Analysis of 20 Elements and Speciation of Arsenic in Vegetables Using Chromatography and Mass Spectrometry

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Introduction

- Arsenic is a naturally occurring element found widely in the environment.
- Main exposure sources for the public:
  - Ingestion of contaminated food and water.
- This project focuses on determining arsenic in locally grown vegetables and mushrooms.

Sources of Arsenic in Agriculture:

- Agricultural and industrial activities (e.g., mining, smelting) introduce arsenic into water.
- Vegetables absorb arsenic from water, converting it into various chemical species

Arsenic Toxicity:

- Toxicity varies by arsenic species:
- Arsenobetaine *(AsB)* – harmless to humans.
- Inorganic arsenite *(iAsIII)* and inorganic arsenate *(iAsV)* – highly toxic, linked to cancer and disease.
- Monomethylarsonic acid *(MMA)* and dimethylarsinic acid *(DMA)* – less toxic but can be converted from inorganic arsenic.

Importance of Speciation:

- High arsenic content ≠ high toxicity.
- Speciation analysis is essential to determine if toxic arsenic species are present in vegetables.

Objective: Identify and quantify arsenic species in the vegetable samples that contained large amounts of arsenic.

Instrumentation

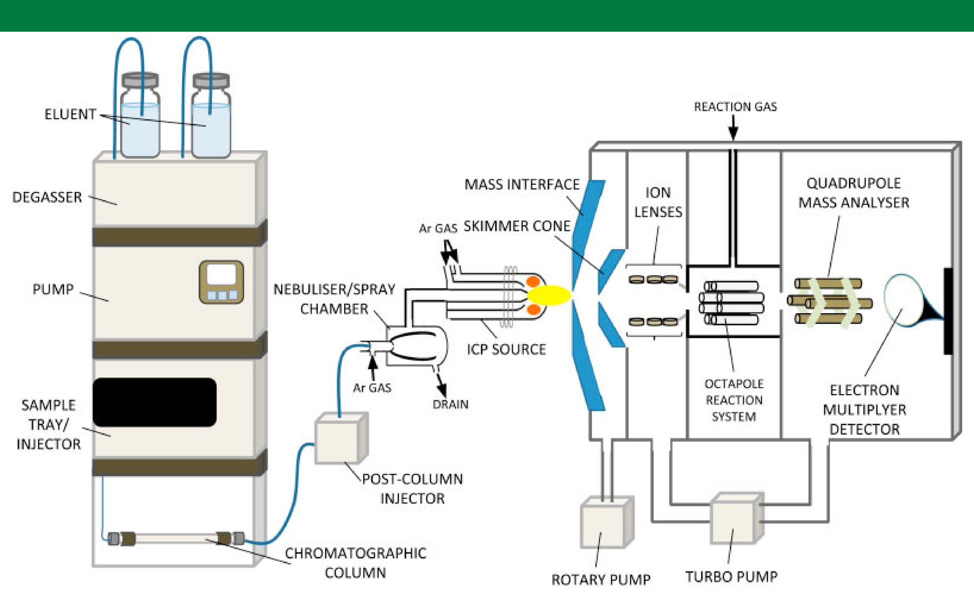
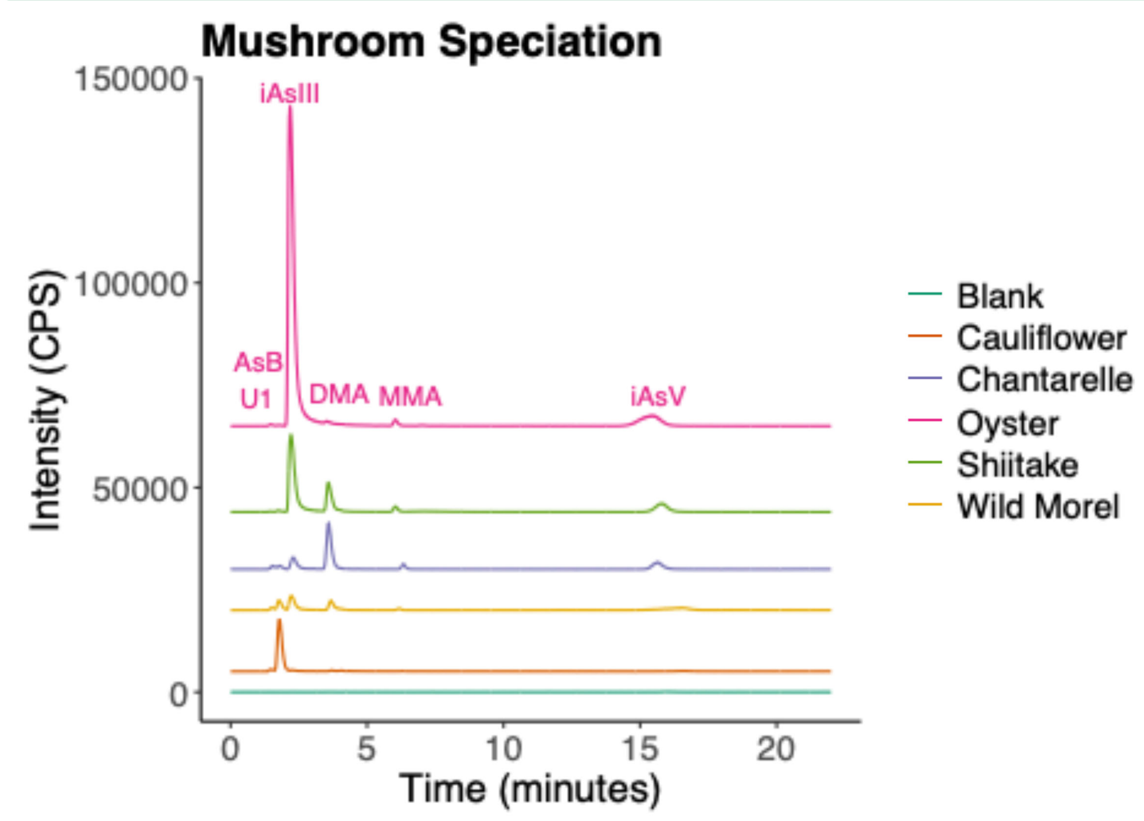


