



Arsenic in soils of the Madison and upper Missouri River valleys
by Kristin Elisabeth Keith

A thesis submitted in partial fulfillment of the requirements for the degree Master of Science in Soils
Montana State University

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Abstract:

Arsenic (As) is a natural element in geothermal waters of Yellowstone National Park, and it is frequently present in concentrations above the national primary drinking water standard of 50 ug/L. The Firehole and Gibbon Rivers, tributaries to the Madison River, drain much of the geothermal water of the western part of the park. An estimated load of 272 kg/day of As is in the Madison River at West Yellowstone. It has been hypothesized that irrigation with As-laden Madison and upper Missouri River waters has resulted in As contamination of the thin alluvial aquifer near Three Forks, MT. However, in the upper Madison and upper Missouri River valleys, As concentrations in groundwater believed to be impacted by irrigation practices were below 10 ug/L.

It has been shown that in oxic conditions, As is strongly adsorbed to soils. Paired irrigated and non-irrigated soils were identified in areas within the Madison and upper Missouri River valleys where groundwater suspected to be impacted by irrigation practices using Madison or upper Missouri River water. Soils were sampled to a depth of 3 meters, then were characterized for total and soluble As. Concentrations of total As in irrigated soils of the upper Madison River valley above Ennis reservoir and in soils of the upper Missouri River valley above Canyon Ferry reservoir were significantly higher than total As in non-irrigated soils within those locations, indicating As removal from irrigation water by sorption of soils. However, total and soluble As concentrations in the soils of the lower Madison River valley near Three Forks are orders of magnitude higher than concentrations observed in soils of the upper Madison and upper Missouri River valleys. Furthermore, total and soluble As concentrations were higher in non-irrigated soils than irrigated soils of the lower Madison River valley. This is a strong indication that the soils near Three Forks are inherently high in As either from a parent material or a historical depositional effect.

Soluble As was monitored for an entire irrigation season in the soil profiles of two sites in the lower Madison River valley. No substantial increase in soluble As concentrations was observed following irrigation events, indicating irrigation is not a major mechanism for As contamination of the alluvial aquifer near Three Forks.

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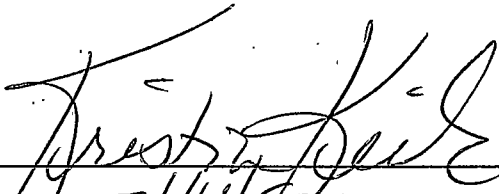
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TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS.....	iv
LIST OF TABLES.....	viii
LIST OF FIGURES.....	x
ABSTRACT.....	xiii
<u>CHAPTERS</u>	
1. INTRODUCTION.....	1
Objectives.....	4
2. LITERATURE REVIEW.....	6
Arsenic in Groundwater of the Madison and Upper Missouri River Valleys.....	6
Arsenic in Irrigation Return Flow of the Madison and Upper Missouri River Valleys.....	8
Arsenic Speciation in Soils and Water.....	9
Arsenic Sorption on Soils.....	12
Arsenic in Groundwater of the United States.....	14
3. MATERIALS AND METHODS.....	16
Study 1	
Statistical Design.....	16
Site Selection.....	17
Site Descriptions.....	18
Granger West.....	18
Granger East.....	19
Valley Garden.....	22
Wigwam.....	22
Anderson South.....	23
Kilgore.....	23
McDonnell North.....	24
McDonnell South.....	24
Anderson North.....	25
Kammerman.....	26
Lane.....	26
VanDyk.....	27
Bruce.....	27

TABLE OF CONTENTS-Continued.

	Page
Hansen.....	28
Hunsaker.....	29
Koehnke.....	29
Sample Collection.....	30
Sample Analyses.....	30
Statistical Analysis.....	31
Study 2	
Statistical Design.....	32
Sample Collection.....	33
Sample Analyses.....	34
Statistical Analyses.....	34
4. RESULTS.....	35
Study 1	
Soluble As Concentrations.....	35
Upper Madison.....	35
Lower Madison South.....	37
Lower Madison North.....	42
Upper Missouri.....	42
Soluble As in Irrigated Versus Non-Irrigated Soils.....	43
Depth Weighted Average Soluble As Concentrations.....	43
Total As Concentrations.....	49
Upper Madison.....	49
Lower Madison South.....	55
Lower Madison North.....	55
Upper Missouri.....	59
Carbonate Coatings.....	62

TABLE OF CONTENTS-Continued

	Page
Irrigated Versus Non-Irrigated Soils.....	64
Mean Depth Weighted Average Total As Concentrations.....	64
Study 2	
Anderson South.....	73
Vandyk.....	76
5. DISCUSSION.....	87
LITERATURE CITED.....	93
APPENDIX.....	96

LIST OF TABLES

Table	Page
1. Arsenic concentrations in the Madison River, upper Missouri River, and major tributaries.....	3
2. Land use practices and sample sites.....	20
3. r^2 values from regression analyses with soluble As and identified sources of variation within the soil profile.....	36
4. Mean soluble As concentrations of irrigated and non-irrigated soil profiles of the four study locations.....	43
5. r^2 values from regression analyses with total As in the fine earth fraction and identified sources of variation within the soil profile.....	51
6. Total As concentrations in carbonate coatings on coarse fragments of selected soil sampling sites..	64
7. Mean total As concentration in the fine earth fraction from irrigated and non-irrigated soil profiles on the four study locations.....	65
8. Mean total As concentration in the bulk fraction from irrigated and non-irrigated soil profiles of the four study locations.....	65
9. Analysis of variance of soluble As in soil samples collected prior to and following the first irrigation event at the Anderson South site.....	78
10. Analysis of variance of soluble As concentration in soil samples collected prior to and following the second irrigation event at the Anderson South site.....	79
11. Mean soluble As concentration with depth at Anderson South site prior to and following the first irrigation event.....	80
12. Mean soluble As concentration with depth at Anderson South site for the second irrigation event.....	80

LIST OF TABLES-Continued

Table	Page
13. Mean soluble As concentration of Anderson South site prior to and following the first irrigation event.....	81
14. Mean soluble As concentration of Anderson South site prior to and following the first irrigation event.....	81
15. Analysis of variance of soluble As concentration in soil samples collected prior to and following the first irrigation event at the VanDyk site.....	83
16. Mean soluble As concentration with depth at the VanDyk site prior to and following the first irrigation event.....	84
17. Mean soluble As concentration of VanDyk site prior to and following the first irrigation event.....	84
18. Analysis of variance of soluble As concentration in soil samples collected prior to and following the second irrigation event at the VanDyk site....	85
19. Mean soluble As concentration with depth at the VanDyk site prior to and following the first irrigation event.....	86
20. Mean soluble As concentration of VanDyk site prior to and following the first irrigation event.....	86
21. Chemical characteristics of sampled soil profiles, analysis of saturated paste extracts.....	97
22. Physical parameters of sampled soil profiles.....	107
23. Soluble As means in ug/L for the first irrigation event at the Anderson South site.....	118
24. Soluble As means in ug/L for the second irrigation event at the Anderson South site.....	118
25. Soluble As means in ug/L for the first irrigation event at the VanDyk site.....	119
26. Soluble As means in ug/L for the second irrigation event at the VanDyk site.....	119

LIST OF FIGURES

Figure	Page
1. Map of the upper Madison River connected to Yellowstone National Park.....	2
3. Upper Missouri River basin in Montana.....	5
2. Eh-pH diagram for As at 25 C and 1 atm.....	11
4. Soluble As concentrations in ug/L in the soil profiles of the Upper Madison location.....	38
5. Soluble As concentrations in ug/L in the soil profiles of the Lower Madison South location.....	39
6. Soluble As concentrations in ug/L in the soil profiles of the Lower Madison North location.....	40
7. Soluble As concentrations in ug/L in the soil profiles of the Upper Missouri location.....	41
8. Mean DWA soluble As (ug/L) in combined irrigated and non-irrigated soil profiles for the four study locations.....	44
9. Mean DWA soluble As (ug/L) in the 0-30 cm depth of combined irrigated and non-irrigated soils of the four study locations.....	46
10. Mean DWA soluble As (ug/L) in the irrigated and non-irrigated soil profiles of the four study locations.....	47
11. Mean DWA soluble As (ug/L) in the 0-30 cm depth of irrigated and non-irrigated soils of the four study locations.....	48
12. Mean DWA soluble As (ug/L) in the irrigated versus non-irrigated soil profiles of the combined four study locations.....	50
13. Mean DWA soluble As (ug/L) in the 0-30 cm depth of irrigated versus non-irrigated soils of the combined four study locations.....	50

LIST OF FIGURES-Continued

Figure	Page
14. Total As concentrations in the fine earth fraction of the soil profiles of the Upper Madison location.....	53
15. Total As concentrations in the bulk soil profiles in the Upper Madison location.....	54
16. Total As concentrations in the fine earth fraction of soil profiles of the Lower Madison South location.....	56
17. Total As concentrations in the bulk soil profiles of the Lower Madison South location.....	57
18. Total As concentrations in the fine earth fraction of soil profiles of the Lower Madison North location.....	58
19. Total As concentrations in the bulk soil profiles of the Lower Madison North location.....	60
20. Total As concentrations in the fine earth fraction of the soil profiles of the Upper Missouri location.....	61
21. Total As concentrations in the bulk soil profiles of the Upper Missouri location.....	63
22. Mean DWA total As (mg/kg) in the fine earth fraction of soils of the four study locations.....	66
23. Mean DWA total As (mg/kg) in the bulk soil profile of the four study locations.....	66
24. Mean DWA total As (mg/kg) in the 0-30 cm depth of the fine earth fraction of soils of the four study locations.....	68
25. Mean DWA total As (mg/kg) in the 0-30 cm depth of the bulk soil profile of the four study locations.....	68
26. Mean DWA total As (mg/kg) in the fine earth fraction of soils of the irrigated and non-irrigated soils of the four study locations...	69

LIST OF FIGURES-Continued

Figure	Page
27. Mean DWA total As (mg/kg) in the bulk soil profile of irrigated and non-irrigated soils of the four study locations.....	69
28. Mean DWA total As (mg/kg) in the 0-30 cm depth of fine earth fraction of irrigated and non-irrigated soils of the four study locations...	71
29. Mean DWA total As (mg/kg) in the 0-30 cm depth of bulk irrigated and non-irrigated soils of the four study locations.....	71
30. Mean DWA total As (mg/kg) in the fine earth fraction of irrigated versus non-irrigated soils of the combined study locations.....	72
31. Mean DWA total As (mg/kg) in the bulk irrigated versus non-irrigated soils of the combined study locations.....	72
32. Mean DWA total As (mg/kg) in the 0-30 cm depth of fine earth fraction of irrigated versus non-irrigated soils of the combined study locations.....	74
33. Mean DWA total As (mg/kg) in the 0-30 cm depth of bulk irrigated versus non-irrigated soils of the combined study locations.....	74
34. Soluble As concentration with depth prior to and following irrigation events at the Anderson South site.....	75
35. Soluble As concentration with depth prior to and following irrigation events at the VanDyk site.....	77

ABSTRACT

Arsenic (As) is a natural element in geothermal waters of Yellowstone National Park, and it is frequently present in concentrations above the national primary drinking water standard of 50 ug/L. The Firehole and Gibbon Rivers, tributaries to the Madison River, drain much of the geothermal water of the western part of the park. An estimated load of 272 kg/day of As is in the Madison River at West Yellowstone. It has been hypothesized that irrigation with As-laden Madison and upper Missouri River waters has resulted in As contamination of the thin alluvial aquifer near Three Forks, MT. However, in the upper Madison and upper Missouri River valleys, As concentrations in groundwater believed to be impacted by irrigation practices were below 10 ug/L.

It has been shown that in oxic conditions, As is strongly adsorbed to soils. Paired irrigated and non-irrigated soils were identified in areas within the Madison and upper Missouri River valleys where groundwater suspected to be impacted by irrigation practices using Madison or upper Missouri River water. Soils were sampled to a depth of 3 meters, then were characterized for total and soluble As. Concentrations of total As in irrigated soils of the upper Madison River valley above Ennis reservoir and in soils of the upper Missouri River valley above Canyon Ferry reservoir were significantly higher than total As in non-irrigated soils within those locations, indicating As removal from irrigation water by sorption of soils. However, total and soluble As concentrations in the soils of the lower Madison River valley near Three Forks are orders of magnitude higher than concentrations observed in soils of the upper Madison and upper Missouri River valleys. Furthermore, total and soluble As concentrations were higher in non-irrigated soils than irrigated soils of the lower Madison River valley. This is a strong indication that the soils near Three Forks are inherently high in As either from a parent material or a historical depositional effect.

Soluble As was monitored for an entire irrigation season in the soil profiles of two sites in the lower Madison River valley. No substantial increase in soluble As concentrations was observed following irrigation events, indicating irrigation is not a major mechanism for As contamination of the alluvial aquifer near Three Forks.

CHAPTER 1

INTRODUCTION

Arsenic (As) is a natural element in geothermal waters of Yellowstone National Park, and it is frequently present in concentrations well above the national primary drinking water standard of 50 ug/L (Stauffer, 1984). Concerns about health effects of As have induced considerations of lowering the national primary drinking water standard in 1997 to 2 ug/L (Mangelson and Brummer, 1994).

The Madison and Missouri River drainage receives significantly high concentrations of As from the Firehole and Gibbon Rivers, tributaries to the Madison River, which drain much of the geothermal water of the western part of Yellowstone Park (Fig 1). An estimated average load of 272 kg/day of As is carried by the Madison River at West Yellowstone (Mangelson and Brummer, 1994).

Dilutionary effects from tributaries of the Madison and upper Missouri Rivers, particularly during runoff, can be observed downstream from the source at Yellowstone National Park to Fort Peck Reservoir. However, even at Fort Peck Reservoir, As concentrations still exceed typical background surface water levels of 2-5 ug/L (Mangelson and Brummer,

1994). Typical As concentrations within the Madison/upper Missouri River system are shown in Table 1. A strong negative correlation exists along the Madison and upper Missouri River corridor between river discharge and As concentration (David Nimick, U.S.G.S., Helena, MT., written communication), indicating that the element behaves conservatively.

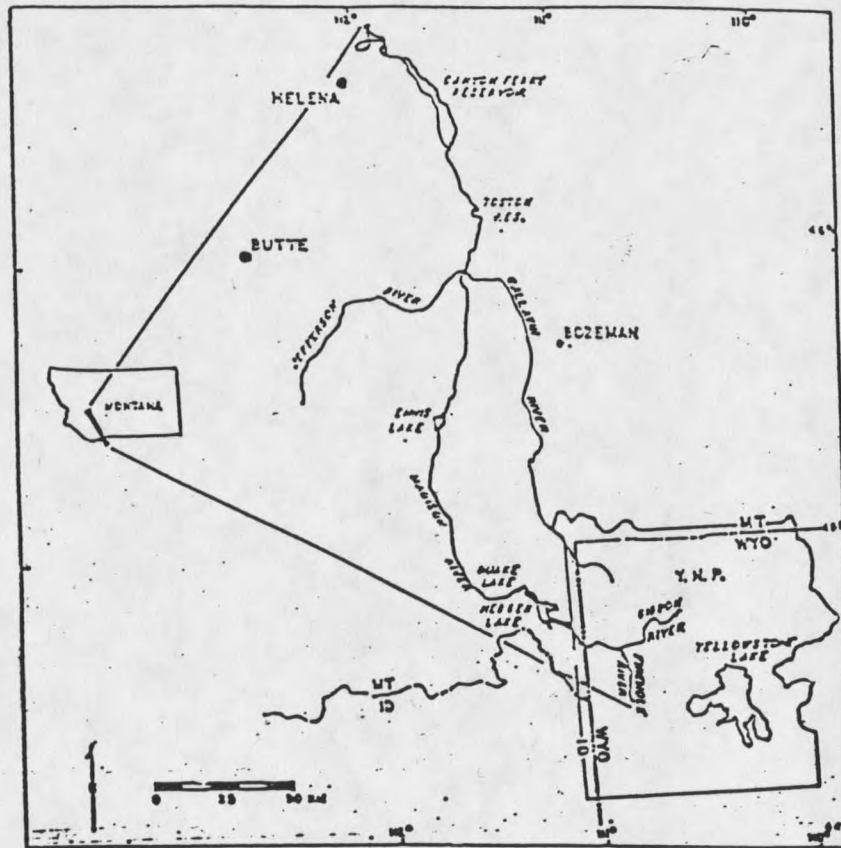


Figure 1. Map of the upper Madison River connected to Yellowstone National Park (Savka, 1993).

Arsenic in the river, to a large extent, exists in the soluble, oxidized (As V) form, as opposed to the adsorbed phase on sediments and particulates (Savka, 1993). Decreases

in As concentrations downstream from Yellowstone National Park can, to a lesser extent, be attributed to adsorption onto sediments and particulates, particularly during times of high discharge. Some of the As is removed by deposition of these sediments and particulates at Hebgen and Canyon Ferry Reservoirs (Savka, 1993; Schulman, 1992).

Table 1. Arsenic concentrations in the Madison River, upper Missouri River, and major tributaries (Mangelson and Brummer, 1994).

Location	min	max
	(ug/L)	
Madison River near West Yellowstone	120	370
Madison River below Hebgen Lake	70	240
Madison River below Ennis Lake	50	100
Madison River at Three Forks	50	90
Missouri River near Toston	10	50
Missouri River below Canyon Ferry	20	35
Missouri River below Fort Peck	2	6
Jefferson River at Three Forks	1	10
Gallatin River at Three Forks	<1	2

Concentrations of As well above the national primary drinking water standard of 50 ug/L have been measured in wells along the lower Madison River from MT Highway 84 downstream to Three Forks (Lori Tuck, U.S.G.S, Helena, MT., written communication; Sonderegger and Ohguchi, 1988). Enough data have been collected to show that these As concentrations do not change significantly during the year. Yet, in the lower

Madison stretch, groundwater well concentrations are not consistent along the river corridor. It is hypothesized that irrigation with As-laden Madison River water is resulting in progressive contamination of the shallow alluvial aquifer near Three Forks (Sonderegger and Ohguchi, 1988; Sonderegger et al., 1989).

