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**ARSENIC IRRIGATED VEGETABLES: RISK ASSESSMENT
FOR SOUTH ASIAN HORTICULTURE**

A Thesis presented in fulfilment of the requirements for the degree of

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ABSTRACT

Arsenic (As) contaminated water is often used in South Asia to irrigate vegetables. These vegetables accumulate As in their edible tissues and once ingested, increase As burden in humans. Despite the apparent risk, the As uptake potential of vegetable species when irrigated with As-contaminated water is not well defined. Most research on As-irrigated vegetables are monitoring surveys that only describe the As concentration levels in various vegetable species from affected areas. Because of the great variability in As concentration of irrigation water, soil type, vegetable species and cultivars, agronomic practices and climatic factors, As uptake potential of an individual vegetable species cannot be described from the monitoring data. Identifying vegetable species and soil conditions that result in high As concentrations in the edible tissues of vegetables is prerequisite for risk assessment and proposing As mitigation strategies.

The objectives of this study were to (i) determine the As uptake response of common vegetable species when irrigated with As-contaminated water, (ii) calculate the risk to humans upon ingestion of As-contaminated vegetable species, (iii) elucidate factors that may increase As concentrations in vegetable species, and (iv) propose management strategies for South Asian countries where As-contaminated water is used for vegetable cultivation.

In the first glasshouse experiment (Chapter 4), four common vegetables, carrot (*Daucus carota*), radish (*Raphanus sativus*), spinach (*Spinacia oleracea*), and tomato (*Solanum esculentum*) were irrigated with a range of As^V enriched water (50 to 1000 $\mu\text{g L}^{-1}$) using two irrigation techniques. These irrigation techniques were (i) non-flooded, where soil moisture was maintained to 70% field capacity (Fc) of soil, and (ii) flooded, where the water was maintained at 110% Fc initially followed by drainage and onset of aerobic conditions until the next irrigation event. Only the 1000 $\mu\text{g As L}^{-1}$ treatment showed a significant increase of As concentration in the vegetables compared to all other treatments. There was a higher concentration of As in the vegetables grown under flood irrigation relative to non-flood irrigation. The trend of As uptake among vegetable species was spinach > tomato > radish > carrot. Only in spinach leaves, the As concentration was above the Chinese food safety standard for inorganic As (0.05 $\mu\text{g g}^{-1}$ fresh weight) by a factor of 1.6 to 6.4 times, when irrigated with 100, 200, and 1000 $\mu\text{g As L}^{-1}$ under flood irrigation and with 1000 $\mu\text{g As L}^{-1}$

under non-flood irrigation. The USEPA carcinogenic and non-carcinogenic risk parameters for the scenario where vegetables are consumed 500 grams per day were calculated. The USEPA Hazard Quotient (HQ) value for spinach leaves ranged from 0.32 to 1.26 for adults and 0.38 to 1.51 for adolescents while the Cancer Risk (CR) value ranged from 1.4×10^{-4} to 5.7×10^{-4} for adults and 1.7×10^{-4} to 6.8×10^{-4} for adolescents for treatment water concentrations $100 \mu\text{g As L}^{-1}$ or greater. An HQ value greater than 1 represents an unacceptable non-carcinogenic risk and a CR value greater than 10^{-4} represents an unacceptable carcinogenic risk.

A laboratory batch experiment (Chapter 5) was conducted using four soils to determine their As adsorption behavior and the soil properties that control As retention in these soils. Soils used in this study were (i) Rangitikei silt loam (the soil which was used in glasshouse experiment 1), (ii) Rangitikei silt loam soil amended with calcium hydroxide to raise the pH to 7.5, to model the soil pH level of South Asian countries, and (iii) two New Zealand soils, Korokoro silt loam and Tokomaru silt loam. Both arsenate (As^{V}) and arsenite (As^{III}) were investigated in the experiment because these As species are mainly present in irrigation water. The results showed that the As^{V} was adsorbed to a greater degree than As^{III} as defined by high adsorption maxima, bonding energy and As partition coefficient values of Langmuir and Freundlich isotherms. Adsorption of both As^{V} and As^{III} was mainly controlled by amorphous Al, total C and Olsen P content of selected soils.

