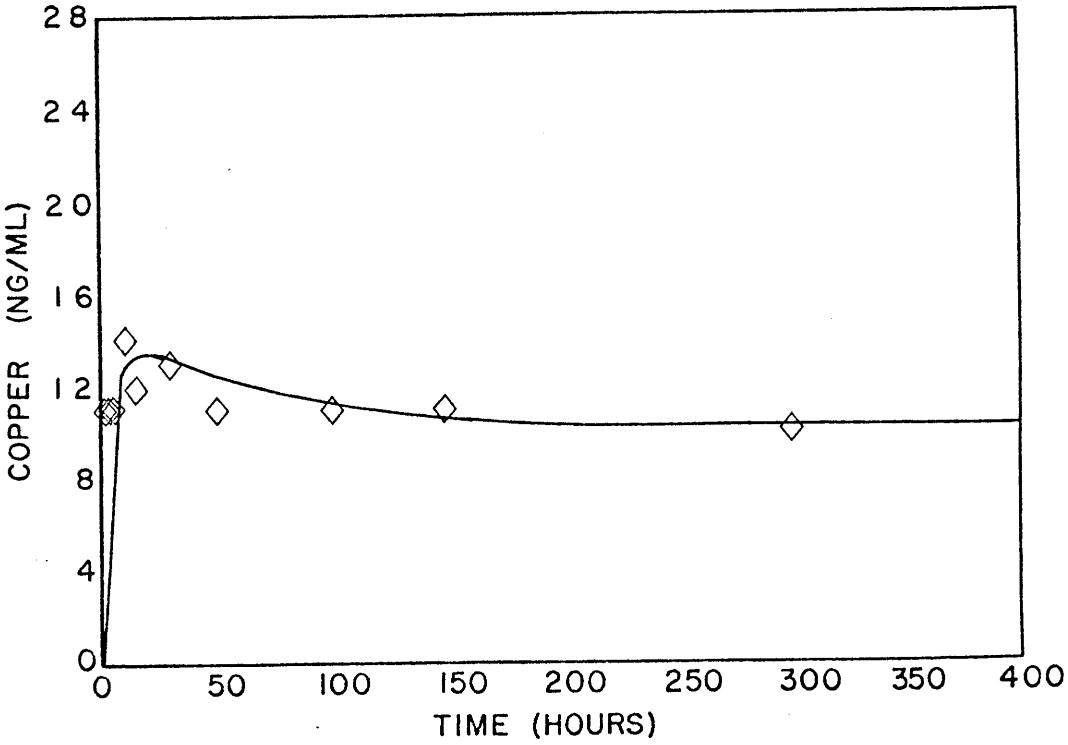

Figure 20 (b). Solubilized Copper in Static Smelterville Soil Solutions.

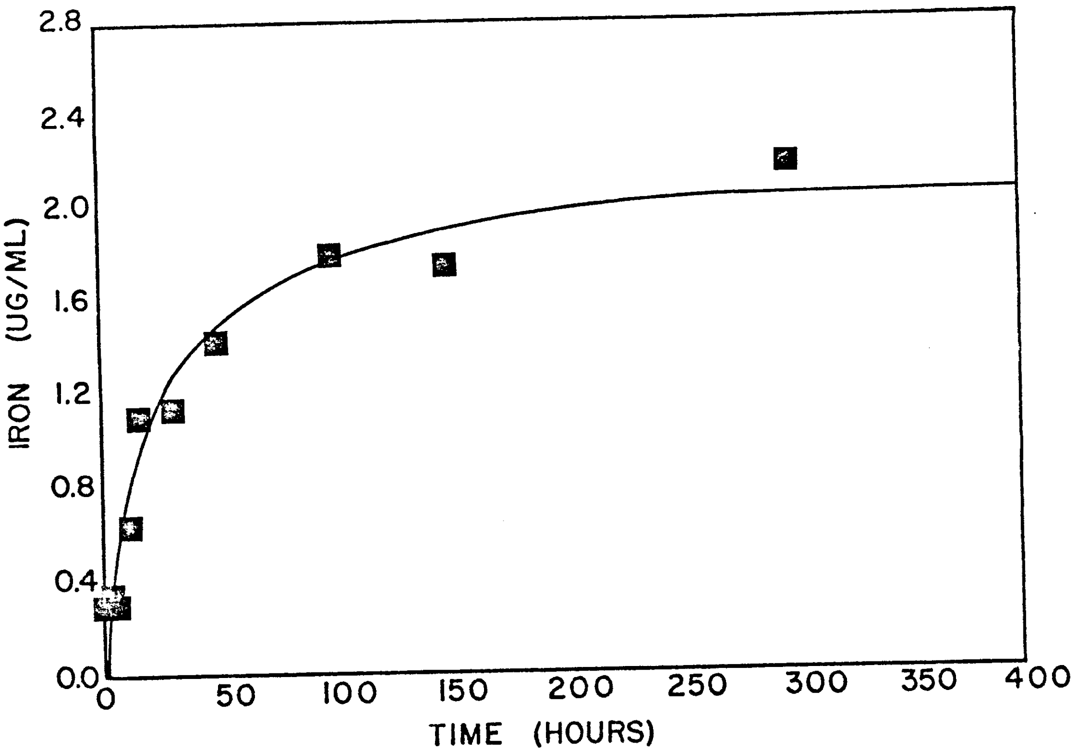

Figure 21 (a). Solubilized Iron in Agitated Smelterville Soil Solutions.

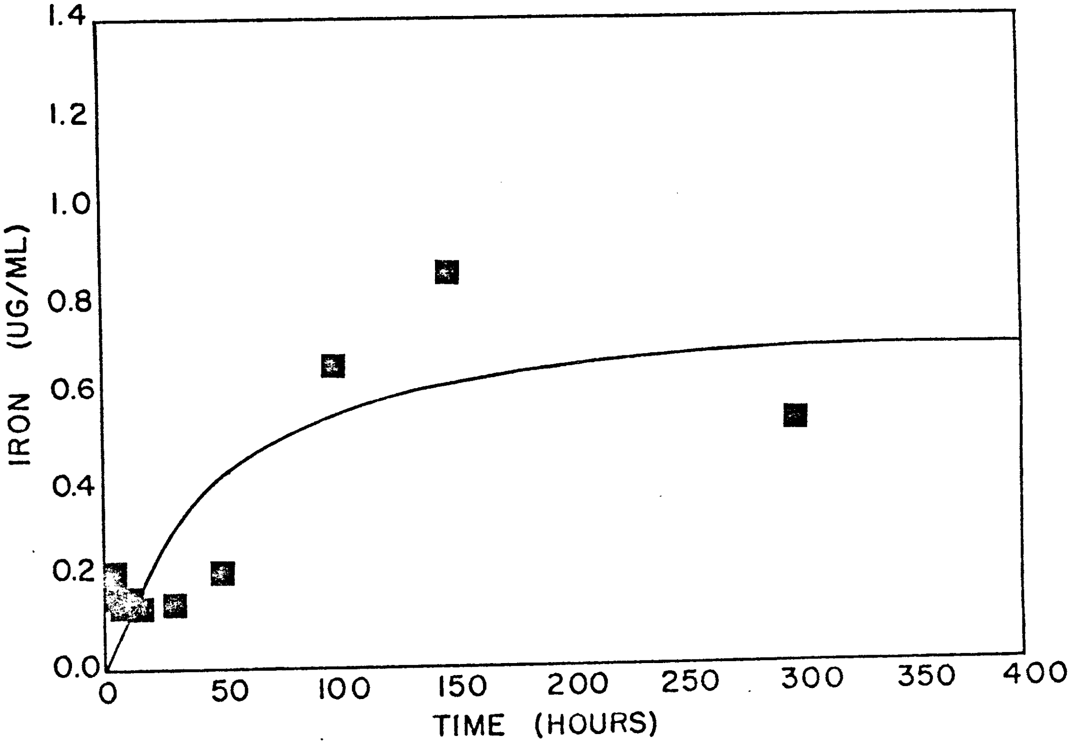

Figure 21 (b). Solubilized Iron in Static Smelterville Soil Solutions.

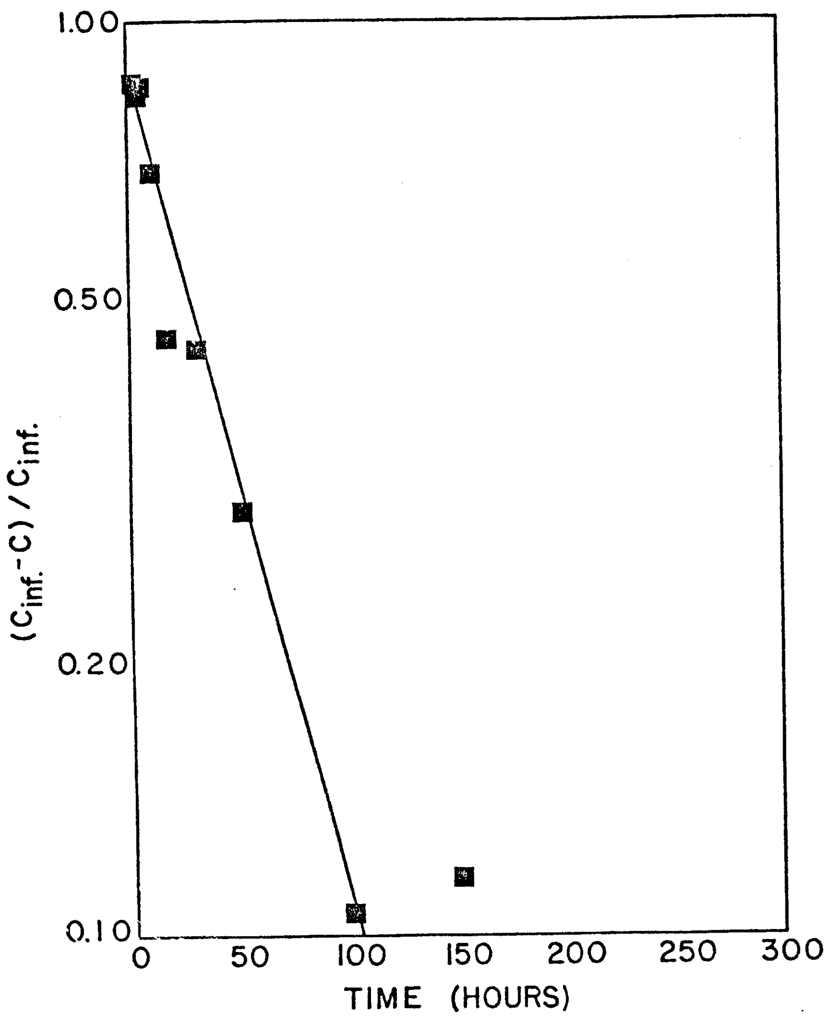

Figure 21-2a. Kinetic Plot for Solubilized Iron in Agitated Smelterville Soil Solutions.

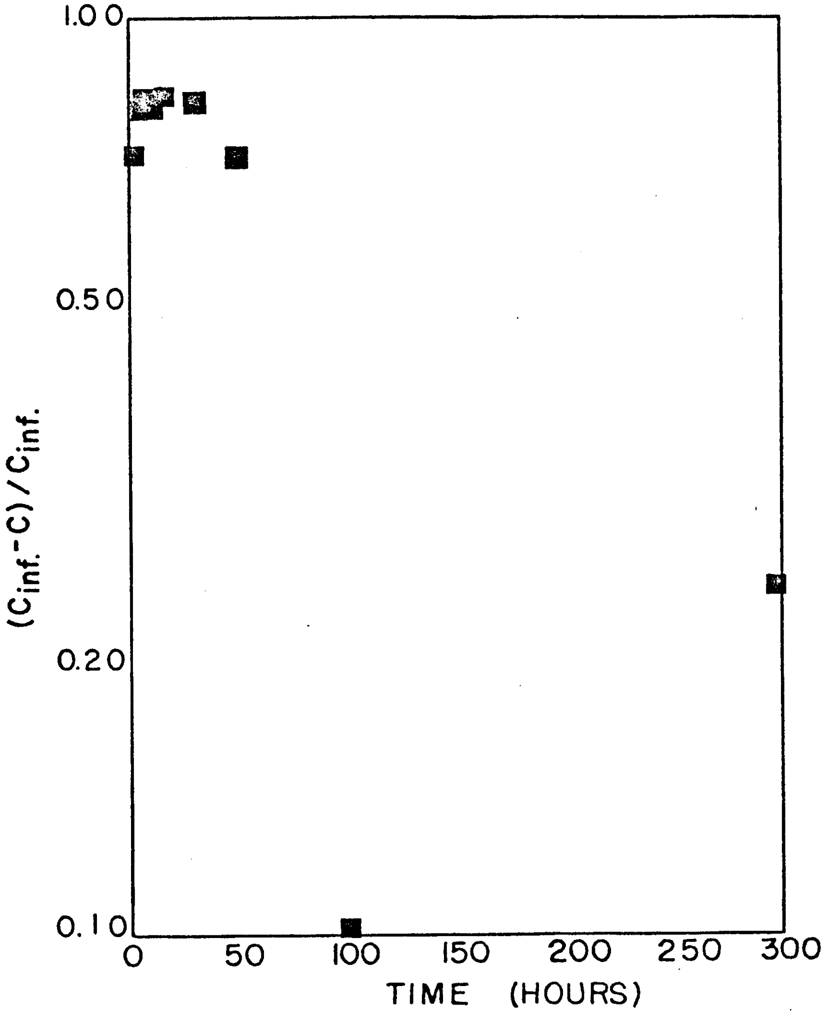

Figure 21-2b. Kinetic Plot for Solubilized Iron in Static Smelterville Soil Solutions.

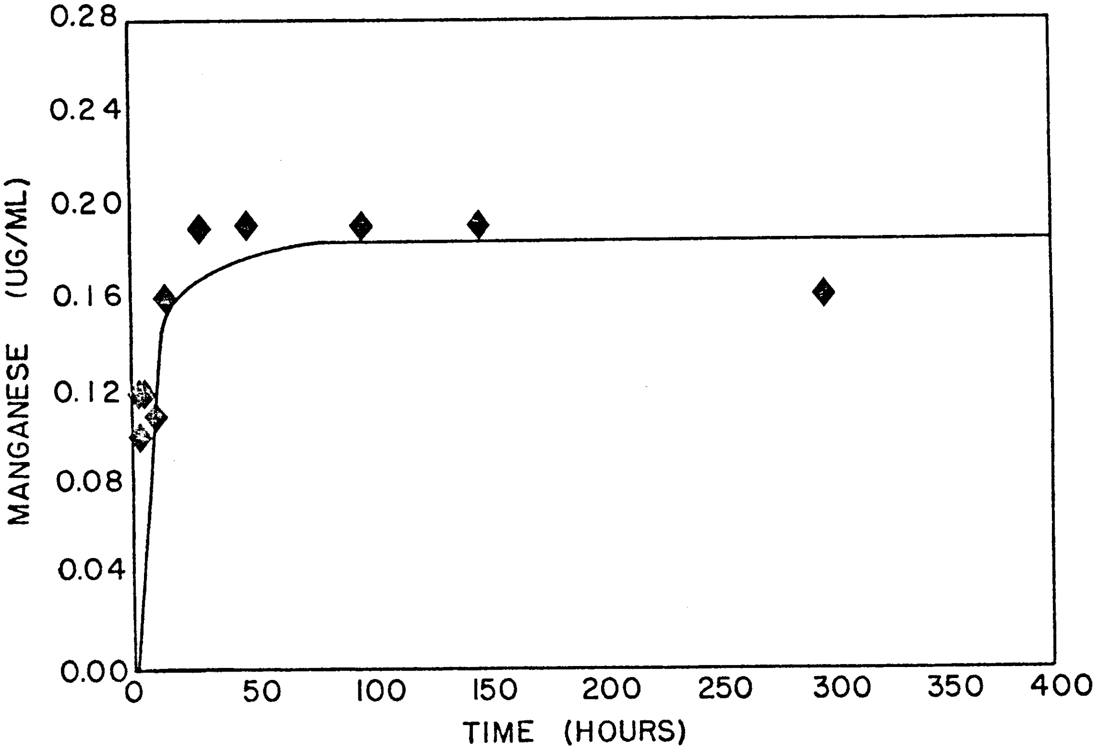

Figure 22 (a). Solubilized Manganese in Agitated Smelterville Soil Solutions.

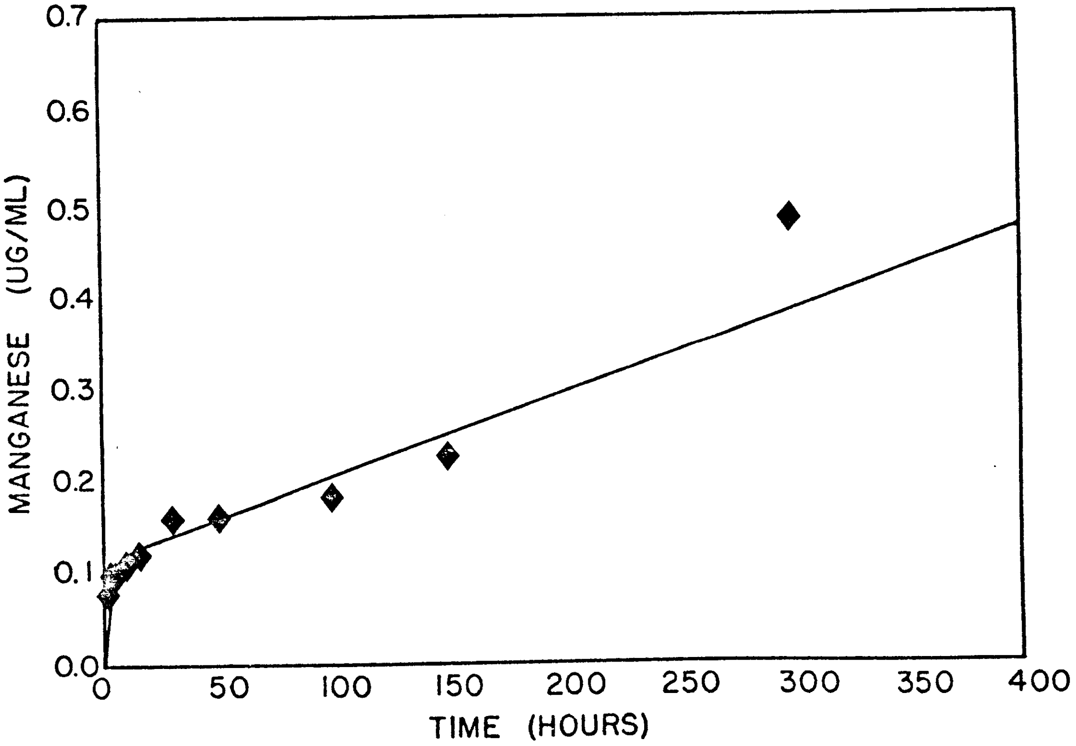

Figure 22 (b). Solubilized Manganese in Static Smelterville Soil Solutions.

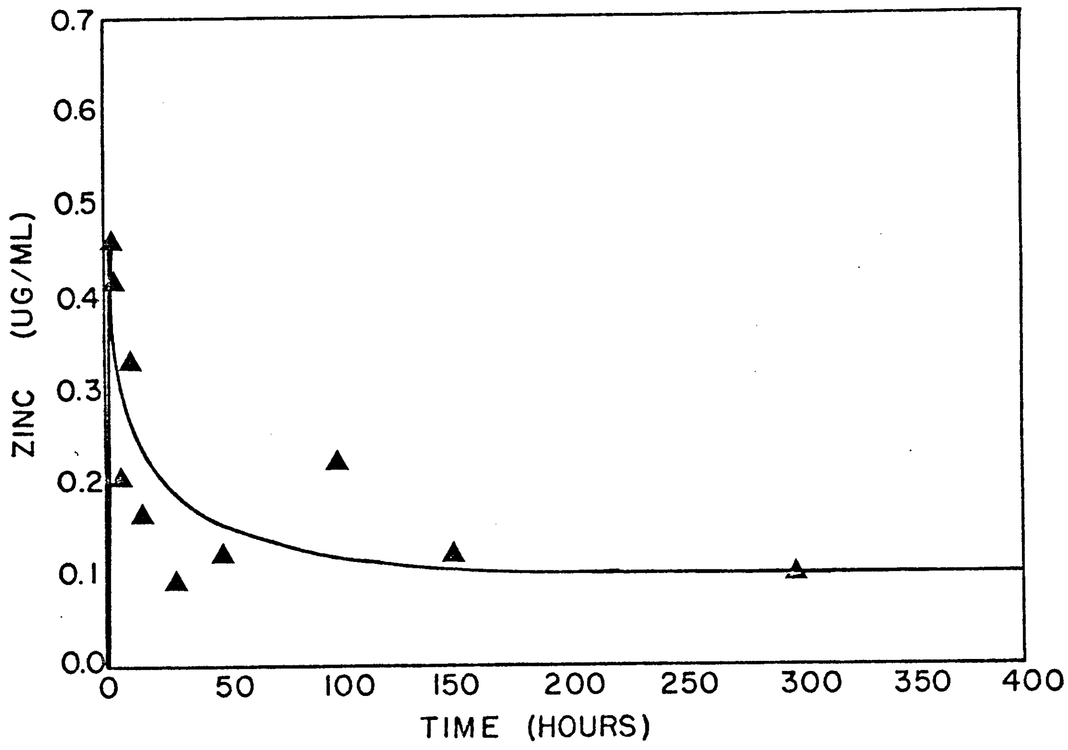

Figure 23 (a). Solubilized Zinc in Agitated Smelterville Soil Solutions.