Objectives

Two studies were conducted during the 1993 and 1994 growing seasons. The study area was located in the Madison and upper Missouri River corridor from the West Fork of the Madison River downstream to Canyon Ferry Reservoir. A map of the study area is shown in Figure 2. The objective of study 1 was to investigate arsenic degradation of shallow groundwater quality from long-term irrigation in the Madison-upper Missouri River corridor through the comparison of soil physical, chemical, and As characteristics of paired irrigated versus non-irrigated soil profiles. The objective of study 2 was to investigate the question of significantly elevated levels of soluble As in the soil profile following irrigation events by monitoring soluble arsenic transport from the soil surface to the saturated zone during an entire irrigation season in soils irrigated with Madison River water.

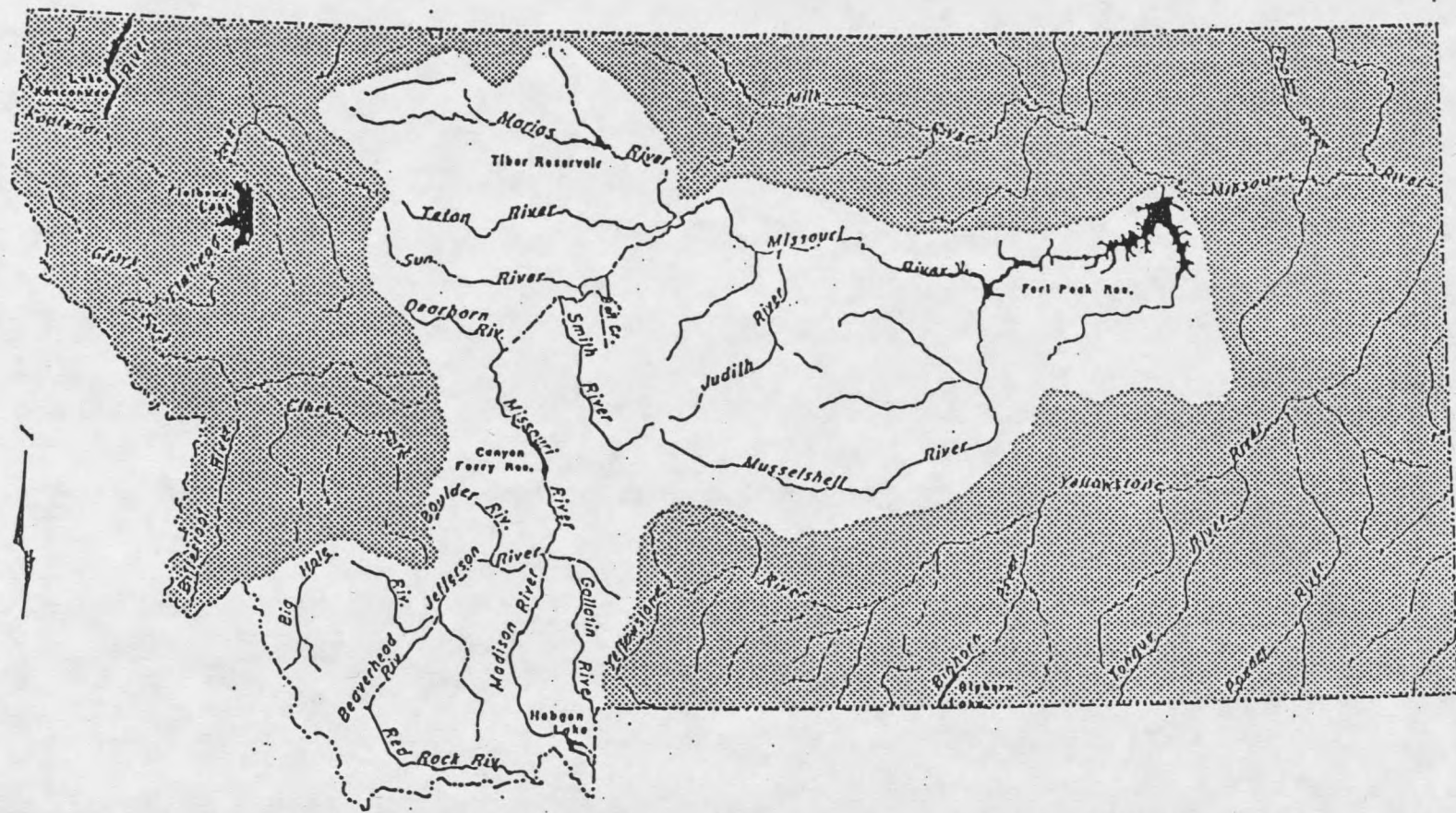


Figure 2. Upper Missouri River basin in Montana--study area is Madison and upper Missouri River valleys (above Canyon Ferry Reservoir).

CHAPTER 2

LITERATURE REVIEW

Arsenic in Groundwater of the Madison
and Upper Missouri River Valleys

Groundwater As concentrations in the southern lower Madison River valley from Montana Highway 84 downstream approximately to the Madison Buffalo Jump State Monument range from 25-50 ug/L. The water in these wells is oxic. Many of the wells on the irrigated side valley along the Buffalo Jump Road have groundwater As concentrations between 55-140 ug/L, with a concentrated group of wells north near the Kammerman and VanDyk ranches having well water As above 100 ug/L. The wells tested just upstream from the confluence of the Gallatin and Jefferson Rivers have groundwater As concentrations between 60-160 ug/L, the majority of which have As concentrations above 100 ug/L. The groundwater in these wells is anoxic (Tuck, U.S.G.S., Helena MT, written communication).

Mangelson and Brummer (1994) sampled domestic and stock watering wells between Ennis and Townsend to determine if As concentrations in well water supplies were greater than concentrations in the upper Madison and upper Missouri River waters. They identified twelve wells in the upper Madison River valley in which water quality degradation may have

occurred as a result of irrigation with Madison River water. Water from only two wells had As concentrations above 10 ug/L (one well had a concentration of 40 ug/L). Both of these wells were located very close to the river, implying a hydrological connection between well water and river water. The rest of the samples contained concentrations of As from below detection limits to 10 ug/L.

Tuck (written communication) also did a reconnaissance of groundwater As concentrations in areas of the upper Madison River valley believed to be impacted by irrigation with river water. The majority of the wells she tested had groundwater As concentrations below 10 ug/L, and the wells with elevated As levels were either very close to the river, or smelled of hydrogen sulfide, indicating reduced groundwater chemistry.

Mangelson and Brummer (1994) additionally tested water from eight wells in the upper Missouri River valley between Toston and Townsend. Only two samples had concentrations of As above 10 ug/L. These wells were in close proximity to the Broadwater-Missouri irrigation canal, implying a hydraulical connection to the canal water.

Tuck also sampled well water in Toston/Townsend area of the upper Missouri River valley. Well water As concentrations ranged from less than detection to approximately 20 ug/L.

Arsenic in Irrigation Return Flow of the Madison
and Upper Missouri River Valleys

Sonderegger et al. (1989) found the concentration of As in the lower Madison River upstream from the densely irrigated acreage to be the same as the concentration of As in the river downstream from the irrigated acreage, except during the irrigation season and during spring runoff. During these times, they observed considerably higher concentrations of As in the river downstream from the irrigated acreage. They hypothesized that evapotranspiration from irrigation ditches and soil pore water concentrate the As. Furthermore, they proposed that deep percolation of this concentrate to groundwater results in much higher concentrations of As in groundwater than in the river. They attributed the seasonal increases in As downstream from the irrigated acreage to groundwater discharge into the river in response to a rise in the water table.

Nimick (written communication) sampled As concentrations in the lower Madison River upstream and downstream from the irrigated acreage. He found no sharp increase in As concentrations in the river during irrigation season, rather he found As concentrations in the river to fluctuate with discharge.

Mangelson and Brummer (1994) addressed the issue of concentrated As in irrigation return flows, and they found the following: within the area between MT Highway 84 north to Three Forks, As concentrations in irrigation ditch water

ranged from 45-80 ug/L. Two primary creeks, Spring Creek and Rey Creek, serve as drains for irrigation water in this area. Groundwater discharge (springs), tailwater from fields, and flow from ends of irrigation ditches also contribute to these creeks. Where the two creeks combine to form Rey Creek (towards the northern end of the valley), As concentrations in the water ranged from 56-81 ug/L.

Nimick sampled As concentrations in drains of the lower Madison River valley and observed As values much like those of Mangelson and Brummer.

Arsenic concentrations in water in irrigation ditches along the upper Madison River range from 42-85 ug/L. Mangelson and Brummer identified a number of springs and seeps in this region which were believed to be irrigation return flow. Most of these seeps were located just west of Ennis Lake. As concentrations in these waters ranged from 4-26 ug/L.

Nimick measured dissolved As in tributary streams and supply canals, and found As levels ranging from below detection to below 30 ug/L. He also identified seeps or drains believed to be influenced by irrigation activity. Dissolved As concentrations in these seeps or drains were less than 20 ug/L.

Arsenic Speciation in Soils and Water

Arsenic is ubiquitous, but its natural abundance is low. Arsenic is present in more than 245 minerals (Gao et al.,

1994), and is in the highest concentration in rocks and minerals of volcanic origin (Welsh, 1988). Arsenic does not exist as a free element in the environment; rather, it is associated with minerals in a 0, +3, or +5 oxidation state. The As(III) and As(V) are the most common oxidation states in soil and water, and as a rule, As(III) is more soluble and more toxic than As(V). Organic species of As can be detected in aquatic systems; these species are typically associated with methyl groups. Two species, monomethylarsenic acid (MMAA) and dimethylarsenic acid (DMMA), have been found in surface water and sediment (Xu et al., 1991). Organic forms of As are more prevalent in soils with high microbial activity. For example, 31-50% DMAA and 11-17% MMAA of total soluble As was observed in agricultural evaporation ponds with high microagal activity (Gao et al., 1994).

Chemical behavior of As is similar to behavior of P, in that As tends to form oxyanions (Kabata - Pendias, 1992). The oxidation state of As and the speciation of the oxyanion are highly dependent on pH and Eh (Fig 2). In well aerated soils, arsenate ($H_nAsO_4^{3-n}$), the +5 oxyanion species of As, is stable. At a neutral pH dihydrogen arsenate ($H_2AsO_4^-$) and hydrogen arsenate ($HAsO_4^{2-}$) are stable. Dissociation of $HAsO_4^{2-}$ to AsO_4^{3-} would not occur until pH 11.5, which is higher than the typical soil pH 4-8 range (Ferguson and Gavis, 1972; O'Neill, 1990).

In anoxic soils ($Eh < 300$ mV), arsenite ($H_nAsO_3^{3-n}$), the +3 oxyanion species of As, is stable. At neutral pH arsenious acid (H_3AsO_3) is stable. Dissociation to dihydrogen arsenite ($H_2AsO_4^-$) would not occur until pH 9.2 (O'Neill, 1990; Ferguson and Gavis, 1972). Speciation of organic forms of As does not depend on Eh (Gao et al., 1994).

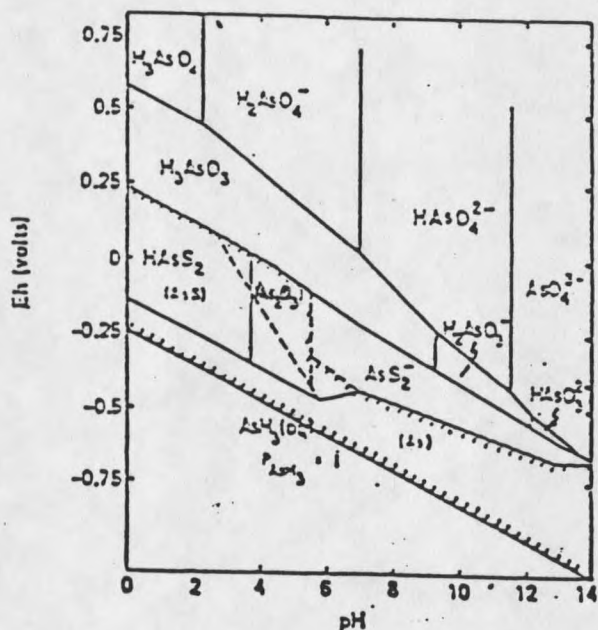


Figure 3. Eh-pH diagram for As at 25 C and 1 atm. with total As 10^{-3} mol/L. Symbols for solid species are enclosed in parentheses in cross-hatched area, which indicates solubility less than 10^{-5} mol/L. Eh = standard oxidation-reduction potential. (Ferguson and Gavis, 1972).

Manganese oxide oxidizes arsenite to arsenate in freshwater lake sediment (Oscarson et al., 1982). Iron and Al oxide coatings on Mn decrease the reaction rate of Mn oxidation of arsenite by masking Lewis acid sites (electron accepting sites) on Mn. Furthermore, a seven-fold decrease in

reaction rate of arsenite oxidation was observed when Mn was coated with CaCO_3 (Oscarson et al., 1982).

Arsenic Sorption on Soils

Arsenic removal from the soil solution does not generally occur by precipitation reactions; rather, it occurs by adsorption reactions (Livesey and Huang, 1981; Woolson et al.; Lemmo et al. (in Gao et al., 1994)). The most prominent As sorbing materials in soils are amorphous Fe and Al oxide minerals (Jacobs, 1970; Goldberg, 1986; Livesey and Huang, 1981). Xu et al. (1991) showed with increasing pH, adsorption of arsenate by alumina (As_2O_3) increased to pH 5, then decreased. Adsorption of arsenate on hematite (Fe_2O_3) was at pH 6, then adsorption decreased with increasing pH. The reported pH_{zpc} for alumina and hematite was 6.5-7.0. The sorptivity of arsenate on alumina was approximately 100-fold higher than on hematite. In the same study, adsorption of arsenite on alumina peaked at pH 7.

Other studies have exhibited a maximum adsorption of As on goethite, gibbsite, and amorphous Al hydroxide in the pH range 3 to 4, followed by a gradual decline with increasing pH (Hingston, Hingston et al., Anderson et al. (in Goldberg, 1986)).

Studies have supported the hypothesis that amorphous Al oxide minerals have a higher sorption capacity for As than amorphous Fe oxide minerals (Ferguson and Gavis, 1972; Livesey

and Huang, 1981). However, Oscarson et al. (1982) reported that amorphous Fe oxides adsorb approximately 3-fold more As than amorphous Al oxides.

The speciation of As is important to its adsorption onto amorphous Fe and Al oxide minerals. Aluminum oxides have a greater sorption capacity for arsenate than arsenite (Oscarson et al., 1982; Ferguson and Gavis 1972; Xu et al., 1991; Goldberg and Glaubig, 1988; Goldberg, 1986). However, some conflict arises as to the sorptivity of amorphous Fe oxide minerals for arsenate and arsenite. Arsenate is more strongly adsorbed onto Fe oxide minerals than arsenite (Goldberg and Glaubig, 1988; Gupta and Chen, Pierce and Moore, Frost and Griffin (in Gao et. al., 1994)). However, Oscarson et al. (1982) report a higher sorptivity of Fe oxides to arsenite than to arsenate.

Other surfaces for As adsorption are positive charges on exposed crystal edges, micas, vermiculites, smectites, chlorites, and kaolinites (Livesey and Huang, 1981). Frost and Griffin (in Gao et al., 1994) report more adsorption of As onto montmorillonite than onto kaolinite. Removal of As from the soil solution by sorption onto calcite may be important in calcareous soils; however, Fe and Al oxides have a greater capacity per unit mass than calcite (Goldberg and Glaubig, 1988; Goldberg, 1986). The retention of As by organic matter in soils is also not significant as compared to Fe and Al oxides or clay (Jacobs, et al., 1970).

Adsorption of As by soils does not vary significantly with introduction of anions such as nitrate, chloride, and sulfate (Livesey and Huang, 1981); however, addition of phosphate or citrate substantially decreases adsorption of As through competition for sorption sites (Livesey and Huang, 1981; Misra and Tiwari, 1963).

Arsenic in Groundwater of the United States

Concentrations of As above the national drinking water standard occur in at least five midwestern United States: Missouri, Iowa, Illinois, South Dakota and Ohio (Korte, 1991). The As in these systems can be linked to no anthropogenic source. Many sites tested were in alluvial groundwater systems that had reducing conditions indicated by elevated levels of soluble Fe and Mn.

Natural occurrences of moderate (10 - 50 ug/L) to high (>50 ug/L) concentrations of As have been identified in groundwater of the western United States. High concentrations were typically associated with four geochemical environments: 1) basin fill deposits of alluvial lacustrine origin, 2) volcanic deposits, 3) geothermal systems, 4) uranium and gold mining (Welch et al., 1988).

Agget and Kriegman (in Korte, 1991) proposed a mechanism for the occurrence of high As concentration in groundwater. Arsenic is adsorbed onto Fe oxides in sediment that gets deposited from stream flow and flooding. Through time, the sediments get buried. Then reducing conditions begin to

persist, and the reduced Fe releases soluble As into the groundwater.

CHAPTER 3

MATERIALS AND METHODS

Study 1: Statistical Design

Study 1 consisted of extensive deep profile soil sampling along the entire study area, followed by chemical and physical characterization of each soil sample. Study 1 was designed as a 4x2x9 factorial experiment with four replications. Main factors were: 1) location, 2) paired irrigated and non-irrigated soils, and 3) depth , as detailed below.

1. locations

- i. the upper Madison River from the West Fork of the Madison River downstream to Ennis Reservoir;
- ii. the lower Madison River at MT Highway 84 downstream to the Madison Buffalo Jump State Monument;
- iii. the lower Madison River at Madison Buffalo Jump State Monument downstream to Interstate 90;
- iv. the upper Missouri River just North of Three Forks downstream to Canyon Ferry Reservoir;

The lower Madison River was divided into two sections due to the elevated levels of As in groundwater in the

northern part of the valley. For future reference, the four locations will be defined as the Upper Madison, the Lower Madison South, the Lower Madison North, and the Upper Missouri.

2. paired irrigated and non-irrigated sites

There were 4 paired sites (replications) within each location.

