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Research Article

Arsenic speciation in cattail (*Typha latifolia*) using chromatography and mass spectrometry

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Typha latifolia, commonly known as cattail, is widely used as traditional food and medicinal ingredients by indigenous people. There have been concerns over the high levels of total arsenic in cattail plants, but the chemical species of arsenic in cattail have not been characterized. We describe here the determination of arsenic species in the various compartments of cattail. Average concentrations of total arsenic from 9 to 19 cattail plants were 1120 μg/kg (range 68–2600 μg/kg) in the fine (hairy) roots, 575 μg/kg (range 16–1400) in the skin of tuber, 26 μg/kg (range 2–82) in the core of the tuber, 6 μg/kg (range 5–12) in the stem, and 420 μg/kg (range 4–1970) in the whole tuber. Speciation analysis using strong anion exchange, ion pairing, and strong cation exchange chromatography separation with MS detection revealed the presence of inorganic arsenite, arsenate, dimethylarsinic acid, and monomethylarsonic acid. The two inorganic arsenic species accounted for >80% of the total arsenic. Further analyses of arsenic and iron concentrations showed a strong correlation between arsenic and iron in the fine roots and skin. These results suggest that arsenic and iron are colocalized (codeposited) in the skin of the cattail plants, consistent with the previous findings. The level of exposure to arsenic from the use of cattail as food and medicine can be substantially reduced by removing the skin of cattail.

Keywords: Arsenic species / Cattail / Methylated arsenic / Speciation analysis / *Typha latifolia*

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1 Introduction

Exposure to arsenic by the general population occurs mainly through ingestion of arsenic present in water and food [1]. For drinking water meeting the arsenic guideline level of 10 μg/L (*e.g.*, by the World Health Organization, United States Environmental Protection Agency, and Health Canada), dietary sources of arsenic could make a significant contribution to the overall exposure to arsenic. For example, the average daily dietary intake of total arsenic was estimated to be 38 μg/day in Canada [2], 62 μg/day in USA [3, 4], 89 μg/day in UK [5], 55 μg/day in New Zealand [6], and 160–280 μg/day in Japan [7, 8]. Meacher *et al*. [9] and Schoof *et al*. [10] further estimated daily inorganic arsenic intake of US adults from food, water, and soil ingestion and from airborne particle inhalation. They found that food is the greatest source of inorganic arsenic intake and that drinking water is the next highest contributor. Inhalation of airborne arsenic-containing particles and ingestion of arsenic-containing soils were negligible contributors. Even in southeastern Michigan, where approximately 8% of the population is exposed to arsenic in drinking water >10 μg/L, food intake accounts for 37.3% of the estimated exposure to inorganic arsenic, second to the contribution from home drinking water (55.1%) [11].

Most dietary arsenic originates from fish, shellfish, and seaweed products. On the basis of the US Food and Drug Administration (FDA) Total Diet Study for Market Baskets collected from 1990 through 1991, Adams *et al*. [12] estimated that food contributed 93% of the total daily intake of arsenic, with seafood accounting for 90%. The major arsenic species found in the fish and shell fish that are usu-

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Abbreviations: **As^{III},** arsenite; **As^{V},** arsenate; **AsC,** arsenocholine; **AsB,** arsenobetaine; **DMA,** dimethylarsinic acid; **DMAE,** dimethylarsinyl ethanol; **ICPMS,** inductively coupled plasma MS; **MMA,** monomethylarsonic acid; **TMAO,** trimethylarsine oxide; **TMA,** tetramethylarsonium

ally eaten is arsenobetaine [$(CH_3)_3As^+CH_2COO^-$, AsB], a ubiquitous major arsenic species in crustaceans. Minor amounts of arsenocholine [$(CH_3)_3As^+CH_2CH_2OH$, AsC], trimethylarsine oxide [$(CH_3)_3AsO$, TMAO], tetramethylarsonium ion [$(CH_3)_4As^+$, TMA], dimethylarsinic acid (DMA), monomethylarsonic acid (MMA), arsenate (As^V), arsenite (As^{III}), and unidentified arsenicals have also been found in marine animals [13–16]. A number of arsenosugars are present at high concentrations in seaweed and bivalves [13–18]. These various arsenic species have a very different degree and nature of toxicity, *e.g.*, AsB is essentially nontoxic compared to the highly toxic As^{III}. Therefore, assessing dietary arsenic exposure requires not only quantifying the concentration of arsenic but also determining arsenic speciation [1, 13–17]. While earlier studies have focused on arsenic speciation in the marine environment [13–16], further research has also extended to the speciation of arsenic in other food items [20–32].

