



The uptake in inorganic arsenic by wheat and alfalfa
by Gwen Dee Gray

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in
Environmental Engineering
Montana State University
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Abstract:

The Madison and the Upper Missouri Rivers typically have 50 - 200 ppb arsenic concentration which exceeds the Federal EPA drinking standard of 50 micrograms per liter for arsenic. Water from these sources has been used for the irrigation of crops in Montana since the late 1800's. There is great concern that crops grown with this water may deliver arsenic to the human population. The goal of the project is to determine arsenic uptake in wheat and alfalfa and the soil in which they were grown as a function of arsenic concentration in irrigation water. In a greenhouse experiment, irrigation water of 4 different arsenic trioxide concentrations of 0, 10, 50, and 100 ppb, were applied to wheat and alfalfa plants for 11 weeks. The plants were then harvested and analyzed for arsenic concentration levels in roots, stems, leaves, and for wheat, seed heads. Soil samples at 0.5 and 10 cm depths were also analyzed for arsenic.

Wheat roots accumulated more arsenic than other plant sections for all application concentrations. No alfalfa plant part consistently accumulated more arsenic than other plant parts, however at the 1 ppm treatment, leaves had significantly higher concentrations. Wheat as a whole stored more arsenic than alfalfa. Regardless of plant species, more arsenic accumulated near the surface than at the 10 cm depth. When alfalfa was grown, soil arsenic concentrations increased more readily at the surface, for all treatments greater than zero, than when wheat was grown. No statistically significant differences were observed in measured plant heights for either species as a function of applied arsenic concentration. No conclusive cellular structure differences could be found between the treated and control, alfalfa and wheat groups except for a possible growth reduction in the wheat leaves. The wheat and alfalfa both appear to be accumulating arsenic but at very low concentrations. Approximately 90% of the arsenic in this experiment is flowing out with the drainage. Therefore at risk populations should be more concerned about the arsenic in drinking water than in food supplies.

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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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Date 4/21/94

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ABSTRACT

The Madison and the Upper Missouri Rivers typically have 50 - 200 ppb arsenic concentration which exceeds the Federal EPA drinking standard of 50 micrograms per liter for arsenic. Water from these sources has been used for the irrigation of crops in Montana since the late 1800's. There is great concern that crops grown with this water may deliver arsenic to the human population. The goal of the project is to determine arsenic uptake in wheat and alfalfa and the soil in which they were grown as a function of arsenic concentration in irrigation water. In a greenhouse experiment, irrigation water of 4 different arsenic trioxide concentrations of 0, 10, 50, and 100 ppb, were applied to wheat and alfalfa plants for 11 weeks. The plants were then harvested and analyzed for arsenic concentration levels in roots, stems, leaves, and for wheat, seed heads. Soil samples at 0.5 and 10 cm depths were also analyzed for arsenic.

Wheat roots accumulated more arsenic than other plant sections for all application concentrations. No alfalfa plant part consistently accumulated more arsenic than other plant parts, however at the 1 ppm treatment, leaves had significantly higher concentrations. Wheat as a whole stored more arsenic than alfalfa. Regardless of plant species, more arsenic accumulated near the surface than at the 10 cm depth. When alfalfa was grown, soil arsenic concentrations increased more readily at the surface, for all treatments greater than zero, than when wheat was grown. No statistically significant differences were observed in measured plant heights for either species as a function of applied arsenic concentration. No conclusive cellular structure differences could be found between the treated and control, alfalfa and wheat groups except for a possible growth reduction in the wheat leaves. The wheat and alfalfa both appear to be accumulating arsenic but at very low concentrations. Approximately 90% of the arsenic in this experiment is flowing out with the drainage. Therefore at risk populations should be more concerned about the arsenic in drinking water than in food supplies.