3. depth increments of soil sampling (in cm):

i. 0-5	iv. 20-30	vii. 90-150
ii. 5-10	v. 30-60	viii. 150-250
iii. 10-20	vi. 60-90	ix. 250-350

Site Selection

Potential cooperators in the Madison and upper Missouri River corridor who operated on property irrigated with Madison or upper Missouri River water were identified. Landowners were contacted and apprised of our purpose and approach. They were questioned about the possibility of existing paired irrigated and non-irrigated sites and about their willingness to assist.

Sites were then visited to determine site suitability. The irrigated site required a history of a least 20 years of irrigation with water from the Madison or upper Missouri Rivers. The non-irrigated site required a history of no exposure to Madison or upper Missouri River irrigation water. Location of paired sites involved a reconnaissance of soil series using soil survey resources, hand sampling and texturing, and comparison of topographical locations.

Additionally, the paired sites were required to be within 60 m of each other at each sampling location.

Site Descriptions

Soil sampling occurred at four sites on ranches within each location as detailed below.

1. Upper Madison

- | | |
|------------------|--------------------|
| i. Granger West | iii. Valley Garden |
| ii. Granger East | iv. Wigwam |

2. Lower Madison South

- | | |
|-------------------|----------------------|
| i. Anderson South | iii. McDonnell North |
| ii. Kilgore | iv. McDonnell South |

McDonnell North is located in the northern section of the valley. It is grouped within this location due to the very low levels of As in the groundwater at this site.

3. Lower Madison North

- | | |
|-------------------|------------|
| i. Anderson North | iii. Lane |
| ii. Kammerman | iv. VanDyk |

3. Upper Missouri

- | | |
|------------|---------------|
| i. Bruce | iii. Hunsaker |
| ii. Hansen | iv. Koehnke |

Granger West

Paired sites were located approximately 11.27 kilometers south of Ennis, in section 10, T7S, R1W at latitude 45.225 degrees North and longitude 111.675 degrees West. Elevation

of this area is 1615 meters, and mean annual precipitation is 30-35 cm. Growing season precipitation is 18-20 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service (1989) as Musselshell gravelly loam (coarse, carbonatic Borollic Calciorthid) with a uniform slope of 2-4%.

The irrigated site was in flood irrigated pasture, with a 35 year history of irrigation with Madison River water from Cameron ditch. The non-irrigated site was in dryland pasture. Additional site information and information from all soil sampling sites is given in Table 2.

Granger East

Paired sites were located approximately 13 kilometers southeast of Ennis, in section 12, T7S, R1W at latitude 45.225 degrees North and longitude 111.675 degrees West. Elevation of this area is 1615 meters, and mean annual precipitation is 30-35 cm. Growing season precipitation is 18-20 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service (1989) as Attewan loam (fine loamy over sandy, mixed Aridic Argiboroll) with a uniform slope of 2-4%.

The irrigated site was in flood irrigated pasture, with a 35 year history of irrigation with Madison River water from Cameron ditch. The non-irrigated site was in dryland pasture.

Table 2. Land use practices at sample sites.

irrigated site	depth to GW (m)	years irrigated irrig method	annual irrig (cm)	crop history	plowing (years)	arsenical pesticide	P
Granger E.	UK	35 - flood	51-76	grass	14 yrs ago	none	none
Granger W.	UK	35 - flood	30-61	grass	15 yrs ago	none	none
Valley Garden	3	80-90 - flood	51-76	grass	25 yrs ago	none	none
Wigwam	UK	> 10	> 61	alfalfa/ grain	12 yrs ago	none	light (2yrs)
Anderson S.	*	*	*	*	*	*	*
Kilgore	UK	95 - flood 12 - sprinkle	30	alfalfa/ grain	every 6-8	1x gopher control	light
McDonnell N.	113	21 - sprinkle	46-61	alfalfa/ grain	never	none	55 lb/acre annually
McDonnell S.	25	85 - flood 10 - sprinkle	51-56	alfalfa/ grain	every 7	none	40 lb/acre annually
Anderson N.	*	*	*	*	*	*	*
Kammerman	UK	89 - flood 18 - sprinkle	30	alfalfa/ grain	UK	none	none
Lane	1.5	25 - flood	30-60	grass	every 5-6	none	none
VanDyk	2-3	82 - flood 15 - sprinkle	30-60	alfalfa/ grain	every 6-8	none	none

Note: UK=unknown; P=phosphorus; *=no information given

Table 2. Continued

irrigated site	depth to GW (m)	years irrigated irrig method	annual irrig (cm)	crop history	plowing (years)	arsenical pesticide	P
Bruce	2-3	35 - sprinkle	30-60	fallow/ grain	annually	none	none
Hansen	12	20 - flood	51-56	alfalfa/ grain	annually	none	36kg/yr
Hunsaker	>3	38 - flood	30-60	alfalfa/ grain	every 2	none	biannually
Koehnke	*	*	*	*	*	*	*

Valley Garden

Paired sites were located approximately 4 kilometers south of Ennis, in section 21, T5S, R1W at latitude 45.375 degrees North and longitude 111.725 degrees West. Elevation of this area is 1494 meters, and mean annual precipitation is 25-30 cm. Growing season precipitation is 15-18 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service (1989) as Thess loam (fine loamy over sandy Borollic Calciorthid) with a uniform slope of 1-3%.

The irrigated site was in flood irrigated pasture, with a 80-90 year history of irrigation with Madison River water from the West Madison Valley ditch. The non-irrigated site was a high spot in the flood irrigated pasture.

Wigwam

Paired sites were located approximately 13 kilometers south of Ennis, in section 20, T7S, R1W at latitude 45.225 degrees North and longitude 111.725 degrees West. Elevation of this area is 1585 meters, and mean annual precipitation is 25-30 cm. Growing season precipitation is 13-15 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service (1989) as Scravo very cobbly sandy loam (sandy skeletal, mixed Borollic Calciorthid) with a uniform slope of 1-3%.

The irrigated site was in flood irrigated alfalfa, with a 20 year history of irrigation with Madison River water from

the Shewmaker ditch. The non-irrigated site was in native range grass.

Anderson South

Paired sites were located approximately 18 kilometers south of Three Forks, in section 21, T1S, R2E at latitude 45.225 degrees North and longitude 111.725 degrees West. Elevation of this area is 1432 meters, and mean annual precipitation is 36-41 cm. Growing season precipitation is 18-20 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service (unpublished data) as Glendive silt loam (coarse loamy, mixed, calcareous, frigid Ustic Torrifuvent) with a uniform slope of 2-4%.

The irrigated site was in flood irrigated alfalfa. The site is irrigated with Madison River water from the Sloan ditch, and the history of irrigation was not given. The non-irrigated site was in native range grass.

Kilgore

Paired sites were located approximately 19 kilometers south of Three Forks, in section 5, T2S, R2E at latitude 45.725 degrees North and longitude 111.475 degrees West. Elevation of this area is 1432 meters, and mean annual precipitation is 36-41 cm. Growing season precipitation is 18-20 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service

(unpublished data) as Chinook fine sandy loam (coarse loamy, mixed Aridic Haploboroll) with a uniform slope of 3-5%.

The irrigated site was in sprinkler irrigated barley, with a 107 year history of irrigation with Madison River water from the Sloan ditch. The non-irrigated site was in native range grass.

McDonnell North

Paired sites were located approximately 6 kilometers east of Three Forks, in section 34, T2N, R2E at latitude 45.975 degrees North and longitude 111.475 degrees West. Elevation of this area is 1341 meters, and mean annual precipitation is 30-36 cm. Growing season precipitation is 18-20 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service (unpublished data) as Kalsted silt loam (coarse loamy, mixed Borollic Calciorthid) with a uniform slope of 3-5%.

The irrigated site was in sprinkler irrigated barley, with a 21 year history of irrigation with Madison River water from the Burrell ditch. The non-irrigated site was in native range grass.

McDonnell South

Paired sites were located approximately 14 kilometers southeast of Three Forks, in section 10, T1S, R2E at latitude 45.775 degrees North and longitude 111.475 degrees West. Elevation of this area is 1372 meters, and mean annual

precipitation is 36-41 cm. Growing season precipitation is 20-23 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service as Glendive silt loam (coarse loamy, mixed, calcareous, frigid Ustic Torrifuvent) with a uniform slope of 3-5%.

The irrigated site was in sprinkler irrigated alfalfa, with a 95 year history of irrigation with Madison River water from the Sloan ditch. The non-irrigated site was in native range grass.

Anderson North

Paired sites were located approximately 14 kilometers southeast of Three Forks, in section 8, T1S, R2E at latitude 45.775 degrees North and longitude 111.475 degrees West. Elevation of this area is 1372 meters, and mean annual precipitation is 36-41 cm. Growing season precipitation is 20-23 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service as Binna-Slickspots Complex (fine loamy over sandy, mixed Aridic Calciboroll) with a uniform slope of 0-2%.

The irrigated site was in sprinkler irrigated alfalfa. The site is irrigated with Madison River water from the Crowley ditch, and the history of irrigation was not given. The non-irrigated site was in native range grass.

Kammerman

Paired sites were located approximately 6 kilometers southeast of Three Forks, in section 15, T1N, R2E at latitude 45.775 degrees North and longitude 111.475 degrees West. Elevation of this area is 1372 meters, and mean annual precipitation is 36-41 cm. Growing season precipitation is 20-23 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service (unpublished data) as Kalsted silt loam (coarse loamy, mixed Borollic Calciorthid) with a uniform slope of 2-4%.

The irrigated site was in sprinkler irrigated alfalfa, with a 113 year history of irrigation with Madison River water from the Sloan ditch. The non-irrigated site was in native range grass.

Lane

Paired sites were located approximately 4 kilometers east of Three Forks, in section 33, T2N, R2E at latitude 45.875 degrees North and longitude 111.475 degrees West. Elevation of this area is 1311 meters, and mean annual precipitation is 25-30 cm. Growing season precipitation is 15-18 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service as Nevka VAR-Toston Aquents Complex with a uniform slope of 0-2%.

The irrigated site was in flood irrigated pasture, with a 25 year history of irrigation with Madison River water from

Rey Creek ditch. The non-irrigated site was in native range grass.

VanDyk

Paired sites were located approximately 6 kilometers southeast of Three Forks, in section 10, T1N, R2E at latitude 45.775 degrees North and longitude 111.475 degrees West. Elevation of this area is 1372 meters, and mean annual precipitation is 36-41 cm. Growing season precipitation is 20-23 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service as Tetonview silt loam (fine loamy, frigid Typic Calciaquoll) with a uniform slope of 2-4%.

The irrigated site was in flood irrigated alfalfa, with a 107 year history of irrigation with Madison River water from the Crowley ditch. The non-irrigated site was in native range grass.

Bruce

Paired sites were located approximately 2 kilometers south of Townsend, in section 4, T6N, R2E at latitude 46.325 degrees North and longitude 111.475 degrees West. Elevation of this area is 1189 meters, and mean annual precipitation is 30-36 cm. Growing season precipitation is 15-18 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service (1977) as Brocko silt loam

(coarse silty mixed, Borollic Calciorthid) with a uniform slope of 1-3%.

The irrigated site was in wheel-line irrigated grass seed production, and during the season of soil sampling the irrigated field was in fallow. The site had a 35 year history of irrigation with Missouri River water from the Broadwater-Missouri canal. The non-irrigated site was in native range grass.

Hansen

Paired sites were located approximately 13 kilometers south of Townsend, in section 10, T5N, R2E at latitude 46.175 degrees North and longitude 111.475 degrees West. Elevation of this area is 1219 meters, and mean annual precipitation is 30-36 cm. Growing season precipitation is 18-20 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service (1977) as Lothair silty clay (fine, mixed Ustic Torriorthent); however, based on the soil profile characteristics, the soil at this site is more likely to be classified as Scravo cobbly loam (sandy skeletal, mixed Borollic Calciorthid). Scravo series soils are commonly found near the Lothair series. The site had a uniform slope of 1-3%.

The irrigated site was in flood irrigated barley, with a 20 year history of irrigation with Missouri River water from the Broadwater-Missouri canal. The non-irrigated site was in native range grass.

Hunsaker

Paired sites were located approximately 29 kilometers south of Townsend, in section 5, T4N, R2E at latitude 46.125 degrees North and longitude 111.475 degrees West. Elevation of this area is 1280 meters, and mean annual precipitation is 30-36 cm. Growing season precipitation is 18-20 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service (1977) as Thess silt loam (fine loamy over sandy Borollic Calciorthid) with a uniform slope of 0-2%.

The irrigated site was in flood irrigated alfalfa, with a 38 year history of irrigation with Missouri River water from the Toston canal. The non-irrigated site was in native range grass.

Koehnke

Paired sites were located approximately 19 kilometers south of Townsend, in section 33, T5N, R2E at latitude 46.125 degrees North and longitude 111.475 degrees West. The elevation of this area is 1280 meters, and mean annual precipitation is 30-36 cm. Growing season precipitation is 18-20 cm (Caprio et al., 1990). Soil at the study site was classified by the U.S.D.A. Soil Conservation Service (1977) as Chinook sandy loam (coarse loamy, mixed Aridic Haploboroll) with a uniform slope of 1-2%. The irrigated site was in sprinkler irrigated barley. The site is irrigated with Missouri River water from the Toston canal. The history of

irrigation was not given. The non-irrigated site was also in barley, but was outside the area sprinkled by the pivot end-gun.

Sample Collection

All of the sites in the Madison and upper Missouri River corridor were sampled in August through October, 1993 except for sites at the VanDyk and Anderson ranches, which were sampled in May, 1994.

At each irrigated and non-irrigated site, a 3 m deep pit was excavated, using a backhoe. If standing water was reached during excavation, excavation and sampling ceased at that depth. To avoid contamination from the backhoe and to avoid any cross-contamination of the profiles during excavation, a fresh surface on the wall of the pit was exposed following excavation. Samples were collected at the appropriate depth, placed in plastic bags, and then placed in a cooler for preservation. To avoid cross-contamination of the profile while sampling, sampling tools were cleaned between depth increments. Samples were stored in refrigeration prior to analysis.

Sample Analyses

Soil samples were sieved with a 2 mm stainless steel sieve in the cooler. The fine earth fraction and coarse material was weighed, then a subsample of the fine earth fraction was dried at 70 C for 1 week. The remaining fine

earth and coarse fractions were returned to refrigeration for storage. Gravimetric moisture content was determined from sample weight measurements prior to and after drying.

A portion of the subsample was used for mechanical analysis using the Bouyoucos hydrometer method (Bouyoucos, 1936; Day, 1965; Gee and Bauder, 1979). The rest of the subsample was submitted to the M.S.U. Soil Analytical Laboratory for analysis of total As, soluble As, Ca^{2+} , Mg^{2+} , Na^+ , electrical conductivity (EC), and pH. Arsenic was analyzed using continuous-flow hydride generation atomic absorption spectrophotometry (HG-AAS). Samples were acidified 1:1 with 6N HCl and pre-reduced with 1% KI prior to arsine generation with 0.6% sodium borohydride (NaBH_4) in 0.5% NaOH. Sample flow rate was approximately 7 mL/min and the NaBH_4 flow rate was approximately 1 mL/min. The generated arsine was analyzed at 193.7 nm and a 0.2 μm slit width in an air-acetylene flame. Soil samples were digested and analyzed for total As by HG-AAS as described by Welsch et al. (1990). Analysis quality assurance consisted of duplicate analysis of every ten total As samples and every 20-30 soluble As samples.

Statistical Analyses

Statistical analyses of the As data were completed using MSUSTAT (Lund, 1991). Regression analyses were performed on soil physical and chemical parameters versus total and soluble As of each soil sample. Then, to determine differences

between irrigated and non-irrigated sites within each location, separate analyses of variance (ANOVA) were performed on total and soluble As data within each location. To compare total and soluble As data between the locations, total and soluble As values were normalized to a load value for each site. A depth weighted average (DWA) value was obtained by multiplying the depth increment of the sample by the As concentration, then summing these numbers throughout the profile to obtain a load value for the entire profile. This load value was divided by the total profile depth to get a DWA value. Eight DWA values were calculated for each location. For example, one value for each irrigated profile and one value for each non-irrigated profile within each location.

Two separate ANOVAs were performed on the transformed numbers. The first ANOVA excluded data from the lower Madison North location. The second ANOVA included the data from all four locations. The same ANOVA procedures were performed using As load values of the top 30 cm of the soil profile only.

Study 2: Statistical Design

The study consisted of soil profile sampling within the Lower Madison South and the Lower Madison North locations prior to and then following irrigation events for an entire growing season. Study 2 was designed as a 2x5x10 split plot repeated measures experiment with 3 replications. The three

main factors were location, day (relative to irrigation event), and depth as detailed below.

1. location

i. Lower Madison North

ii. Lower Madison South

Three soil sampling replications were completed for each sampling event at each location.

2. day

i. 1 day pre-irrigation

ii. 1 day post-irrigation

iii. 2 days post-irrigation

iv. 4 days post-irrigation

v. 8 days post-irrigation

3. depth (centimeters)

i. 0-15	v. 62-76	ix. 138-168
ii. 16-31	vi. 77-91	x. 169-198
iii. 32-46	vii. 92-107	xi. 199-229
iv. 47-61	viii. 108-137	xii. 230-259

Sample Collection

Sampling occurred in the 1994 growing season at the Anderson South and the VanDyk irrigated sites. Two irrigation events, one in June and one in July, occurred at each site. Sampling occurred prior to and 1, 2, 4, and 8 days after each irrigation event. Samples were collected with a Gidding's probe down to 2.4 m, or until a saturated depth was reached where a representative soil core could not be obtained. Three

profile replications were sampled at each site. The replications were approximately 9 m apart.

Soil cores were placed in prelabeled plastic bags, sealed, then placed on ice for temporary storage. To avoid cross-contamination of soil cores, the probe tube was rinsed with deionized water between core sampling, then dried. Upon return to the lab, samples were immediately placed in a freezer prior to analysis.

Two replicate samples of the irrigation water (from the ditch) were also obtained during the first sampling day following an irrigation event and analyzed for soluble As.

Sample Analyses

Samples were removed from the freezer, thawed, and subsampled for determination of moisture content. Saturated pastes were made from moisture-intact samples from the first irrigation events at each location. Extracts were filtered (0.45 μm), then analyzed for soluble As as described earlier.