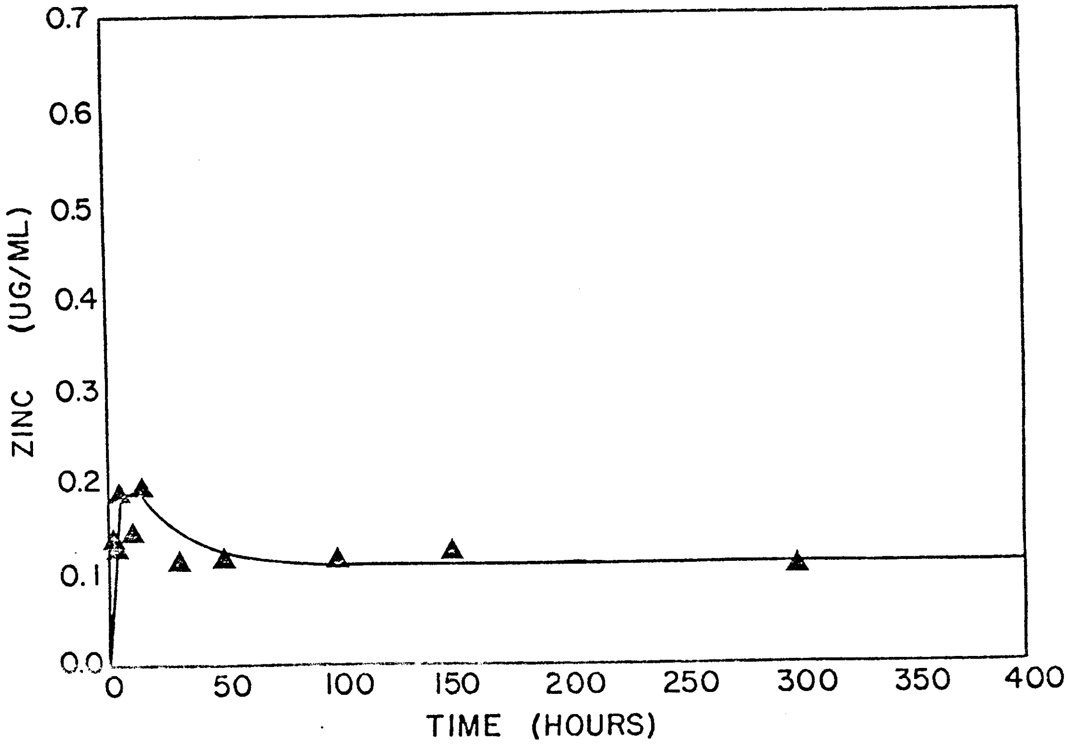

Figure 23 (b). Solubilized Zinc in Static Smelterville Soil Solutions.

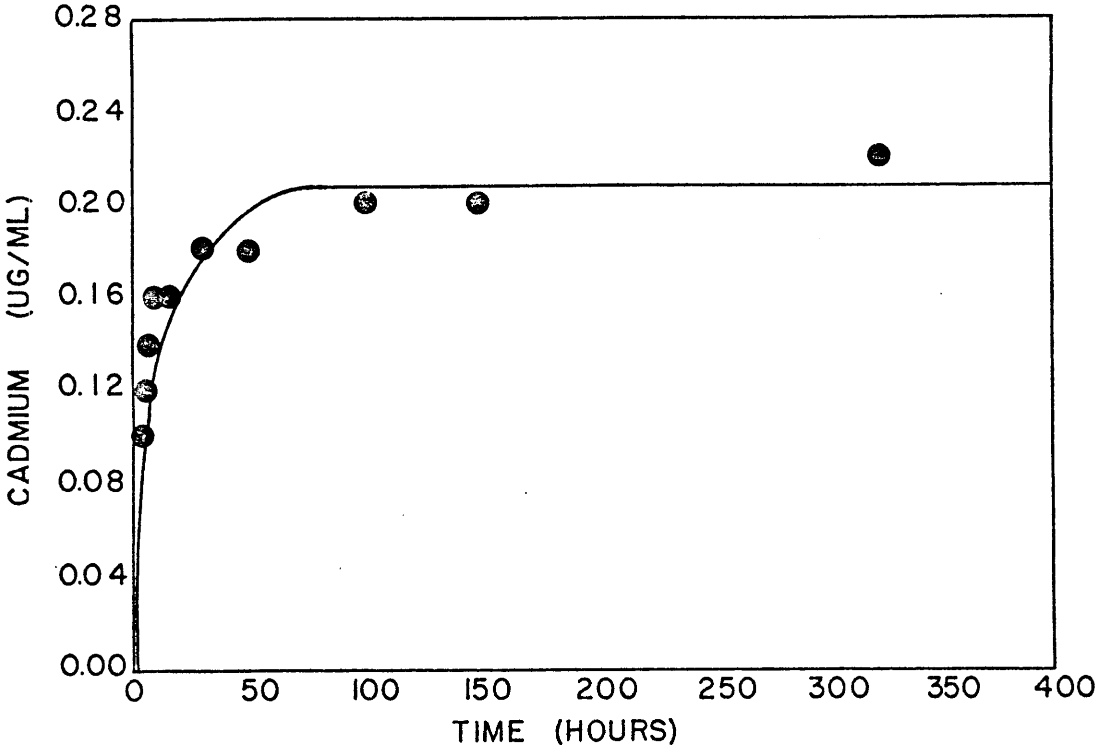

Figure 24 (a). Solubilized Cadmium in Agitated Osburn Tailings (Dried, Sieved) Solutions.

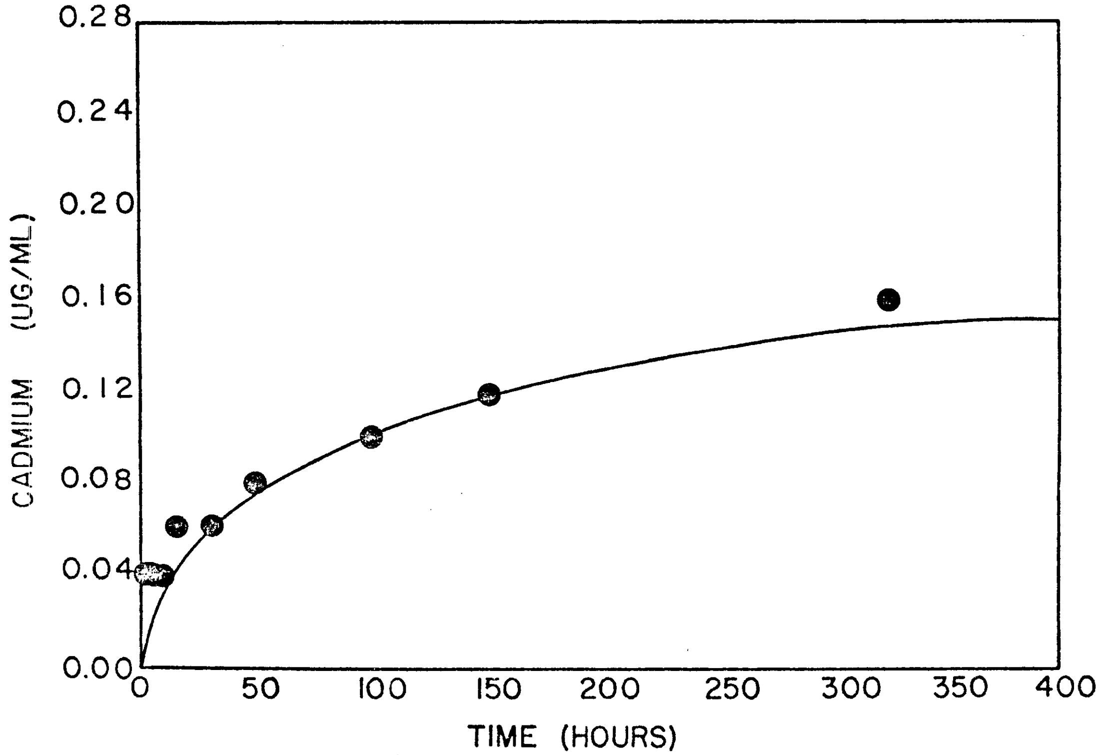

Figure 24 (b). Solubilized Cadmium in Static Osburn Tailings (Dried, Sieved) Solutions.

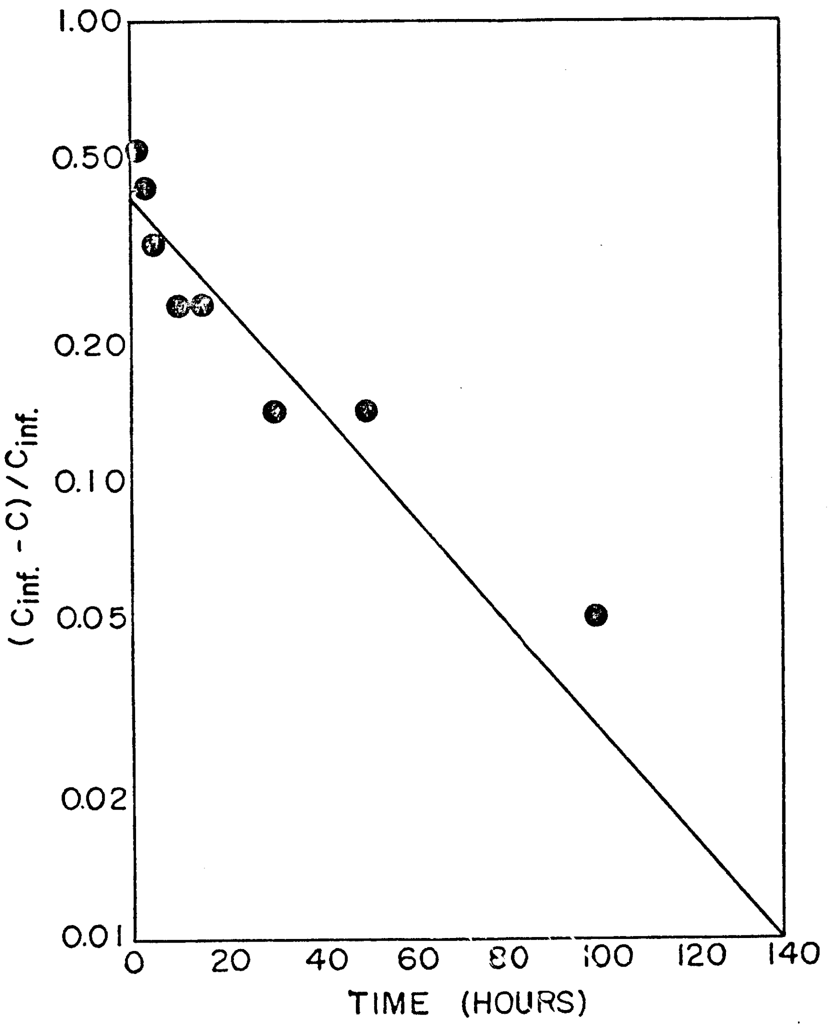

Figure 24-2a. Kinetic Plot for Solubilized Cadmium in Agitated Osburn Tailings (Dried, Sieved) Solutions.

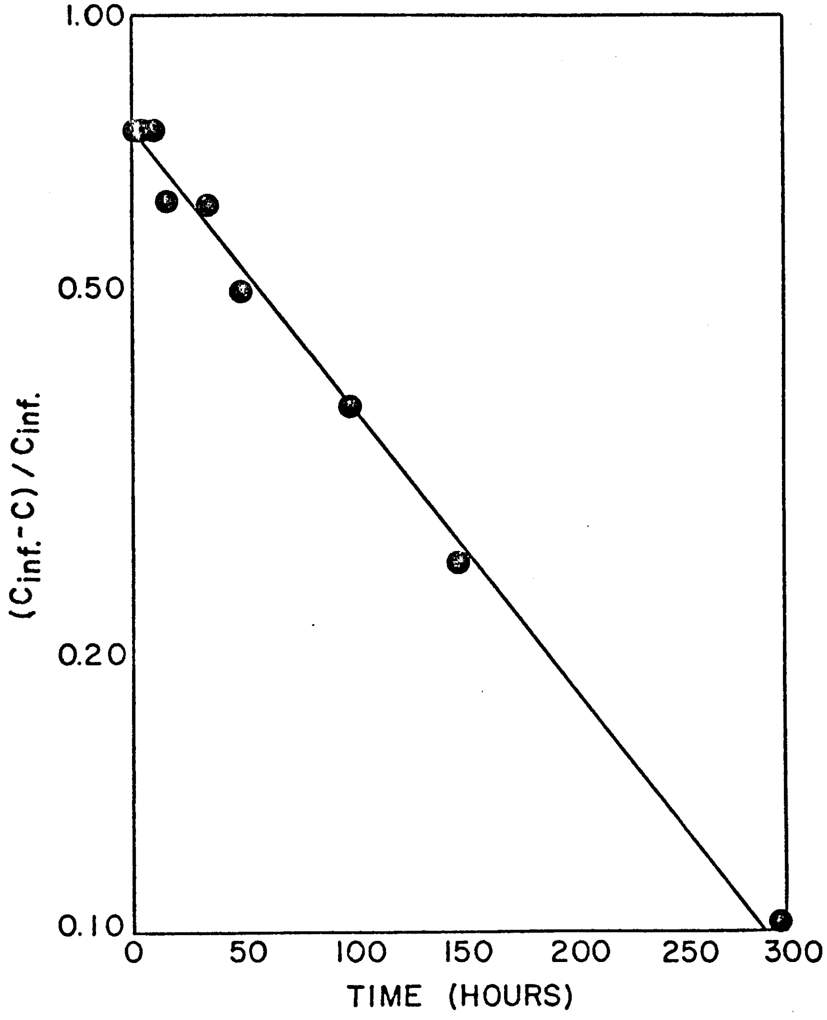

Figure 24-2b. Kinetic Plot for Solubilized Cadmium in Static Osburn Tailings (Dried, Sieved) Solutions.

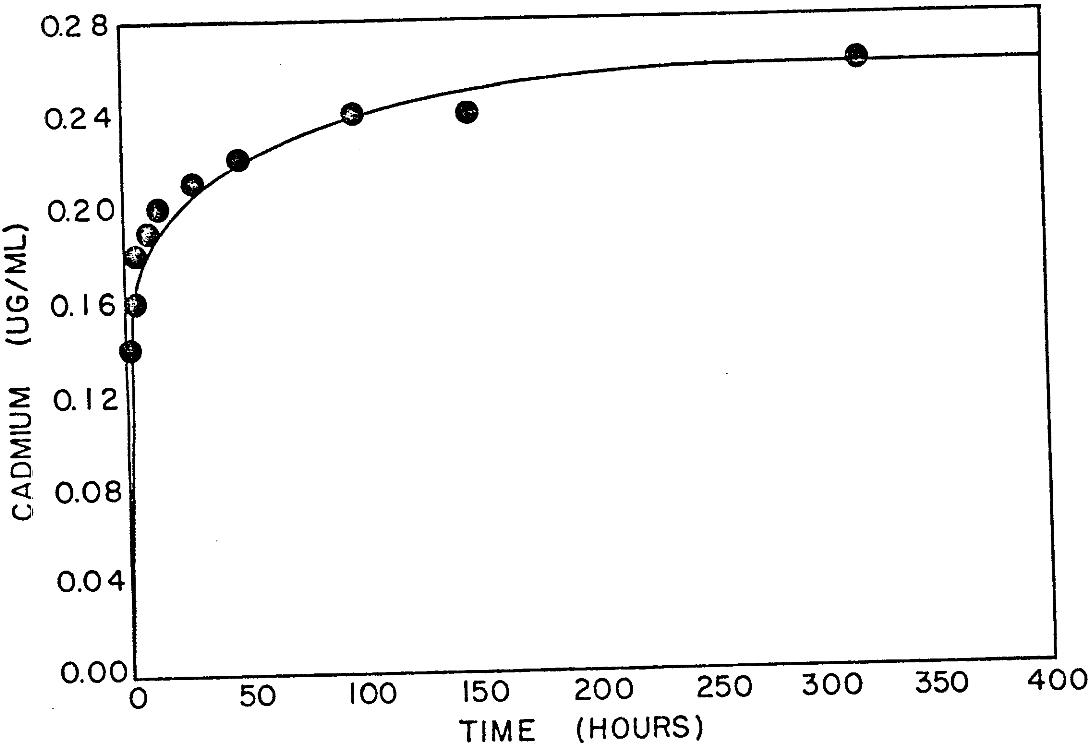

Figure 25 (a). Solubilized Cadmium in Agitated Osburn Tailings (Native) Solutions.

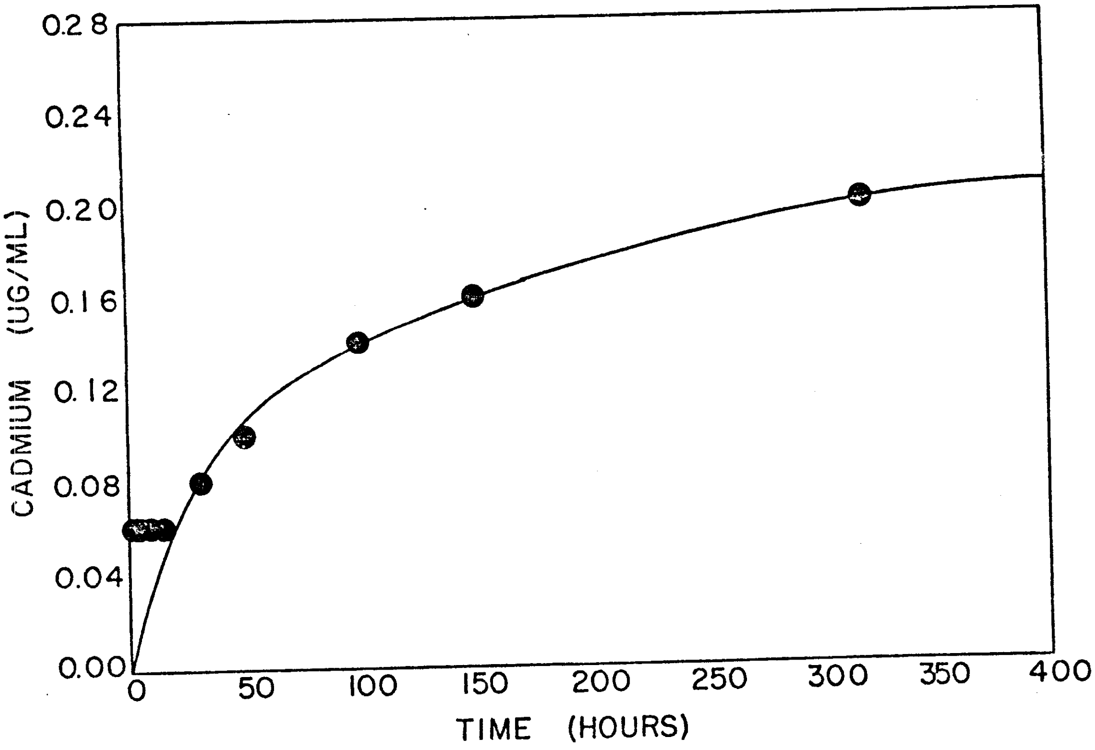

Figure 25 (b). Solubilized Cadmium in Static Osburn Tailings (Native) Solutions.