Typha latifolia (or cattail) is a common wetland plant (grown in marshes, swamps, ditches, and stagnant water) and is widely consumed as food and medicine. It is claimed that "the cattail's every part has uses." "It was a major staple for the American Indians", and it is "easy to harvest, very tasty, and highly nutritious" [33]. In northern Alberta, Canada, the Aboriginal people commonly use cattails as a source of food for various specialty dishes and as a medicinal herb. In a preliminary monitoring of environmental contaminants commissioned by a local oilsand industry, variable (and generally high) levels of arsenic were found in a few samples of *T. latifolia* collected from northern Alberta. Although the results were variable between cattail plants collected from the same location, the news about arsenic in cattail caused much concern in the local community. However, little is known about the chemical speciation of arsenic in cattail. The primary objective of the present study is to identify and quantify individual arsenic species in cattail. A second objective is to investigate the variability of arsenic concentration between cattail plants. We have achieved arsenic speciation analysis in cattail by using LC separation with inductively coupled plasma MS (ICPMS) and ESI MS detection. We have further determined the distribution of arsenic in the fine root, skin, and core of the cattail tuber. The localization of arsenic in the skin of cattail is probably responsible for the apparent difference in arsenic concentration between cattails of different sizes (and therefore different surface area).

2 Materials and methods

2.1 Instrumentation

An Agilent 7500 ce octopole reaction system ICPMS (Agilent Technologies, Japan) was operated with the helium mode. A 4000Q-Trap MS/MS (Applied Biosystems, MDS SCIEX, Ontario, Canada) was equipped with an electrospray ion source. The detailed operating conditions were described previously [34]. A liquid chromatograph (1100 series, Agilent Technologies, Santa Clara, CA) with an autosampler and column temperature controller was used for the separation. Chromatographic separation of arsenic species was achieved using three columns, including RP (ODS-3, 150×4.6 mm^2, 3 μm particle size, Phenomenex, Torrance, CA), strong anion exchange (PRP-X100, 150×4.1 mm^2, Hamilton, Reno, NV), and strong cation exchange (PRP-X200, 150×4.1 mm^2, Hamilton).

2.2 Reagents and standards

Solutions of standard arsenic compounds, As^{III}, As^V, DMA (Aldrich, Milwaukee, WI), MMA (Chem Service, West Chester, PA), and AsB (Tri Chemical Laboratories, Japan) were prepared by appropriate dilutions with deionized water from 1000 mg/L stock solutions. AsC, TMAO, and TMA iodide were obtained from Tri Chemical Laboratories, Japan. Dimethylarsinyl ethanol (DMAE) was kindly provided by Dr. K. A. Francesconi (Karl-Franzens University Graz, Austria). The standard reference materials SRM1640 (Trace Elements in Natural Water), SRM1566b (Oyster Tissue), and SRM1573a (Tomato Leaves) were purchased from National Institute of Standards and Technology (NIST, Gaithersburg, MD). Tetrabutylammonium hydroxide (Aldrich), malonic acid (Fisher), methanol (Fisher), ammonium bicarbonate (Sigma), pyridine (Aldrich), and formic acid (Fluka) were used for preparation of the mobile phase solutions, which were filtered through a 0.45 μm membrane prior to use for chromatography separation. UltraPure nitric acid and sulfuric acid (Fisher) were used for digestion of solid samples.

