

The Role of Speciation for Selenium Treatment and Compliance with Site-Specific Aquatic Life Criteria

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I. Overview of Selenium Regulations

II. Relevance of Speciation to Selenium Treatability and Bioavailability

III. Impact of Speciation on Accuracy of Total Selenium Measurements

Why Care about Selenium?

- Narrow range between deficiency & toxicity
- Impacts invertebrates, fish, and waterfowl in the aquatic environment
- Bioaccumulates & biomagnifies
- Sources include mining (C, S, P, Fe, U)



Toxic drainwater from irrigated farmland in California and other Western states has created an environmental calamity in ROBERT H. BOYLE 4.3 How is the models into its account of the model intertion of the one operation in the start of the start base. The start has inter-shown a start of the start is start of the start of the inter-shown a start of the start of the start of the start is the start of the start of the start of the start of the inter-start of the start of the encaded start of the start of the start of the start of the encaded start of the start of the start of the start of the encaded start of the start of the start of the start of the encaded start of the start of the start of the start of the encaded start of the start of the start of the start of the encaded start of the start of the start of the start of the encaded start of the start of the start of the start of the encaded start of the start of the start of the start of the encaded start of the start of the start of the start of the encaded start of the start of the start of the start of the encaded start of the start of the start of the start of the encaded start of the start of the start of the start of the encaded start of the start of the start of the start of the encaded start of the start of the start of the start of the encaded start of the encaded start of the encaded start of the encaded start of the encaded start of the encaded start of the encaded start of the start of th

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Source: Sports Illustrated (March 22, 1993)



Challenges with Regulating Selenium

Se.,,,,C

- Selenium (Se) concentrations of waters are *not* directly predictive of toxicity
 - Bioavailability depends on the molecular form (species) of Se & other sample components
 - Organisms convert Se into organic forms that may be more bioavailable & toxic
- Uptake rates will therefore vary from one location to another!

Site-Specific Criteria for Se

USEPA Recommended Freshwater Ambient Chronic Water Quality Criterion

Fish Tissue	Water Column
15.1 mg/kg dw Egg/Ovary	1.5 μg/L Monthly average for Lentic Systems
8.5 mg/kg dw Whole Body	3.1 μg/L Monthly Average for Lotic Systems
11.3 mg/kg dw Muscle	Intermittent Exposure Equation for Short-Term Exposures

British Columbia Water Quality Guidelines for Selenium for Protection of Aquatic Life

Fish Tissue	Other Matrices	
11 mg/kg dw Egg/Ovary	2.0 μg/L Monthly Average in Water Column	
4 mg/kg dw Whole Body	2 mg/kg in Sediment (Alert Concentration)	
4 mg/kg dw Muscle (Interim)	4 mg/kg in Invertebrate Tissue (Interim)	

Monitoring water is still more practical (cost, frequency, equilibrium considerations)

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Se Treatability Affected by Speciation

<u>Se(IV)</u> Precipitation with FeOOH

Biological reduction

Chemical reduction

Se(VI) Biological reduction Adsorption Reverse osmosis Chemical reduction

Anion exchange

<u>SeCN</u> Chemical oxidation (Fenton's reagent)

Biological oxidation

ncreasing Cost of Treatment

Must know what is present before implementing any treatment system

Biological Treatment for Se Removal

- Uses biological organisms to convert soluble Se into a form that can be easily removed from solution (typically Se⁰)
- Field-proven to treat WWs from mg/L $\rightarrow \mu$ g/L





Source: J Hazard Mater. 2014 Mar 30;269:98-109

Regular monitoring required for optimal treatment efficiency

Issues with Uncontrolled Bioreactors

- Can produce non-target Se species
- Bioavailability of some organoselenium species shown to be orders of magnitude higher than inorganic Se
 - Effluent bioavailability
 may be greater than
 the influent even if
 total Se concentration
 decreases!
 - Requires methods
 that can quantitate
 very low amounts of
 these species



Without Regular Monitoring...



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Se78 Signal

Why Speciation Matters for Treatability

 Critical indicator of bioreactor health to help maintain treatment efficacy

Selenium Species	Potential Indication
Selenocyanate	Overfeeding; Toxic reactor conditions (cell death)
Selenosulfate	Excess Se(0) buildup; ORP too low (sulfate reduction)
Elemental Se	Ionic strength too high; Improper Se(0) retention mechanism
Volatile Se (DMSe, DMDSe)	Improper bacteria strain; Improper degassing of system
Seleno-amino acids	Improper bacterial strain
	Bacteria colony has not equilibrated; Flow too high; Underfeeding
Initial Se Species	Concentration of other contaminants too high (toxic)

 Minimizing formation of more bioavailable Se species during treatment maximizes the likelihood of compliance with aquatic life criteria for Se

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Methods for Total Se Quantitation

- Typically ICP-MS methods (e.g., USEPA 200.8, 1638, 6020)
- Collection & preservation →
- Digestion:
 - Not always required for dissolved (filtered) fractions
 - External, open-vessel digestion most common for total (unfiltered) fractions
- Not designed to account for selenium's unique chemistry





Indicators of Issues with Standard Methods

• Diss Se > Total Se

Raw Wastewater Results (µg/L)				
Total Rec. Se	Diss. Se			
246	393			
210	333			

• Se Speciation > Diss or Total Se

_ffluent Results (μg/L)				
Total Rec. Se	∑ Se Species			
76.6	150			

Irreproducible Results (within and between labs)

Effluent Results (µg/L)				
Initial Digest	Re-digest			
32.0	16.4			

What can cause these issues?

What about Volatile Se Species?

 ICP-MS response assumed to be species-independent – but is it?

Sample Type	Total Rec. Se	Diss. Se (Undigested)	Diss. Se (Digested)
Influent	153	155	-
Effluent	27.5	185	22.1

 Volatile species will have increased mass-transport in typical ICP-MS systems unless converted to a non-volatile form



Source: www.qmx.com

What happens during open-vessel digestion?

What about Reduced Se Species?

- Reduced species like SeCN⁻ and SeSO₃²⁻ can degrade to Se⁰ upon acidification
- Se^o adsorbs onto polymer surfaces and is "left behind" when sample aliquot is removed for external digestion





Solutions!

Generating accurate Se results may require deviation from standard methods:

- <u>Collection</u>: Borosilicate glass instead of HDPE
- <u>Preservation</u>: None, or
 oxidant much stronger than
 dilute nitric
- <u>Digestion</u>: Closed-vessel instead of open-vessel; both total & dissolved fractions



Conclusions

- Compliance with Aquatic Life Criteria for Se can be achieved more rapidly & cost-effectively by incorporating speciation into sampling plans
- Treatment should lower both Se loading and bioavailability
- Speciation data should be viewed as an additional quality control check on dissolved Se measurements
- Be cautious of anyone who advises that speciation analysis or "unknown Se species" are unimportant!
- More research still needed on the fate and bioavailability of various Se species

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