Statistical Analyses

Statistical analyses of the data were completed using MSUSTAT (Lund, 1991). Analysis of variance (ANOVA) were performed on samples representing each irrigation event, then comparing the two irrigation events at each site.

CHAPTER 4

RESULTS

Study 1: Soluble As Concentrations

The results of regression analyses between soluble As and total As, Mg, Na, Ca, EC, pH, and percent clay of the soil profiles of the four study locations are presented in Table 3. Although strong correlations do exist at some individual sampling sites between As and other chemical or physical parameters, no pattern exists across the four paired sites or among the sampling sites within the four study locations. Therefore, no conclusions uniform to all sites can be drawn between soluble As and the parameters of interest in the Upper Madison, Lower Madison South, Lower Madison North, and Upper Missouri locations.

Soluble As concentrations from saturated pastes of the sampled soil profiles within the four study locations are represented in Figures 4, 5, 6, and 7.

Upper Madison

Typical concentrations in the irrigated and non-irrigated saturated pastes are below 50 ug/L. The upper 20 cm. of the irrigated sites have soluble As concentrations closer to the

Table 3. r^2 values from regression analyses of soluble As in the fine earth fraction and identified sources of variation within the soil profile.

Site	-----Source of Variation-----						
	Total As	Mg	Ca	Na	EC	pH	% clay
Granger E.							
I	.51	.79	---	.83	.83	---	---
NI	---	.39	---	.04	.08	---	.52
Granger W.							
I	---	.17	.53	.47	.45	.31	---
NI	.11	---	---	---	.17	.11	.06
Valley Garden							
I	---	.43	.33	.57	.46	.13	---
NI	---	.66	.60	.45	.61	.25	.13
Wigwam							
I	.06	.35	---	.96	.92	.76	.02
NI	---	.17	.10	.74	.16	.71	.29
Anderson S.							
I	.26	.76	.83	.76	.77	.73	.03
NI	.32	.13	---	---	---	.18	---
Kilgore							
I	.51	.09	.57	.31	---	.03	.01
NI	.69	.52	.21	---	---	.27	.07
McDonnell N.							
I	.11	---	---	---	---	---	---
NI	---	---	---	---	---	.20	.05
McDonnell S.							
I	.68	---	---	---	---	---	---
NI	.10	.33	.18	.26	.35	.23	---
Anderson N.							
I	---	.28	.42	---	.24	---	---
NI	---	---	---	---	---	---	---
Kammerman							
I	.42	.03	.05	.02	.04	.36	.65
NI	.02	---	---	---	---	.34	---
Lane							
I	---	.46	.15	.40	.52	.35	.01
NI	.88	---	.39	.09	.31	.86	---

Note: I=irrigated site; NI=non-irrigated site; -- designates $r^2=0$.

Table 3. continued

Site	-----Source of Variation-----						
	Total As	Mg	Ca	Na	EC	pH	% clay
VanDyk							
I	---	---	---	---	---	.10	.03
NI	.24	.62	.48	.85	.52	.44	---
Bruce							
I	.28	---	---	---	---	.02	---
NI	.62	.35	---	.54	.42	---	.13
Hansen							
I	.40	.64	---	.59	.57	---	.68
NI	.80	---	---	.16	.09	---	.46
Hunsaker							
I	---	.07	---	.10	.09	---	---
NI	.14	---	---	---	---	---	.15
Koehnke							
I	---	---	.01	.26	---	---	---
NI	---	---	---	---	---	---	---

70-240 ug/L soluble As range in the upper Madison River. Arsenic levels in the irrigated sites are similar to those in the non-irrigated sites at profile depths greater than 20 cm.

Lower Madison South

Soluble As concentrations do not follow a consistent pattern with depth as in the Upper Madison location, but rather are quite variable among the four sampling sites. With the exception of a few depths in the soil profiles at the McDonnell North and Anderson South sites, soluble As seems to be at or below the concentration of the Madison river water, which ranges from 50-100 ug/L in this part of the valley.

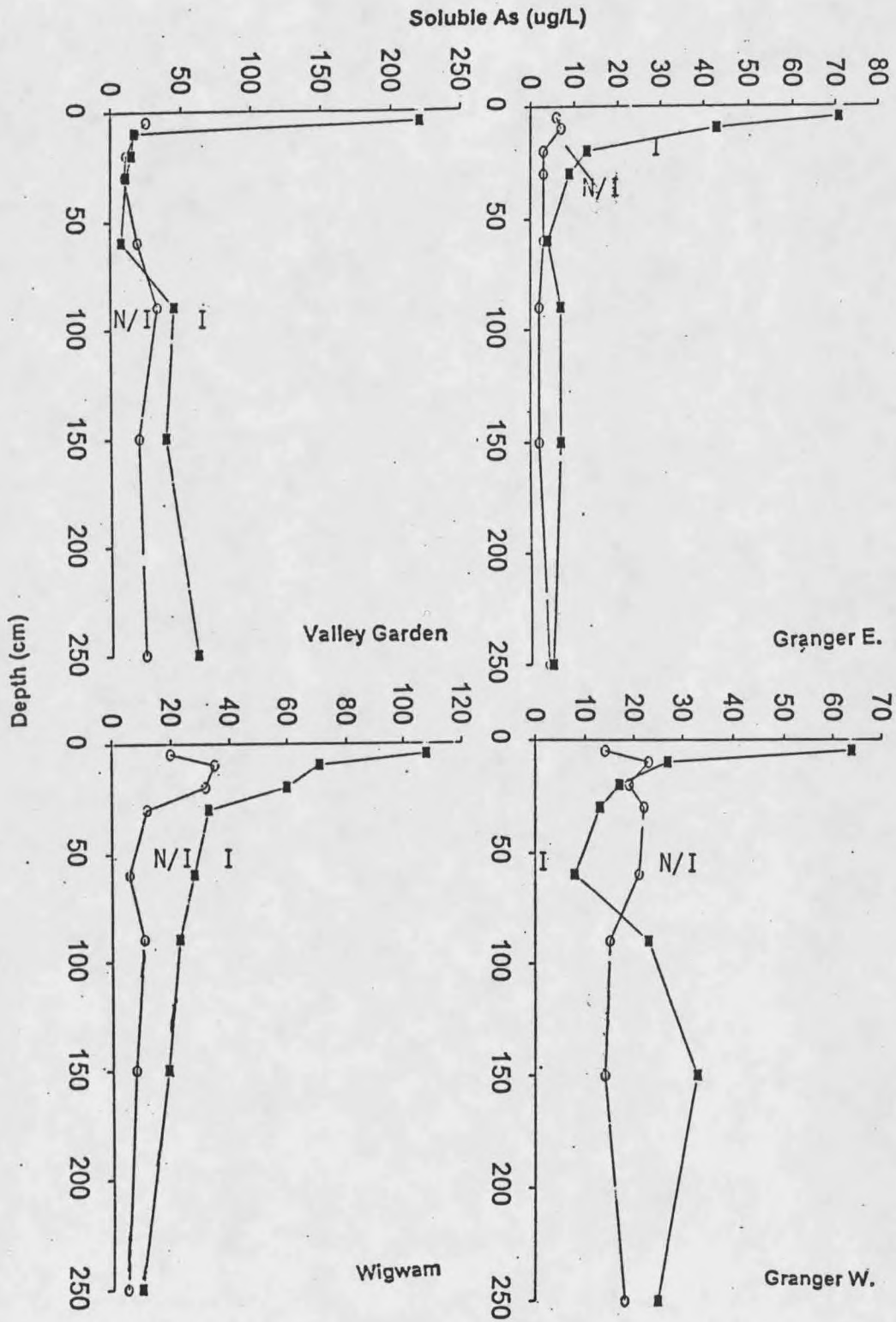


Figure 4. Soluble As concentrations in $\mu\text{g/L}$ in the soil profiles of the Upper Madison location.

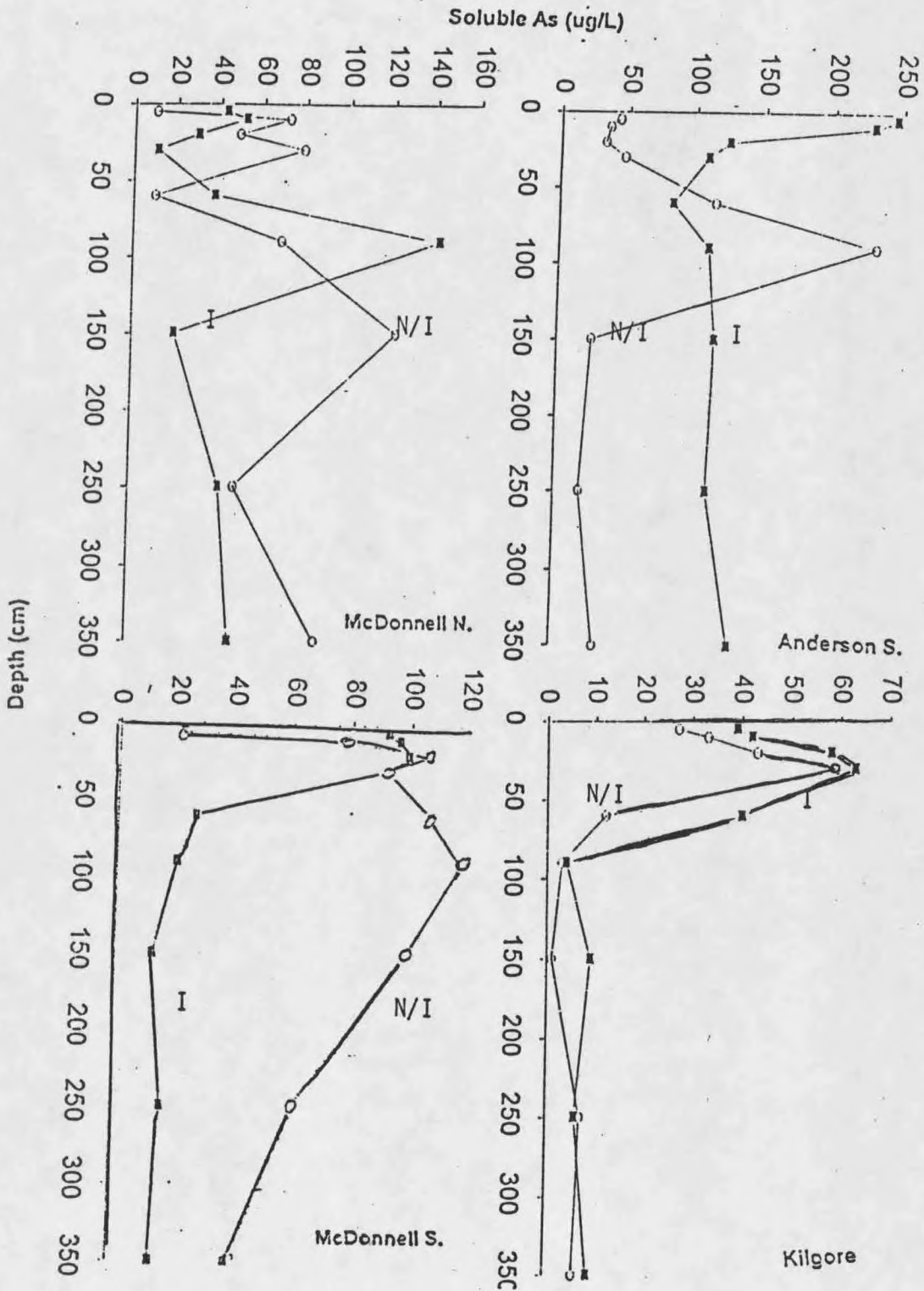


Figure 5. Soluble As concentrations in ug/L in the soil profiles of the Lower Madison South location.

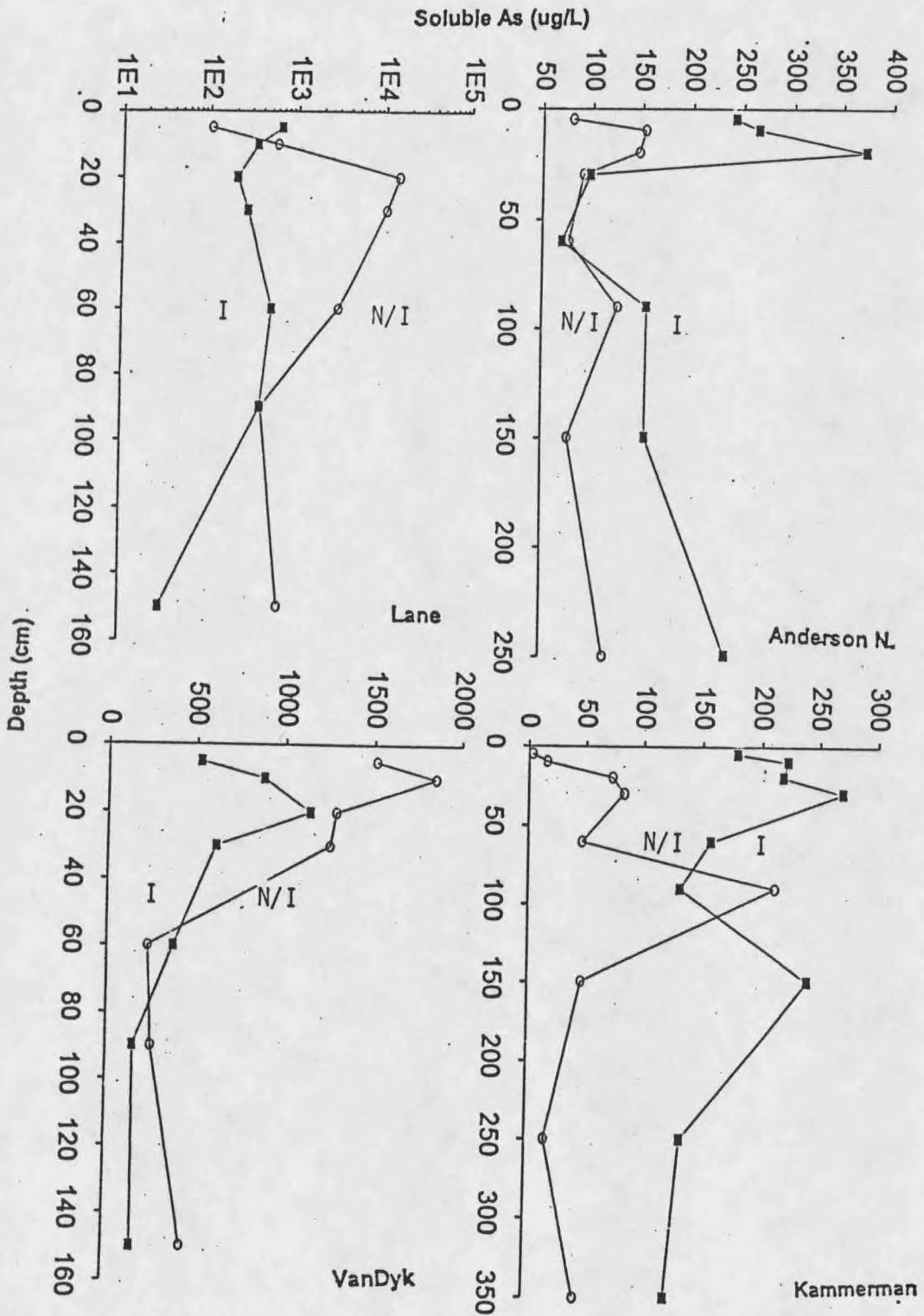


Figure 6. Soluble As concentrations in $\mu\text{g/L}$ in the soil profiles of the Lower Madison North location.

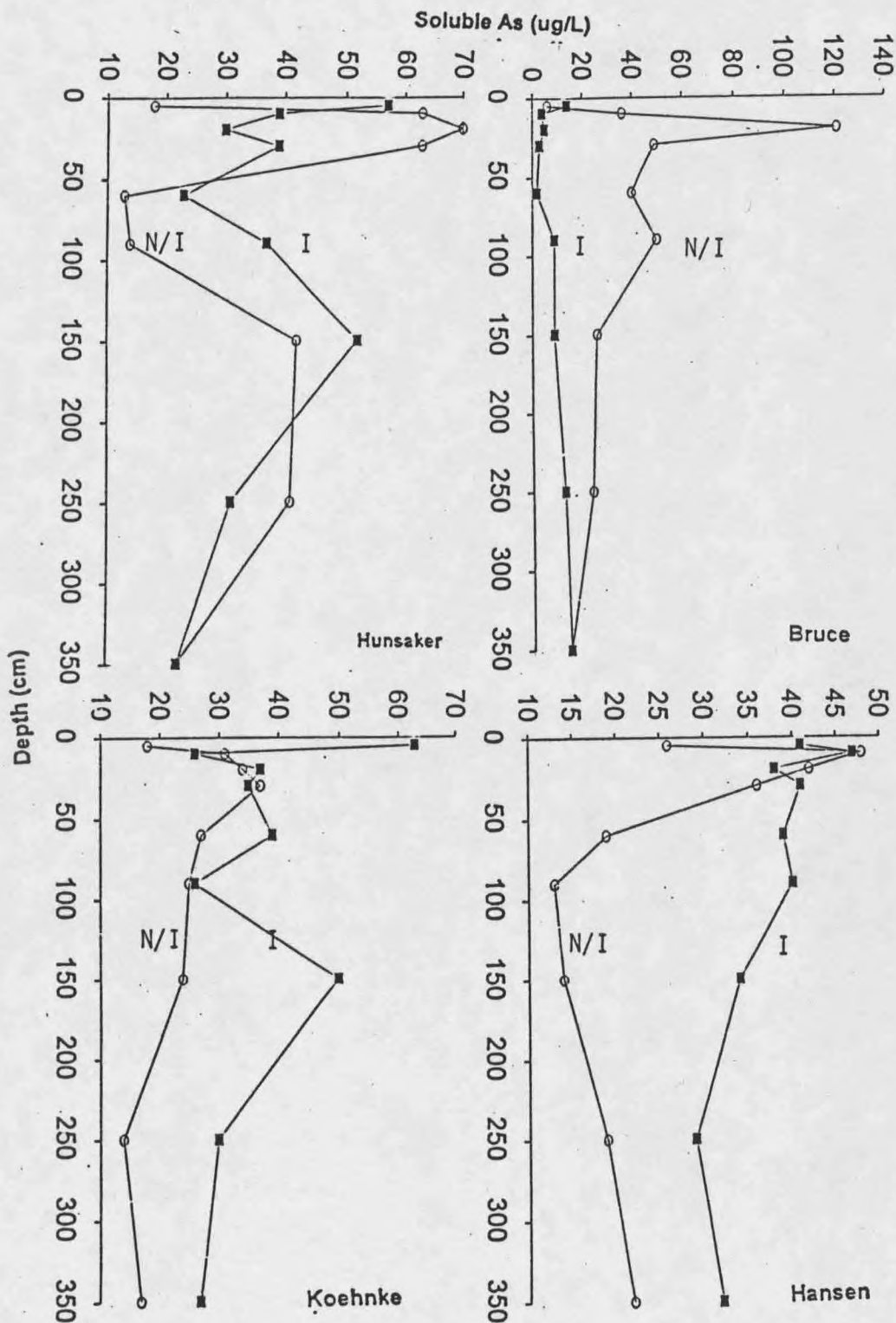


Figure 7. Soluble As concentrations in $\mu\text{g/L}$ in the soil profiles of the Upper Missouri location.