INTRODUCTION

The Madison and the Upper Missouri Rivers frequently exceed the federal Environmental Protection Agency (EPA) drinking water standard for total arsenic of 50 micrograms per liter. Natural geothermal springs are the major source of arsenic in the Madison River. Water from the Madison River has been used for irrigation since the late 1800's and this arsenic laden water is believed to be the source of extensive ground water contamination and chronic (long term) arsenic poisoning of resident animal and human populations. The Madison and Missouri Rivers are drinking water sources for many Montana cities including Helena and Great Falls. Chronic health problems in humans have been documented when arsenic levels in drinking water exceed 80 micrograms per liter (Water Management Bureau, 1992). EPA may soon lower the acceptable arsenic limit for drinking water to 15 micrograms per liter. In a personal communication, Dr. Abraham Horpestad of the Montana Water Quality Bureau estimated the increased risk of cancer due to arsenic for water consumers near the upper Missouri is 1 per 2000 people. Gallatin County health officers attribute chronic arsenic poisoning in the Gallatin valley to combined effects of arsenic in drinking water, garden produce, locally grown chicken and beef, and dermal contact.

The experiment described herein was designed to answer four questions:

1. In what plant tissues does arsenic accumulate when introduced through water in a typical Montana monocot, e.g. wheat, and dicot, e.g. alfalfa?
2. Where in the soil profile does arsenic accumulate?
3. Does arsenic accumulation affect plant growth characteristics?
4. Is there discernible damage in the plant cell tissues due to accumulation?

Inorganic Arsenic General Chemistry

Arsenic is a toxic metalloid found in almost all natural waters and rocks.

Determining the pathways of arsenic mobility through the environment is essential if we are to understand arsenic toxicity effects. The abbreviated periodic chart (Figure 1) shows that arsenic is the thirty-third element and is located in the same group column as phosphorus. Elements in the same group have the same number of electrons in their valence shell. The Group V elements, arsenic and phosphorus, therefore behave similarly in chemical reactions in biochemical pathways. Arsenic (As) is a conservative member, an element that cannot be removed by nuclear decay, of Group V, the metalloid group. Metalloids are elements that are technically non-metals but often behave like metals (Schulman, 1992). Inorganic arsenic is stable in four oxidation states: -3, 0, +3, and +5. Arsenic (0) is very rare and As (-3) only occurs at low redox values, which do not commonly occur in Montana river waters (Baudo, 1990). Arsenic (+3) is volatile, but oxidizing conditions can prevent loss. Organoarsenic compounds differ in their stability to oxidation. It should be recognized that arsenic exists in several oxidation states of limited interconvertability (Penrose, 1974). A list of arsenic species commonly found in environmental samples are listed in Table 1.

Figure 1. Abbreviated Periodic table displaying arsenic (Schulman, 1992).

IV		V		VI	
7	2, 4, 0, -4	8	1, 2, 3, 4, 5, 0, -1, -2, -3	9	-2
C	Carbon	12.011	N	Nitrogen	14.007
14	2, 4, 0, -4	15	3, 5, 0, -3	16	4, 6, 0, -2
Si	Silicon	28.086	P	Phosphorus	30.974
32	2, 4, 0	33	3, 5, 0, -3	34	4, 6, 0, -2
Ge	Germanium	72.59	As	Arsenic	74.922
50	2, 4, 0	51	3, 5, 0, -3	52	4, 6, 0, -2
Sn	Tin	118.69	Sb	Antimony	121.75
				Te	Tellurium
					127.60

Table 1. Common arsenic species found in environmental samples (Holm et. al., 1979).

Species	Name(s)	Oxidation State
AsO_4^{3-}	Arsenate	+5
AsO_3^{3-}	Arsenite	+3
$\text{CH}_3\text{AsO}(\text{OH})_2$	Methanearsonic Acid Monomethyl Arsonic Acid	+3
$(\text{CH}_3)_2\text{AsOOH}$	Hydroxydimethyl Arsine Oxide Dimethyl Arsinic Acid Cacodylic Acid	+1
AsH_3	Arsine	-3
$(\text{CH}_3)_2\text{AsH}$	Dimethyl Arsine	-3
$(\text{CH}_3)_3\text{As}$	Trimethyl Arsine	-3

Arsenic is difficult to categorize because its chemistry is so complex. It can exist in either a pentavalent (+5) or trivalent (+3) state and can combine with other elements to form many different compounds and ions, the most common being arsenic trioxide (+3).

Conversion from the trivalent state (arsenite) to the pentavalent state (arsenate) is reversible in solution without the use of catalysts, and both species can occur simultaneously. Free energies of formation for arsenic species at 25° C and 1 atmosphere are listed in Table 2.