Figure 1. Schematic of high-performance liquid chromatography—inductively-coupled plasma mass spectrometry (HPLC-ICPMS) instrumentation.[3]

Speciation Results



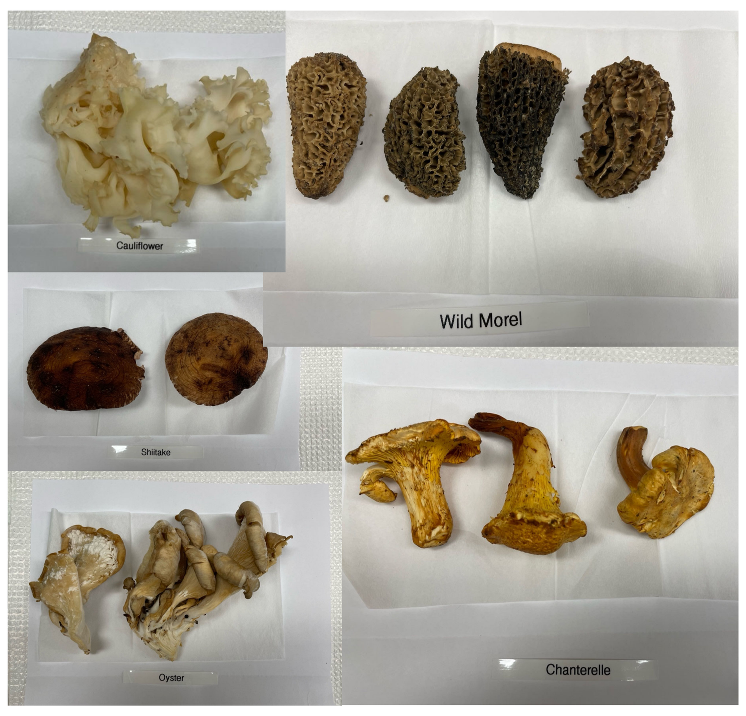


Figure 2. Representative chromatogram obtained from HPLC-ICPMS analysis of five mushroom species.

