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

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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MONTANA STATE UNIVERSITY
Bozeman, Montana

August 1995

APPROVAL

of a thesis submitted by

Kristin Elisabeth Keith

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

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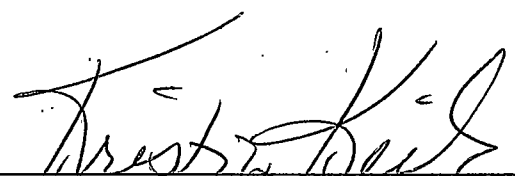
Signature 

Date 7/14/98

ACKNOWLEDGMENTS

I offer my sincere appreciation and gratitude to my major professor Dr. James Bauder for his encouragement, confidence, and positive attitude towards myself and my work. Without him I could not have endured.

My sincere appreciation to my committee members; Dr. Earl Skogley, Dr. Gerald Nielsen, and Dr. William Inskeep, for sharing their time and advice in review of this manuscript.

Special thanks to Bernard Schaff for his generous time and hard labor in the field, and to my colleague Clain Jones for his valuable insight and advice in my research.

I am grateful to the tremendous generosity and friendliness of the producers who offered their time and land for the purpose of this project.

Most of all, I am deeply grateful to my husband, Gene, for his encouragement and support while I was working towards this degree.

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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.

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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.

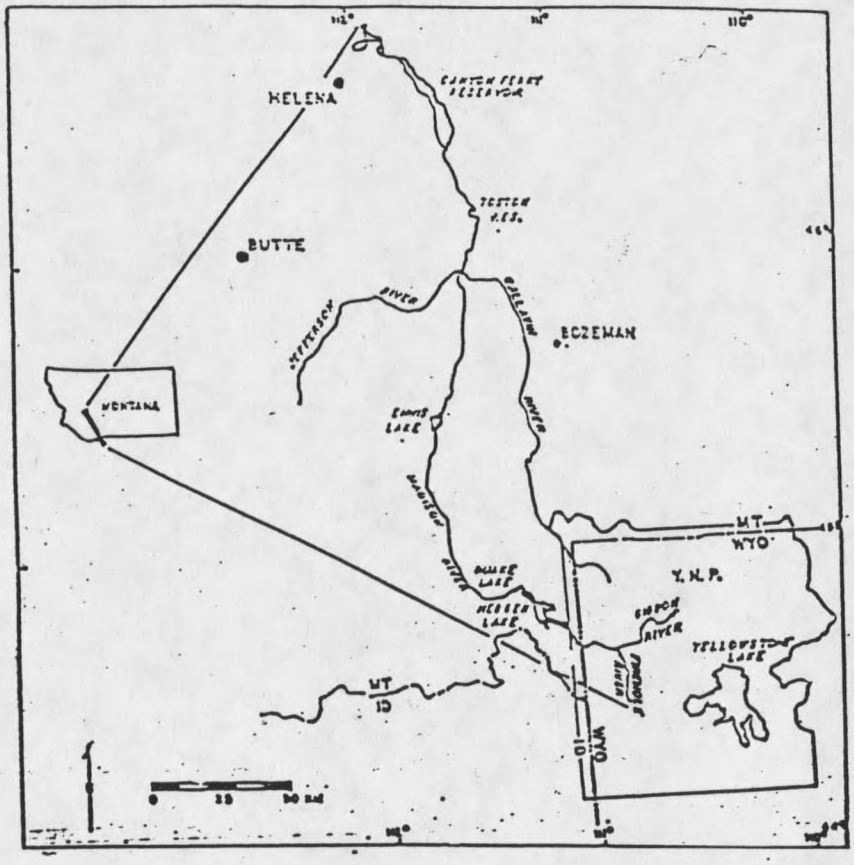

Figure 1. Map of the upper Madison River connected to Yellowstone National Park (Savka, 1993).

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.