At the Anderson South and McDonnell South sites, the irrigated profiles have substantially higher soluble As concentrations than the non-irrigated sites in the top 10 cm of the soil profile.

Lower Madison North

Soluble As concentrations are quite variable with depth, and show no consistent pattern across the sites. In both the non-irrigated and the irrigated profiles, soluble As is often well above the 50-90 ug/L range in lower Madison River water. In an extreme case, soluble As from the non-irrigated Lane site reached above 10,000 ug/L. Both the non-irrigated sites at the Lane and VanDyk sites have concentrations above their irrigated pair for most of the profile.

Upper Missouri

Soluble As concentrations are quite variable with depth, and show no significant pattern across the sites. In general, concentrations remain near or below the 10-50 ug/L range of As in the upper Missouri River. Soluble As is higher in the non-irrigated than the irrigated profile at the Bruce site. At the time of sampling, the irrigated site was in fallow for the second year, which may suggest that some soluble As moved below the 3 m sampling depth.

Soluble As in Irrigated versus
Non-irrigated Soils

Mean soluble As concentration of each soil profile was determined from the ANOVA of soluble As concentrations in irrigated and non-irrigated soils of the four study locations. Significance of differences between mean soluble As concentrations of irrigated and non-irrigated soil profiles within each study location are presented in Table 4. The only significant difference between the irrigated and non-irrigated sites exists within the Upper Madison location.

Table 4. Mean soluble As concentrations of irrigated and non-irrigated soil profiles of the four study locations.

Mean Soluble As Concentration (ug/L)				
	Upper Madison	Lower Madison South	Lower Madison North	Upper Missouri
Irrigated	36 ^B	77 ^A	323 ^A	30 ^A
Non- Irrigated	15 ^A	48 ^A	1356 ^A	32 ^A

Note: Means of irrigated and non-irrigated sites within the same study location having the same superscript do not differ significantly at the p=0.05 level of probability.

Mean DWA Soluble As Concentration

Results of the ANOVAs of Depth Weighted Average (DWA) soluble As concentration in the entire profile of soils from

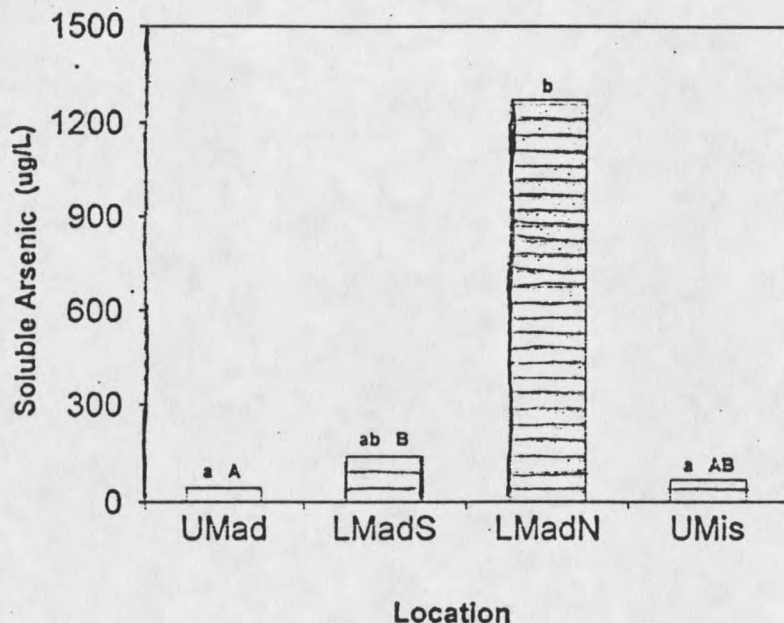


Figure 8. Mean DWA soluble As (ug/L) in combined irrigated and non-irrigated soil profiles of the four study locations. Note: Means of locations having the same superscript do not differ significantly at the $p=0.05$ level of probability. Lower case letters include data from the Lower Madison North location. Upper case letters exclude data from the lower Madison North location.

the four locations are illustrated in Figure 8. Values in Figure 8 are mean DWA soluble As concentrations in the soils of the irrigated and non-irrigated sites combined within each location. At the Upper Madison and Upper Missouri locations, mean DWA soil water As concentrations are at, or below the concentration in the river at those locations. Slightly higher As concentrations occur in the soil water than in the river water at the Lower Madison South location. Comparing these results with the Lower Madison North location, a significantly higher mean DWA soluble As concentration occurs in the soil water at that location than at the Upper Madison

and Upper Missouri locations. Mean DWA soil water As is also approximately an order of magnitude higher than the As concentration in the river water at that location. Furthermore, the mean DWA As concentration in the soil water from these soils is significantly greater than that which is observed in the highest As concentrations of groundwater in this section of the river corridor (Nimik, written communication; Mangelson and Brummer 1994).

Results of the ANOVA of DWA soluble As concentrations in the top 30 cm depth of each soil profile are shown in Figure 9. The values are mean DWA soluble As concentrations in the irrigated and non-irrigated sites combined within each location. Analysis of variance of the data set excluding the data from the Lower Madison North location indicated a significant difference between the mean DWA soluble As concentrations in Lower Madison South location and the Upper Madison and Upper Missouri locations. Although the mean DWA soluble As concentration of the Lower Madison South location is more than 10-fold greater than concentrations at the other locations, when it is included into the analysis there is no statistical difference between mean DWA soluble As concentrations of that location and the three other locations. The As concentrations at each Lower Madison North sampling site were too variable to account for a significant difference at that location.

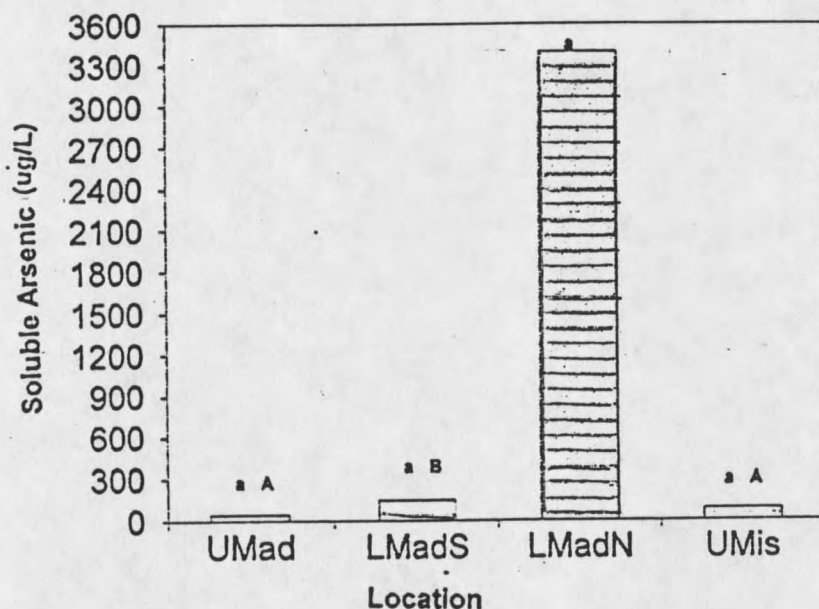


Figure 9. Mean DWA soluble As (ug/L) in the 0-30 cm depth of combined irrigated and non-irrigated soils of the four study locations.

Results of the ANOVA of the DWA soluble As concentrations of the entire profile of the irrigated and non-irrigated sites across the four locations is illustrated in Figure 10. Differences in mean DWA soluble As concentrations in the irrigated sites of the Upper Madison, Lower Madison South, and Upper Missouri locations were not significant. Mean DWA soluble As in the irrigated sites of the Lower Madison North location is significantly different from the other locations when including it into the analysis. Mean DWA soluble As concentrations in the non-irrigated sites did not differ significantly between the four locations.

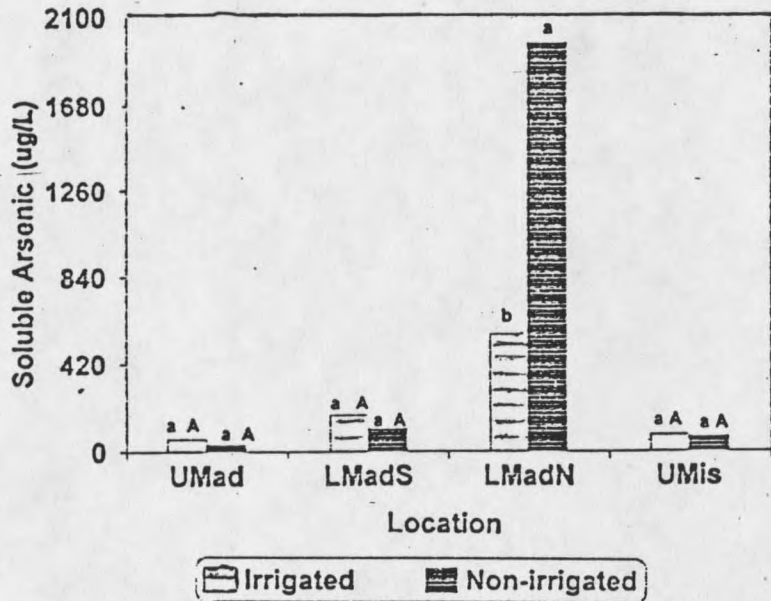


Figure 10. Mean DWA soluble As (ug/L) in the irrigated and non-irrigated soil profiles of the four study locations. Note: Means of locations having the same superscript do not differ significantly at the $p=0.05$ level of probability. Lower case letters include data from the Lower Madison North location. Upper case letters exclude data from the lower Madison North location.

Mean DWA soluble As concentrations in the 0-30 cm depth in the irrigated sites of the Upper Madison, Lower Madison South, and Upper Missouri locations did not differ significantly (Fig. 11). Mean DWA soil water As concentrations of the Lower Madison North location were significantly different from the mean DWA soil water As concentrations of the Upper Madison, Lower Madison South and Upper Missouri locations.

Differences in mean DWA soluble As concentration of the 0-30 cm depth of the non-irrigated sites were significant when the ANOVA was completed excluding the data from the non-irrigated sites of the Lower Madison North location. Although the mean DWA soluble As concentrations of the Lower Madison

North location are substantially greater than the mean DWA soluble As concentrations of the other locations, when the Lower Madison North location is included into the ANOVA, no significant differences exist. Furthermore, the mean DWA soluble As concentration of the non-irrigated profiles is substantially greater than the mean DWA soluble As concentration of the irrigated profiles of the Lower Madison North location.

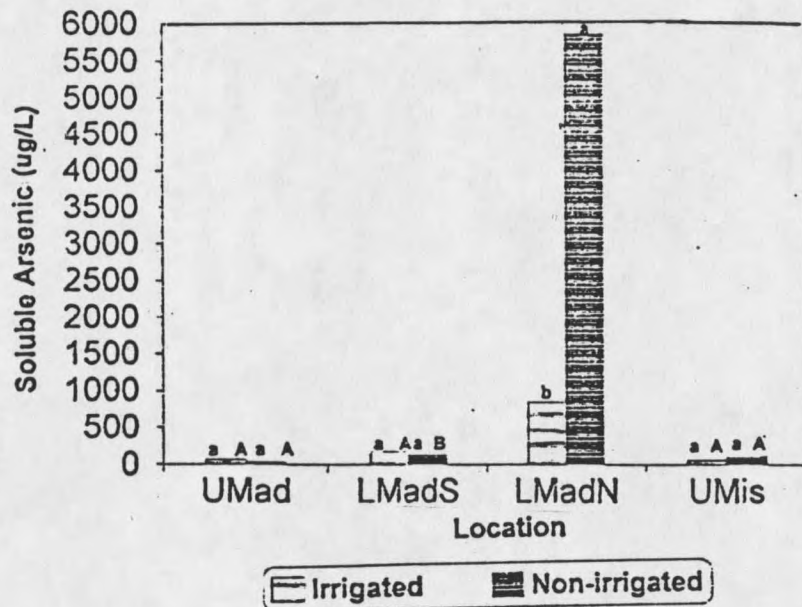


Figure 11. Mean DWA Soluble As (ug/L) in the 0-30 cm depth of irrigated and non-irrigated soils of the four study locations.

Mean DWA soluble As concentrations in the entire soil profile and in the 0-30 cm depth of irrigated versus non-irrigated soils of the four locations combined are shown in

Figures 12 and 13. There is no significant difference between soluble As concentration in irrigated and non-irrigated sites, whether or not the data from the Lower Madison North location are included into the analysis.

Total As Concentrations

The results of regression analyses between total As and Mg, Na, Ca, EC, pH, and percent clay of the soil profiles of the four study locations are presented in Table 5. Although strong correlations do exist at some individual sampling sites between total As and other chemical or physical parameters, no pattern exists across the four paired sites within each study location. Therefore, no conclusions can be drawn between total As and the parameters of interest in the Upper Madison, Lower Madison South, Lower Madison North, and Upper Missouri locations.

Upper Madison

Total As concentrations for the fine earth fraction of the sampled soil profiles of the Upper Madison River valley are represented in Figure 14. Total As concentrations in the irrigated sites range from 6 to 24 mg/kg in the top 60 cm of the soil profiles. With exception of the Valley Garden site, total As concentrations in the non-irrigated sites are generally less than the total As concentrations

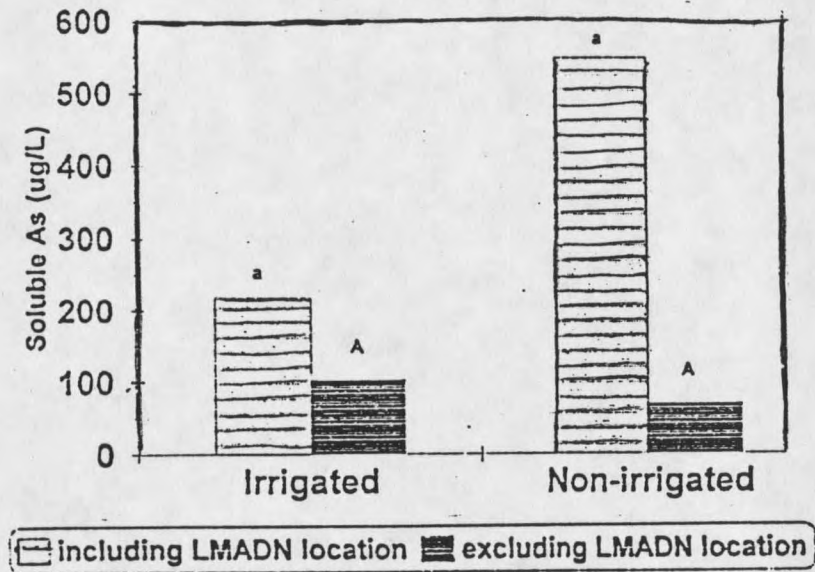


Figure 12. Mean DWA soluble As (ug/L) in the irrigated versus non-irrigated soil profiles of the combined four study locations.

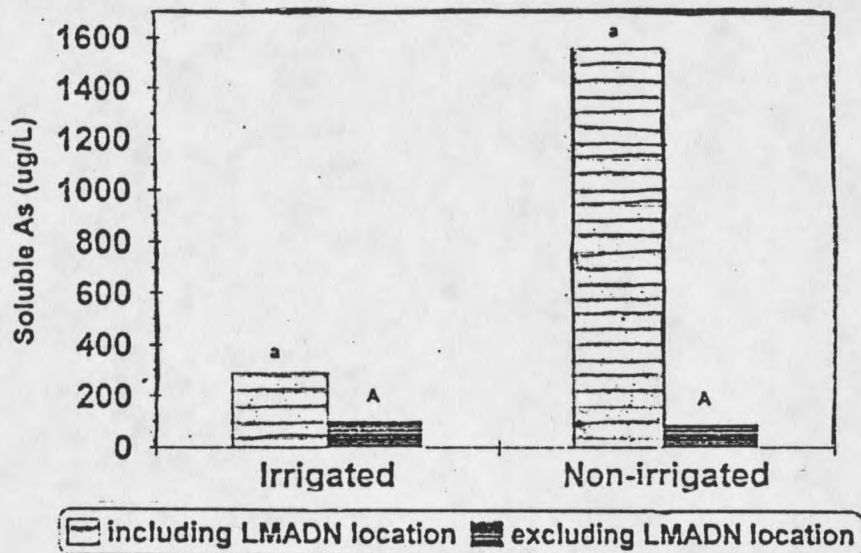


Figure 13. Mean DWA soluble As (ug/L) in the 0-30 cm depth of irrigated versus non-irrigated soils of the combined four study locations.

Table 5. r^2 values from regression analysis of total As in the fine earth fraction and identified sources of variation within the soil profile.