A glasshouse experiment (Chapter 6) was conducted to explore those factors which can promote As concentration in plants. The following factors which are likely to affect horticulture in South Asia were included: two As species (As^{V} and As^{III}), four As concentration levels of irrigation water (50 to $1000 \mu\text{g L}^{-1}$), two soil pH levels (6.1 and 7.5), and two soil amendments (biochar and cattle manure). The control treatment for this experiment was no As in irrigation water and no soil amendment. Spinach was selected for this work due to its high uptake potential described in the earlier glasshouse experiment (Chapter 4). The findings of this experiment showed that the As concentration in spinach leaves was dependent on As concentrations in water and soil amendments and was independent of soil pH and As species under flood irrigation. Spinach plants grown in biochar and cattle manure amended soils had significantly higher As concentration in their leaves when compared with spinach plants grown with no amendment. In both biochar and

cattle manure amended soils, the As concentration in spinach leaves exceeded the Chinese food safety standard ($0.05 \mu\text{g g}^{-1}$ fresh weight) by a factor of 1.6 to 8.3 times, where the concentration of As in irrigation water was $200 \mu\text{g L}^{-1}$ or greater. The CR values for spinach grown in cattle manure amended soil was greater than the critical value of 1×10^{-4} for the scenarios where vegetable consumption is 205 grams and/or 500 grams per day. This increase was found where the As concentration in irrigation water was $200 \mu\text{g L}^{-1}$ or greater. The HQ value was above the critical value of 1 for the scenario where the vegetable consumption is 500 grams per day. This increase was observed for spinach grown in cattle manure amended soil with an As concentration in irrigation water $500 \mu\text{g L}^{-1}$ or greater. Arsenic daily intake (mg kg^{-1} body weight) associated with the ingestion of spinach leaves corresponds to proposed ATSDR (Agency for Toxic Substances and Disease Registry) and drinking water daily intake values that may lead to development of cancer (bladder, lung and skin), skin lesions, and intellectual impairment in children. The As intake through ingestion of spinach correlates to an As concentration in drinking water that is $10 \mu\text{g L}^{-1}$ or greater.

Overall, the results of glasshouse studies indicate that the As concentrations greater than $50 \mu\text{g L}^{-1}$ should be avoided for spinach cultivation where flood irrigation is practiced. Addition of cattle manure can further intensify the risk by increasing the As concentration in plant tissues, therefore its usage in South Asian horticulture is questionable. I propose that the As concentration in vegetables should not be overlooked as they can alone be a major source of As poisoning in humans.

DEDICATION

This work is dedicated to my parents for their hard work

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Table of Contents

Abstract	i
Acknowledgements.....	v
Table of Contents.....	vi
List of Tables	xi
List of Figures and Equations	xiii
Chapter 1 Introduction	1
1.1 Background	1
1.2 Theme of the current research	2
1.3 Research hypothesis	3
1.4 Brief description of the objectives of this research	3
1.5 Thesis structure	3
1.6 References	5
Chapter 2 Literature review	8
2.1 Introduction	8
2.2 Sources of arsenic	8
2.3 Arsenic in soil	10
2.3.1 Arsenic concentration in soil	10
2.3.2 Arsenic speciation in soil	10
2.3.3 Biogeochemistry of arsenic in soil	12
2.3.3.1 Adsorption reaction	12
2.3.3.2 Factors affecting adsorption reaction	12
2.3.3.3 Redox reactions	17

2.4	Arsenic concentration in water	17
2.5	Arsenic in plants	19
2.5.1	Arsenic toxicity to terrestrial plants	19
2.5.2	Factors affecting As toxicity to plants	21
2.5.3	Arsenic accumulation in vegetables	25
2.5.4	Risk assessment of arsenic	34
2.5.5	Arsenic distribution in vegetable tissues	35
2.5.6	Factors affecting As accumulation and distribution in vegetables/crops	36
2.6	Toxicity of arsenic to humans	41
2.7	Objectives of this research	43
2.8	Stakeholders in this research	44
2.9	References	46
Chapter 3	Materials and methods	57
3.1	Introduction	57
3.2	Methodology to analyse total arsenic in plants	57
3.2.1	Determination of total arsenic in plants using GFAAS	59
3.2.2	Determination of total arsenic in plants using HGAAS	64
3.3	Methodology for analysing total arsenic in soil using HGAAS	66
3.4	Quality control	67
3.5	Choice of soil for experiments and its relevance to South Asian soils	67
3.6	Methods adopted to determine physical and chemical properties of soil	70
3.7	References	72

Chapter 4	Risk assessment of vegetables irrigated with arsenic contaminated water	75
4.1	Introduction	75
4.2	Materials and methods.....	76
4.2.1	Crops	76
4.2.2	Pot preparation and soil	77
4.2.3	Irrigation	78
4.2.4	Plant harvest and analysis	78
4.2.5	Soil analysis	79
4.2.6	Statistical analysis	79
4.2.7	Human health risk assessment	80
4.3	Results and discussion	81
4.3.1	Arsenic concentration in vegetables	81
4.3.2	Arsenic content in vegetables and possible factors affecting accumulation in plants	87
4.3.3	Risk assessment	89
4.3.4	Arsenic concentration in soil after vegetable harvest	91
4.4	Conclusions	94
4.5	References	96
Chapter 5	Arsenic adsorption in soils.....	99
5.1	Introduction	99
5.2	Materials and methods	101
5.2.1	Soils	101
5.2.2	Soil analysis	101

