

Impact of Different Analytical Techniques on Risk Assessment: A Case Study on Arsenic in Saline Groundwater

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Why is Arsenic in Florida Groundwater a Concern?

- More than 90% of the potable water in Florida comes from groundwater sources.
- Arsenic is classified by the International Agency for Research on Cancer (IARC) and the U.S. EPA as a “known human carcinogen” based on studies from several countries showing high rates of cancers of the bladder, lung, skin and several other organs among populations in which high levels of arsenic are present in drinking water.

We still do not fully know many things about arsenic

- What level of arsenic in groundwater poses human health risks?
- Which forms of arsenic pose the greatest human health risks?
- How is arsenic transformed and mobilized in the environment?
- What are the best ways to measure arsenic in different environmental matrices?

What level of arsenic in groundwater poses human health risks?

- In 2001, The U.S. EPA changed the allowable level of total arsenic in public drinking water from 50 ug/L to 10 ug/L.
- However, even at 10 ug/L, there is still a much greater theoretical cancer risk compared to other carcinogens on the U.S. EPA MCL list.
- Arsenic sometimes occurs naturally in water at higher levels than 10 ug/L, and it is too costly or not possible to reduce to significantly lower levels.
- Is arsenic a threshold carcinogen? Is arsenic a necessary component of the human diet? Can arsenic have beneficial effects (hormesis) at low levels?

Which forms of arsenic pose the greatest human health risks?

TABLE 3-1 Some Arsenic Compounds and Species Known to be Present in Water and Food Consumed by Humans

Name	Abbreviation	Chemical Formula
Arsenous acid	As(III)	H ₂ AsO ₃
Arsenic acid	As(V)	H ₂ AsO ₄
Oxythioarsenic acid		H ₂ AsO ₃ S
Monomethylarsonic acid	MMA	CH ₃ AsO(OH) ₂
Methylarsonous acid	MMA(III)	CH ₃ As(OH) ₂ (CH ₂ AsO) _n
Dimethylarsinic acid	DMA	(CH ₃) ₂ AsO(OH)
Dimethylarsinous acid	DMA(III)	(CH ₃) ₂ AsOH(((CH ₃) ₂ As) ₂ O)
Trimethylarsine	TMA	(CH ₃) ₃ As
Trimethylarsine oxide	TMAO	(CH ₃) ₃ AsO
Tetramethylarsonium ion	Me ₄ As ⁺	(CH ₃) ₄ As ⁺
Arsenocholine	AsC	(CH ₃) ₃ As ⁺ CH ₂ CH ₂ OH
Arsenobetaine	AsB	(CH ₃) ₃ As ⁺ CH ₂ COO ⁻
Arsenic-containing ribosides	Arsenosugar X-XV ^a Arsenolipid ^b	

Different arsenic species have different toxicities

- The type of toxic arsenic effects, as well as the degree of toxicity and carcinogenicity depend on the arsenic form (*i.e.*, trivalent vs. pentavalent, organic vs. inorganic arsenic).
- Toxicity information from animal studies and from studies using human cell lines indicates MMAIII > AsIII > AsIV > MMAIV >> high M.W. organoarsenicals

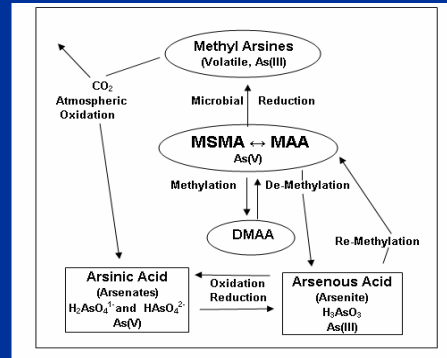
Humans are generally more susceptible than animals to arsenic toxicity and carcinogenicity

- AsIII LD50 mice = 15 to 48 mg/kg bw
- AsIII LD50 human = 1 to 3 mg/kg bw

In laboratory animals,

- AsIV: Inadequate evidence of cancer
 - AsIII: Limited evidence of cancer
- DMA: Sufficient evidence of bladder cancer in rats given high doses

How is Arsenic Transformed in the Environment?



Arsenic Species in Natural Waters

- **Groundwater** typically contains mostly **inorganic** arsenic species
- **Marine** water typically contains mostly **organic** arsenic

Arsenic Species in Natural Waters

- **Groundwater:** Arsenate, arsenite, methylarsonic acid (MMA), dimethylarsinic acid (DMA), arsines
- **Marine water:** Arsenate, arsenite, methylarsonic acid (MMA), dimethylarsinic acid (DMA), arsines, but **also** arsenobetaine, arsenocholine, tetramethylarsonium salts, arsenosugars, arsenic-containing lipids

Treatment and Removal Alternatives may vary with Arsenic Species

- Different arsenic species bind differently to various elements in the soil, and therefore have different potentials for contaminating groundwater

What are the best ways to measure arsenic in different environmental matrices?