Site	-----Source of Variation-----						
	Soluble As	Mg	Ca	Na	EC	pH	% clay
Granger E.							
I	.51	.51	.09	.51	.50	.27	.01
NI	---	.17	.54	.47	.45	.31	---
Granger W.							
I	---	.39	---	---	.07	---	.52
NI	.11	---	---	---	.00	.04	---
Valley Garden							
I	---	---	---	---	---	---	---
NI	---	---	---	---	---	---	.35
Wigwam							
I	.06	---	.11	---	---	.03	.29
NI	---	---	---	---	---	---	.00
Anderson S.							
I	.26	.62	---	---	.60	.54	.62
NI	.32	---	---	---	---	.00	.11
Kilgore							
I	.51	---	.45	.44	.22	---	.04
NI	.69	---	.05	---	---	.42	.55
McDonnell N.							
I	.11	---	---	---	---	---	---
NI	---	---	---	.10	---	---	.12
McDonnell S.							
I	.68	---	---	---	---	---	---
NI	.10	.06	---	---	---	---	.61
Anderson N:							
I	---	.43	---	.47	.50	.63	.70
NI	---	---	---	.17	.53	.68	---
Kammerman							
I	.42	.14	.18	.13	.16	.35	.50
NI	.02	---	---	---	---	---	---
Lane							
I	---	---	.28	---	---	---	---
NI	.88	---	.42	.26	.34	.73	.02

Note: I=irrigated site; NI=non-irrigated site; -- designates $r^2=0$.

Table 5. continued

Site	-----Source of Variation-----						
	Soluble As	Mg	Ca	Na	EC	pH	% clay
VanDyk							
I	---	.20	.06	---	.55	---	.15
NI	.24	.52	.40	.51	.48	.37	---
Bruce							
I	.28	.21	---	.68	.49	.34	---
NI	.62	.04	---	.07	---	---	---
Hansen							
I	.40	.43	.08	.25	.31	---	.47
NI	.80	---	---	.44	.36	---	.68
Hunsaker							
I	---	.39	.08	.02	.14	.12	.43
NI	.14	---	---	.01	---	.04	---
Koehnke							
I	---	.15	.80	.25	.24	.59	.05
NI	---	---	.54	.33	.10	.15	.59

in the irrigated sites of the Upper Madison location, particularly in the upper 30 cm of the soil profiles.

Total As per unit weight of bulk soil in the profile of the Upper Madison sites after adjusting for coarse fragments is illustrated in Figure 15. The adjustment for coarse fragments assumes a minimum ability of the coarse fragments to adsorb As. Total As concentrations in the bulk soil profile of soils having significant amounts of coarse fragments are somewhat less than those observed in the fine earth fraction. Furthermore, the difference in total As between the irrigated and non-irrigated sites is not as clear as was shown in Figure 14. Only at the Granger East site does the irrigated soil

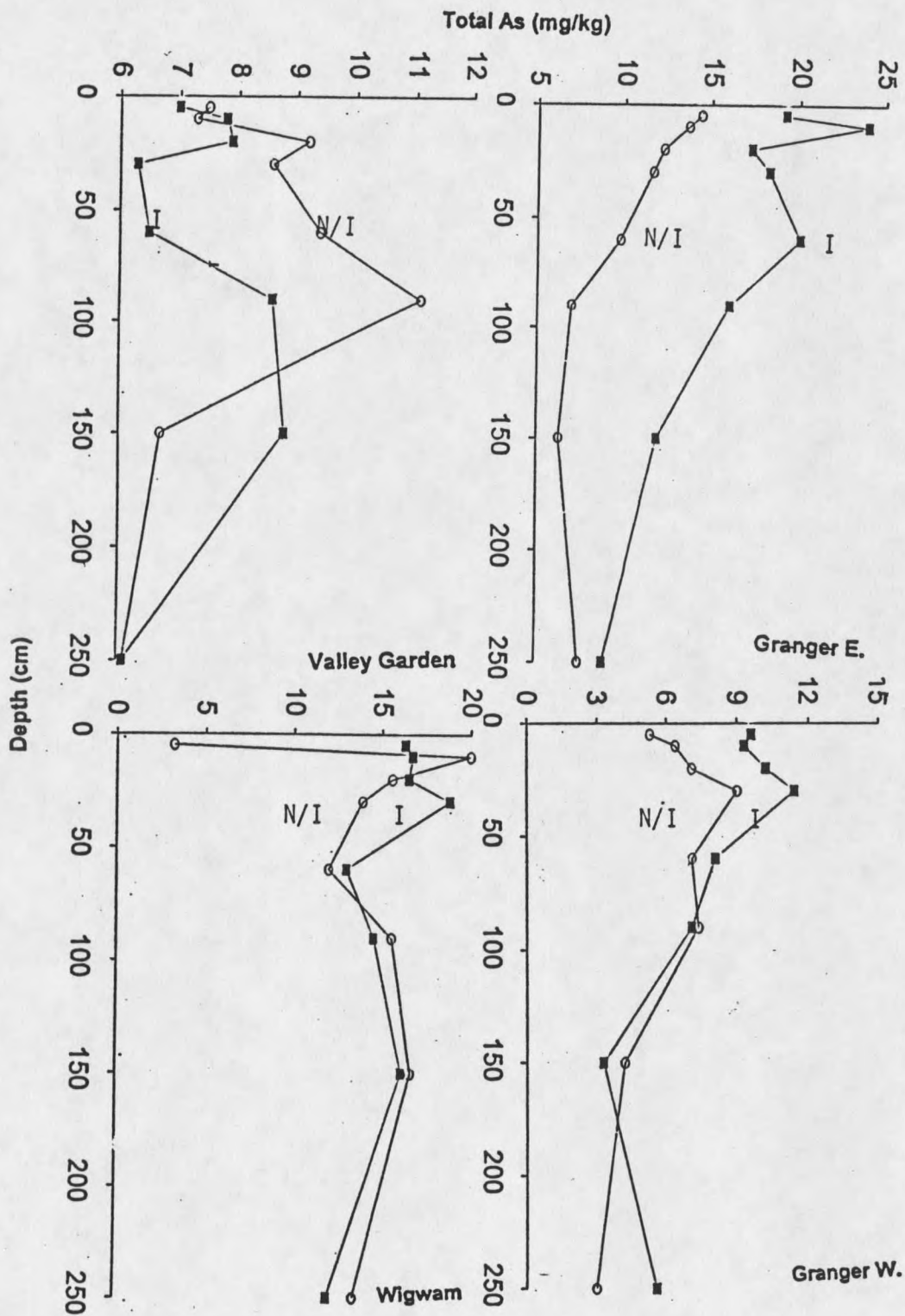


Figure 14. Total As concentrations in the fine earth fraction of the soil profiles of the Upper Madison location.

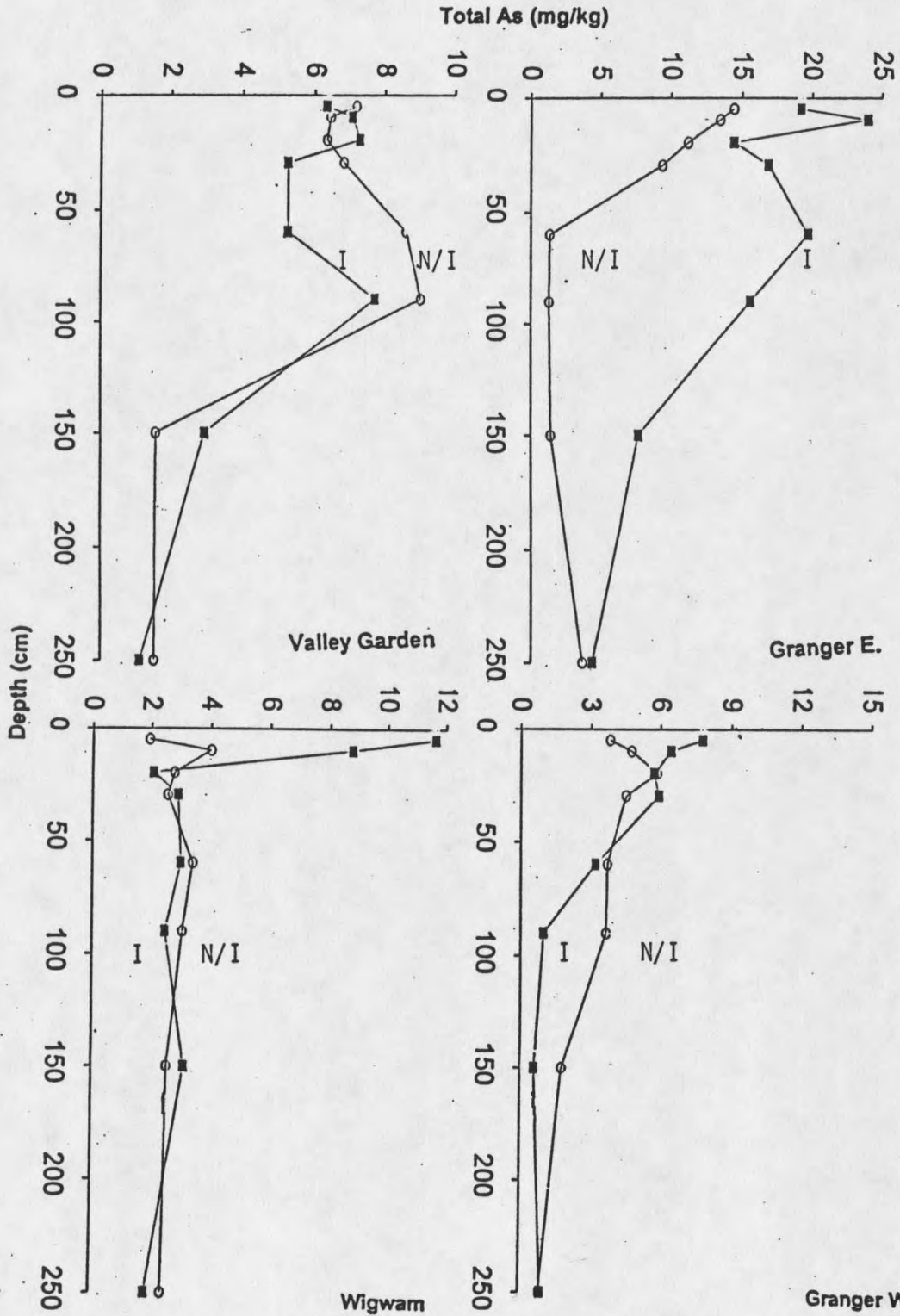


Figure 15. Total As concentrations in the bulk soil profiles in the Upper Madison location.

have higher total As concentrations than its non-irrigated pair.

Lower Madison South

Total As concentrations for the fine earth fraction of the sampled soil profiles of the Lower Madison South location are represented in Figure 16. Total As the non-irrigated sites does not exceed 10 mg/kg. Total As concentrations in the irrigated sites approach 14 mg/kg at some depths in the McDonnell North and Anderson South sites, and they are generally higher than in the non-irrigated sites, with the exception being the Kilgore site. The adjustment for total As in the bulk soil profile shows no noticeable change in the total As profile at each site (Fig. 17). The percentage of coarse fragments in the soils sampled at the Lower Madison South locations is relatively low compared to the Upper Madison sites.

Lower Madison North

Total As concentrations for the fine earth fraction of the sampled soil profiles of the Lower Madison North location are presented in Figure 18. The total As concentrations in these profiles are significantly greater than those seen upstream in the Madison River valley. For example, the maximum concentration of total As at the non-irrigated VanDyk site is 132 mg/kg, approximately 10-fold greater than any concentration measured at the previous two locations. The

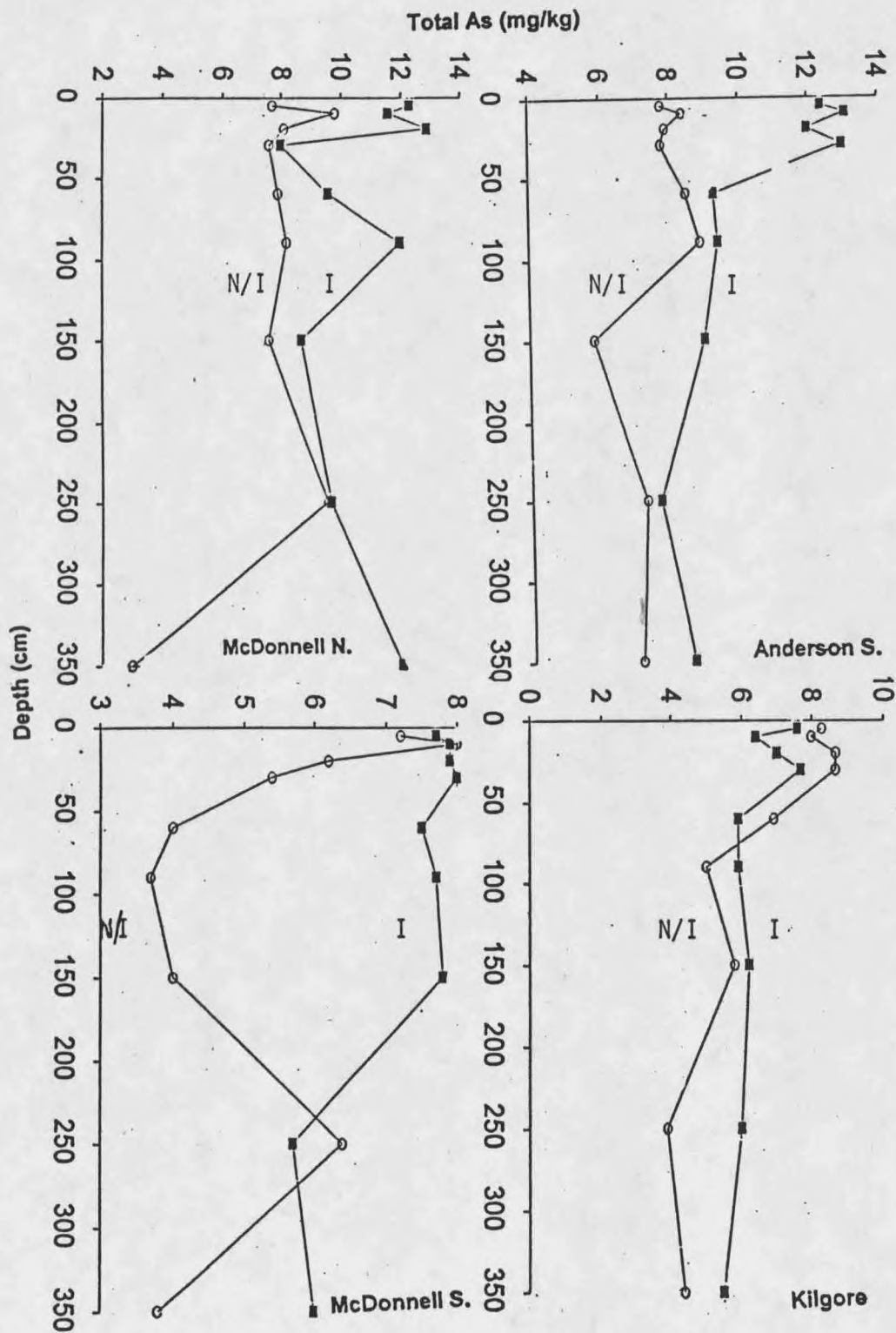


Figure 16. Total As concentrations in the fine earth fraction of soil profiles in the Lower Madison South location.

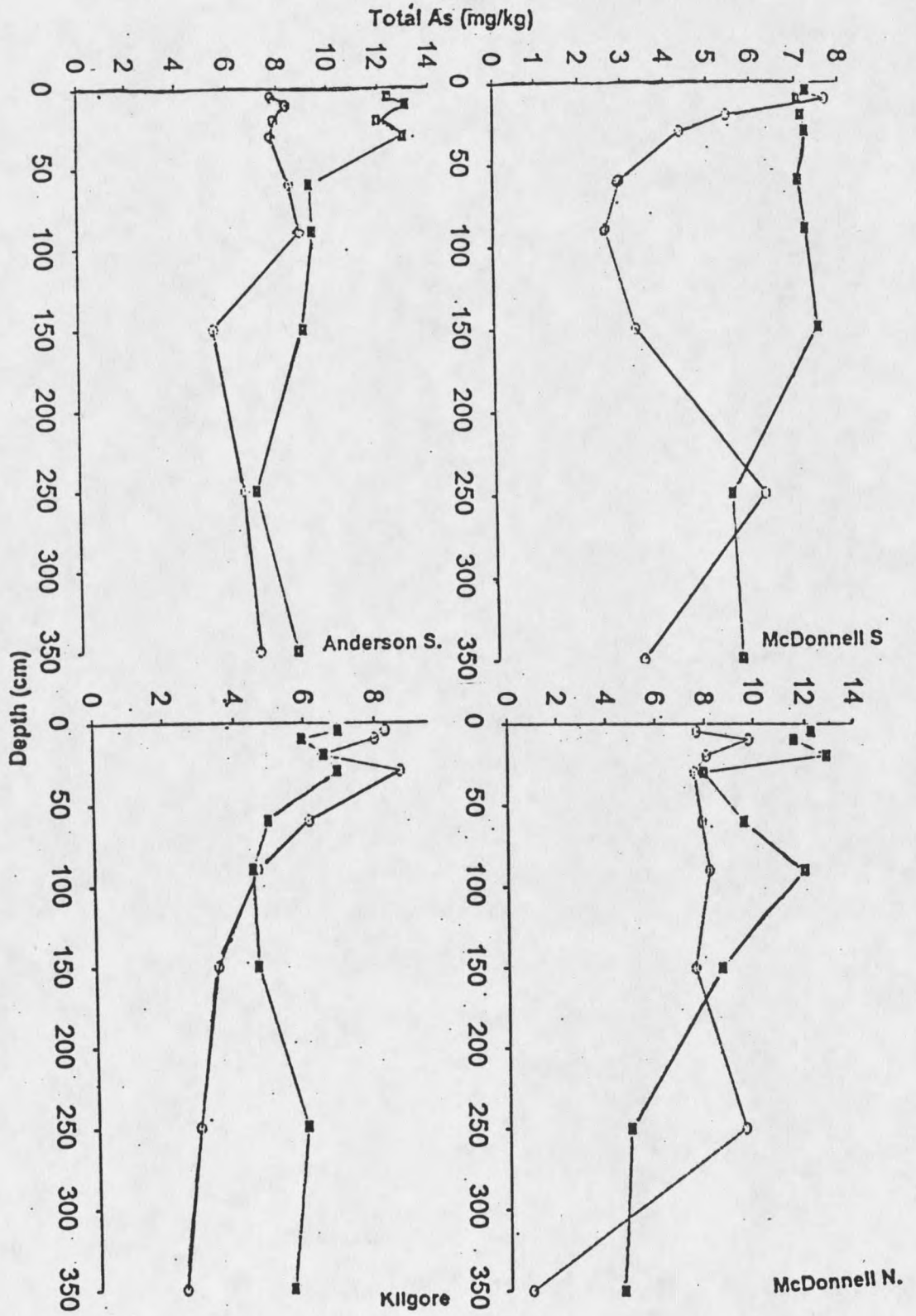


Figure 17. Total As concentrations in the bulk soil profiles of the Lower Madison South location.