An Eh-pH diagram for arsenic in a system including oxygen, water, and sulfur is shown in Figure 2, the Eh is a measure of the amount of electrons measure in voltage units. At the high Eh values encountered in oxygenated waters, arsenic acid species (H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-} , and AsO_4^{3-}) are stable. At Eh values characteristic of mildly

reducing conditions, arsenous acid species (H_3AsO_3 , H_2AsO_3^- , and HAsO_3^{2-}) become stable. Except at extremely low Eh values, organic arsenics are unstable with respect to oxidation of the organic part of the molecule. Very little information about the rates of arsenic reactions in solution exists, and specific rate constants are unknown (Ferguson and Gavis, 1972). Arsenite is approximately ten times more toxic than arsenate and about thirty-five times more toxic than organic arsenic forms (Schulman, 1992). Table 3 gives the solubility product for some soluble arsenates that may limit the arsenic concentration in the aqueous phase. Due to arsenic's complexity, the inorganic form is assumed in this paper unless noted otherwise.

Inorganic Arsenic in Water

In well oxygenated water at a pH of 7-9, HAsO_4^{2-} is the dominant form of dissolved arsenic (Schulman, 1992). The solubility of arsenic in freshwater depends on oxygen concentration, ferric and sulfur hydroxides, pH, and suspended particle content. Increasing concentrations of these substances cause arsenic to precipitate into the sediment of natural water bodies (Baudo et al., 1990; Brannon et al., 1987). In seawater, under normal pH and dissolved oxygen conditions, arsenic should exist at equilibrium as arsenate, but marine bacteria can reduce added arsenate to arsenite, therefore creating a dynamic equilibrium between chemical oxidation and biological reduction. In aerated streams, arsenate is the dominant species; in anaerobic reservoirs, it is arsenite (Penrose, 1974).

Table 2. Free energies of formation for arsenic species at 25° C and 1 atmosphere
(Ferguson and Gavis, 1972).

Species	State	dG _t
H ₃ AsO ₄	aq.	-184.0
H ₂ AsO ₄ ⁻	aq.	-181.0
HAsO ₄ ²⁻	aq.	-171.5
AsO ₄ ³⁻	aq.	-155.8
H ₃ AsO ₃	aq.	-154.4
H ₂ AsO ₃ ⁻	aq.	-141.8
HAsO ₃ ²⁻	aq.	-125.3
HAsS ₂	aq.	-11.61
AsS ₂ ⁻	aq.	-6.56
AsS	s.	-16.81
As ₂ S ₃	s.	-40.25
As	s.	0.0
AsH ₃	aq.	23.8
AsH ₃	g.	16.5
As ₂ O ₃	s.	-140.8
As ₂ O ₅	s.	-186.9

Legend

aq = aqueous

g = gas

s = solid

Figure 2. The Eh-pH diagram for As at 25 °C and 1 atm with total arsenic 10^{-5} M and total sulfur 10^{-3} M. Solid species are enclosed in parentheses in cross-hatched area, which indicates solubility less than $10^{-5.3}$ M (Ferguson and Gavis, 1972).