2.3 Sampling

Cattails were collected by Alberta Health and Wellness from ponds in the Fort McMurray region, northern Alberta, Canada. Residual mud was washed off with water before cattail tubers, along with fine roots were delivered to our laboratory, on the same day of collection. The fine (hairy) roots were cut off from the tuber. The skin of the tuber was then peeled off from the core. Each component (fine roots, skin, and core) was separately ground, and the homogenized samples were kept at –20°C for up to 2 months before analysis. These samples were either digested with nitric acid–sulfuric acid for the determination of total arsenic concentrations or extracted with methanol–water solution for the speciation of arsenic.

2.4 Determination of total arsenic in the samples

The separate cattail samples and standard reference materials (SRM1566b and SRM1573a) were digested using a mixture of nitric acid and sulfuric acid. Triplicate cattail

samples (5–10 g wet weight) or SRM (1 g dry weight) were each weighed into a 100 mL beaker, to which 20 mL nitric acid and 60 mL sulfuric acid were added. The beaker was covered and the mixture left overnight. The mixture in the beaker was then heated to ~100°C for 2 h, and further boiled for 4 h. The glass cover was removed and the contents heated to evaporate the acids to almost dryness. The digested content was redissolved in 15 mL of 1% nitric acid. The solution was analyzed for total arsenic and iron concentrations by ICPMS. Parallel triplicate blanks containing the acids were included with each set of samples.

2.5 Determination of arsenic speciation in the samples

Duplicate cattail samples (1–10 g wet weight) were extracted three times with a mixture of 50% methanol and 50% water. Each sample was weighed into a 50 mL centrifuge tube, to which 7.5 mL methanol and 7.5 mL deionized water were added. The mixture in the tube was sonicated for 15 min. The tube was centrifuged and the supernatant transferred to a 100 mL beaker. The extraction/sonication/centrifugation procedures were repeated two more times on the residue, and the supernatant pooled in the beaker. The combined supernatant from the three repeat extractions was evaporated at 40°C to almost dryness. The content was dissolved in 3 mL deionized water. The solution was filtered through a 0.45 μm syringe filter before liquid chromatographic analysis of arsenic species.

To determine and confirm arsenic species in the sample extracts, three sets of chromatography separations were carried out: strong anion exchange, ion pairing, and strong cation exchange. A strong anion exchange column (PRP-X100, 150×4.1 mm^2; Hamilton) was used with a mobile phase containing 35 mM ammonium bicarbonate and 5% methanol in deionized water. The flow rate was 0.8 mL/min during the first 4 min, and then increased to 1.7 mL/min for the remaining 10 min of separation. Ion pairing separation was performed on an RP column (ODS, 150×4.6 mm^2, 3 μm particle size, Phenomenex) with a mobile phase (pH 5.9) containing 5 mM tetrabutylammonium hydroxide, 3 mM malonic acid, and 5% methanol, under similar conditions as described previously [35, 36]. The flow rate of the mobile phase was 1.2 mL/min. Strong cation exchange separation was performed on a PRP-X200 column (250×4.1 mm^2, Hamilton) with a mobile phase containing 4 mM pyridine and 5% methanol. Its pH was adjusted to 2.8 by using formic acid and the flow rate was 1.0 mL/min.

ESI MS/MS was performed on a 4000Q-Trap MS/MS system (Applied Biosystems). One-third of the effluent from the HPLC column was split and mixed with the same amount of methanol either at pH 10 (adjusted by ammonium hydroxide for positive ionization mode) or pH 3.0 (adjusted by formic acid for negative ionization mode) [34]. The multiple reaction monitoring (MRM) transitions 139/121 and 139/91 were monitored for DMA, and MRM transitions 141/123 and 141/107 were monitored for As^{V}.