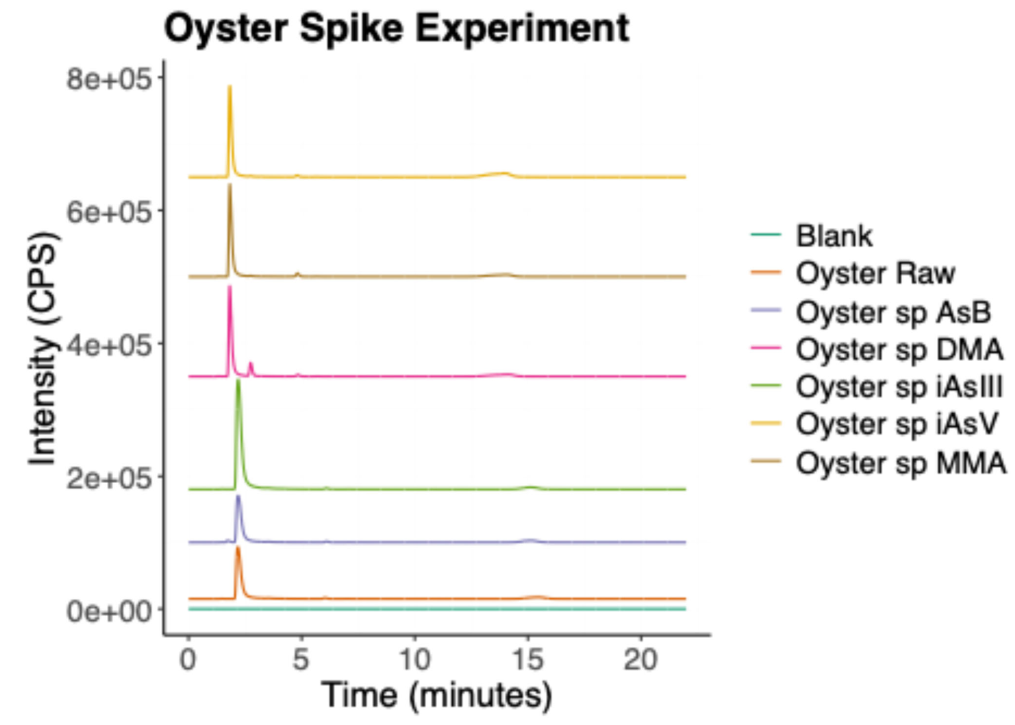


Figure 3. Representative chromatogram obtained from HPLC-ICPMS analysis of Oyster mushrooms spiked with AsB, DMA, iAsIII, iAsV, MMA