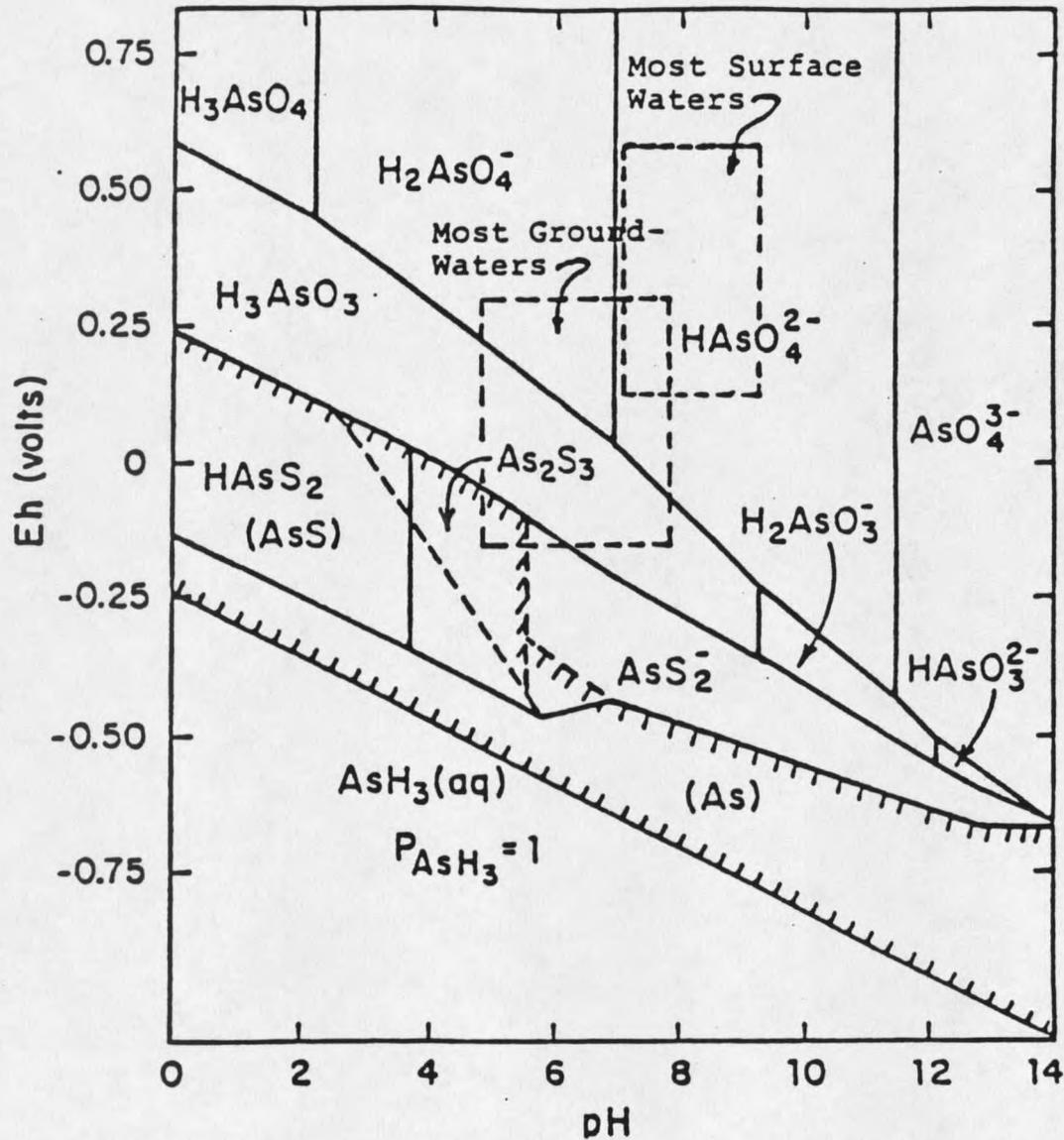


Table 3. Stability constants for the arsenic acid system and some soluble arsenates at 25° C (Allard and Grimvall, 1988).

Reaction		log K
$H^+ + H_{n-1}AsO_4^{n-4} = H_nAsO_4^{n-3}$	n=1	11.5
	n=2	6.9
	n=3	2.2
$AlAsO_4 (s) = Al^{3+} + AsO_4^{3-}$		-15.8
$FeAsO_4 (s) = Fe^{3+} + AsO_4^{3-}$		-20.2
$Ca_3(AsO_4)_2 (s) = 3Ca^{2+} + 2AsO_4^{3-}$		-18.2

The local cycle of arsenic in a stratified lake is shown in Figure 3. In natural waters, arsenic can be absorbed by microorganisms, which in some cases can detoxify arsenic by methylating it (the compound becomes lipid soluble). In this form, arsenic is 35 times less toxic than in the inorganic form. The methylated compounds produced in these phytoplankton are readily ingested by fish or shellfish and accumulated in their tissues. Concentrations of 2 milligrams per kilogram (mg/kg) to 50 mg/kg of arsenic have been measured in shellfish (Baudo et al., 1990). Stonefly and caddisfly larvae also accumulate arsenic and are currently being used as arsenic indicators in freshwater streams (Bedwell, 1992). Even though arsenic is rapidly excreted by the ingesting organism, the rate of uptake can be greater than the rate of elimination. Biomagnification through other parts of the food web has yet to be scientifically proven (Ferguson and Gavis, 1972).