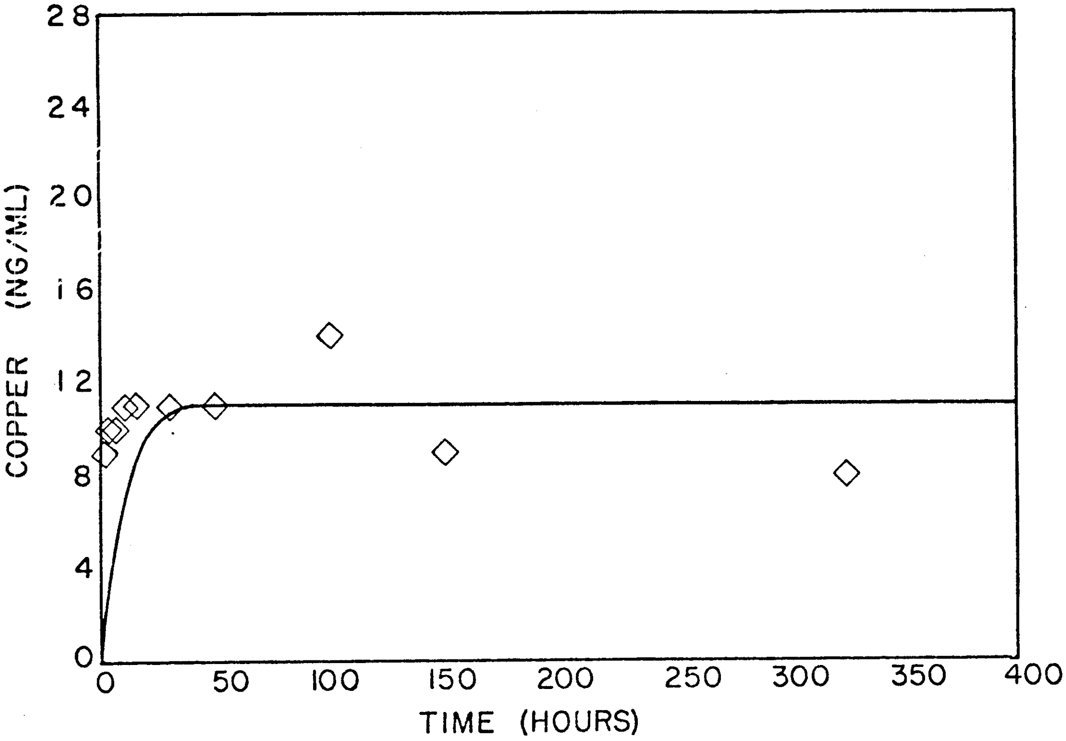

Figure 26 (a). Solubilized Copper in Agitated Osburn Tailings (Dried, Sieved) Solutions.

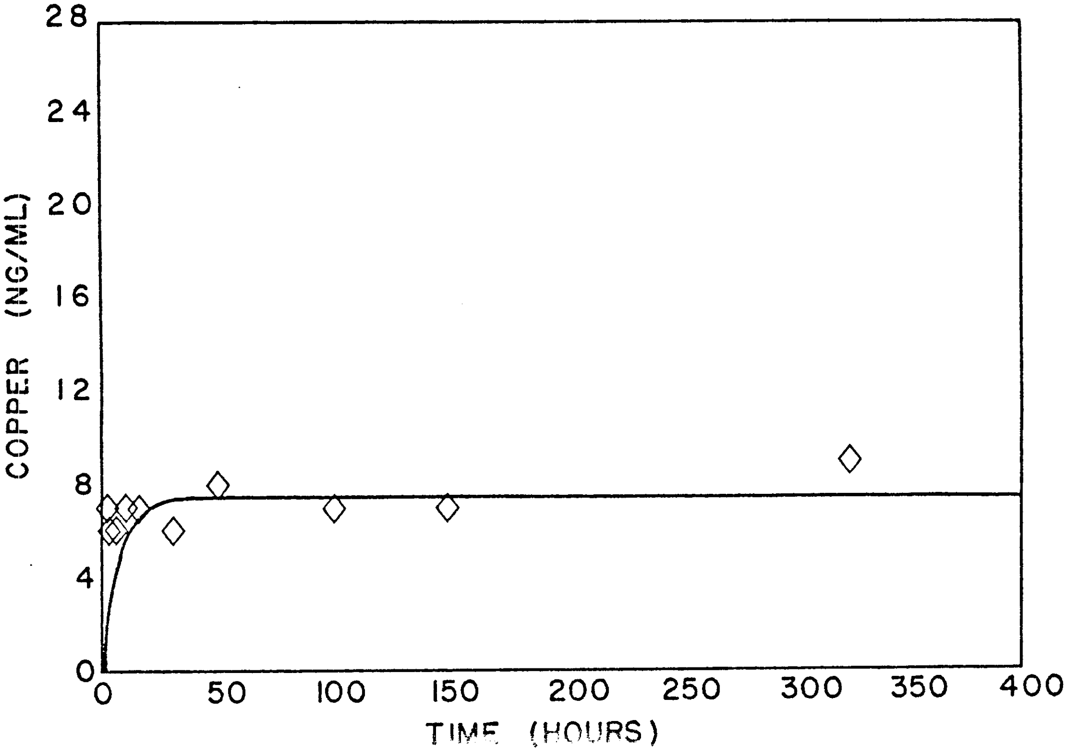

Figure 26 (b). Solubilized Copper in Static Osburn Tailings (Dried, Sieved) Solutions.

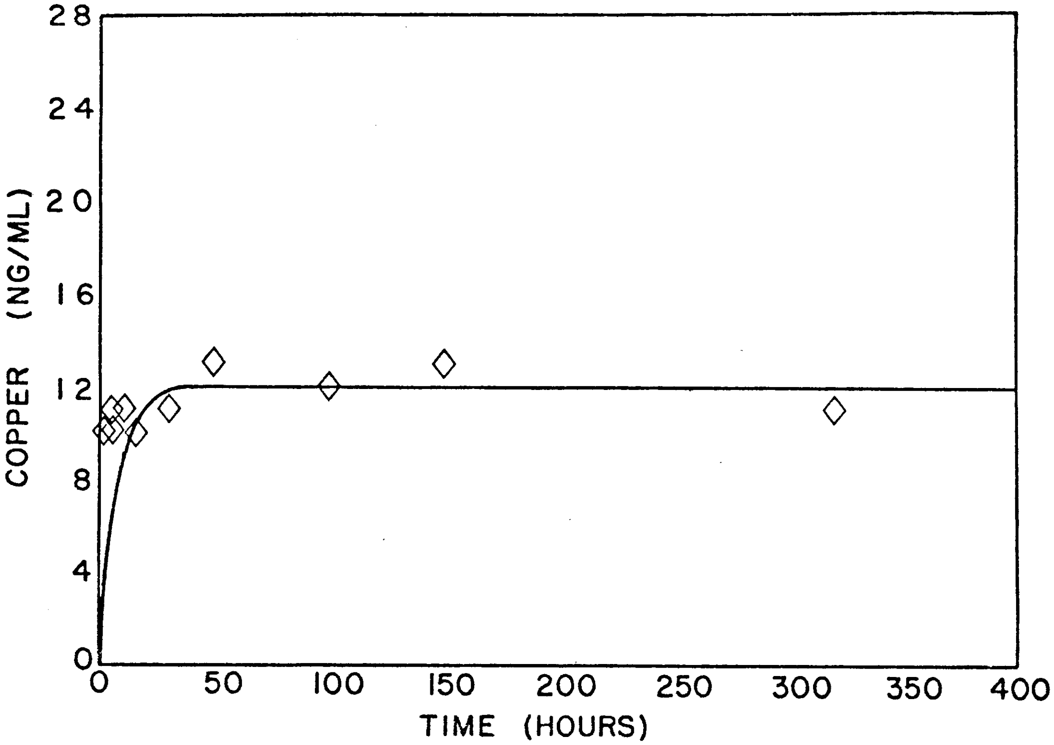

Figure 27 (a). Solubilized Copper in Agitated Osburn Tailings (Native) Solutions.

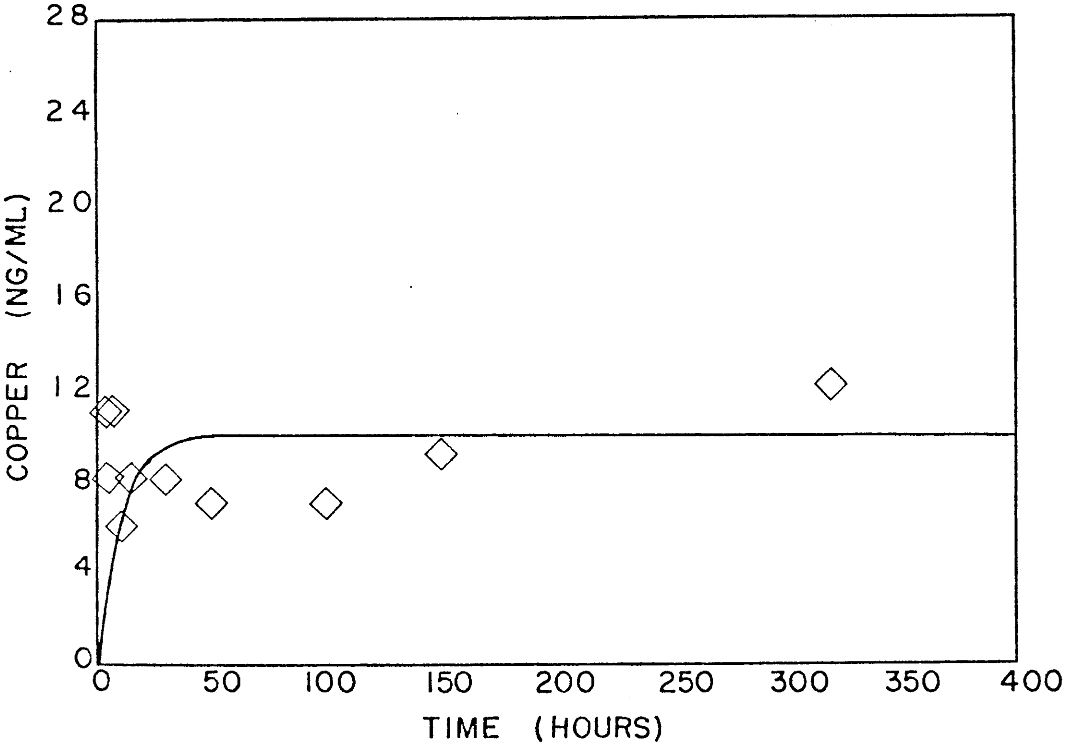

Figure 27 (b). Solubilized Copper in Static Osburn Tailings (Native) Solutions.

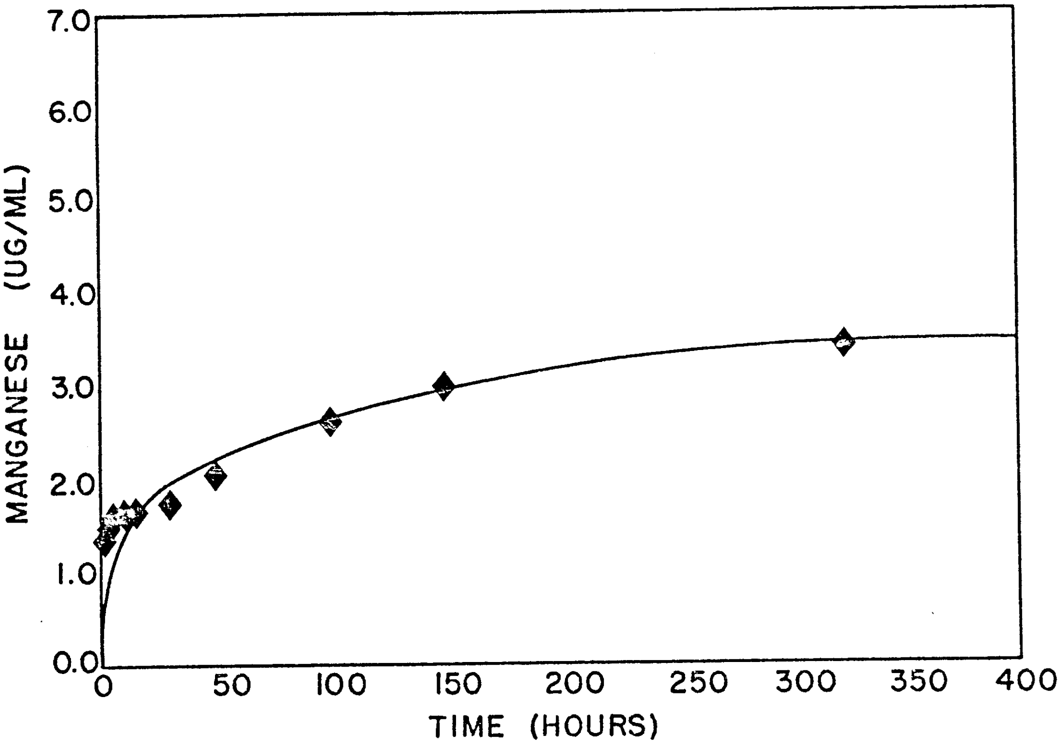

Figure 28 (a). Solubilized Manganese in Agitated Osburn Tailings (Dried, Sieved) Solutions.

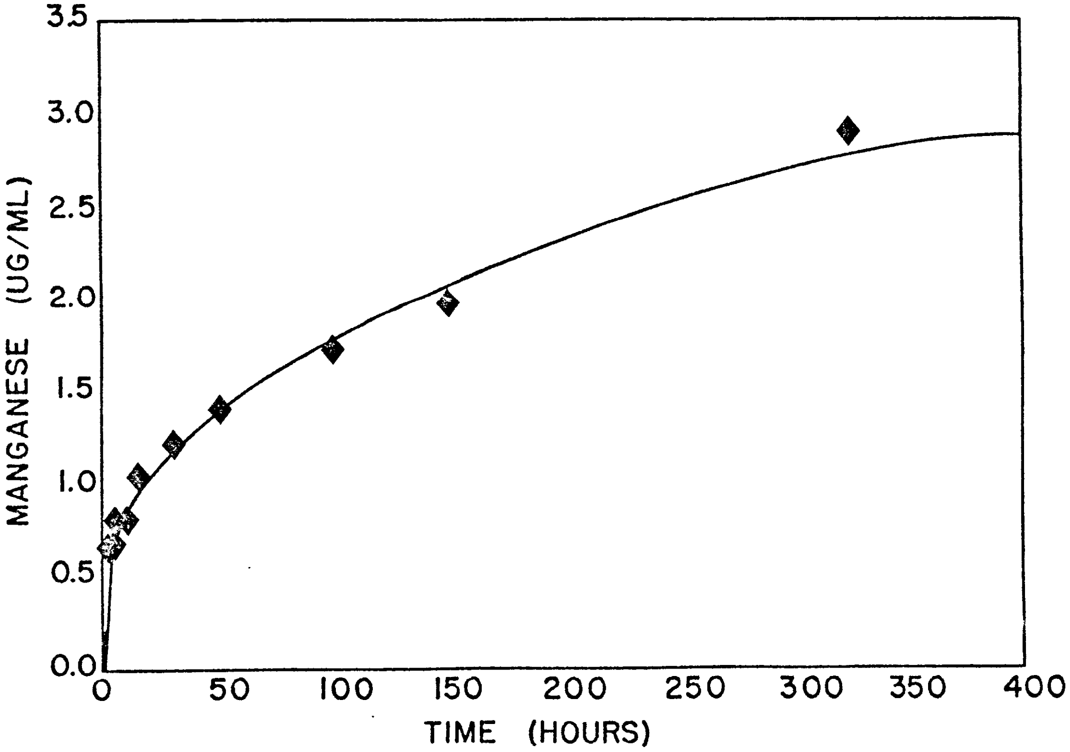

Figure 28 (b). Solubilized Manganese in Static Osburn Tailings (Dried, Sieved) Solutions.

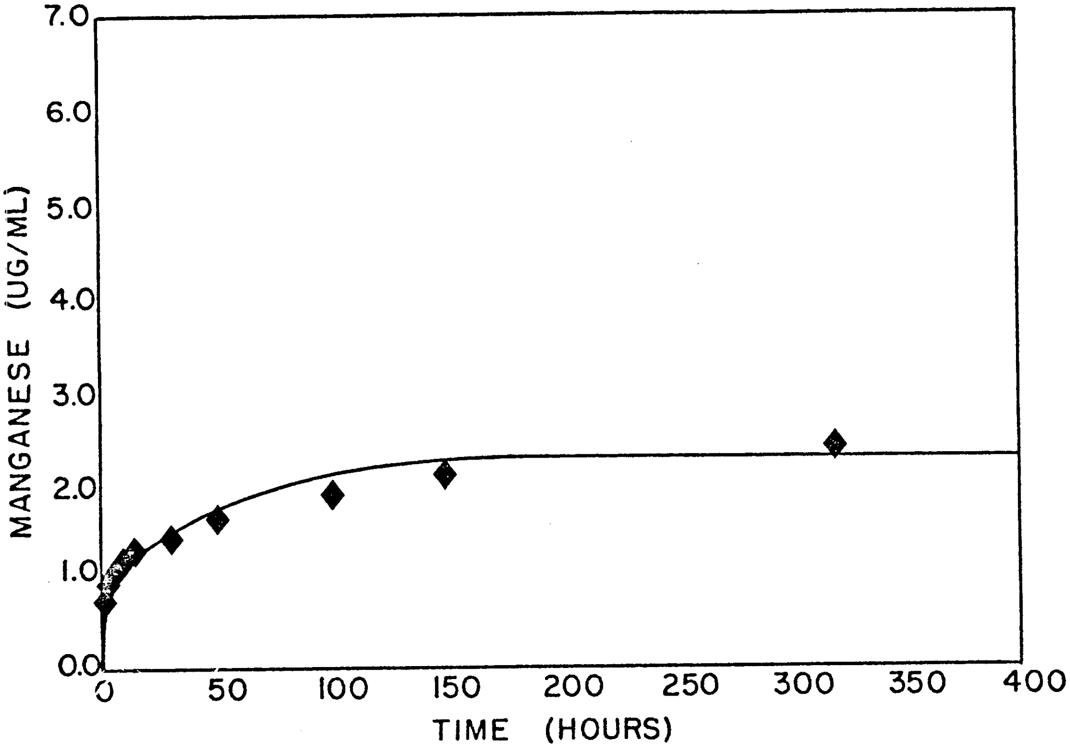

Figure 29 (a). Solubilized Manganese in Agitated Osburn Tailings (Native) Solutions.

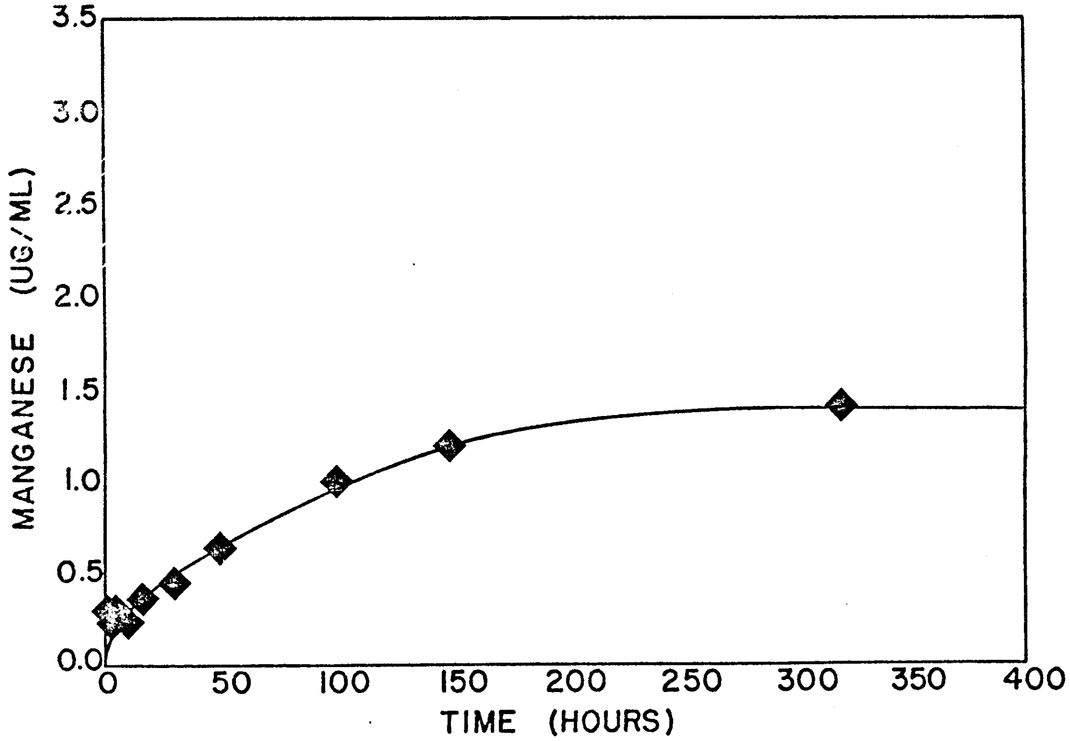

Figure 29 (b). Solubilized Manganese in Static Osburn Tailings (Native) Solutions.