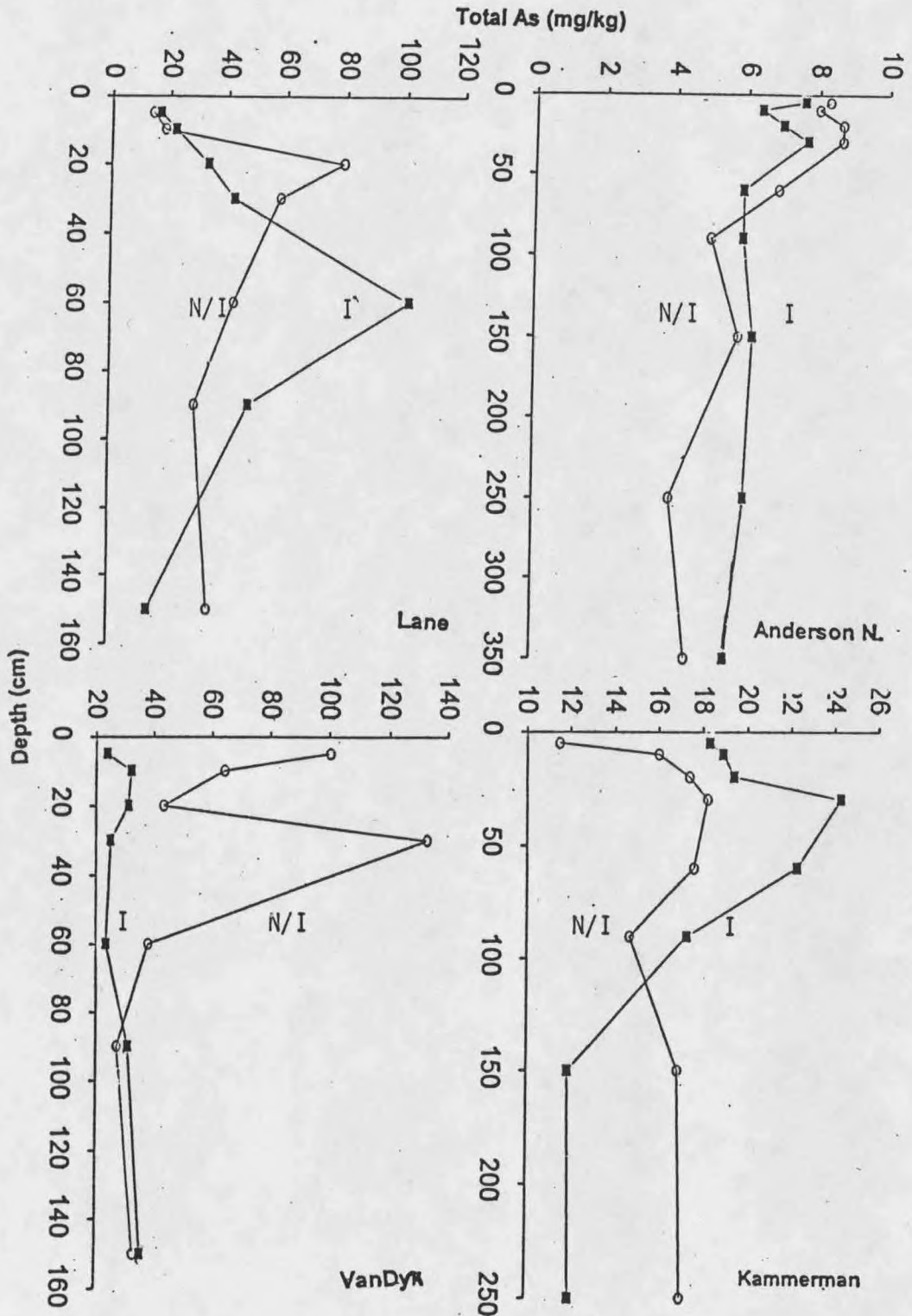


Figure 18. Total As concentrations in the fine earth fraction of soil profiles of the Lower Madison North location.

non-irrigated soils at the VanDyk sites have greater total As concentrations than the irrigated soils. However, no consistent pattern of change in total As concentration with depth can be observed among the four sites.

Only the Anderson North site in the Lower Madison North location had a substantial amount of coarse fragments in the soil profile. After adjusting the data from this site for total As concentrations in the bulk soil profile, the non-irrigated soil has a greater total As concentration than the irrigated soil (Fig. 19).

Upper Missouri

Total As concentrations for the fine earth fraction of the sampled soil profiles of the Upper Missouri location are presented in Figure 20. In general, total As concentrations in both the irrigated and non-irrigated soils are between 5 and 20 mg/kg, approximately the same range as was observed in the soils of the upper Madison and lower Madison South locations. Total As concentrations in the irrigated soils are greater than the total As concentrations of the non-irrigated soil at the Bruce site. The irrigated soil has greater total As concentrations than the non-irrigated soil at the Hunsaker and Hansen sites between the 50 and 150 cm depths. However, no difference between the irrigated and non-irrigated soil was observed at the Koehnke site.

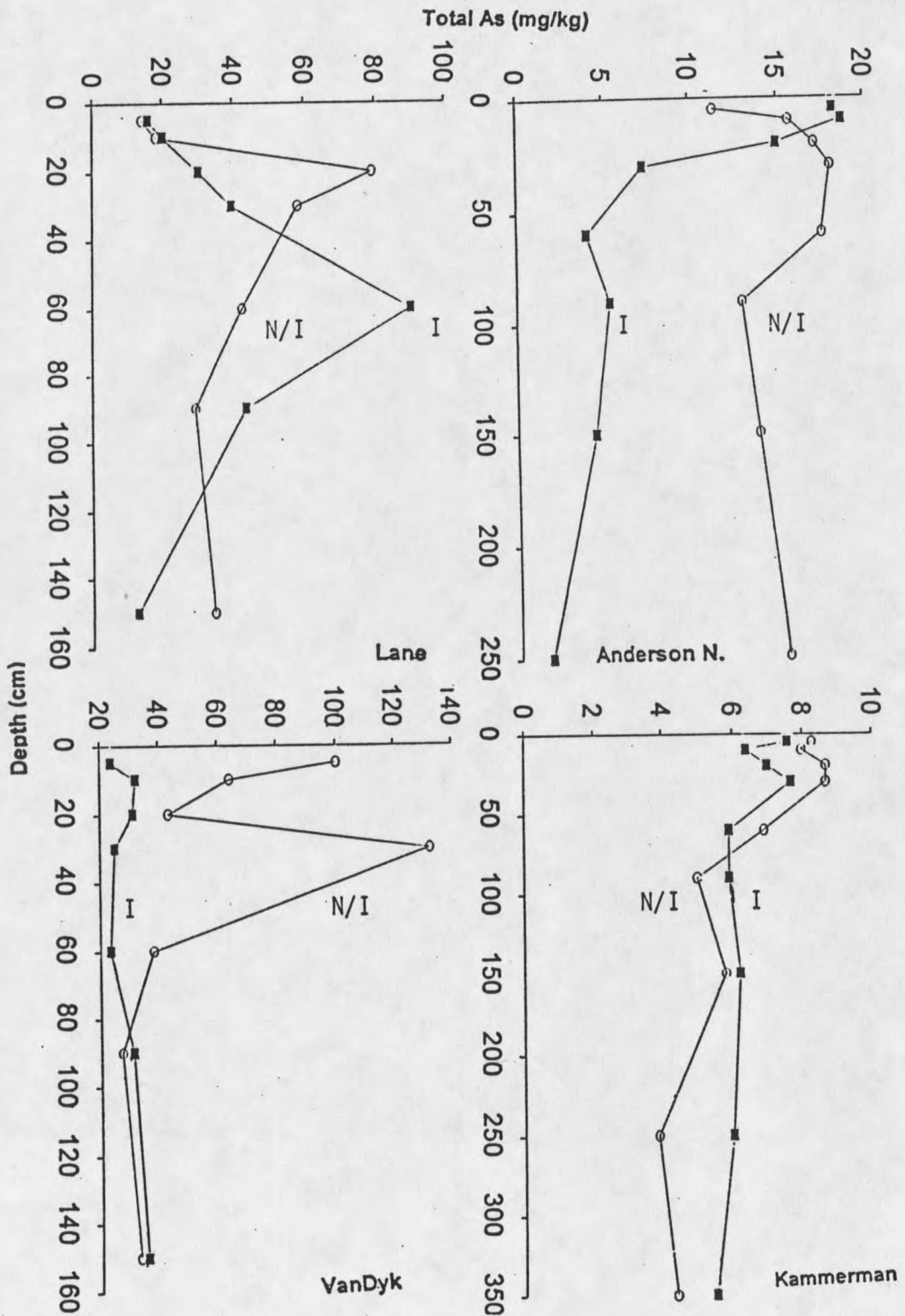


Figure 19. Total As concentrations in the bulk soil profiles of the Lower Madison North location.

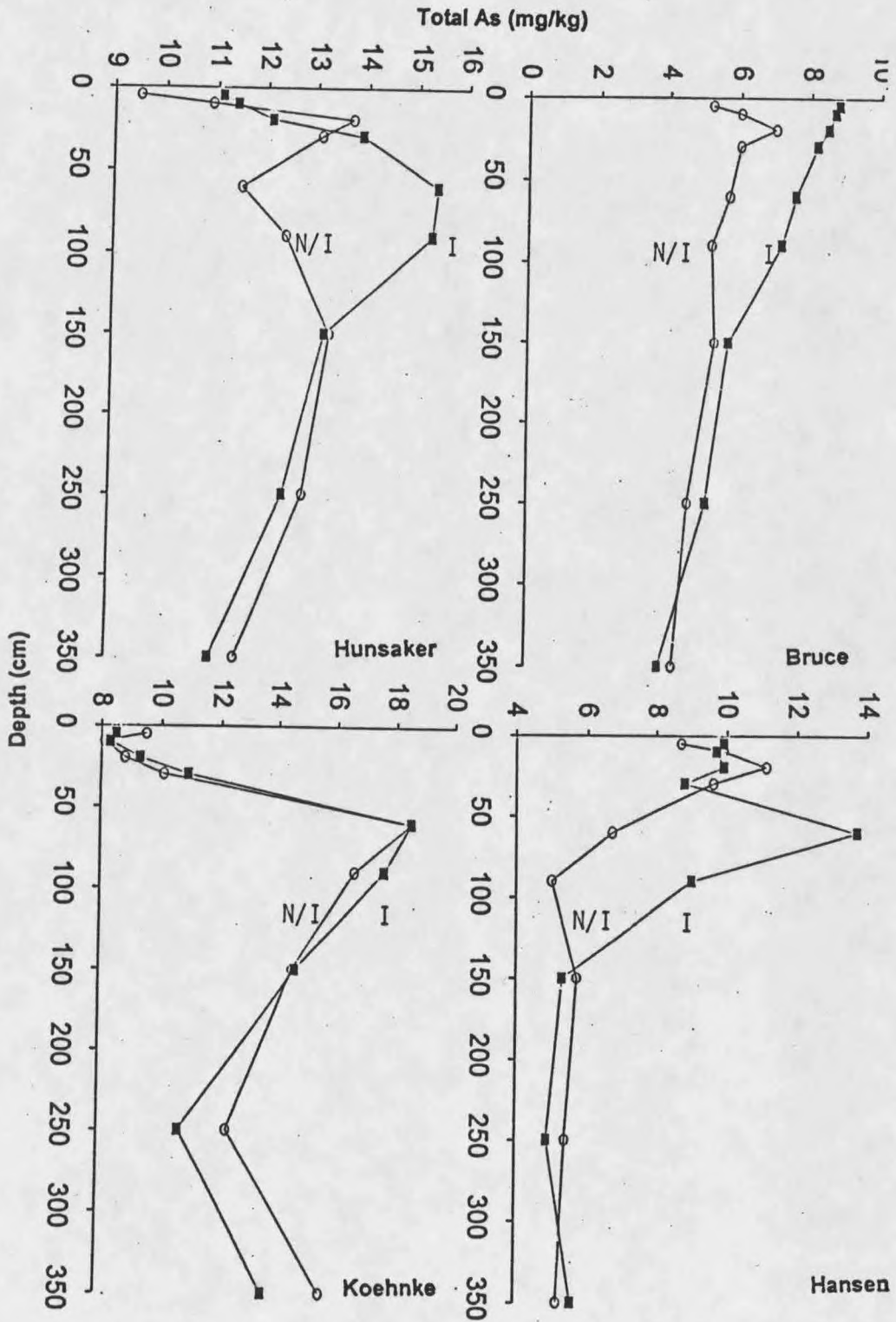


Figure 20. Total As concentrations in the fine earth fraction of soil profiles of the Upper Missouri location.

A general trend of a decrease in total As concentration with depth occurs.

After adjustment for total As concentration in the bulk soil profile, the only significant change in the As profile is at the Hansen site (Fig. 21). The total As profile looks much like that at the Bruce site where the irrigated soil is higher in As than the non-irrigated soil, and total As concentration decreases with depth.

Carbonate Coatings

To address the assumption that coarse fragments do not adsorb As, calcium carbonate coatings on coarse fragments selected from four sites were analyzed for total As content. Although it has not been shown that calcium carbonate adsorbs As, calcite is known to adsorb As. The results from the analysis are provided in Table 6.

Total As concentration in the carbonate coatings is substantial at the Anderson North site. However, it is inconclusive whether the higher concentration in the irrigated site is an irrigation effect. When comparing the surface area occupied by the coatings on the coarse fragments to the surface area of the fine earth fraction, the coatings on the coarse fragments may not significantly change the total As load in the entire soil profile. Furthermore, some carbonate coatings were observed on sand particles at many of the sites.

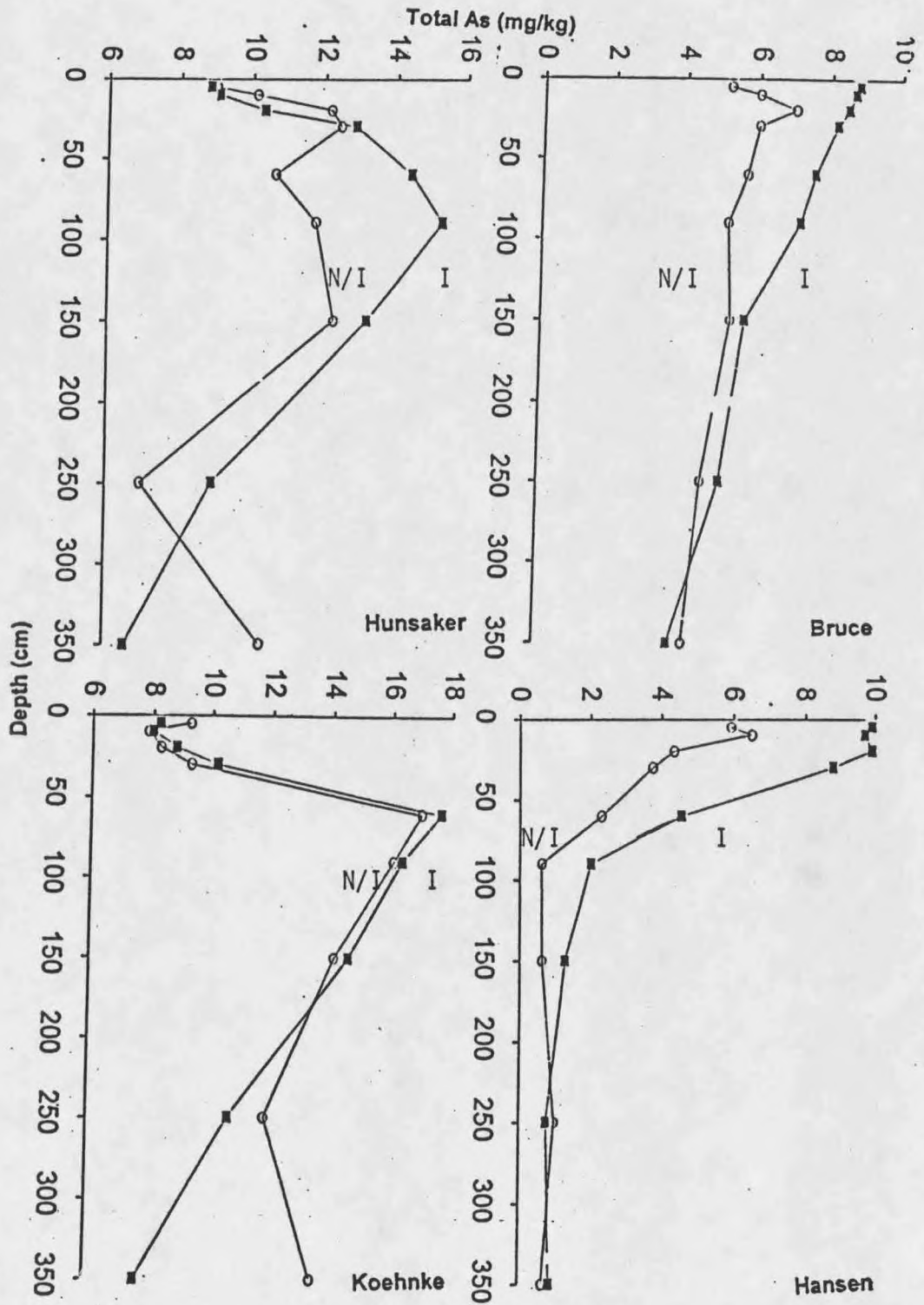


Figure 21. Total As (mg/kg) in the bulk soil in profiles of the Upper Missouri location.

Table 6. Total As concentrations in carbonate coatings on coarse fragments of selected soil sampling sites.