3 Results and discussion

Initial analysis of cattail samples collected from the same location showed variable concentrations of arsenic. The total arsenic concentrations from three cattail tubers (bulbs) collected from the same location were 200, 635, and 939 μg/kg, respectively. Triplicate analyses of the same cattail sample gave an RSD of less than 5%, suggesting good precision of the analysis. Determination of arsenic in standard reference materials including SRM1640 (Trace Elements in Natural Water), SRM1566b (Oyster Tissue), and SRM1573a (Tomato Leaves) showed good agreements with the certified values. Our measured values and the certified (reference) values were: 27.04 ± 0.97 ($n = 14$) and 26.67 ± 0.41 for SRM1640, 7.80 ± 0.53 ($n = 12$) and 7.65 ± 0.65 for SRM1566b, 0.116 ± 0.014 ($n = 11$) and 0.112 ± 0.004 for SRM1573a, respectively. Therefore, the variability observed from the analyses of the three cattail plants was not due to errors in analysis but rather due to differences between the cattail samples.

Previous work has shown heterogeneous distributions of arsenic in plants, typically higher concentrations of arsenic in the roots and skin than in the stem and interior of the plant or grain [29, 31, 37]. Therefore, we suspected that the observed variability of arsenic concentration between the cattail tubers (skin and core of the tuber) was due to the difference in the size of the tuber. Indeed, the highest arsenic concentration was in the smallest tuber among the three initial cattail samples. This is understandable because the smaller tuber had a higher unit surface area and contained a higher percentage of skin by weight, and therefore, presented a higher concentration of arsenic.

We then separated the various compartments of cattail, in particular, the fine hairy roots, the skin of the tuber, and the core of the tuber (skin removed). Analysis of the separate compartments of the plants indicate the highest concentration of arsenic in the fine root and skin (Table 1). These results are consistent with previous findings [29, 31, 37]. Previous study has also indicated the colocalization of arsenic and iron plaque in the plant skin [37, 38]. To confirm this finding, we further analyzed iron concentrations. Our results show a good correlation between arsenic and iron (Table 1).

We further determined arsenic speciation in the fine root and tuber of cattail. The speciation analysis was achieved by LC separation and ICPMS detection. Figure 1 shows ion pair chromatography separation and ICPMS detection of arsenic standards and a root skin sample, suggesting the presence of As^{III}, DMA, MMA, and As^{V}. Further analyses using strong anion exchange chromatography separation and ICPMS detection (Fig. 2) also support the presence of

Table 1. Summary of arsenic and iron concentrations in the various components of cattail

Cattail samples	Arsenic concentrations (μg/kg)		Iron concentrations (mg/kg)		Correlations	
	Mean (*n*)	Range	Mean	Range	R^2	*p*-Values
Fine roots	1.12 (10)	0.068–2.6	1.47	0.071–4.59	0.8121	0.0004
Skin of tuber	0.575 (9)	0.016–1.4	0.99	0.11–1.97	0.8931	0.0001
Core of tuber	0.026 (9)	0.002–0.082	0.026	0.009–0.12	–	–
Whole tuber	0.42 (19)	0.004–1.97	0.14	0.008–0.75	0.8569	0.0003
Stem	0.006 (13)	0.005–0.012	0.13	0.004–0.71	0.0312	0.5638

Number shown in the parenthesis (*n*) is the number of cattail samples analyzed, and R^2 represents correlation between the concentrations of arsenic and iron in the cattail samples. Note that fine roots, skin of tuber, and core of tuber were from the same cattail plants, while results of whole tuber were obtained from 19 other cattail plants that were not separated into the three components. See also Supporting Information Fig. S1.

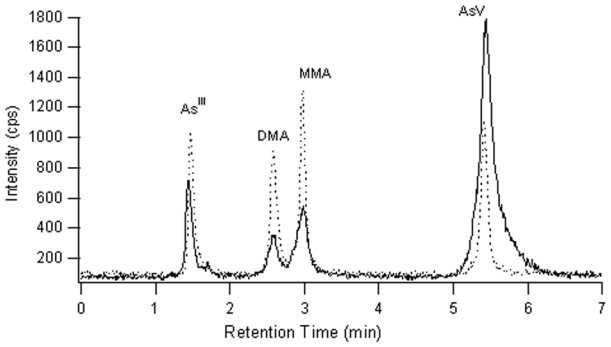

Figure 1. Chromatograms showing analysis of a cattail skin sample (solid trace) and four arsenic standards (dotted trace) using ion pairing chromatographic separation with ICPMS detection. An RP column (ODS, 150 × 4.6 mm^2, 3 μm particle size, Phenomenex) was used with a mobile phase (pH 5.9) containing 5 mM tetrabutylammonium hydroxide, 3 mM malonic acid, and 5% methanol. The flow rate of the mobile phase was 1.2 mL/min.