- Q: Will it be necessary to speciate the arsenic?
- Q: Will the sample matrix cause interference and detection limit problems?



Low-level As determination in complex environmental matrices is difficult!

- Two problems:
 1. Speciation of Arsenic is a moving target. The species of As in the environment can change over time with changes in the physical, chemical, and biological environment (*e.g.*, redox, pH, microbes).
 2. Analytical methods for arsenic determination are often prone to false positive or false negative results.

Who Cares?

- Problem 1: The speciation of arsenic is important to toxicologists, geologists, soil scientists, and other researchers, but is of a lesser concern to most governmental regulators, since most water regulations are based on total arsenic.
- Problem 2: Reporting arsenic at levels greater or less than true levels concerns everyone involved, including regulators, researchers, the business and legal community, environmental groups, *etc.*

Analytical Considerations

- What are the potential interfering chemicals that might make a given method problematic for a given type of matrix?
- Is the laboratory capable (*e.g.*, equipment, expertise) of doing the selected method?
- Is it necessary to use an approved U.S. EPA method for regulatory or legal purposes?

Some U.S. EPA Arsenic Methods

<u>Method No.</u>	<u>Instrument</u>
■ 200.5, 200.7, 200.15, 6010B	ICP-AES
■ 200.8, 6020	ICP-MS
■ 200.9, 200.12, 7060A	GFAA
■ 245.1, 1631	CV-AFS
■ 1632, 7060A, 7061A, 7062	HG-AAS
■ 7063	ASV

Method pitfalls in testing marine or brackish groundwater for arsenic

- **ICP-AES:** Inductively coupled plasma-atomic emission spectrometry methods are subject to positive interference from high levels of some chemicals present in saltwater (*e.g.*, Na, Cl, K, Al, Cr, V, polyatomic compounds).

Method pitfalls in testing marine or brackish groundwater for arsenic

- **ICP-MS:** Inductively coupled plasma-mass spectroscopy is subject to positive interference from chloride, which reacts with the argon gas used in the method, forming argon chloride, which has the same mass of 75 as arsenic. ICP-MS is also subject to non-spectral interference from seawater.

Options to reduce interference from saltwater

- For GFAA and ICP-AES methods: Use matrix modifiers, background correction, or method of standard additions. These may decrease, but not necessarily eliminate false positives.
- Dilute the sample. This may help, but may greatly increase the detection limit and make the sample result useless for risk assessments.
- Use a method not prone to interference from components of saltwater, such as HG-AAS or ASV.

Options to reduce interference from saltwater

- Read the U.S. EPA arsenic methods.
- Review the scientific literature for options.
- Contact analytical instrument sales and technical staff for the best approach. They are aware of the most cost-effective and efficient, modern technologies, and they will find the best options to suit your particular needs.

Gas Hydride Methods

- Following the murder of his grandfather by arsenic poisoning, an English chemist named James Marsh developed an analytical gas hydride technique for detecting arsenic in the body.
- Marsh J. 1836. Account of a method of separating small quantities of arsenic from substances with which it may be mixed. Eddinburgh New Philosophical Journal 21: 229-236.

Gas Hydride Methods

- Arsenic forms gaseous hydrides when reacted with strong reducing agents. This property has been exploited to allow for the selective removal of arsenic from complex liquid matrices such as saltwater. This technique has been combined with various detectors to achieve high sensitivity with very little matrix interference, and has also been used in some studies for arsenic speciation.

A Case Study

- The principle goal of this study was to compare the anomalous results between two U.S. EPA approved methods for arsenic analysis in a groundwater matrix that varied from somewhat fresh to highly saline, due to saltwater intrusion from the surrounding Tampa Bay.
- The two methods used for arsenic determination were U.S. EPA Method 6010B (ICP-AES) and U.S. EPA Method 7061A (HGAAS).

A Case Study

- Shallow groundwater samples were collected throughout the northern half of Perico Island, FL.
- The site was comprised of approximately 320 acres of former agricultural land, containing several canals.
- Historical land use did not suggest that significant amounts of arsenic were used at the site (*e.g.*, no record of lead arsenate, MSMA, or fertilizers containing high levels of arsenic).

A Case Study

- **Method 6010B (ICP-AES):** Thirty-seven samples were tested using U.S. EPA Method 6010B. Twenty-one of those samples were greater than the MCL of 50 ug/L that was in place at the time. Six samples were reported to be less than the detection limit of 5 ug/L, and nine samples were between the detection limit and the MCL (>5 to <50 ug/L).