Soil Sampling Site	As (mg/kg)
Anderson North Irrigated	78.7
Anderson North Non-irrigated	67.5
Granger West Irrigated	5.8
Hansen Irrigated	7.3

Irrigated versus Non-irrigated Soils

Differences in total As concentrations between irrigated and non-irrigated fine earth fractions and bulk soil profiles within each location were not significant (Table 7 and 8). However, total As concentration in the fine earth fraction and bulk soil of the irrigated sites is greater than the non-irrigated sites, except at the Lower Madison North location.

Mean DWA Total As Concentrations

Results of the ANOVAs of mean DWA total As concentration in the four locations are illustrated in Figures 22 and 23. Values are the mean concentration of DWA total As in the fine earth or in the bulk soils of the combined irrigated and non-irrigated sites within each location. Differences between mean DWA total As in the combined irrigated and non-irrigated soils of the Upper Madison, Lower Madison South, and Upper Missouri locations are not significant. However, DWA total

Table 7. Mean total As concentration in the fine earth fraction from irrigated and non-irrigated soil profiles of the four study locations.

Mean Total As Concentration (mg/kg)				
	Upper Madison	Lower Madison South	Lower Madison North	Upper Missouri
Irrigated	12.0 ^A	8.8 ^A	24.8 ^A	10.2 ^A
Non- Irrigated	9.6 ^A	6.9 ^A	32.9 ^A	9.4 ^A

Note: Means of irrigated and non-irrigated profiles within a study location followed by the same superscript do not differ significantly at the $p=0.05$ level, based on LSD test.

Table 8. Mean total As concentration in the bulk irrigated and non-irrigated soil profiles of the four study locations.

Total As (mg/kg)				
	Upper Madison	Lower Madison South	Lower Madison North	Upper Missouri
Irrigated	7.2 ^A	8.1 ^A	21.4 ^A	8.7 ^A
Non- Irrigated	5.0 ^A	6.4 ^A	32.4 ^A	7.7 ^A

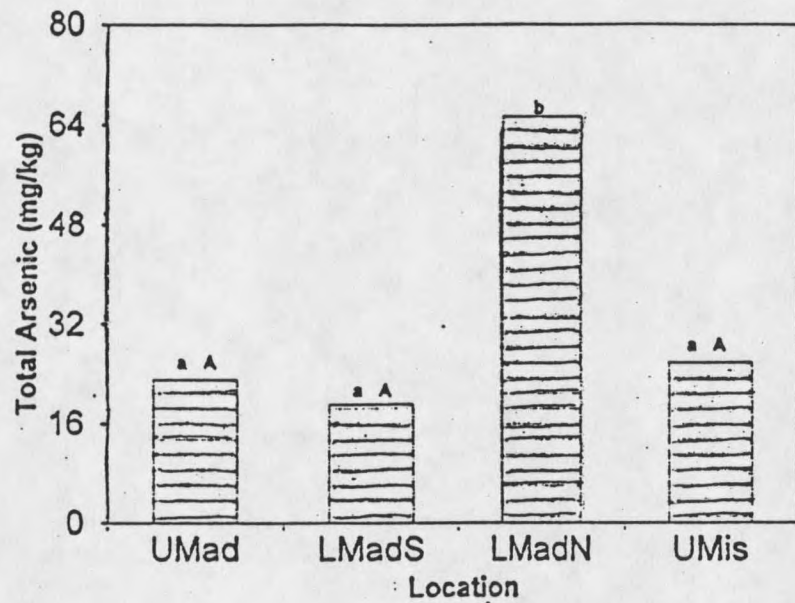


Figure 22. Mean DWA total As (mg/kg) in the fine earth fraction of soils of the four study locations. Note: Means identified with the same upper or lower case letter do not differ significantly at the $p=0.05$ level, base on LSD test. Upper case letters apply to LSD analysis excluding data from the Lower Madison North location.

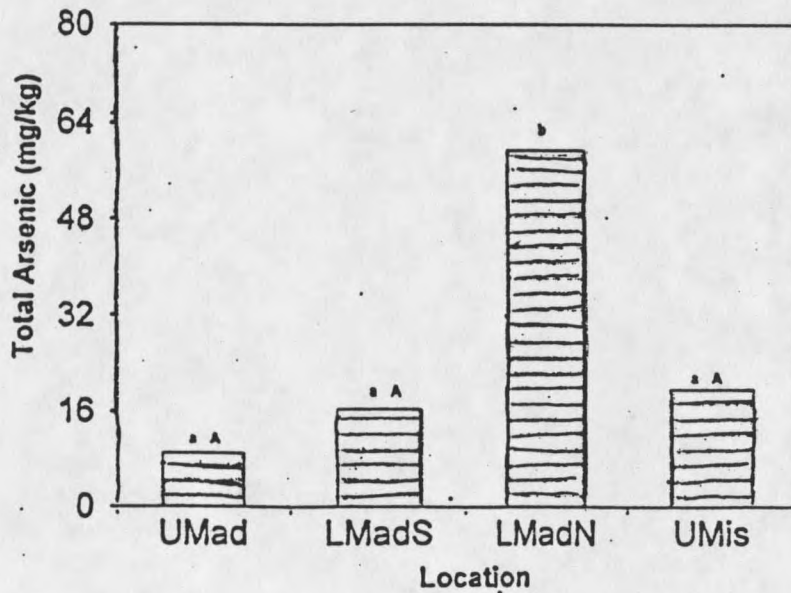


Figure 23. Mean DWA total As (mg/kg) in the bulk soil profile of the four study locations.

As concentration in the Lower Madison North location is significantly different than mean DWA total As concentration of the other three locations.

Results of the ANOVA of mean DWA total As concentration in the top 30 cm of all profiles of each study location are shown in Figures 24 and 25. Differences in mean DWA total As concentrations of the Upper Madison, Lower Madison South, and Upper Missouri locations are not significant. However, the mean DWA total As concentration is significantly different between the Lower Madison North location and the other locations.

Results of the ANOVA of mean DWA total As concentrations in the irrigated and non-irrigated soils of the four locations are illustrated in Figures 26 and 27. Mean DWA total As concentrations in the fine earth fraction of the irrigated sites of the Upper Madison, Lower Madison South, and Upper Missouri locations are not significantly different. Mean DWA total As concentrations in the fine earth fraction of the irrigated sites of the Lower Madison North location are significantly different from the other locations, being 2-3 times greater than the concentrations of the other three locations.

After adjusting for coarse fragments in the soil profile, the only significant difference in mean DWA total As concentrations is between the irrigated sites in the upper Madison location and the lower Madison North location.

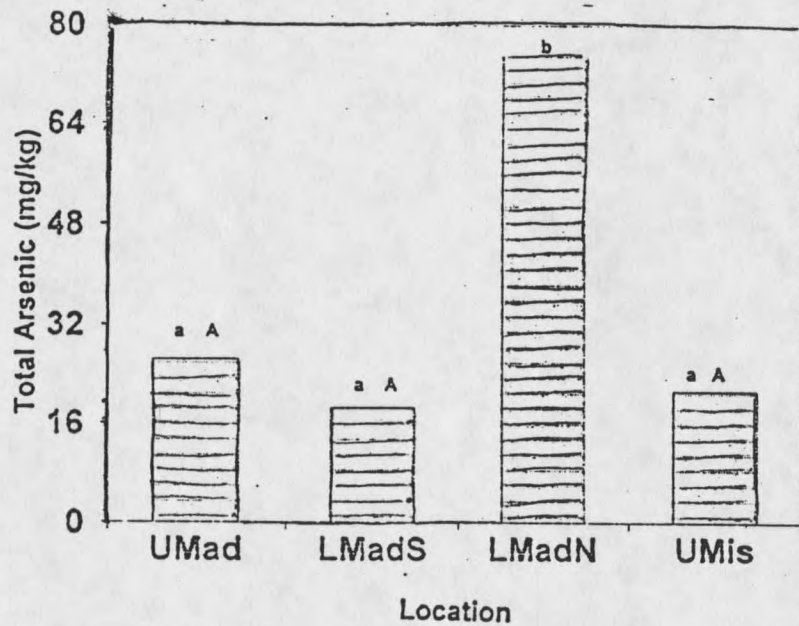


Figure 24. Mean DWA total As concentrations (mg/kg) in the 0-30 cm depth of the fine earth fraction of soils of the four study locations.

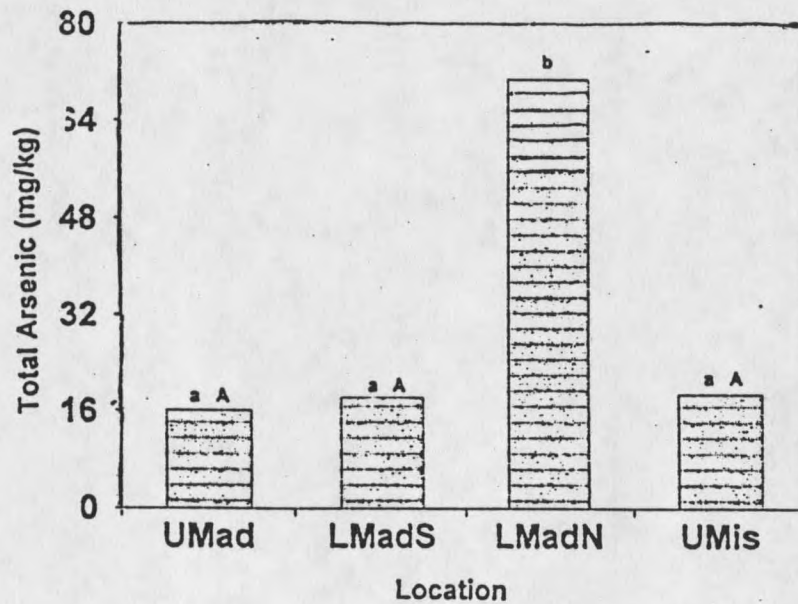


Figure 25. Mean DWA total As concentrations (mg/kg) in the 0-30 cm depth of the bulk soil profile of the four study locations.

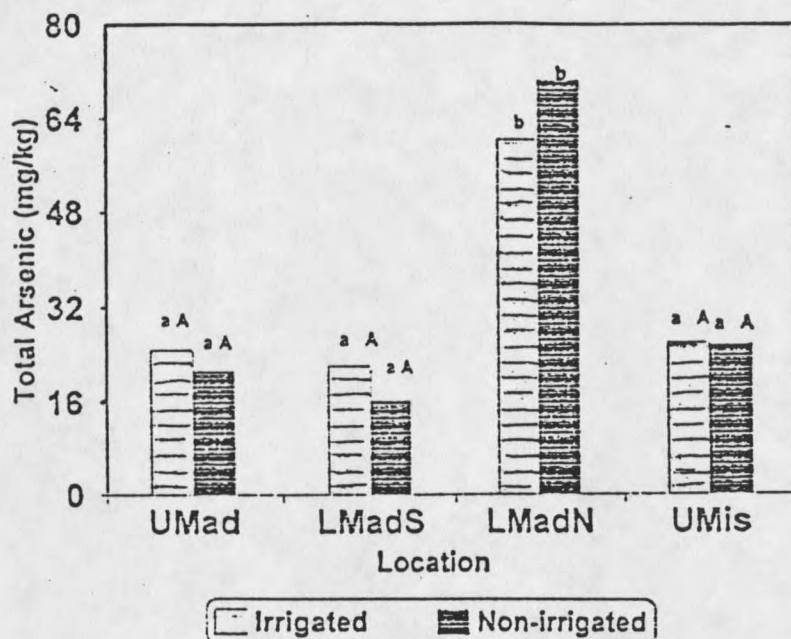


Figure 26. Mean DWA total As concentrations (mg/kg) in the fine earth fraction of soils of irrigated and non-irrigated soils of the four study locations.

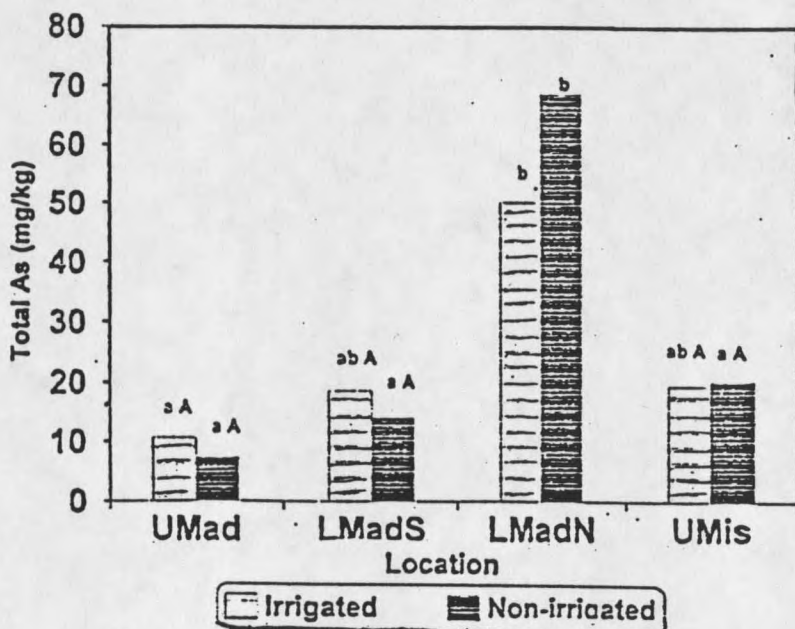


Figure 27. Mean DWA total As concentrations (mg/kg) in the bulk soil profile for the irrigated and non-irrigated soils of the four study locations.

Analysis of variance of mean DWA total As concentrations in the top 30 cm of irrigated and non-irrigated soil profiles indicated no significant difference between the total As in the irrigated sites of the Upper Madison, Lower Madison South, and Upper Missouri locations (Fig. 28 and 29). Mean DWA total As concentrations of the lower Madison North location are significantly greater than mean DWA total As concentrations of the other three locations.

Mean DWA total As concentrations in the non-irrigated sites of the Upper Madison, Lower Madison South, and Upper Missouri locations do not differ significantly. Mean DWA total As concentrations of the lower Madison North location are significantly greater than the mean DWA total As concentrations of the other three locations. The same pattern exists for mean DWA total As concentrations in the upper 30 cm of the soil profile. Furthermore, mean DWA total As concentrations in the non-irrigated site is greater than the irrigated site at the Lower Madison North location. Figures 30 and 31 illustrate the differences in mean DWA total As concentrations between irrigated versus non-irrigated soils of the four locations combined or the locations excluding the data from Lower Madison North location. Depth weighted average total As concentrations in the fine earth fraction of irrigated sites are significantly different from the DWA total As concentrations in the non-irrigated sites when excluding

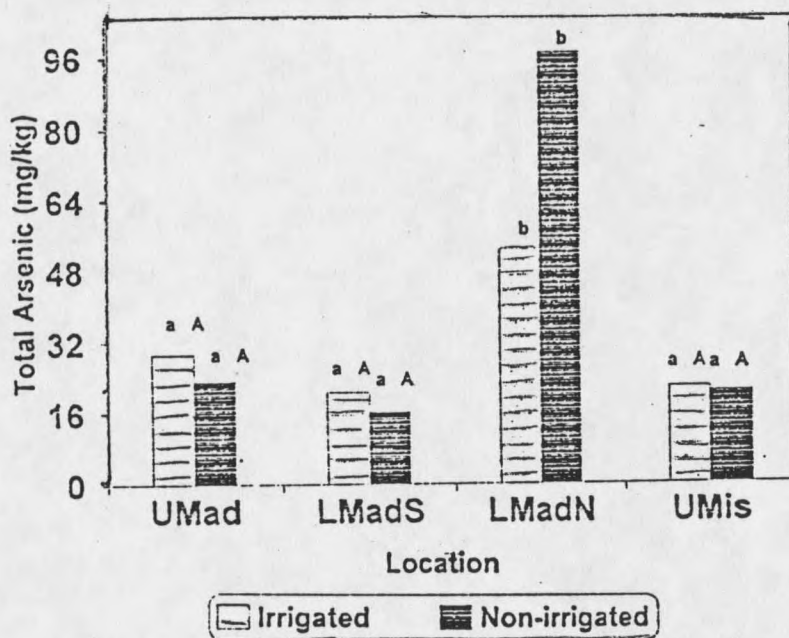


Figure 28. Mean DWA total As concentrations (mg/kg) in the 0-30 cm depth of fine earth fraction of irrigated and non-irrigated soils of the four study locations.

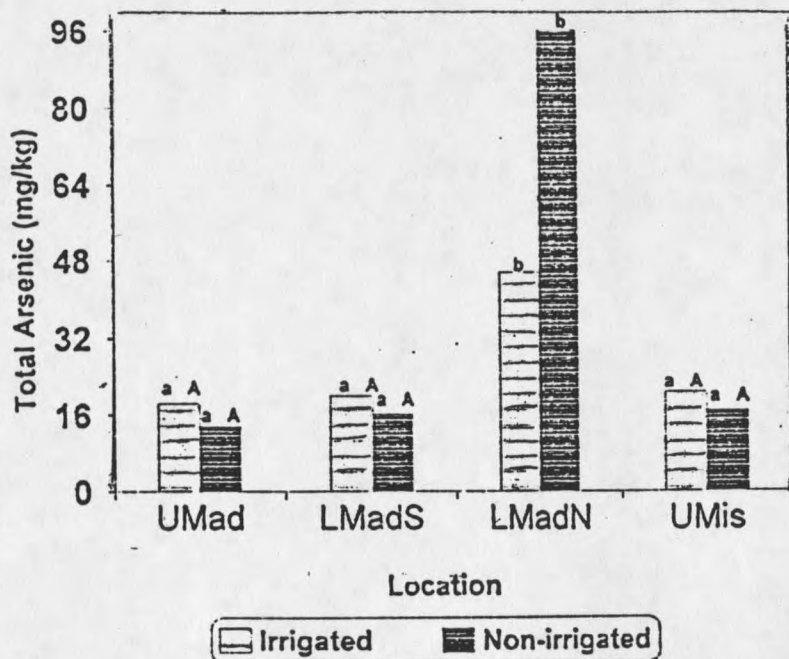


Figure 29. Mean DWA total As concentrations (mg/kg) in the 0-30 cm depth of bulk irrigated and non-irrigated soils of the four study locations.