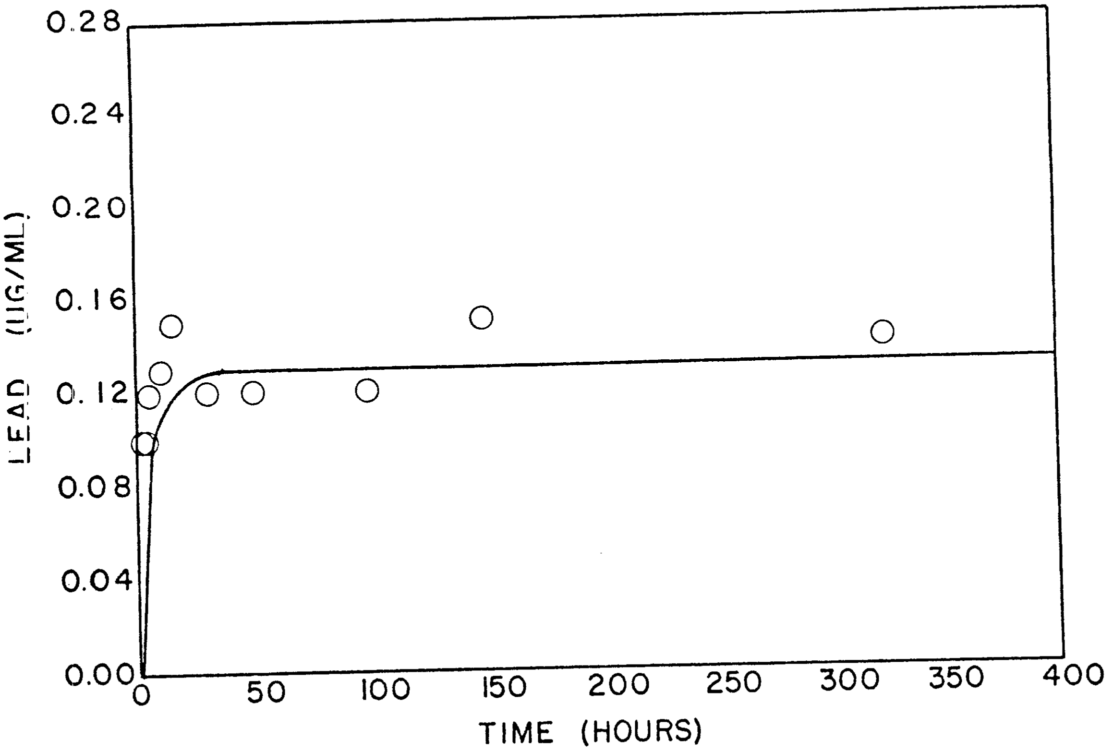

Figure 30 (a). Solubilized Lead in Agitated Osburn Tailings (Dried, Sieved) Solutions.

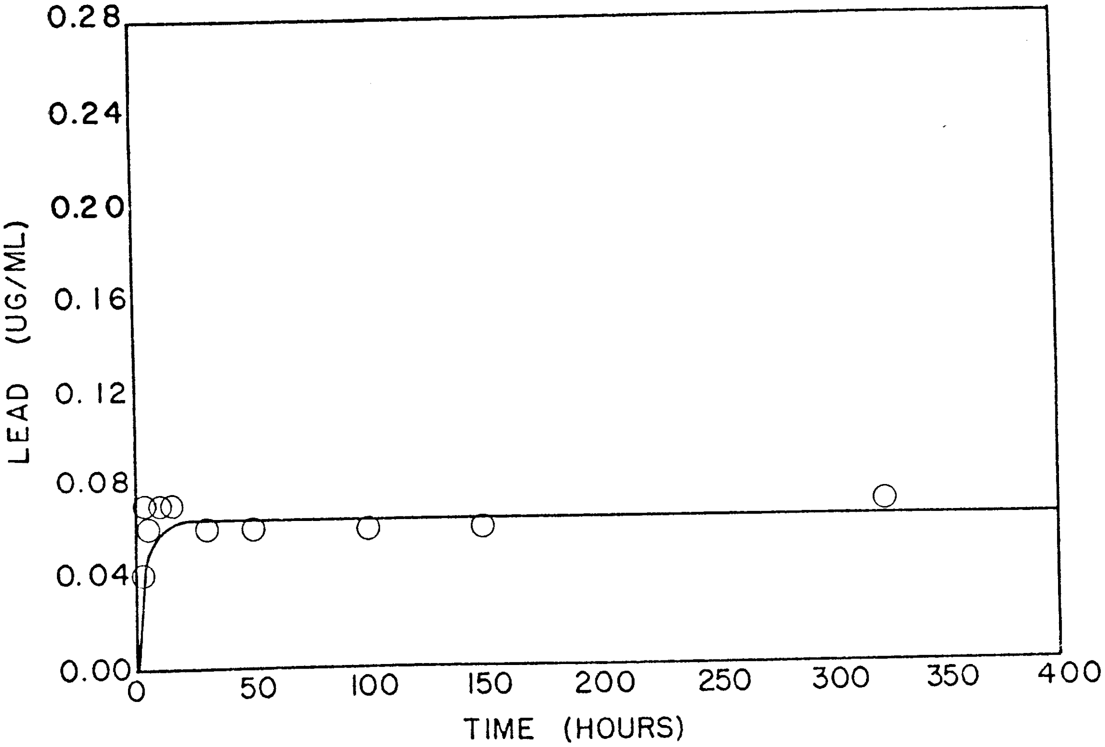

Figure 30 (b). Solubilized Lead in Static Osburn Tailings (Dried, Sieved) Solutions.

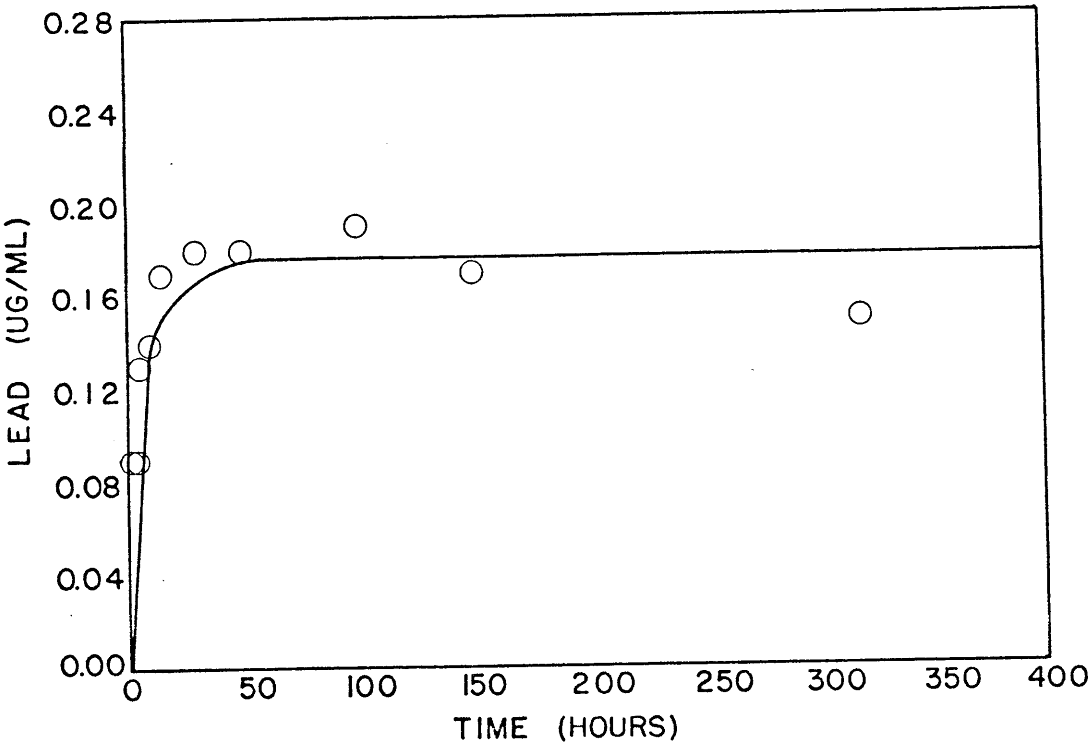

Figure 31 (a). Solubilized Lead in Agitated Osburn Tailings (Native) Solutions.

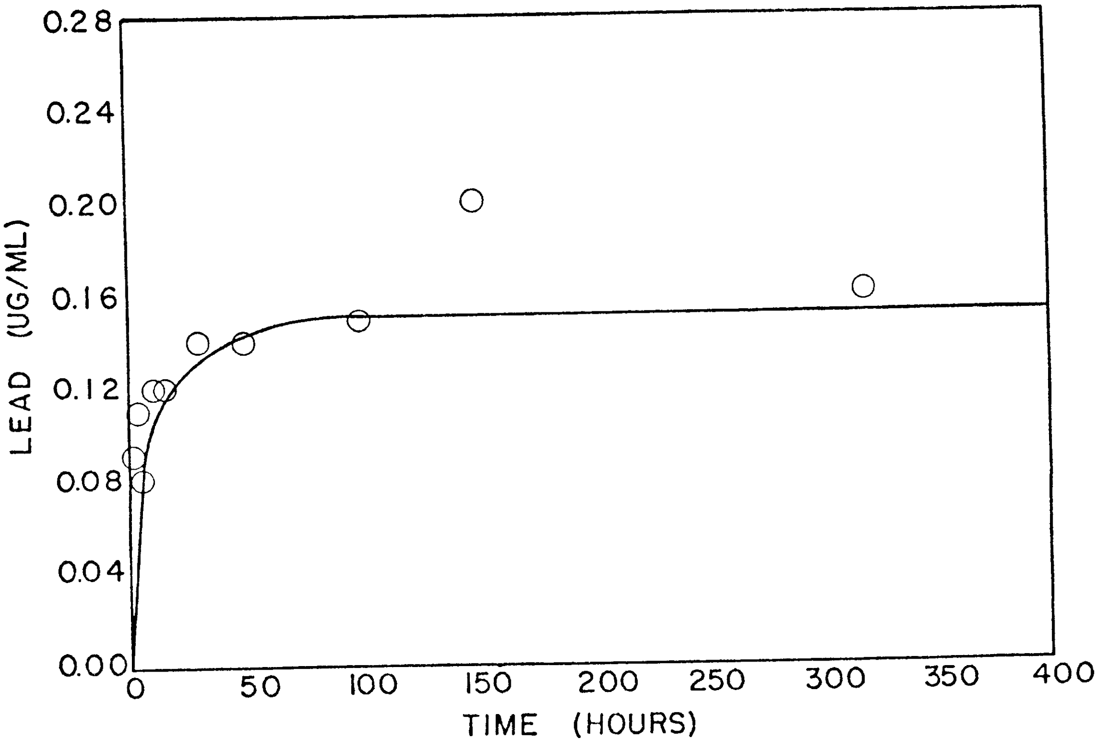

Figure 31 (b). Solubilized Lead in Static Osburn Tailings (Native) Solutions.

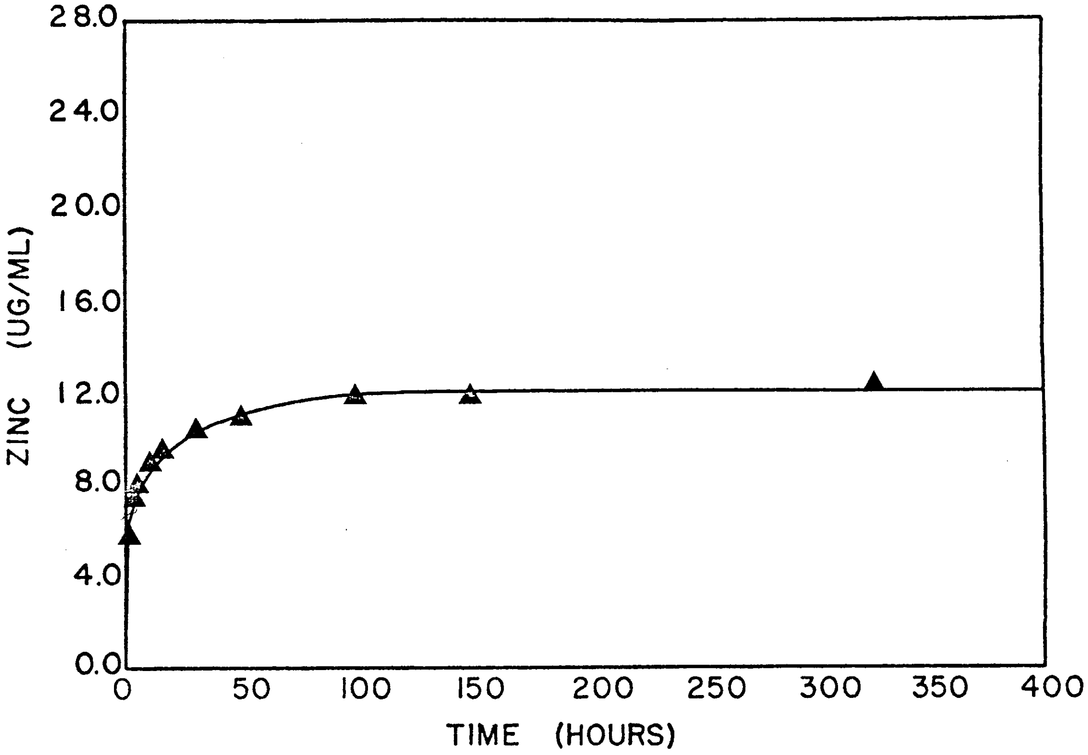

Figure 32 (a). Solubilized Zinc in Agitated Osburn Tailings (Dried, Sieved) Solutions.

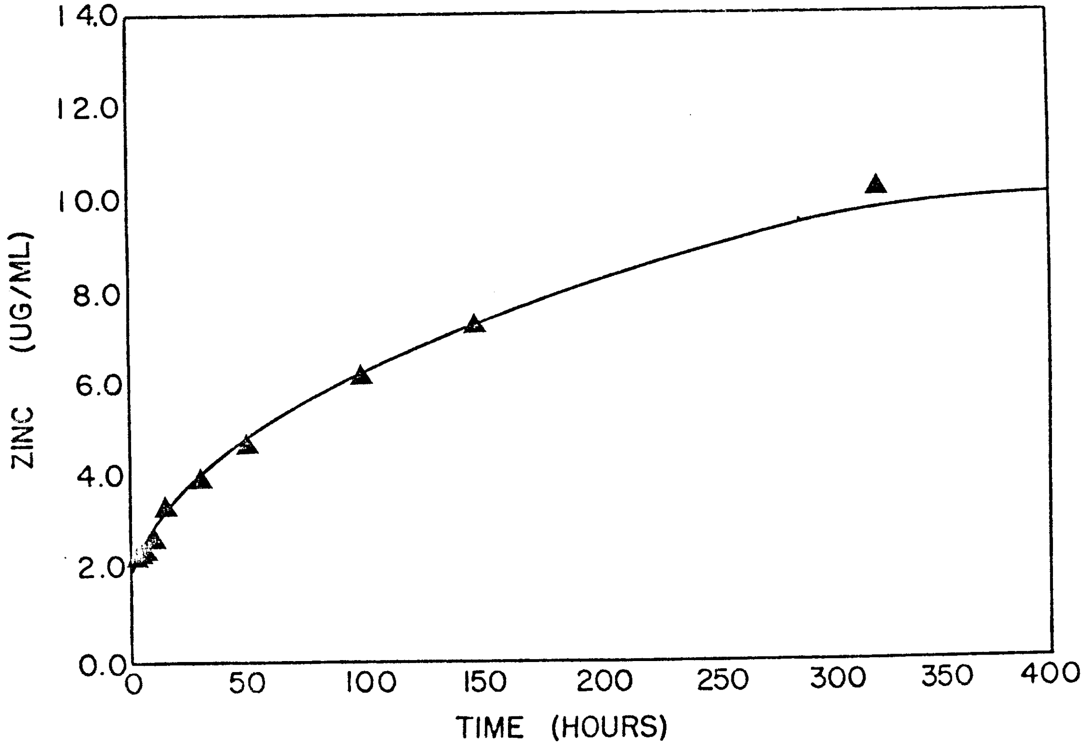

Figure 32 (b). Solubilized Zinc in Static Osburn Tailings (Dried, Sieved) Solutions.

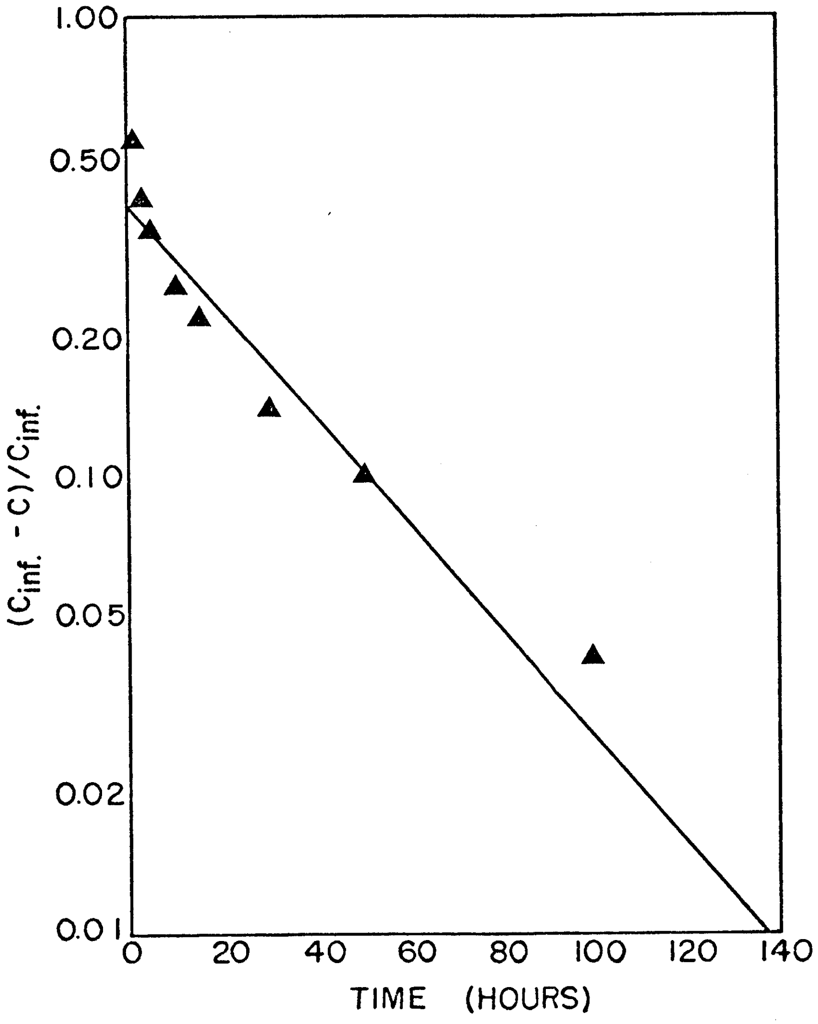

Figure 32-2a. Kinetic Plot for Solubilized Zinc in Agitated Osburn Tailings (Dried, Sieved) Solutions.

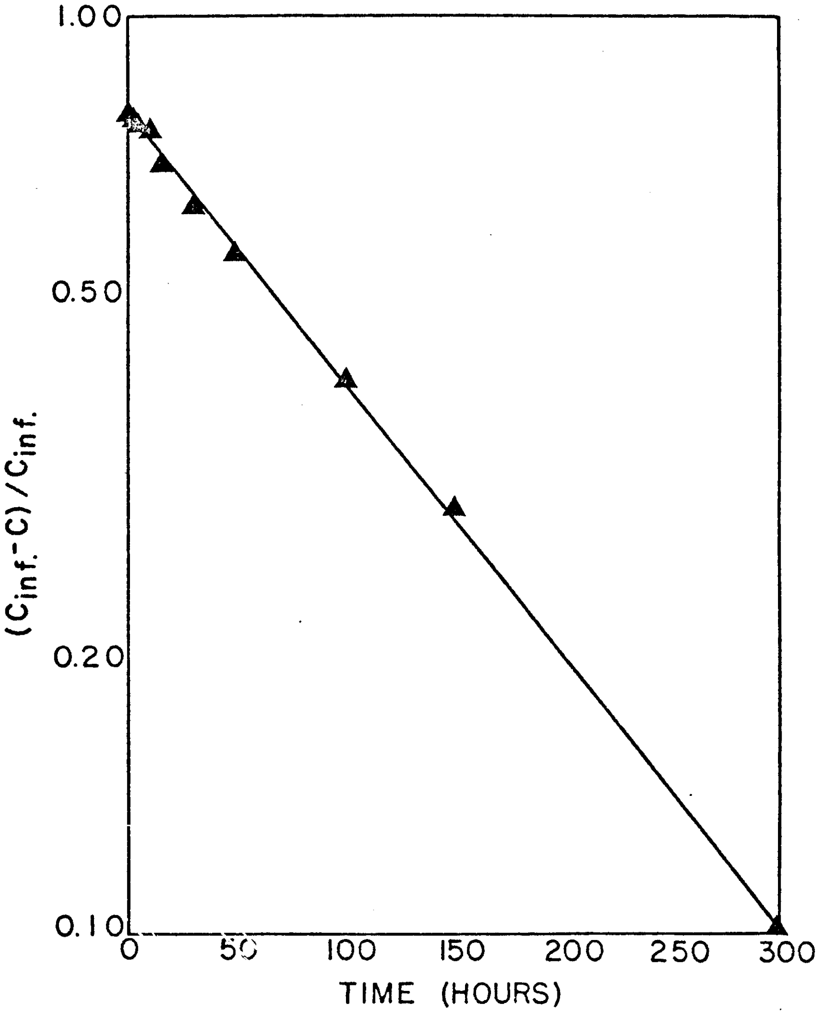

Figure 32-2b. Kinetic Plot for Solubilized Zinc in Static Osburn Tailings (Dried, Sieved) Solutions.