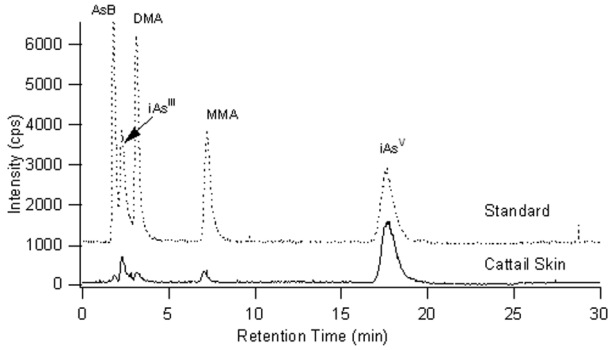

Figure 2. Chromatograms showing analysis of a cattail skin sample (solid trace) and five arsenic standards (dotted trace) using strong anion exchange separation and ICPMS detection. A strong anion exchange column (PRP-X100, 150 × 4.1 mm^2; Hamilton) was used with a mobile phase containing 35 mM ammonium bicarbonate and 5% methanol in deionized water. The flow rate was 0.8 mL/min for the first 4 min, and then increased to 1.7 mL/min for the remaining 10 min of separation.

As^{III}, DMA, MMA, and As^{V} based on retention time matches between arsenic standards and the sample. The identities of As^{III}, DMA, MMA, and As^{V} species in cattail samples were confirmed by analyses of the cattail sample spiked with As^{III}, DMA, MMA, and As^{V} standards and by additional analyses using ESI MS/MS (data not shown).

In the analysis of arsenic species by strong anion exchange chromatography separation and ICPMS detection (Fig. 2), we observed a small peak at the retention time of AsB. To examine whether AsB and/or other arsenic species, such as AsC [$(CH_3)_3As^+CH_2CH_2OH$), TMAO [$(CH_3)_3AsO$], TMA ion [$(CH_3)_4As^+$], and DMAE, may be present in the cattail sample, we have further separated these arsenic species on a strong cation exchange column. Figure 3 shows chromatograms obtained from the analyses of three cattail skin samples and standards of AsB, AsC, TMAO, TMA, and DMAE. Clearly, none of the arsenic species present in the cattail skin samples correspond to AsB, AsC, TMAO, TMA, or DMAE. Peaks 1 and 2 match retention times of As^{III}, DMA, MMA, and As^{V} standards (data not shown), which are not completely resolved under the strong cation exchange chromatography conditions. The early eluting small peak in Fig. 2 remains as unidentified arsenic species.

The concentrations of individual arsenic species in the fine root, skin, core, and the whole tuber are summarized in Table 2. Inorganic As^{III} and As^{V} are predominant, and MMA and DMA account for <10% of the total arsenic concentration in cattail.

Typha sp., including cattail, thrives well in the high arsenic soil [39] and sequesters arsenic in root surface iron plaque [37]. It is not surprising that the concentration of arsenic in cattail is higher than many other common food items for human consumption [40]. Comprehensive analyses of food collected in Canadian cities in the years 1985–1988 showed that the food groups containing the highest mean arsenic concentrations were fish (1662 μg/kg), poultry and meat (24.3 μg/kg), cereals and bakery goods (24.5 μg/kg), and fats and oils (19.0 μg/kg) [41]. These were based on the measurement of total arsenic in market basket food items. More recent work has focused on arsenic speciation; with extensive assessment of arsenic species in

Table 2. Concentration (μg/kg) and percentage of arsenic species in the various components of cattail