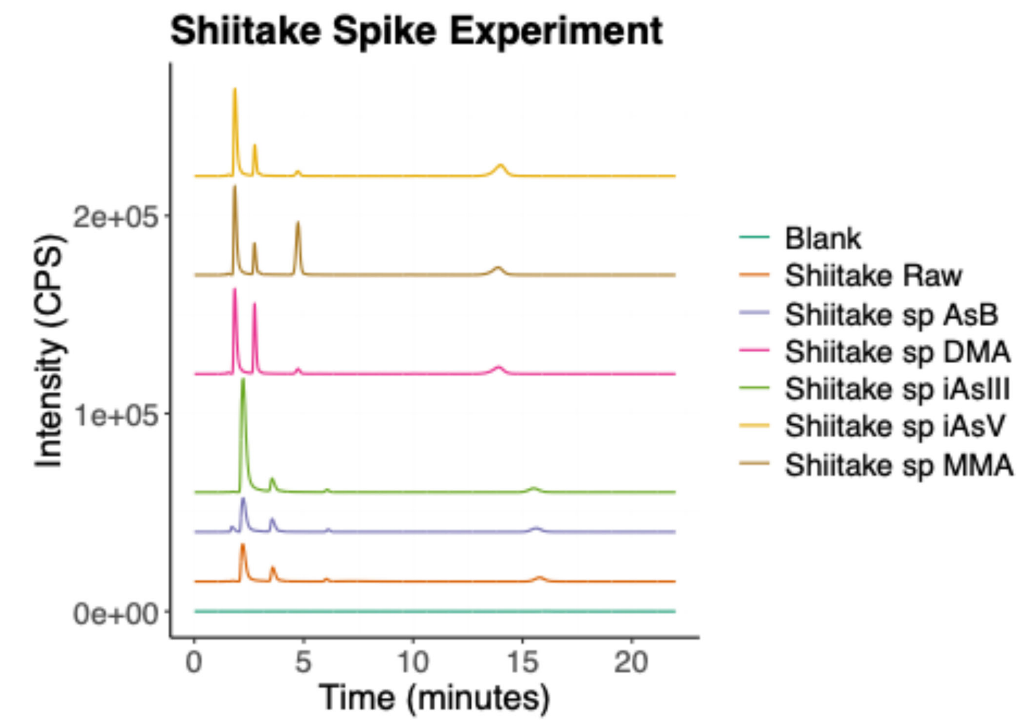


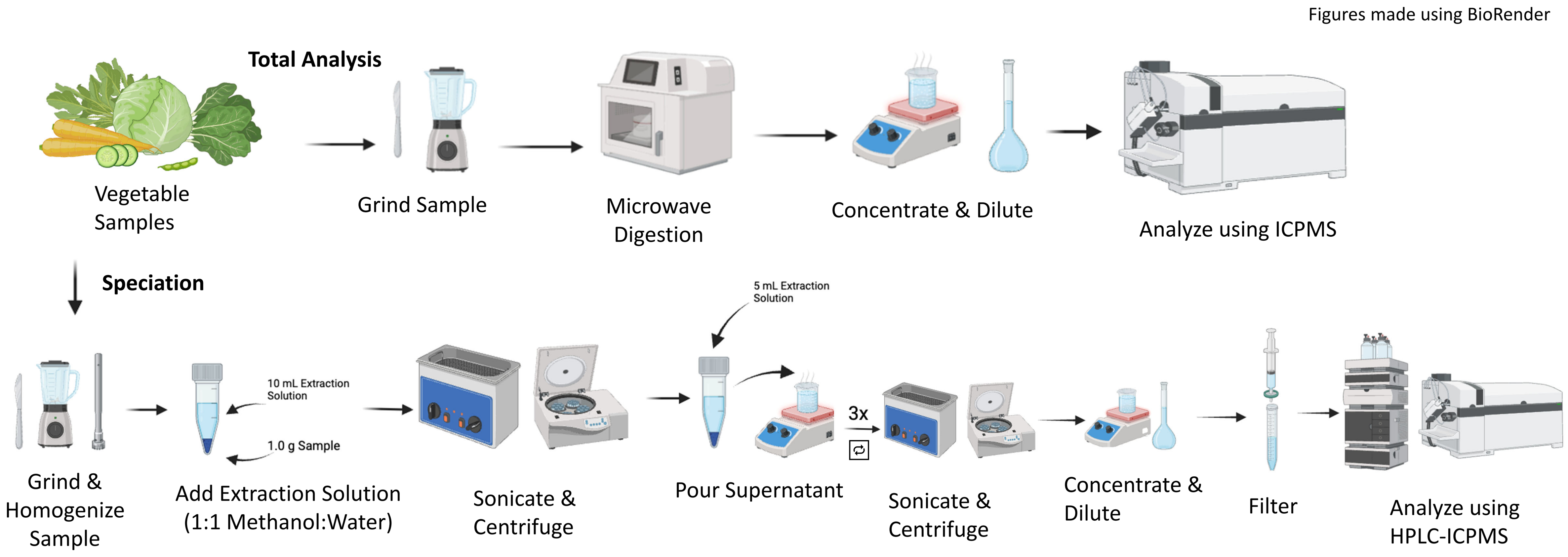
Figure 4. Representative chromatogram obtained from HPLC-ICPMS analysis of Shiitake mushrooms spiked with AsB, DMA, iAsIII, iAsV, MMA

Table 2. Concentrations of AsB, iAsIII, DMA, MMA, iAsV (µg/kg) in Wild Morel, Shiitake, Cauliflower, Oyster, and Chanterelle Mushrooms.

Mushroom Type	AsB	iAsIII	DMA	MMA	iAsV
Wild Morel	1.29 ± 0.08	5.22 ± 0.03	1.53 ± 0.07	0.328 ± 0.003	3.03 ± 0.08
Shiitake	0.287 ± 0.007	48.8 ± 0.2	8.42 ± 0.05	2.55 ± 0.05	11.47 ± 0.02
Cauliflower	7.29 ± 0.09	0.30 ± 0.02	<LOD	<LOD	0.29 ± 0.01
Oyster	<LOD	132 ± 2	0.28 ± 0.04	1.78 ± 0.03	17.7 ± 0.3
Chantarelle	0.40 ± 0.02	3.47 ± 0.02	6.9 ± 0.2	0.985 ± 0.005	4.2 ± 0.3

Methodology

Figures made using BioRender



Total Analysis Results

Table 1. Concentrations of elements (µg/kg) in 18 vegetable samples analyzed.