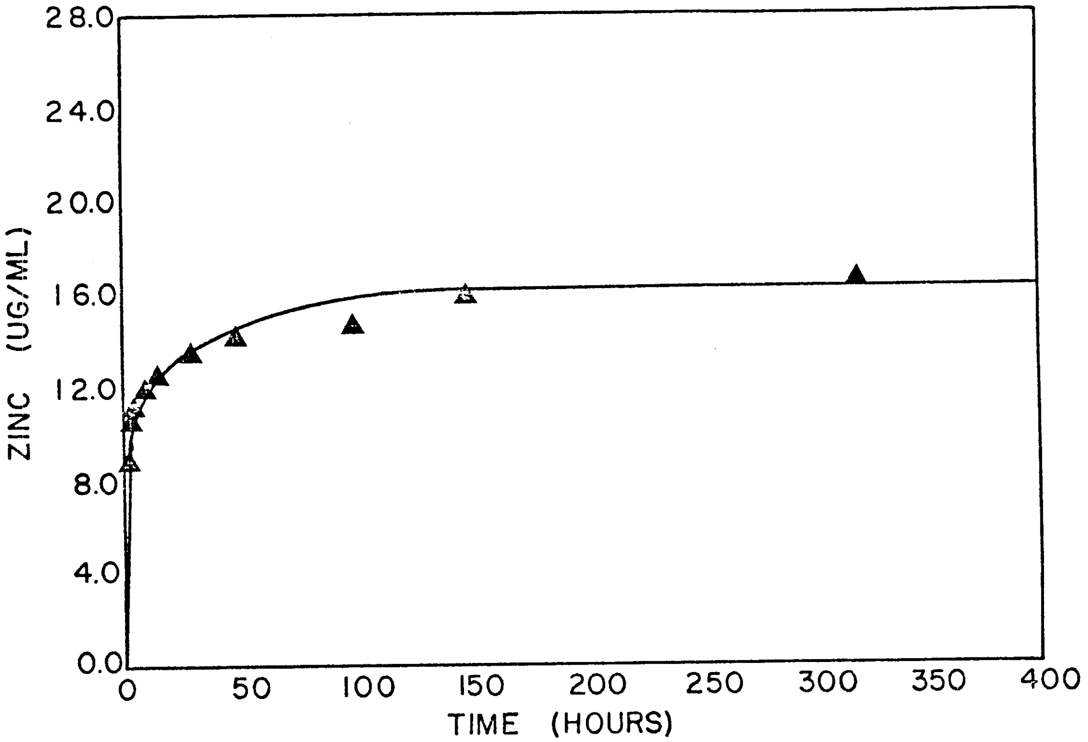

Figure 33 (a). Solubilized Zinc in Agitated Osburn Tailings (Native) Solutions.

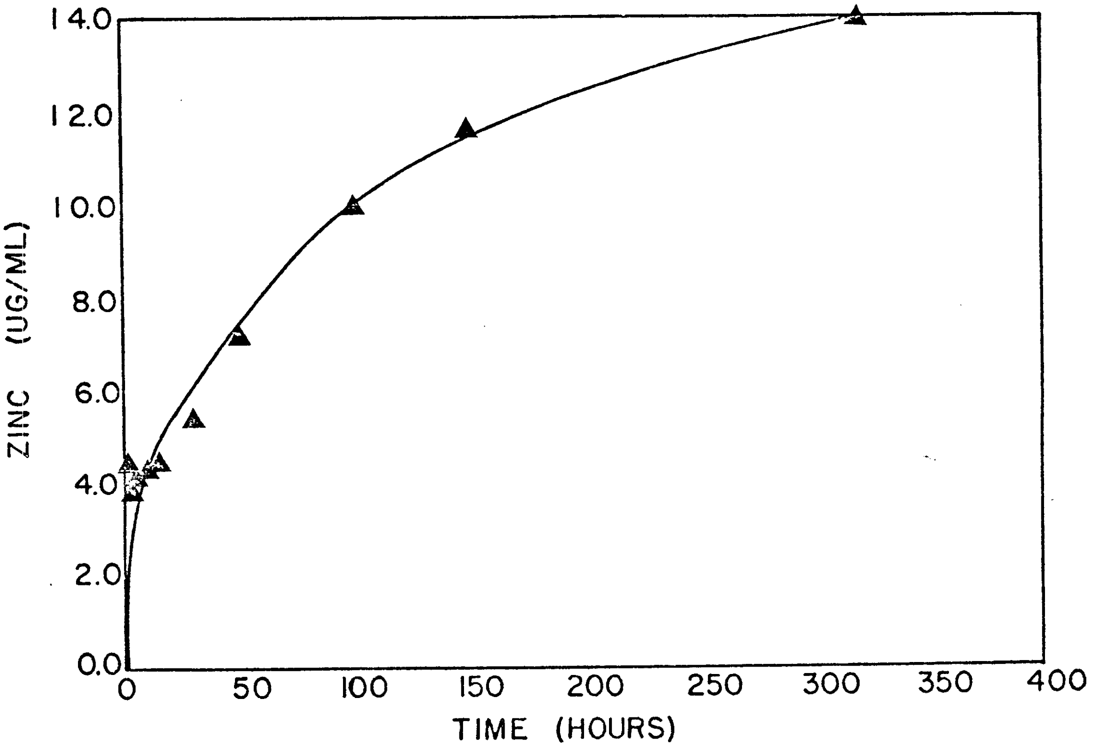

Figure 33 (b). Solubilized Zinc in Static Osburn Tailings (Native) Solutions.

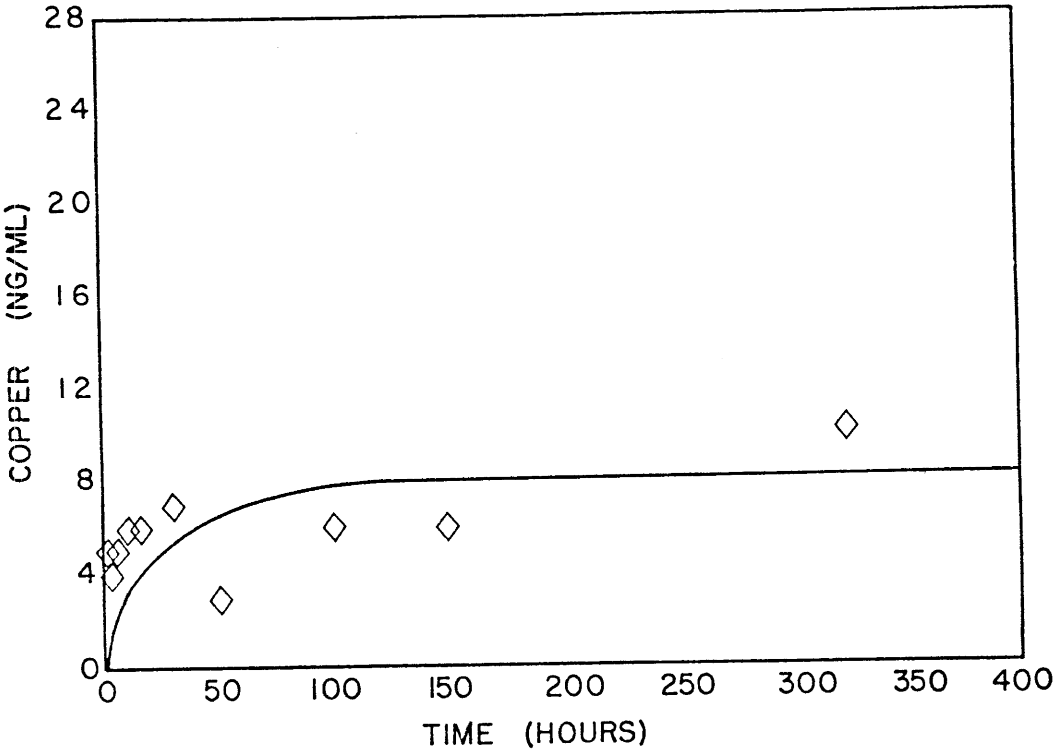

Figure 34 (a). Solubilized Copper in Agitated Cataldo Sediment (Dried, Sieved) Solutions.

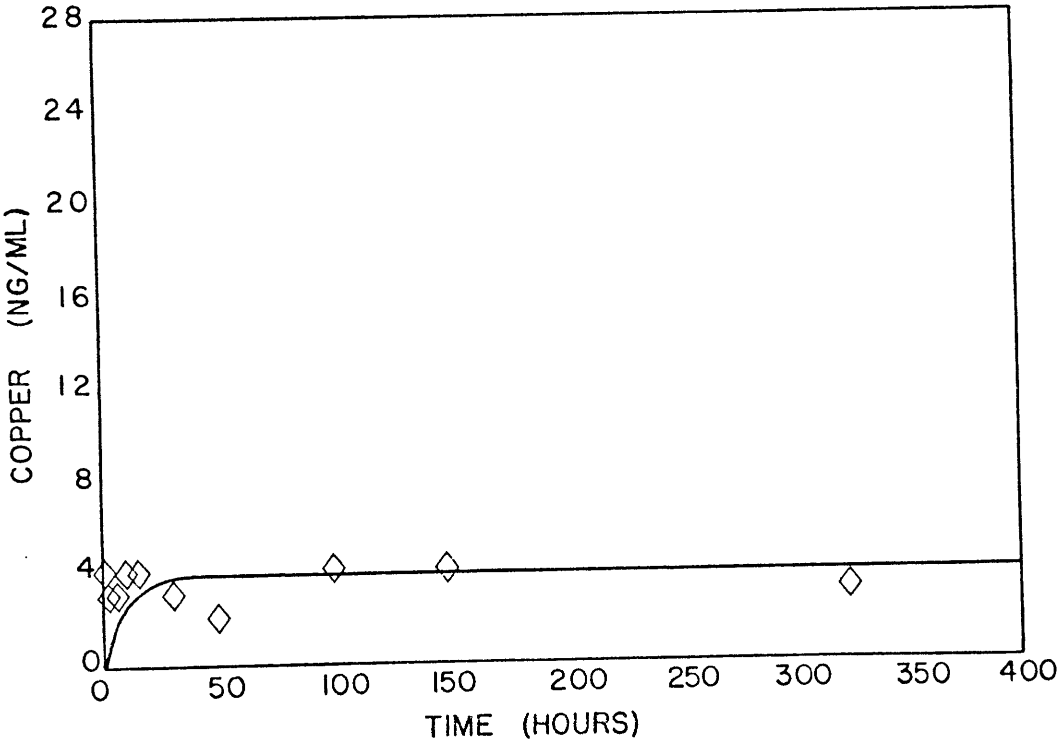

Figure 34 (b). Solubilized Copper in Static Cataldo Sediment (Dried, Sieved) Solutions.

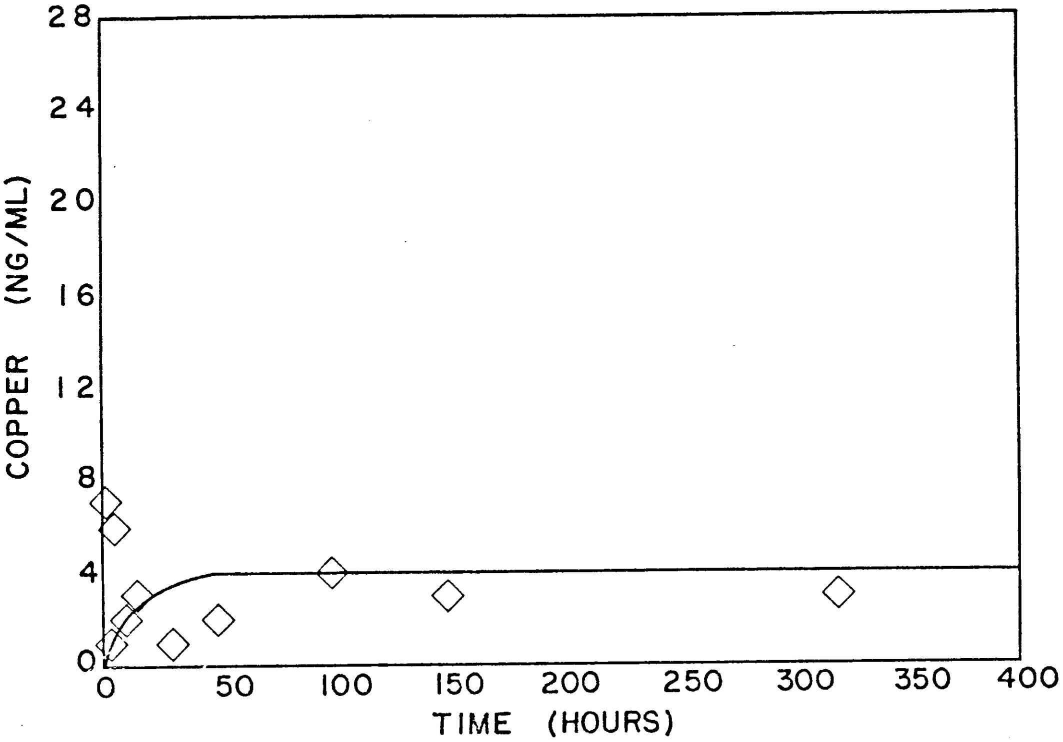

Figure 35 (a). Solubilized Copper in Agitated Cataldo Sediment (Native) Solutions.

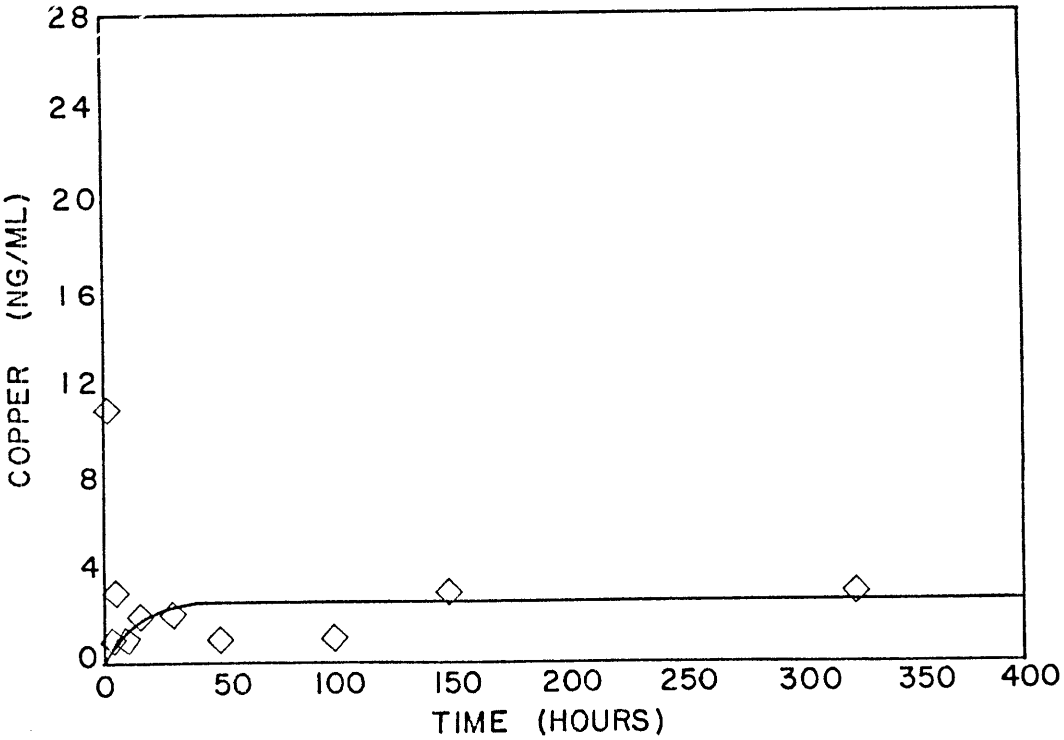

Figure 35 (b). Solubilized Copper in Static Cataldo Sediment (Native) Solutions.

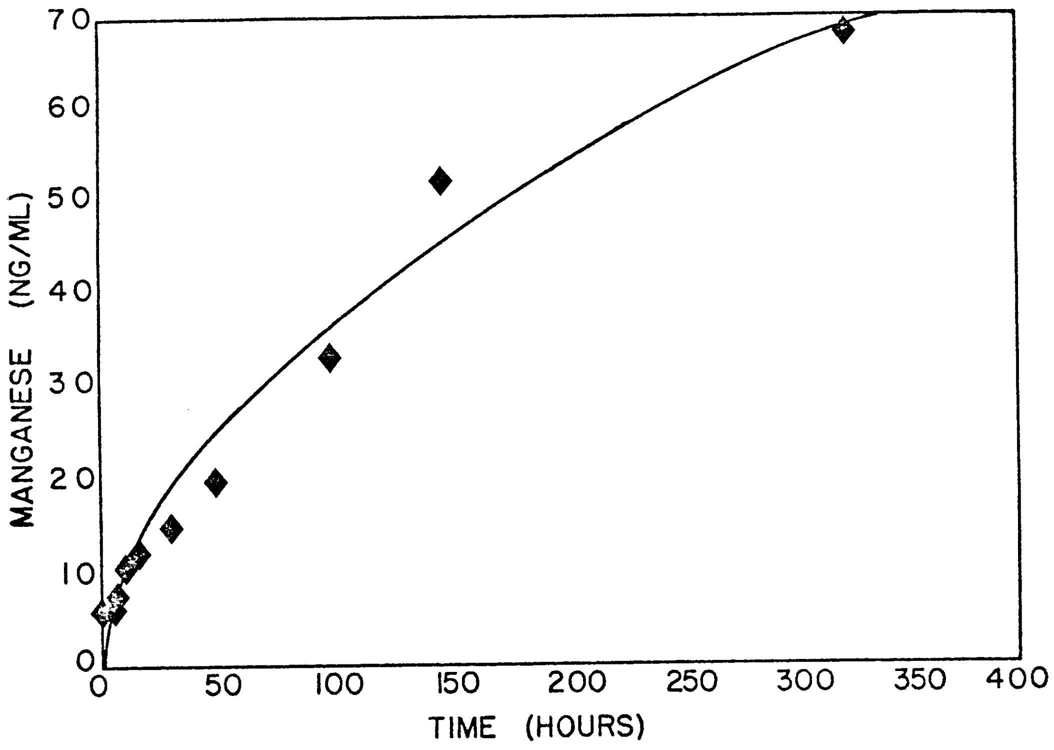

Figure 36 (a). Solubilized Manganese in Agitated Cataldo Sediment (Dried, Sieved) Solutions.

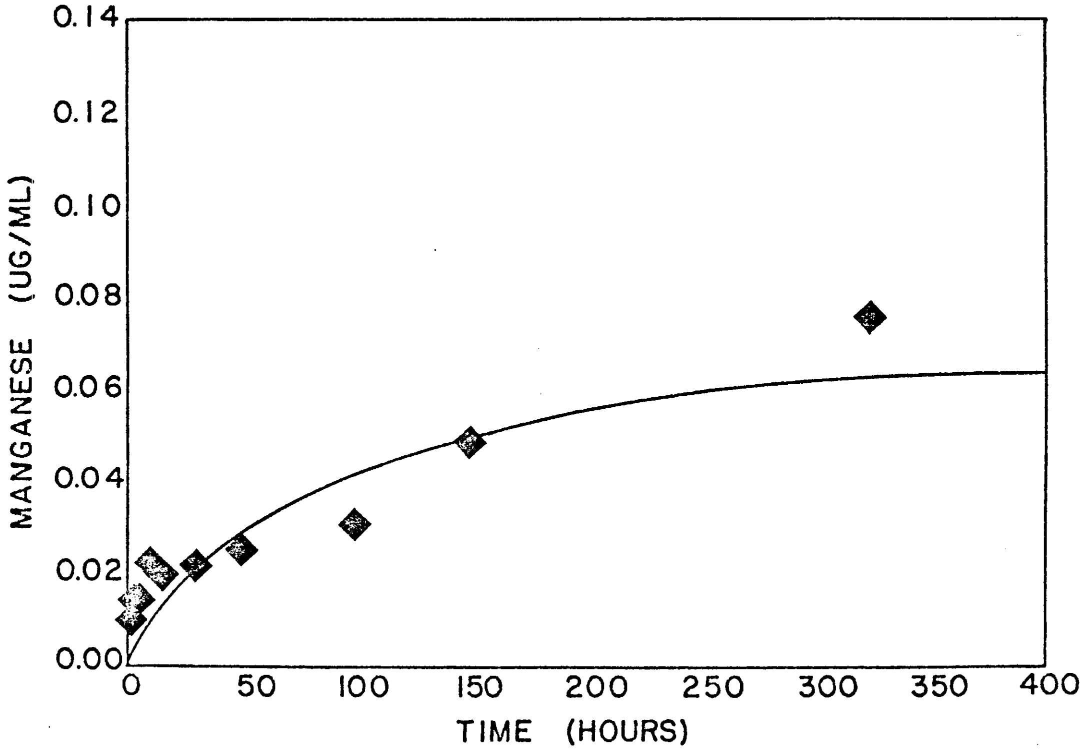

Figure 36 (b). Solubilized Manganese in Static Cataldo Sediment (Dried, Sieved) Solutions.