Cattail samples	DMA		MMA		As^{III}		As^{V}		Unknown	
	μg/kg	%	μg/kg	%	μg/kg	%	μg/kg	%	μg/kg	%
Fine roots	62 ± 6	5.2	15 ± 3	3.6	38 ± 8	3.2	912 ± 132	76	124 ± 20	12
Skin	12 ± 4	2	17 ± 5	2.8	49 ± 6	8.1	516 ± 26	86	8 ± 2	1.3
Core	1.3 ± 0.2	4.9	0.3 ± 0.1	1.1	11 ± 1	42	13 ± 2	49	0.7 ± 0.1	2.7
Whole tuber	23 ± 4	5.5	12 ± 2	2.9	97 ± 10	23	277 ± 19	66	11 ± 2	2.6

Note that fine roots, skin of tuber, and core of tuber were from the same cattail plants, while results of whole tuber were obtained from different cattail plants that were not separated into the three components.

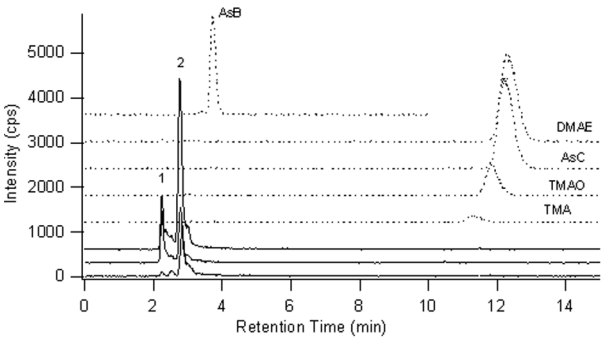

Figure 3. Chromatograms showing analysis of three cattail skin samples (bottom three solid trace) and five individual arsenic standards (top five dotted traces) using strong cation exchange separation and ICPMS detection. A strong cation exchange column (PRP-X200, 250 × 4.1 mm^2, Hamilton) was used with a mobile phase containing 4 mM pyridine and 5% methanol (pH adjusted to 2.8 by with formic acid). Peak 1 is due to As^{III} and MMA, and peak 2 corresponds to DMA and As^{V}, determined by match of retention time of these arsenic standards.

seafood and rice [42–44]. Schoof and Yager [42] summarized available data on inorganic arsenic, DMA, and MMA in fish and seafood from 20 studies, and they concluded that inorganic arsenic concentrations were 10–20 μg/kg (wet weight) in freshwater, anadromous, and marine fish, and 40–50 μg/kg in crustaceans and molluscs. DMA concentration averaged 10 μg/kg in freshwater fish and 45–95 μg/kg in anadromous fish, marine fish, crustaceans, and mollusks. In freshwater fish, inorganic arsenic accounted for 10% of total arsenic. For marine and esturine fish, crustaceans, and mollusks 2–3% of total arsenic was inorganic arsenic. Zavala *et al*. [43] have recently derived a "global normal range" of 80–200 μg/kg for arsenic concentration in rice. They conclude that the mean arsenic concentrations for rice from the US and Europe (both 198 μg/kg) were statistically similar and significantly higher than rice from Asia (70 μg/kg). They [43], Williams *et al*. [31], and Heitkemper *et al*. [32] found that the high concentration of arsenic in US rice, regardless of type, color, variety, and location of production, is primarily associated with DMA, whereas the primary arsenic species in rice from Asia is inorganic arsenic.

4 Concluding remarks

Cattail plants are widely used by the aboriginal people as food and medicine. For a consumption of 0.1 kg of whole tuber having a mean arsenic concentration of 400 μg/kg, the intake of arsenic is 40 μg. This is higher than the consumption of 2 L of water containing 10 μg/L arsenic (the maximum contaminant level in US and Canadian drinking water). Arsenic concentration in cattail varies between the skin, roots, and core of the plant. Because the highest arsenic concentration is localized in the skin of cattail, removal of the skin before consumption will decrease the amount of arsenic and reduce the intake of arsenic from cattail.

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