5.2.3	Arsenic adsorption kinetics	102
5.2.4	Arsenic adsorption isotherms	103
5.2.5	Arsenic adsorption modelling	103
5.2.6	Statistical analysis	104
5.3	Results and discussion	104
5.3.1	Soil characteristics	104
5.3.2	Arsenate and arsenite adsorption kinetics	104
5.3.3	Arsenate and arsenite adsorption: Langmuir and Freundlich isotherms	107
5.3.4	Soil properties affecting arsenic adsorption parameters	112
5.4	Conclusions	115
5.5	References	117
Chapter 6	Response of spinach to arsenic contaminated water in soils amended with biochar and cattle manure.....	120
6.1	Introduction	120
6.2	Materials and methods	122
6.2.1	Pot preparation and soil amendments	122
6.2.2	Irrigation	123
6.2.3	Plant harvest and analysis	124
6.2.4	Soil analysis	124
6.2.5	Biochar and cattle manure analysis	124
6.2.6	Statistical analysis	126
6.2.7	Human health risk assessment	126
6.3	Results	128

6.3.1 Overall picture	128
6.3.1.1 Arsenic concentration in spinach tissues (leaves and roots)	129
6.3.1.2 Arsenic concentration in soil after spinach harvest	129
6.3.2 Detailed assessment of treatments effect on the As concentration in spinach tissues and soil after spinach harvest	133
6.3.2.1 Effect of the As concentrations in irrigation water and soil amendments for a particular species-pH combination	133
6.3.2.2 Effect of As species and soil pH for a specific soil amendment	138
6.4 Discussion	142
6.5 Risk assessment	147
6.6 Conclusions	156
6.7 References	158
Chapter 7 Key findings from this research: scale of risk and recommendations for food safety	163
7.1 Introduction	163
7.2 Objectives of the study	163
7.3 Role of stakeholders	169
7.4 Recommendations for future work	171
7.5 References	173
Appendixes	174

List of Tables

Table 2.1	Arsenic concentration in agricultural soils as a function of As in irrigation water	11
Table 2.2	Arsenic concentration in drinking water in selected studies around the world	18
Table 2.3	Arsenic concentration in irrigation water used for cultivation of food crops around the world	20
Table 2.4	Total As concentrations ($\mu\text{g g}^{-1}$) in edible parts of various vegetable species under different growth conditions	26
Table 2.5	Effects of arsenic exposure to humans	42
Table 3.1	Acid digestion techniques to determine total As in vegetables tissues	58
Table 3.2	Reported As concentration (ng g^{-1} dry weight) in plants selected for methodology development	60
Table 3.3	Arsenic concentration (ng g^{-1}) in selected plants on GFAAS as a function of pyrolysis temperatures with $\text{Mg}(\text{NO}_3)_2$ modifier	61
Table 3.4	Arsenic concentration (ng g^{-1}) in selected plants on GFAAS as a function of modifiers at $800\text{ }^\circ\text{C}$ pyrolysis temperature	62
Table 3.5	Arsenic concentration (ng g^{-1}) in vegetable species as a function of plant mass (g) under pyrolysis temperature $800\text{ }^\circ\text{C}$ and Ni modifier (2000 mg L^{-1}) on GFAAS	63
Table 3.6	Arsenic concentration (ng g^{-1}) in vegetable species with plant mass (1.0 g) under pyrolysis temperature $800\text{ }^\circ\text{C}$ and Ni modifier (2000 mg L^{-1}) on GFAAS	63
Table 3.7	Arsenic concentration (ng g^{-1}) in various plant species and As standard solutions on HGAAS	65
Table 3.8	Characteristics of soils of Karachi	69
Table 3.9	Comparison of experimental soil with selected South Asian soils where As contamination is reported	70
Table 3.10	Methods adopted to determine soil properties	71
Table 4.1	Physical and chemical properties of the Rangitikei silt loam soil used for the experiment	80
Table 4.2	Total arsenic concentration ($\mu\text{g g}^{-1}$ fresh weight) in the edible parts of four common vegetables	90
Table 4.3	Daily average vegetable intakes (gram fresh weight) per capita around the world	92