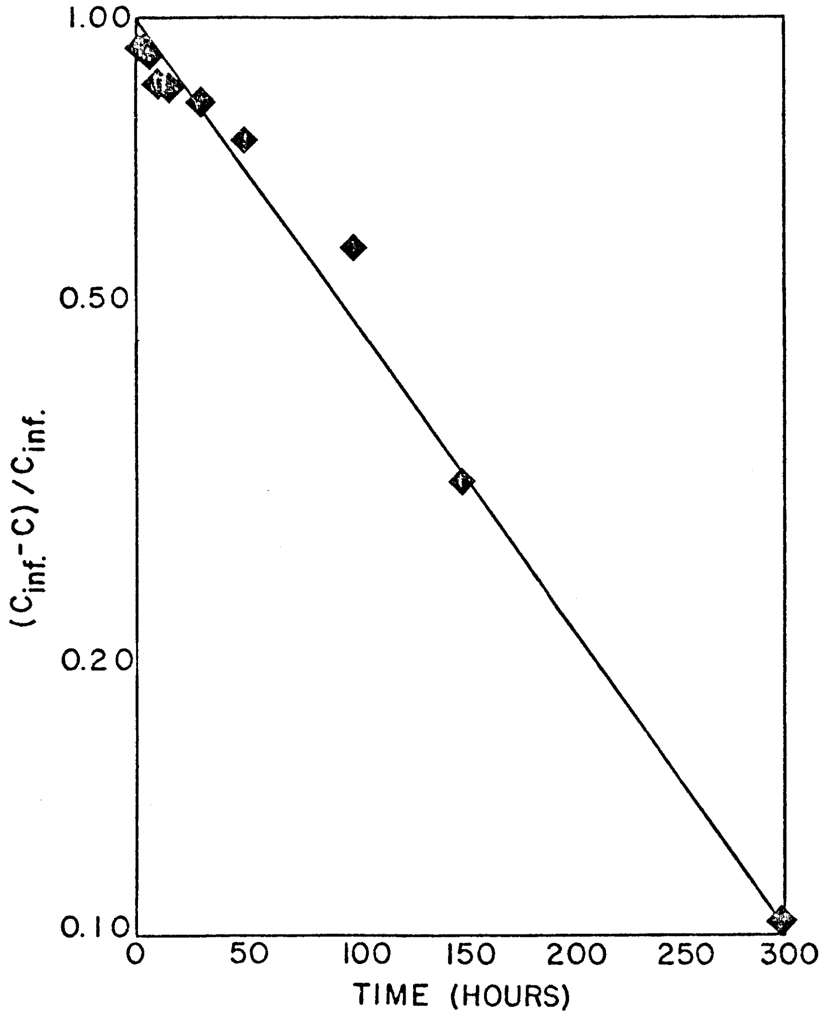

Figure 36-2a. Kinetic Plot for Solubilized Manganese in Agitated Cataldo Sediment (Dried, Sieved) Solutions.

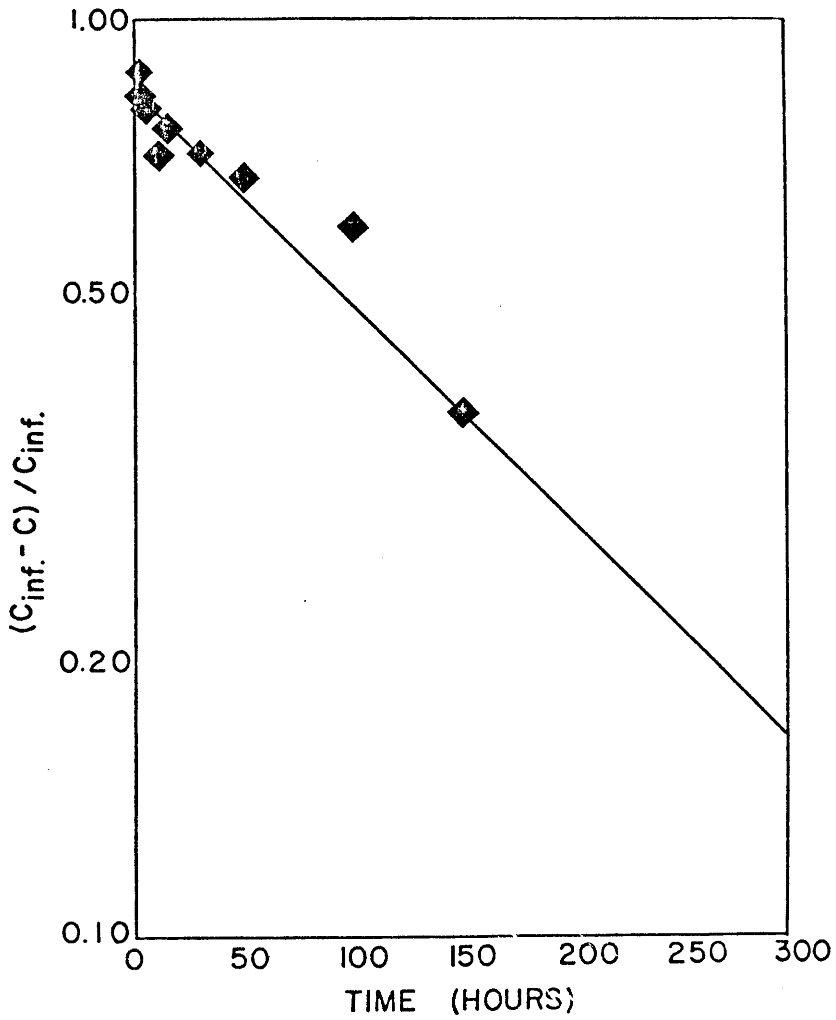

Figure 36-2b. Kinetic Plot for Solubilized Manganese in Static Cataldo Sediment (Dried, Sieved) Solutions.

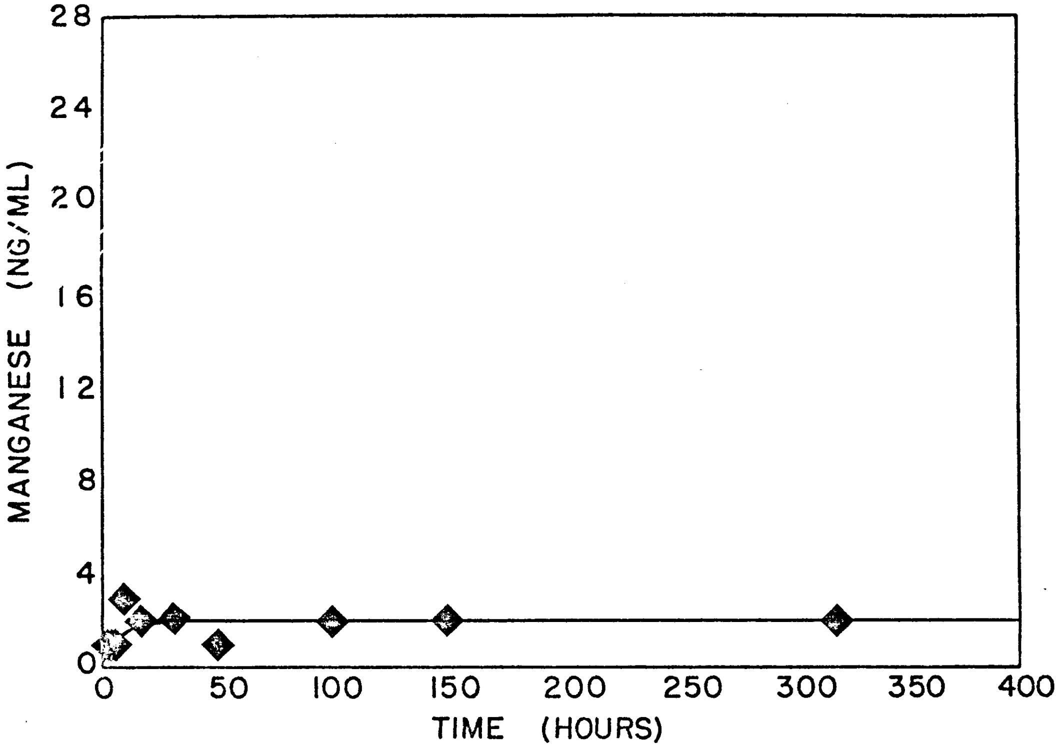

Figure 37 (a). Solubilized Manganese in Agitated Cataldo Sediment (Native) Solutions.

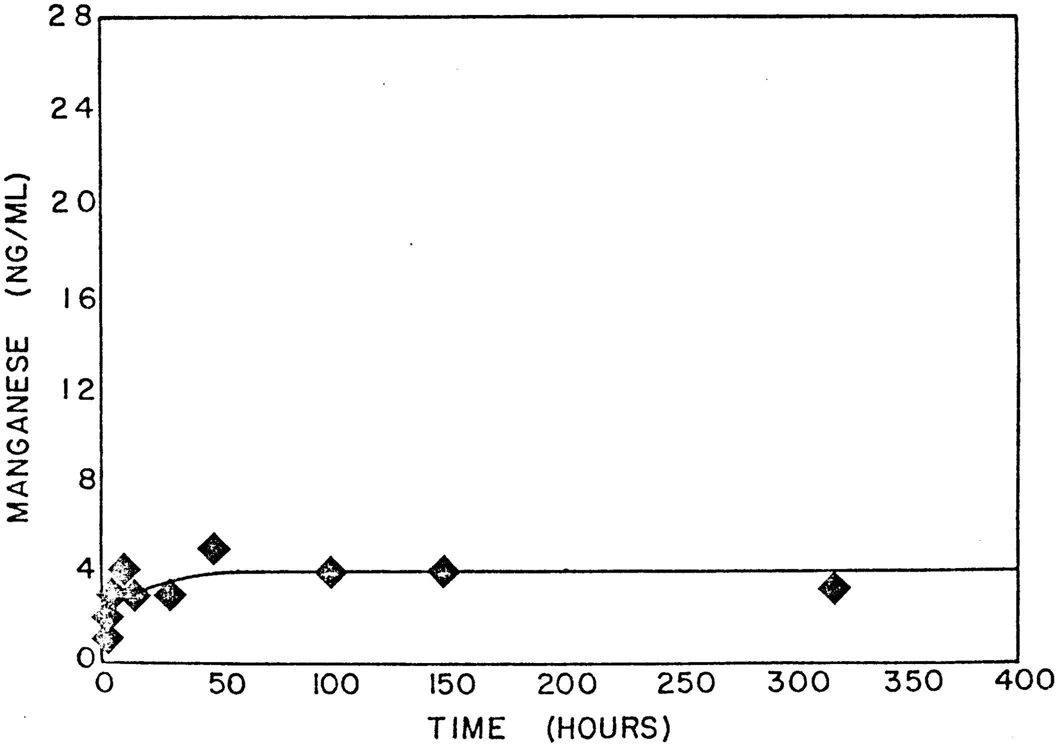

Figure 37 (b). Solubilized Manganese in Static Cataldo Sediment (Native) Solutions.

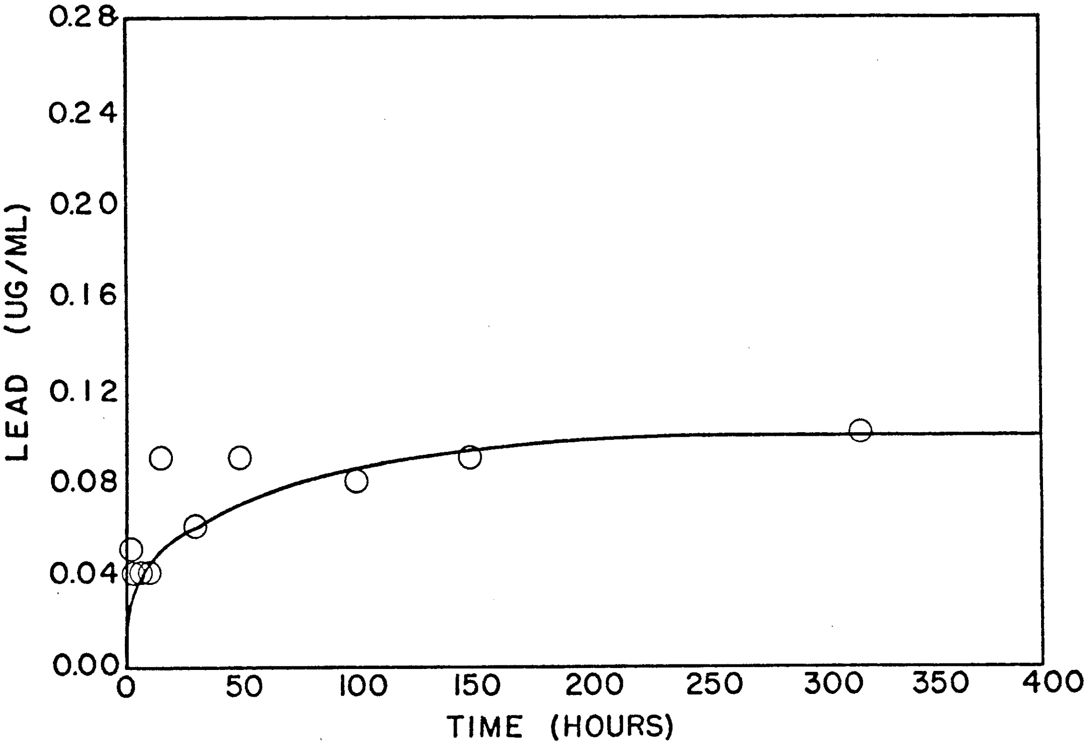

Figure 38 (a). Solubilized Lead in Agitated Cataldo Sediment (Native) Solutions.

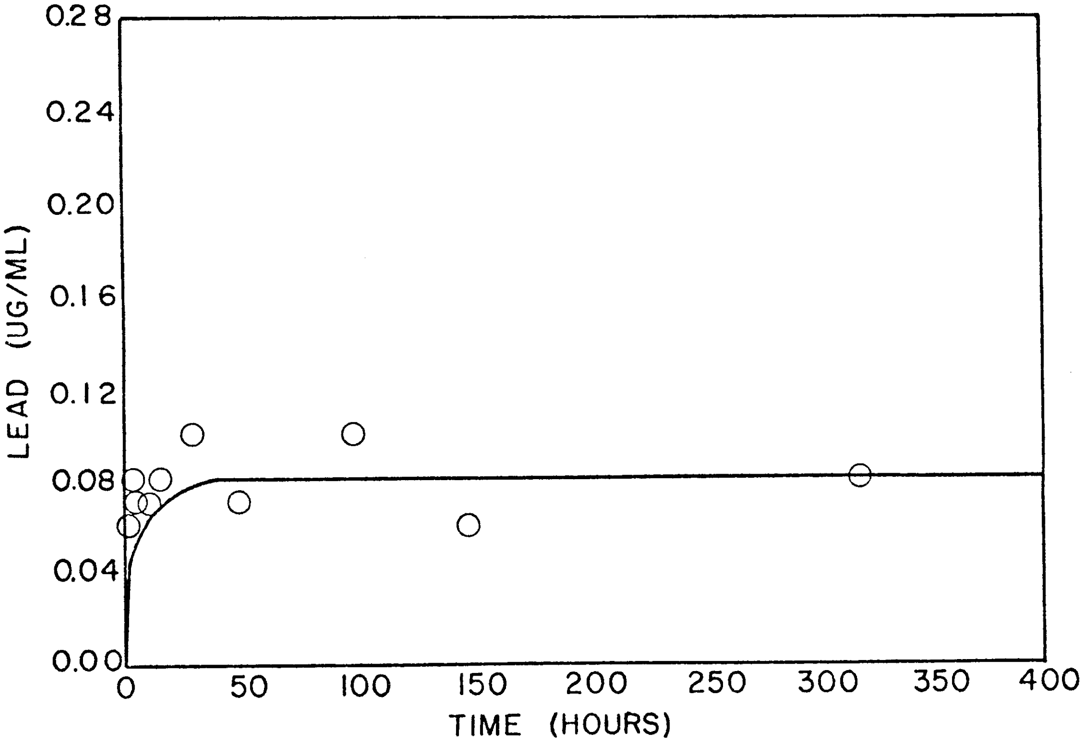

Figure 38 (b). Solubilized Lead in Static Cataldo Sediment (Native) Solutions.

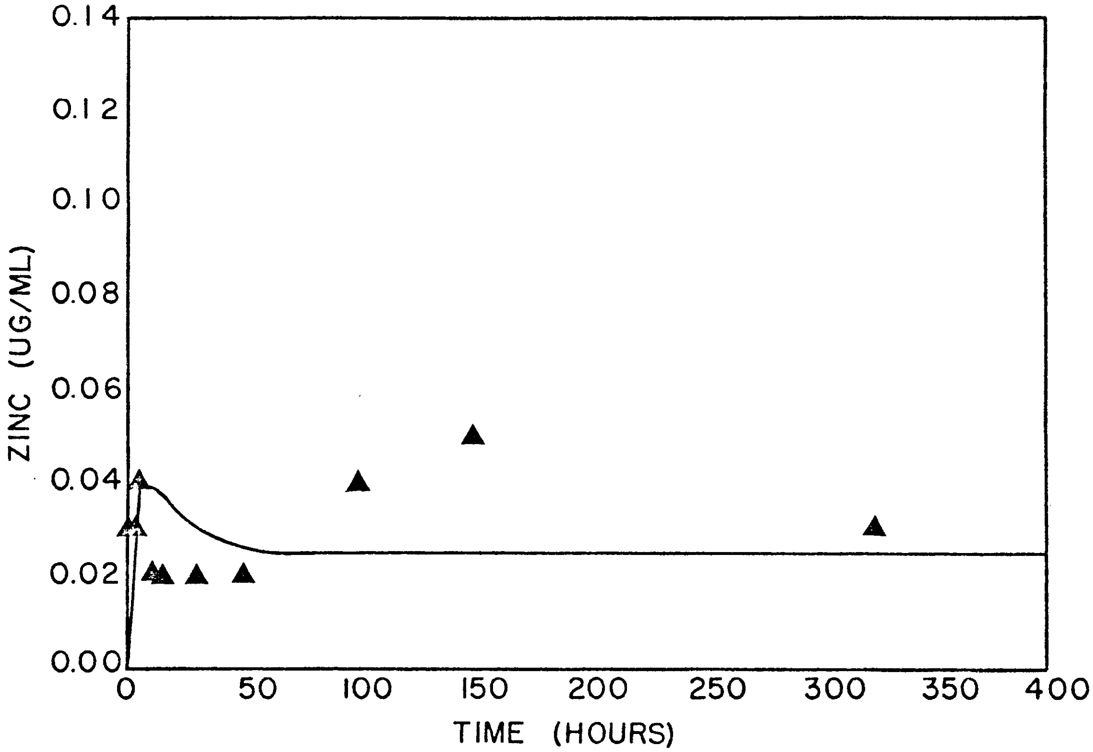

Figure 39 (a). Solubilized Zinc in Agitated Cataldo Sediment (Dried, Sieved) Solutions.