A Case Study

- **Method 7061A (HG-AAS):** The 21 samples that exceeded the MCL Method 6010B were submitted for testing by Method 7061A. All but one of the 21 samples were less than the MCL of 50 ug/L when tested by Method 7061A. The one sample exceeding the MCL (57 ug/L) was much lower than the value of 180 ug/L reported using Method 6010B.

A Case Study

As seen in this table an approximation of potential saline matrix interference using Method 6010B can be obtained from the sample conductivity. A high correlation was found (R=0.87) between increased conductivity and an increase in the difference between the two arsenic method results.

Sample ID	Method 6010B As (ug/L)	Method 7061A As (ug/L)	Difference As (ug/L)	Conductivity (uS/cm)
TMW-34	63	12	48	12740
TMW-32	59	5	54	17330
TMW-8	67	9	58	16200
TMW-26	67	6	61	19150
TMW-35	63	<1	62	18570
TMW-15	75	<1	74	16800
TMW-27	81	5	76	>20000
TMW-25	79	1	78	18520
TMW-7	120	18	102	>20000
TMW-33	120	<1	119	>20000
TMW-4	180	57	123	>20000
TMW-6	155	8	127	>20000
TMW-29	155	<1	154	>20000
TMW-28	140	<1	139	>20000
TMW-36	145	<2	143	>20000
TMW-37	145	<2	143	>20000
TMW-31	180	23	157	>20000
TMW-12	160	<1	159	>20000
TMW-22	165	<1	164	>20000
TMW-5	200	34	166	>20000
TMW-24	195	<1	194	>20000

A Case Study

- A sample with little or no arsenic having a conductivity of approximately 13,000 uS/cm could potentially result in a reported level of arsenic above 50 ug/L using U.S. EPA Method 6010B. A few thousand (*e.g.*, 3,000) uS/cm might result in a false positive arsenic result exceeding 10 ug/L.

A Case Study

- Arsenic in seawater may be as high as 6 ug/L or more, but it is typically less.
- The arsenic results reported by the gas hydride method (EPA Method 7061A) are largely consistent with arsenic levels being at slightly greater than expected background, although 5 of the 21 groundwater samples still exceed the new arsenic MCL of 10 ug/L.

A Case Study

- The origin of the elevated arsenic in these wells remains uncertain, although it may have been the result of domestic dumping near those wells. Speciation, which was not conducted in this study, could have potentially shed more light on the origin of the arsenic at the site.

Implications for Risk Assessment and Remediation

- With the results from the gas hydride arsenic analysis, only one of the 37 groundwater samples exceeded the MCL of 50 ug/L.
- Based on these results, The Florida Department of Environmental Protection did not require the large-scale cleanup that would have been required without having re-tested the samples by Method 7061A.
- \$\$\$\$\$\$ Savings!

Salinity may vary greatly within a relatively confined area.

- For example, whereas saltwater in the Florida Bay has chloride levels of 15,000 to 35,000 mg/L and a specific conductivity of between 20,000 and 50,000 uS/cm, fresh water found in the nearby Everglades National Park typically has a chloride ion concentration of about 40 mg/L and a specific conductivity of 450 uS/cm.

Salinity may vary greatly within a relatively confined area.

- At the interface between saltwater and freshwater zones in groundwater, some of the samples may be differentially affected by saltwater interference resulting in false positive detects, or artificially elevated arsenic, when using a method prone to interference from saline groundwater.

A Cautionary Note

- Gas hydride methods are useful, but they also have their limitations. Some arsenicals present in marine water, such as arsenobetaine and arsenocholine, do not readily form hydrides, so care must be taken to properly digest all of the arsenicals and convert them to a trivalent inorganic state before derivatization.
- The arsine gases formed are toxic.
- Gas hydride methods are indirect test methods.

Conclusions

- In this case study, the saline sample matrix greatly biased high the reported arsenic levels in groundwater.
- Some U.S. EPA methods are better than others under different circumstances.
- The lower arsenic MCL of 10 ug/L makes false arsenic detects resulting from salinity an even more important consideration in selecting an appropriate arsenic method when testing groundwater in coastal areas of Florida, where much of the population resides.

Conclusions

- In cases where saltwater intrusion into the groundwater may be of concern, conductivity may serve as a general guide in choosing the best analytical method for the determination of arsenic.
- Significant cost savings can be achieved by selecting the most appropriate analytical test method, by avoiding unnecessary remediation and legal fees.

Thank You!

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