Table 4.4	Hazard Quotient (HQ) and Cancer Risk (CR) for the ingestion of spinach leaves as a function of the concentration of As in irrigation water and the irrigation technique used	92
Table 4.5	Total arsenic concentration ($\mu\text{g g}^{-1}$) in soil after vegetable harvest under variable As treatments and irrigation techniques	93
Table 5.1	Characteristics of the experimental soils	105
Table 5.2	Langmuir and Freundlich isotherm parameters for As adsorption onto experimental soils	110
Table 5.3	Selected studies detailing Langmuir and Freundlich isotherm parameters for As adsorption, and soil properties influencing these parameters	113
Table 5.4	Regression equation and Pearson's correlation coefficient (r) between soil properties and Langmuir-Freundlich equation parameters	114
Table 6.1	Properties of biochar and cattle manure used in the experiment	125
Table 6.2	Total As concentration ($\mu\text{g g}^{-1}$ dry weight) in spinach leaves as influenced by the As concentrations and species in irrigation water, soil pH and amendments	130
Table 6.3	Total As concentration ($\mu\text{g g}^{-1}$ dry weight) in spinach roots as influenced by the As concentrations and species in irrigation water, soil pH and amendments	131
Table 6.4	Total As concentration ($\mu\text{g g}^{-1}$) in soil after harvest of spinach as influenced by the As concentrations and species in irrigation water, soil pH and amendments	132
Table 6.5	Total As concentration in spinach leaves ($\mu\text{g g}^{-1}$) as a function of the As concentration in irrigation water and soil amendments	149
Table 6.6	Hazard quotient (HQ) and cancer risk (CR) for the ingestion of spinach leaves grown in cattle manure amended soil	151
Table 6.7	Arsenic daily intake (mg kg^{-1} body weight) for the ingestion of spinach leaves grown in cattle manure amended soil	152
Table 6.8	Summary of the health effects of arsenic	153
Table 6.9	Effects and symptoms linked to various concentrations of As in drinking water	154
Table 7.1	Hazard quotient (HQ) and cancer risk (CR) for the ingestion of vegetable species eaten every day of the year	164

List of Figures and Equations

Figure 2.1	Major sources of arsenic in soil and aquatic ecosystems	9
Figure 2.2	Generalized charge distributions on soil colloids	13
Equation 2.1	pH dependency of As ^V and As ^{III} compounds in aqueous solutions ...	14
Figure 4.1	Image of the pot designed to model flood irrigation	77
Figure 4.2	Total arsenic concentration ($\mu\text{g g}^{-1}$ dry weight) in various parts of radish (top) and tomato (bottom) grown under non-flooded irrigation	82
Figure 4.3	Total arsenic concentration ($\mu\text{g g}^{-1}$ dry weight) in various parts of spinach grown under variable As treatments and irrigation techniques	84
Figure 4.4	Total arsenic concentration ($\mu\text{g g}^{-1}$ dry weight) in various parts of carrot grown under variable As treatments and irrigation techniques	86
Figure 4.5	Arsenic content (μg) in four vegetables as a function of As treatments and irrigation techniques	88
Figure 5.1	Adsorption kinetic of As ^V (top) and As ^{III} (bottom) for studied soils ..	106
Figure 5.2	Langmuir isotherm plots for the adsorption of As species onto experimental soils	108
Figure 5.3	Freundlich isotherm plots for the adsorption of As species onto experimental soils	109
Figure 6.1	Arsenic concentration in spinach leaves ($\mu\text{g g}^{-1}$ dry weight) as influenced by the As concentrations in water and soil amendments for a defined species-pH combination	135
Figure 6.2	Arsenic concentration in spinach roots ($\mu\text{g g}^{-1}$ dry weight) as influenced by the As concentrations in water and soil amendments for a defined species-pH combination	136
Figure 6.3	Arsenic concentration in soil ($\mu\text{g g}^{-1}$) after spinach harvest as influenced by the As concentrations in water and soil amendments for a defined species-pH combination.....	137
Figure 6.4	Arsenic concentration in spinach leaves ($\mu\text{g g}^{-1}$ dry weight) as influenced by the As species in water and soil pH for a defined soil amendment	139
Figure 6.5	Arsenic concentration in spinach roots ($\mu\text{g g}^{-1}$ dry weight) as influenced by the As species in water and soil pH for a defined soil amendment	140

Figure 6.6	Arsenic concentration in soil ($\mu\text{g g}^{-1}$) after spinach harvest as influenced by the As species in water and soil pH for a defined soil amendment	141
Figure 6.7	Possible mechanism of As concentration in spinach tissues (leaves and roots) when irrigated with As treatment waters and amended with biochar and cattle manure	148