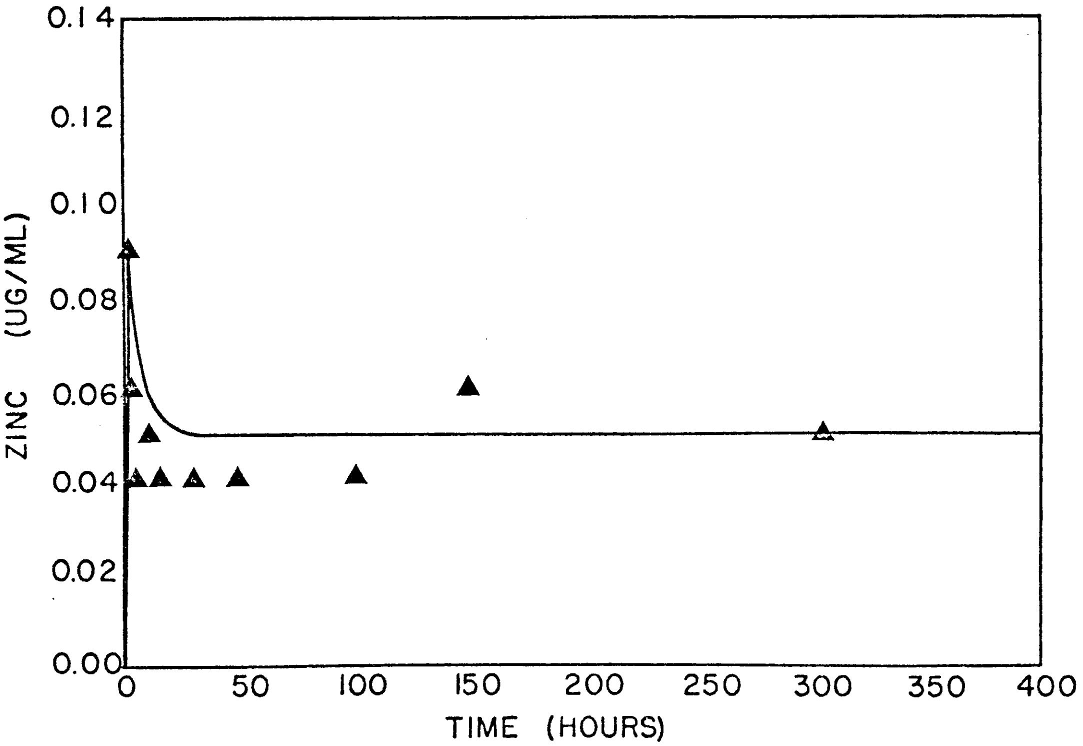

Figure 39 (b). Solubilized Zinc in Static Cataldo Sediment (Dried, Sieved) Solutions.

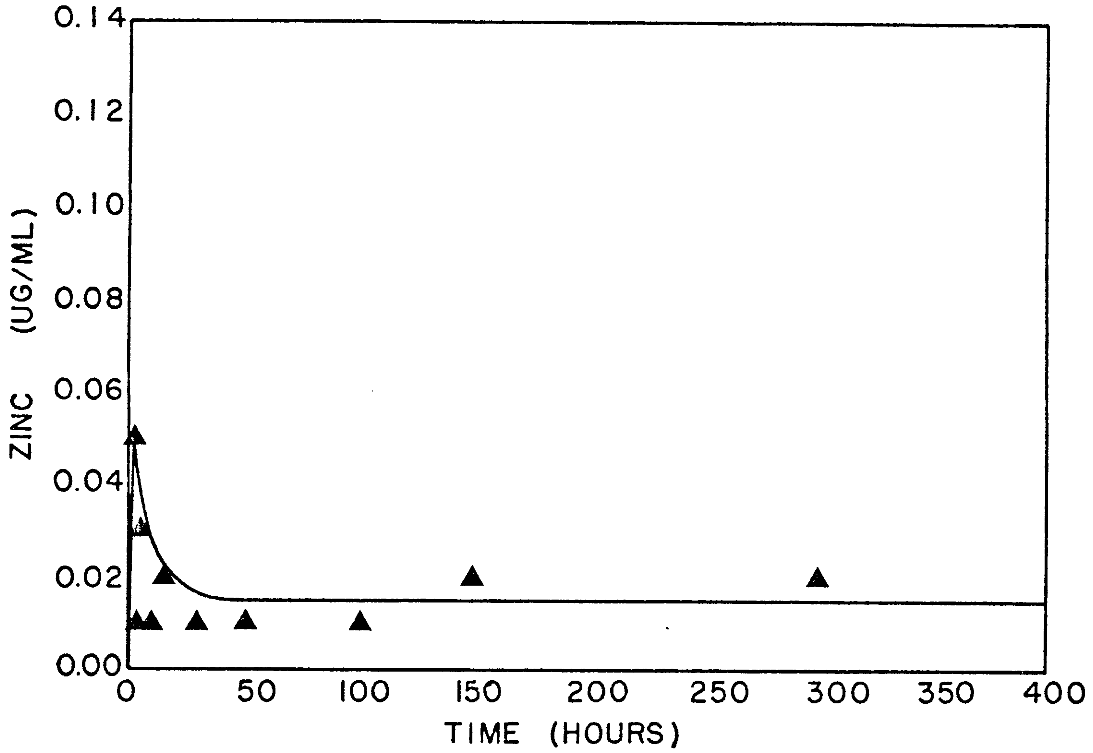

Figure 40 (a). Solubilized Zinc in Agitated Cataldo Sediment (Native) Solutions.

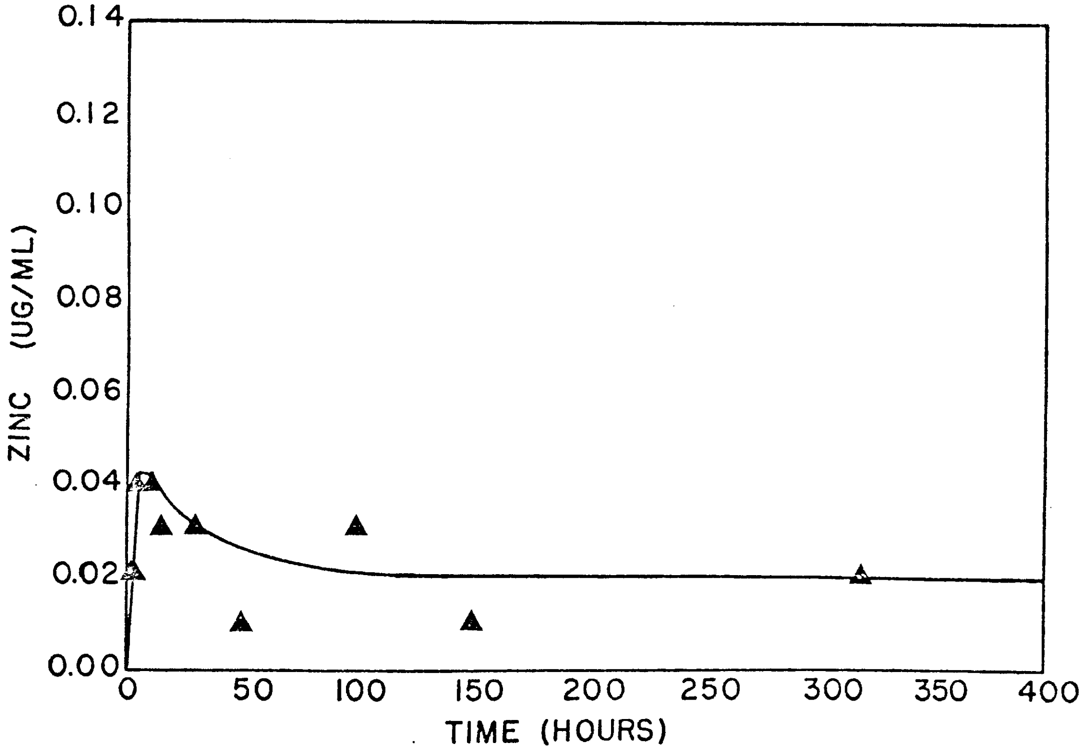

Figure 40 (b). Solubilized Zinc in Static Cataldo Sediment (Native) Solutions.

TABLE 12

ESTIMATED (FITTED CURVE) CADMIUM, COPPER, AND LEAD SOLUBILIZATION CONCENTRATIONS FOR SELECT TIME INTERVALS (ug/ml)

	Cadmium			Copper			Lead		
	$C_{24\text{ hr.}}$	$C_{48\text{ hr.}}$	$C_{\propto}$	$C_{24\text{ hr.}}$	$C_{48\text{ hr.}}$	$C_{\propto}$	$C_{24\text{ hr.}}$	$C_{48\text{ hr.}}$	$C_{\propto}$
Kellogg Agitated	0.12	0.11	0.10	0.022	0.021	0.015	0.50	0.43	0.31
Kellogg Static	0.07	0.07	0.07	0.022	0.018	0.015	0.50	0.53	0.19
Smelterville Agitated	<0.01	<0.01	<0.01	0.016	0.021	0.022	<0.01	<0.01	<0.01
Smelterville Static	<0.01	<0.01	<0.01	0.013	0.012	0.010	<0.01	<0.01	<0.01
Osburn (dried) Agitated	0.17	0.20	0.21	0.10	0.11	0.11	0.13	0.13	0.13
Osburn (dried) Static	0.05	0.07	0.16	0.07	0.07	0.08	0.06	0.06	0.06
Osburn (native) Agitated	0.20	0.22	0.26	0.11	0.12	0.12	0.16	0.18	0.18
Osburn (native) Static	0.07	0.10	0.22	0.09	0.10	0.10	0.13	0.15	0.15
Cataldo (dried) Agitated	<0.01	<0.01	<0.01	0.005	0.006	0.008	<0.01	<0.01	<0.01
Cataldo (dried) Static	<0.01	<0.01	<0.01	0.004	0.004	0.004	<0.01	<0.01	<0.01
Cataldo (native) Agitated	<0.01	<0.01	<0.01	0.003	0.004	0.004	0.06	0.07	0.10
Cataldo (native) Static	<0.01	<0.01	<0.01	0.002	0.003	0.003	0.07	0.08	0.08

TABLE 13

ESTIMATED (FITTED CURVE) IRON, MANGANESE, AND ZINC SOLUBILIZATION CONCENTRATIONS FOR SELECT TIME INTERVALS (ug/ml)

	Iron			Manganese			Zinc		
	$C_{24\ hr.}$	$C_{48\ hr.}$	$C_{\propto}$	$C_{24\ hr.}$	$C_{48\ hr.}$	$C_{\propto}$	$C_{24\ hr.}$	$C_{48\ hr.}$	$C_{\propto}$
Kellogg Agitated	0.20	0.17	<0.01	2.25	2.75	3.30	1.32	1.42	1.43
Kellogg Static	0.50	0.50	6.75	1.65	2.15	10.00	0.88	0.97	0.98
Smelterville Agitated	1.18	1.48	2.00	0.17	0.18	0.18	0.20	0.15	0.10
Smelterville Static	0.25	0.40	0.70	0.13	0.15	0.50	0.15	0.12	0.10
Osburn (dried) Agitated	<0.01	<0.01	<0.01	0.18	0.22	3.50	9.80	10.47	12.00
Osburn (dried) Static	<0.01	<0.01	<0.01	1.10	1.40	2.85	3.80	4.80	10.25
Osburn (native) Agitated	<0.01	<0.01	<0.01	1.35	1.69	2.25	13.15	14.45	16.00
Osburn (native) Static	<0.01	<0.01	<0.01	0.40	0.65	1.40	5.62	7.33	15.00
Cataldo (dried) Agitated	<0.01	<0.01	<0.01	0.017	0.025	0.075	0.03	0.03	0.03
Cataldo (dried) Static	<0.01	<0.01	<0.01	0.019	0.029	0.076	0.05	0.05	0.05
Cataldo (native) Agitated	<0.01	<0.01	<0.01	0.002	0.002	0.002	0.02	0.02	0.02
Cataldo (native) Static	<0.01	<0.01	<0.01	0.003	0.004	0.004	0.03	0.02	0.02

which can be obtained by taking the anti-log of both sides of the integrated equation (Adamson, 1973).

Obviously, if $A_o = 0$, such as is true in the case of the undissolved salts in these experiments, then it is much more convenient to plot the fraction of dissolved salt (reaction product) relative to the equilibrium concentration of dissolved salt; e.g. a plot of $\log [(A_\infty - A) \div A_\infty]$ vs. time. Regardless of which manner of presentation is employed, a log plot of A versus time will yield a straight line if the relationship between the concentration of A and reaction time is a linear one.

In summary those solubilization plots which are very smooth "elbow-shaped" (exponential) curves yield excellent straight line plots for the kinetic plots (plots of $\log [(C_\infty - C) \div C_\infty]$ vs. time), which indicate a first order dissolution of the trace metal. Values of sample concentrations (C) which are greater than the equilibrium concentration (C_∞) cannot be plotted because the logarithm of a negative number cannot be calculated. Therefore, any concentrations greater than the extrapolated C_∞ will not yield a point on the corresponding kinetic plot. The data for each solubilized soil are now presented individually.

Kellogg Soil

The general solubilization behavior of this soil can be characterized as first order. Commonly a rapidly rising slope asympotically approaches an equilibrium concentration, usually within two days (Tables 12 and 13). Manganese in the agitated solution (Fig. 17a) is a typical first order/linear relationship example. Manganese in the static solution (Fig. 17b) had not yet reached equilibrium before the experiment terminated;

therefore, the resulting kinetic plot (Fig. 17-2b) reflected that fact. There is an initial surge of copper and zinc (Fig. 15 and 19) ions entering the solution because of the high solubility of the oxidized (weathered) layer on the surface of the soil grains. However, the remainder of the plotted data to which the zinc and copper solubilization curves were fit quickly yielded stable equilibrium concentrations. Most of the other trace metal ions follow the same path (Fig. 14 and 18), iron is the sole exception (Fig. 16).

The plot of solubilized iron concentrations versus time for the agitated version of the experiment illustrates the effects of two distinct parameters, oxygenation and pH. It is suggested that the systematic exposure of the entire surface of each grain to the oxygen rich solution in the agitated Kellogg soil solution duplicates caused rapid dissolution of the oxidized surfaces with concomitant precipitation of iron and a drop in pH. (The average terminal pH of the agitated Kellogg soil solution duplicates was 4.03 whereas that of the static soil solution duplicates was 4.56.) This suggestion is consistent with the experimental design and results given here and with mechanisms reported in the literature.

The experimental design and results have been introduced; however, an amplification of the factors affecting the initial pH of the soil solutions is useful here. The pH of the ultrapure water used to initiate these experiments was determined to be 5.20. The difference between this value (5.20) and the theoretical 7.00 pH value that one normally assumes for ultrapure water is due entirely to the equilibrium of naturally occurring carbon dioxide in air and dissolved carbon dioxide in the water. Boiling the ultrapure water prior to use would have sufficiently raised the temperature of the solution to have converted the dissolved carbon dioxide to gaseous carbon dioxide, removing it from solution, and would have produced water of pH 7.00. This procedure was deemed unnecessary because the experiment was not designed to exclude atmospheric contact since rainwater and other natural waters are in atmospheric contact under normal field conditions.

Mechanisms reported in the literature, such as those by Ghosh and others (1966), have shown that the aeration caused by continuous stirring raises the initial pH of an aqueous solution by stripping carbon dioxide and simultaneously introducing oxygen for the oxidation of iron II to iron III. Iron III is unstable at pH >3 and precipitates according to the reaction

$$Fe^{+3} + 3H_2O \rightarrow \underline{Fe(OH)_3} + 3H^+$$

The overall reaction can be shown as

$$2Fe^{++} + 5H_2O + \tfrac{1}{2}O_2 \leftrightarrows \underline{2Fe(OH)_3} + 4H^+$$

where it is seen that acidic hydrogens are released, resulting in a low pH. This iron precipitation and acid production process is apparently first order with respect to pH. Ghosh and others (1966) determined that the oxygenation rate and removal of iron II from natural groundwaters in Illinois had a first order dependence on pH.

Iron II hydroxide is insoluble in alkaline solutions and soluble in acidic solutions whereas iron III hydroxide is insoluble over a broad range of pH (Weast, 1977). O'Melia and Stumm (1967) have constructed a log concentration - pH solubility phase diagram for iron which shows that concentrations down to approximately 10^{-6} moles/liter would precipitate at pH 4.0 (which is the same as saying that all but approximately 5 parts per billion of ferric iron would be precipitated as iron III hydroxide at pH 4.0). Their work did not specify whether or not an attempt was made to maintain a specific pE during the experiments leading to construction of their phase diagram. Rather, their diagram was based on equilibrium concentrations at specified pH's, maintained by addition of acid or base.

Natural waters have variable pE's which must fall between the oxidizing and reducing limits of water, which are given by $pE = 20.75 - pH$ and $pE = -pH$, respectively (Manahan, 1975). The importance of pE is that a reducing environment, low pE, will allow high levels of iron to be solubilized as iron II--such as often occurs for ground waters. In an oxidizing environment, high pE--such as can occur in a turbulent stream, the precipitation of iron III hydroxide is favored.

This discussion is also in accord with Applebaum (1956), who determined that high suspended solids favor the oxygenation of iron II to iron III as a result of available ferrous ion adsorption sites. Smith and others (1968a, 1968b) agree with this explanation in as much as they state that oxygen is necessary for the electron transfer occuring during oxidation of iron II to iron III at ferrous ion adsorption sites on pyrite crystals (and hence, for the precipitation of iron as iron III hydroxide). Pyrite is, of course, known to be one of the principal iron-bearing minerals in the Coeur d'Alene River Valley soils and mine tailings (Reece, 1974).

It is postulated therefore, that agitation of the Kellogg soil solutions caused sufficient oxygenation of solubilized ferrous ions to result in precipitation of iron as iron III hydroxide. The static soil solution, on the other hand, remained largely unaffected by precipitation because the ferrous ions were not oxygenated. Hence, the solubilized iron concentrations of the oxygen-poor/reducing static soil solutions were controlled by iron II hydroxide, which is soluble in an acidic environment.

The hydration products of the remaining trace elements are soluble in acidic solutions and would not be expected to form precipitates in the Kellogg soil solutions.

Smelterville Soil

Much like the Kellogg soil, the solubilization behavior of this soil can be described as first order. The surges of zinc ions alluded to in the Kellogg soil solutions are distinctly prevalent in these Smelterville soil solutions (Fig. 23). Again, this behavior is believed to be due to the high solubility of the oxidized layer on the surfaces of the soil grains. It is quite probable that slightly soluble zinc sulfide is rapidly oxidized to highly soluble zinc sulfate under field conditions (weathering). Marcy (1979) found zinc sulfate to be the principal component of surface precipitates on tailings piles near Smelterville.

The solubilized copper concentrations of the static Smelterville soil solutions (Fig. 20b) are mildly influenced in the same manner as zinc, as was the solubilized copper in the static Kellogg soil solutions (Fig. 15b). Manganese (Fig. 22) solubilization curves for Smelterville soil solutions follow first order kinetics fairly well, just as was true of the agitated Kellogg soil solution. The similarities between the

Kellogg and Smelterville soil solutions end there, however; the solubilized iron behaviors for the two soils are considerably different. In the ensuing discussion it will be advantageous to note that the Smelterville soil solutions reached only mildly acidic pH values of 5.84 and 6.27 for agitated and static experiments, respectively (Table 6).

O'Melia and Stumms' (1967) (log concentrations -pH solubility) phase diagram indicates that the agitated Smelterville soil solution would precipitate all but 0.5 parts per billion of ferric ion as iron III hydroxide. That is, iron should be approximately tenfold less soluble in the Smelterville soil solutions than in the agitated Kellogg soil solution, yet no such event occurred. The iron concentrations were found to reach an equilibrium concentration of 2.03 ug/ml in the duplicate agitated Smelterville soil solutions. Due to the agitation of these solutions it must be assumed that adequate dissolved oxygen was available so that these solutions were not reducing; therefore, such an explanation for soluble iron does not apply. Apparently other factors are responsible for this observation; a plausible explanation follows.

According to Oldham and Gloyna (1969), iron transport in humic soils is dependent on the oxidation of organic matter by the iron II-iron III redox couple, which acts as an electron transfer catalyst. The end result is formation of a soluble iron III-organic complex rather than precipitated iron III hydroxide. An important side effect of such a reaction scheme is that the net pH of the solution is not lowered as it was by the production of hydrogen ions in the oxygenation of the Kellogg soil solution; this seems to be the case for the Smelterville solutions.

One might wonder why the Kellogg and Smelterville agitated soil solutions did not yield identical behavior, as both are classified as humic soils. Precipitation of iron III hydroxide in the agitated Kellogg soil solution suggests that the oxygenation (oxidation) of iron II to iron III competed successfully with complexation of the organic components of the soil. This is not true in the agitated Smelterville soil solution. The discrepancy can be explained by the lower complexation capacities of humus in the more acidic Kellogg environment. Qualitative support for the interpretation given here can be gathered from published studies regarding factors affecting the complexation capacities of humus.