Metal	Lion Mane	Wild Morel	Portabella	Chanterelle	Crimini Brown	White	Oyster	Cauliflower	King Oyster	Shiitake	Lettuce Leaf-1	Lettuce Stem-1	Lettuce Leaf-2	Spinach	Lettuce Leaf-3	Cucumber	Carrot	Lettuce Stem 2
Be	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
V	1.6 ± 0.14	46 ± 13	1.1 ± 0.14	45 ± 5.8	16 ± 1.5	1.6 ± 0.18	2.6 ± 0.1	1.7 ± 0.17	2.1 ± 1.6	3.8 ± 0.19	1.6 ± 0.18	2.4 ± 0.24	8.2 ± 0.21	40 ± 3.5	20 ± 0.93	0.40 ± 0.24	22 ± 1.2	5.4 ± 0.69
Cr	3.4±0.45	20±5.7	4.4±2.4	110±13	9.2±2	6.5±5.3	3.5±0.45	4.1±0.41	<LOD	4.8±0.84	10±1.3	4.6±2.7	10±2.7	27±3.8	13±0.66	3.1±2.7	42±6.5	4.9±1
Mn	2500±150	13000±2100	740±68	7400±850	1100±130	760±51	2100±98	430±55	1700±750	2400±52	5300±410	2000±160	4200±390	4800±400	2400±100	1500±46	1800±30	810±9.4
Co	1.3±0.12	45±7	0.47±0.34	440±49	2.3±0.25	0.35±0.07	1.1±0.078	1.4±0.087	4.3±5.8	10±0.21	9.6±1.2	2.8±0.22	5.4±2.1	15±1.2	7.3±0.2	0.72±0.22	8.7±1.1	<LOD
Ni	17±0.81	95±14	7.9±2.7	360±33	15±1.9	5.7±2.8	19±1.3	9±2	9.4±2.4	10±0.66	55±4.3	15±3.2	29±4.7	39±3.4	30±1.4	5.9±3.4	87±14	10±0.9
Cu	3200±250	2400±310	3200±240	5400±260	4300±510	3300±270	1600±55	<LOD	1100±590	1500±69	<LOD	<LOD	<LOD	920±71	<LOD	<LOD	<LOD	<LOD
As	5.4±0.26	21±2.5	13±1.2	36±3	13±0.83	17±1.8	150±3.2	18±1.1	26±44	77±9.5	3.2±0.24	3.3±0.37	4.7±0.25	4.9±0.28	3.2±0.17	13±0.38	15±0.81	2.2±0.14
Se	310±21	8.7±1.5	330±41	15±2.1	320±33	450±61	32±1.1	2±0.13	29±11	44±8.8	3±0.033	<LOD	<LOD	36±3	2.4±0.35	<LOD	11±1.2	<LOD
Mo	30±3.1	25±3.4	29±1.5	4.3±0.27	32±3.2	22±2	14±0.52	2.4±0.96	18±25	43±1.3	26±3.3	13±2.1	57±6.9	75±5.3	4.4±1.2	62±1.4	57±4.9	24±2.4
Ag	5.8±0.66	60±5.7	69±3.6	23±1.5	12±1.2	26±1.5	6.7±0.3	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Cd	93±5.7	93±7	2.9±0.059	30±2.4	3±0.27	5.5±0.92	25±1.3	4.3±0.34	32±38	71±1.9	12±0.83	9.7±0.91	11±0.7	55±5.6	23±9	<LOD	15±4.1	4.8±0.17
Sb	<LOD	2.2±0.34	4.8±0.46	14±1.5	4.5±0.58	<LOD	3±0.14	<LOD	<LOD	3.9±0.24	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ba	<LOD	650±65	<LOD	940±89	44±2.4	<LOD	<LOD	54±4.1	<LOD	<LOD	400±16	400±17	750±18	1100±31	650±59	75±3.2	520±5	630±110
Tl	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	3±0.3	<LOD	<LOD	<LOD	<LOD	<LOD	8.5±0.28	<LOD	<LOD	<LOD	<LOD
Pb	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Th	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
U	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Al	2900±4000	22000±3000	5.2±2600	36000±5100	7600±2000	4700±6100	7500±11000	1500±2400	<LOD	3600±6000	9600±4200	<LOD	2900±1600	23000±4400	13000±5100	6500±9000	2300±2300	2300±4300
Zn	14000±200	19000±700	6100±830	8700±480	9200±380	6200±660	12000±1100	2200±450	9600±200	14000±330	5900±640	2100±210	4100±280	6000±290	2900±430	2500±670	1800±88	1700±210

Note: Samples selected for arsenic speciation are highlighted.

Conclusions

- Mushrooms had higher levels of arsenic than the other vegetables tested.
- Speciation of five mushrooms with elevated levels of arsenic identified the presence of five arsenic species:
  - Arsenobetaine (AsB)
  - Inorganic arsenite (iAs^{III})
  - Inorganic arsenate (iAs^{V})
  - Monomethylarsonic acid (MMA)
  - Dimethylarsinic acid (DMA)
- Oyster and Shiitake mushrooms had the highest levels of inorganic arsenic, confirmed by a qualitative spike experiment.

Future work:

- Test mushrooms from different regions of Alberta.
- Examine the impact of various cultivation methods.

Acknowledgements

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Left to right: Kayla LaPorte, Dr. Chris Le, Gursevak Uppal

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