The complexation capacities of humic materials are synonomous with their cation exchange capacities, as cation exchange with the humic material is the process which results in organic complex formation in soil solutions. An active organic (humic) binding site which is unable to attract a metal ion in an acidic environment certainly cannot be expected to bind such an ion so as to form a complex. According to Bower and others (1952, pp. 251-261) (the paper on which the American Society of Agronomy's reference method for cation exchange capacity determinations is based (Black, 1964)):

> "Numerous investigations have shown that values obtained for the cation-exchange capacity of soils depend somewhat on the pH values of the salt solution employed for saturation of the exchange complex; capacity values tend to increase as the pH value of the salt solution is increased. There appear to be two principal reasons for the increases in observed values: (a) as the pH value of the salt solution increases, hydrogen ions compete to a lesser extent for positions on the exchange complex, and (b) with increases in the hydroxyl-ion activity, weakly acidic groups on the complex are neutralized with resultant adsorption of cations used for saturation. The former occurs to an appreciable extent at pH values below 7, whereas the latter is important mainly at pH values considerably above 7."

Therefore, the less acidic Smelterville agitated soil solutions favored soluble iron III organic complexes whereas the highly acidic Kellogg agitated soil solutions favored precipitated iron III hydroxide. The solubilized copper and manganese ions in the Smelterville soil solutions may have formed organic complexes and equilibrated with adsorption and exchange processes because they have fairly active redox couples; however, their hydration products are soluble in mildly acidic solutions (like the Smelterville soil solution) so that their precipitation would be unlikely anyway.

In the case of zinc (Fig. 23) it is suggested that the highly soluble oxidized surfaces of the Smelterville soil grains immediately released high levels of zinc ions into solution at the onset of the experiment. The rapidly solubilized zinc ions then progressed towards an equilibrium concentration during the remainder of the experiments.

This examination of the Kellogg and Smelterville soils has led to some general conclusions concerning the solubility characteristics of Coeur d'Alene River Valley soils. In highly acidic humic soils solubility of trace metal ions appears to be primarily dependent on the solubilities of their hydration products (hydroxides and oxyhydroxides) due to the predominance of acid forming processes, whereas in mildly acidic soils the trace metal salts may undergo simple hydration/solvation or may form organic complexes with the humic matter present due to the predominance of ion exchange processes.

Osburn Tailings

It is not surprising that the Osburn Tailings solutions did not exhibit solubilization effects similar to those of the Kellogg and

Smelterville soil solutions. There were no abrupt surges of solubilized copper and zinc (Fig. 26 and 32), and the solubilized iron concentrations were non-detectible (below 0.01 parts per million), even though the iron content of the Osburn tailings is fourfold that of the Kellogg soil and sixfold that of the Smelterville soil (Tables 7 and 8).

In the case of the agitated Osburn tailings solution, no visible humus was present and only very minor amounts were confirmed by carbon and nitrogen elemental analyses (Table 5), and therefore available for complexation at the onset of the experiment so that oxygenation and the low solubility of iron III hydroxide in an acidic environment were the determining factors which led to a lack of solubilized iron at detectable levels.

The remaining trace metals, cadmium (Fig. 24), manganese (Fig. 28), and lead (Fig. 30), all yielded first order solubilization curves of the classical type generated by Reece (1974) in the leaching of river sedimented mill tailings and ores from the Coeur d'Alene Mining District.

Cataldo Sediments

The Cataldo soil samples shared many of the characteristics of the Osburn Tailings, as well they should since they are composed of river sedimented tailings-type materials. As was stated previously, they contained no visible humus and had high carbon/negligible nitrogen contents (Table 5). (It is suggested than an inorganic source of carbon such as calcite or dolomite, is responsible for the high carbon content. This could not be readily confirmed by X-ray diffraction analysis of the native Cataldo material due to its' poly-mineralic nature.) However, they were fine enough to look and feel like clays and therefore have special properties differing from the Osburn tailings as a result.

Similar to the Osburn tailings, no soluble iron concentrations were detected. The solubilization responses of the remaining trace metals, however, were much more erratic than the ideal first order plots generated for the Osburn tailings. Significant surges of solubilized zinc were observed (Fig. 39 and 40) and the solubilized copper concentrations (Fig. 34 and 35) fluctuated widely. These pronounced effects are attributed to the adsorption and ion-exchange phenomena so prevalent in clays. This is especially viable in view of the fact that the average terminal pH of the agitated and static Cataldo tailing solutions were 7.74 and 7.78 respectively (Table 13), which would indicate that the acid forming iron redox reactions so predominant in Coeur d'Alene ores and tailings are either neutralized by calcite or dolomite in this soil or are absent.

Neutrality tends to be a focal point for adsorption and ion-exchange activities because of the relatively minimal energies required for association compared to those energies needed to stabilize such processes at the extreme ends of the pH scale. Fuersterau and others (1970) have shown that adsorption of most metal ions increases from near zero to one hundred percent adsorption over very small critical pH ranges and that there are only minor differences in the location of the critical pH range for different substrates. Most of these critical pH ranges are located near neutrality and few are wider than one pH unit. The neutral (mildly alkaline) Cataldo soil solutions evidently yielded solubilization curves characteristic of predominant adsorption/ion exchange processes.

Oven Dry vs. Native

The preparation of oven-dry soils in this study for solubilization experiments may have altered the hydrated form and solubility of certain cations (e.g. calcium), but the cation exchange/adsorption properties of the soil were apparently unaffected. Comparisons of the terminal pH (Table 6), equilibrium concentrations (Tables 12 and 13), and solubilization curves for the oven-dry and native versions of the Osburn and Cataldo soils (Figures 24-33, and Figures 34-40, respectively) indicate that oven-drying these soils did not yield significantly different results for the two methods of pretreatment.

The equilibrium concentrations ($C_{\propto}$) of lead and zinc were generally slightly lower for the oven-dry version of the Osburn soil, but the reverse was true for the Cataldo soil (Tables 12 and 13). This observation might be explained on the basis that the native lead and zinc hydrated forms were converted to forms which were slightly more soluble in acidic solutions (Osburn), rendering them slightly less soluble in neutral/alkaline solutions (Cataldo) (Table 6). The equilibrium concentrations of solubilized manganese were generally higher for the oven-dry versions of both Osburn and Cataldo soils (Table 13). Cadmium equilibrium concentrations from soil solutions of oven-dried Osburn soil were higher in the static solutions than their native static soil solution counterparts; but were lower in the agitated soil solution than cadmium concentrations in the corresponding native agitated soil solutions (Table 12).

Whether or not these observations are sufficient to prove that hydrated lead and zinc were converted to slightly more acid soluble hydrated forms or that hydrated manganese and cadmium were or were not converted to more soluble hydrates is relatively unimportant. What is important is that the solubilization processes (as illustrated by the solubilization vs. time plots) were not significantly altered. The basic geometry of the native and oven-dry versions of each trace metal for these two soils were negligibly different (Osburn: Fig. 24-33, Cataldo: Fig. 34-40). This implies that the mechanisms of acid dissolution, cation-exchange, and adsorption phenomena associated with these soils were relatively unchanged by hydration changes potentially induced by oven-drying at 105°C.

Field Predictions

In essence the overall process by which trace metals in soils affect the quality of surface and ground waters can be viewed as a sequence of three mechanisms. Firstly, the waters must be brought into contact with the soils. Secondly, the chemical solubilization of the trace metals must occur. Lastly, the dissolved metals must be transported and mixed by the surface and ground waters in question.

The solubilization mechanism has already been discussed in detail. The contact and transport mechanisms will now be briefly considered.

Contact Mechanism

The following discussion is a simplified description of those facets of the hydrologic cycle which result in waters being brought into direct contact with soils. The occurrance of precipitation causes soil to be wetted. When the soil moisture storage is satisfied, water will infiltrate downward through the soil and underlying media to recharge, or add to, ground waters. If the rainfall intensity exceeds the infiltration rate then the excess water becomes available for overland flow to surface waters.

The rainfall contribution to surface waters should not, however, be viewed as separate and distinct from that for ground waters. Surface waters may gain water from, or lose water to, ground waters. For example; the base flow of a stream is that portion of the total flow which is contributed by ground water influx even through periods of little or no precipitation. Conversely, the bank storage of a stream is excess water temporarily held in storage in the stream banks due to the passage of flood waters and is slowly released to surrounding ground waters. Additionally, in the case where the water table of the ground waters rises above the surface of a free flowing stream, the ground waters will discharge into the stream; or a stream may lose water through its (permeable) streambed to ground water below.

Many factors affect the amount of precipitation which eventually contributes to surface and ground waters; among them are interception, evaporation, transpiration, and field capacity. The magnitudes of these factors at any specific location depend on the soil cover/vegetation and the soil composition there. It is not necessary to explain each of these factors in detail to arrive at the point of this discussion, however. Suffice it to say that precipitation is the ultimate source of water to solubilize trace metals from the soils and that some fraction of precipitation eventually contributes those dissolved constituents to surface and ground waters. The contributions may be by direct precipitation as just described or they may arise from contaminated soils being brought into contact with uncontaminated surface and ground waters by stream flooding or by rising water tables, respectively.

Transport Mechanism

Estimates of overland flow/runoff to surface waters are usually arrived at semi-empirically. When given the area of the drainage basin (A, in acres), the average rainfall intensity (i, in inches/hour), and an empirical/basin dependent runoff coefficient (C), the peak flow (Q_p, in acre-inches/hour) can be calculated using the rational equation:

$$Q_p = CiA$$

Alternatively, stream depths or stages are recorded prior to, during, and after runoff occurs and a streamflow hydrograph is plotted (streamflow versus time). A runoff hydrograph is then obtained by subtracting groundwater base flow from the streamflow hydrograph.

In either case the quantity/volume of runoff (in acre-inches or in gallons) may be readily obtained by multiplying the total runoff flow (in acre-inches/hour or gallons/hour) by the time over which runoff occurred (in hours). The average velocity of runoff can be arrived at by dividing the total basin flow by the area of the drainage basin. However, detailed analysis of the runoff contributions from small segments of the drainage basin are virtually impossible to isolate and quantify. The mechanism of transportation of dissolved contaminants by surface waters is, therefore, normally only crudely approximated.

The transportation of dissolved constituents by ground waters can be reasonably described by the Darcy equation for flow through porous media:

$$Q = KIA \text{ or } Q/A = v = KI$$

where Q = flow, in units of volume/time
K = coefficient of permeability (hydraulic conductivity); a psuedo-constant which is characteristic of the inertial

force-to-resistive force ratio of the fluid and of the geometry of the porous media voids through which flow occurs, but which varies directly with temperature due to changes in resistive force (viscosity) with temperature = a measure of the ability of a material to transmit water, in units of length/time

I = hydraulic gradient; a dimensionless variable expressing the head loss, or vertical water level decline, over a specified horizontal distance

A = gross cross-sectional area through which flow occurs

v = velocity, in units of length/time

The reader is referred to an elementary text for the assumptions, derivations, limitations, and special adaptations of these general flow equations (Todd, 1959). What is important to note here is that groundwater flow is dependent on the physical properties of the media and the fluid, and on the hydraulic gradient.

For example, flow through sands and gravels is greater than flow through clays (for the same fluid under the same hydraulic gradient), warm fluids yield greater flow than cold fluids (through the same media under the same hydraulic gradient), and a steep hydraulic gradient causes greater flow than a gradual hydraulic gradient (for the same fluid in the same media).

Flow through saturated media is greater than flow through unsaturated media, such as occurs during infiltration, for similar reasons--the apparent resistance to flow is greater for unsaturated flow due to the discontinuous nature of such flow (wetting the soil, building up a hydration layer on each particle, etc.). The Darcy equation is, therefore, an appropriate description for groundwater flow in saturated and unsaturated porous media. In applying the Darcy equation, it must simply be appreciated that unsaturated flow results in an effective decrease in hydraulic conductivity.

Shoshone County

Approximately 25 to 30% of the gross surface area of the Coeur d'Alene River Valley in Shoshone County is valley floor while the remaining 70 to 75% is steep mountainsides--of which 30 to 40%, the Kellogg-Smelterville area, is barren of vegetation and well developed soils. The valley floor is subject to stream flooding and ground water flooding (by rising water tables) during the spring and early summer, and it has highly contaminated soils and a significant acreage of exposed mine tailings. The mountainsides of the Coeur d'Alene River Valley which are barren, especially the Kellogg-Smelterville area, promote vigorous overland flow to the valley surface waters. Such flow carries a considerable load of suspended solid soil particles, as well as dissolved constituents due to the steepness of the mountainsides. In fact, the visible surface erosion in that area testifies to the rapid shedding of muddy waters following precipitation events. Hence, these surface and ground waters have a great potential for contamination from solubilized soil trace metals--especially since the solubilization concentrations linearly increase with time of soil-water contact, according to data presented here.

The remainder of the mountainsides of the Coeur d'Alene River Valley in Shoshone County, the vegetated portion, must allow considerably less overland flow due to interception and transpiration. However, because those soils still bear fairly high concentrations of trace metals, the solubilizations of trace metals and the use of the resultant contaminated waters by the vegetative cover is undoubtedly in progress. Evidence for trace metal contamination of vegetation in that locale has been given previously (Keely and others, 1976, Reginni and others, 1977, and Yankel and others, 1977).

Kootenai County

The Coeur d'Alene River Valley is appreciably wider in Kootenai County than in Shoshone County. Well over half of the gross surface area is occupied by valley floor, of which easily half is subject to annual flooding. Flooding, over the years, has caused discharged mine wastes and tailings to contaminate those floodplains so that active solubilization of trace metals from the sedimented materials has great potential. The remainder of the valley floor (which does not flood) and the mountainsides (which are not contaminated, of gradual slope, and which have fair to deep soil cover and vegetation) of the Coeur d'Alene River Valley in Kootenai County are not contaminated with trace metal laden soils--barring, perhaps, the easternmost edge adjacent to Shoshone County (which may be within the outermost fringe of the aerial deposition of smelter emissions). Therefore, only the floodplains of the Coeur d'Alene River Valley in Kootenai County should be considered to have a potential contribution of solubilized trace metals to its' surface and ground waters.

General Comments

Streams, and surface waters in general, have the mobility to limit the effective concentrations of trace metals in solution by infinite dilution because equilibrium is never attained. Hence the maximum rate of solubilization is maintained even though the resultant solubilized trace metal concentrations are lower than what the equilibrium concentrations would be. On the other hand; the relatively long contact time of ground waters with porous media meterials allows the solubilized trace metal concentrations to approach equilibrium, but the rate of solubilization necessarily declines exponentially as this happens. Although the surface and ground water solubilization of trace metals occur at different rates and reach different maximum concentrations, both have potentially significant contributions to the total trace metal contamination load of the Coeur d'Alene River Valley hydrosphere. The potential for such contributions can be quantified by performing solubilization experiments of the kind described here along with detailed field examinations of the surface and groundwater flows. However, the actual contributions may deviate considerably from the potential contributions due to the errors inherent in perparing such estimates, as previously described.

Conclusions

The solubilization of the majority of the trace metals in aqueous solutions of widely differing Coeur d'Alene River Valley surface materials can generally be characterized as having a linear relationship with time (first order). Cadmium, lead, and silver were solubilized at concentrations so low as to be non-detectible in most cases (less than 0.01 ppm). In those instances where cadmium and lead were at measurable concentrations, solubilization curves which yielded good first order relationships were well fit to plots of the respective data sets. Copper and manganese solubilization concentration-time plots yielded first order curves in virtually every case. They are assumed to have formed soluble hydration products by simple solvation/hydration and in humic soil solutions may have formed metallo-organic complexes.

The concentrations of solubilized iron have been shown to be heavily dependent on humic content, pH, ion-exchange capacity, and oxygenation of the soil solutions. Stumm and Singer (1966) are among several investigators who have noted major interferences in the oxygenation of iron II caused by the formation of stable iron III-organic complexes in humic soil solutions. The solubilized iron data for the Smelterville soil solutions generated in this study are consistent with those observations. The solubilized iron data for the Kellogg static (non-oxygenated) soil solution are also consistent with those observations. However, the agitated Kellogg soil solution iron data must be explained by the successful competition of oxygenation of iron II to iron III over oxidation and complexation of organic matter by iron II at the lower pH, and hence, lower complexation capacity of this soil solution.

The adsorption and ion-exchange properties of the soil solution in these experiments are plausible explanations of the behavior of solubilized zinc and copper. In many respects it is not surprising that the neutral clayey Cataldo tailings solutions gave good evidence of adsorption. Adsorption experiments are commonly conducted using silaceous materials (quartz, silicon dioxide, etc.) as the substrate, such as those by Fuerstenau and others (1970), referred to earlier in this report. Such experiments indicate that neutrality is a focal point for adsorption of cations onto silaceous substrates. X-ray diffraction analysis of both of the native Cataldo and Osburn materials confirmed several strong matching quartz peaks.

These solubilization studies have shown the dependence of solubilized trace metal concentrations on soil solution pH, agitation (oxygenation), and soil characteristics. The differences in these dependencies from one trace metal to the next have been explained on the basis of soluble hydration products, redox potential (pE), metallic-organic complexes, and adsorbed and/or exchanged ions. Pretreatment of these soils by oven-drying at 105°C has been shown experimentally to have little influence on the solubilization process.

Field studies appear to support some of these qualitative relationships. Williams and Mink (1975) noted that high concentrations of trace metals and lowered pH values in ground waters near Wallace, Idaho were caused by contact of the local water table with mine tailings. An examination of plants and ground waters associated with mine tailings in the Coeur d'Alene River Valley by Galbraith (1971) indicated that the ground waters could be contaminated by contact with the mine tailings. Galbraith and others (1972) then demonstrated a definite relationship between the two while attempting to determine the migration of the solubilized (leached) metals.

Estimates of the potential for contamination of surface and ground waters by solubilized trace metals from contaminated surface materials/ soils must be derived by consideration of the chemical properties of the soils and soil solutions, the applicable flow equations for transport of the dissolved contaminants, and the geologic structure (geometric orientation) of the flow paths. It is suggested that the following ranking, in descending order, be given to these factors in preparing such estimates:

(1) Trace metal content of the soils
(2) Acidity of the soil solutions
(3) Humic content of the soils
(4) Physical characteristics of the soils (e.g. grain size and mineral composition)

(5) Physical and chemical properties of the water (e.g. temperature and pE)
(6) Surface and ground water flow regimes

No attempt is made here to rank the relative importance of the contribution of solubilized trace metals by overland flow versus that by groundwater fluctuations. Barren slopes which contain high concentrations of trace metals are areas where overland flow impacts predominate. Trace metals are transferred from mine wastes along the valley floor predominantly by ground water mechanisms. Both of these solubilization and transport mechanisms thus add to a low level non point source pollution problem in the Coeur d'Alene River Valley. The data necessary to differentiate and quantify the contributions from these processes can be obtained by field testing.

CHAPTER FOUR

SUMMARY

Surveys of the trace metal concentrations in soils of the South Fork (Shoshone County) and Main Stem (Kootenai County) Valleys of the Coeur d'Alene River indicate that the South Fork Valley soils are contaminated primarily as a consequence of smelter emissions, with the exception of the riverbanks and floodplains of the Coeur d'Alene River. The Main Stem Valley soils are largely unaffected by the smelter emissions but also have highly contaminated riverbanks and floodplains due to the discharge of industrial mining wastes upstream.

Controlled greenhouse experiments with trace metal contaminated soils and tailings have shown that some species are able to survive in such soils. The successful planting of resistant species (e.g. spring wheat) would solve several problems associated with the hundreds of acres of tailings and contaminated soils in the Coeur d'Alene River Valley. Revegetation of the soil cover would not only stabilize the soil erosion and wind-blown transport but would provide organic matter capable of adsorption, ion-exchange, and complexation with the trace metal contaminants. The organic layer so created would also tend to neutralize and buffer the acidity of these soils and tailings, resulting in greater adsorption and a lowered potential solubility for most of the trace metals.

The solubilizations of most of the trace metals from selected Coeur d'Alene River Valley soils generally follow first order reaction kinetics and rapidly reach equilibrium concentrations. In highly acidic humic and non-humic soil solutions the soluble hydration products of the trace metals predominate. In mildly acidic humic soil solutions soluble hydration products and metallo-organic complexes may be formed. Trace metals may be adsorbed and/or ion-exchanged depending on the pE and pH of non-humic soil solutions (which may be affected significantly by the presence of pyrite, calcite, or dolomite), neutrality being most favorable for such processes. Preparation of soils and exposed sediments and tailings by oven-drying at 105°C did not significantly alter the solubilization process.

Anomalous trace metal concentrations in the Coeur d'Alene River Valley waters may be produced by solubilization of trace metals due to overland flow and infiltration of tailings overburden and contaminated soils by precipitation events. With the soils thus acting as secondary, non-point contaminant sources these mechanisms are responsible for interfacing trace metal contaminants in airborne smelter emissions to the local hydrosphere.

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