



NOT-SO-RARE EARTH ELEMENTS PREVALENCE, ANALYSIS AND REMEDIATION STRATEGIES

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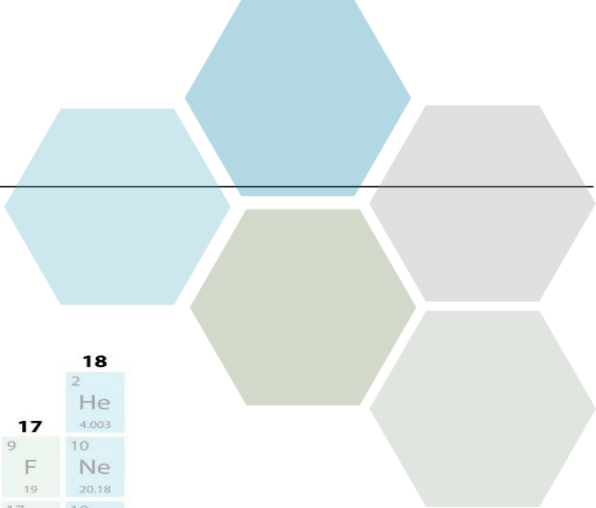
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1. Introduction to Rare Earth Elements (REEs) and their impact to sites
2. Analytical Challenge: Concentrations of Arsenic and Selenium
3. Application: REEs in various matrices
4. Solubility & opportunities for remediation and recovery
5. Conclusions

1. INTRODUCTION



Period	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18	
1	H 1.008																	He 4.003	
2	Li 6.941	Be 9.012											B 10.81	C 12.01	N 14.01	O 16	F 19	Ne 20.18	
3	Na 22.99	Mg 24.31											Al 26.98	Si 28.09	P 30.97	S 32.07	Cl 35.45	Ar 39.95	
4	K 39.10	Ca 40.08	Sc 44.96	Ti 47.88	V 50.94	Cr 52	Mn 54.94	Fe 55.85	Co 58.47	Ni 58.69	Cu 63.55	Zn 65.39	Ga 69.72	Ge 72.59	As 74.92	Se 78.96	Br 79.9	Kr 83.8	
5	Rb 85.47	Sr 87.62	Y 88.91	Zr 91.22	Nb 92.91	Mo 95.94	Tc (98)	Ru 101.1	Rh 102.9	Pd 106.4	Ag 107.9	Cd 112.4	In 114.8	Sn 118.7	Sb 121.8	Te 127.6	I 126.9	Xe 131.3	
6	Cs 132.9	Ba 137.3	La 138.9	Hf 178.5	Ta 180.9	W 183.9	Re 186.2	Os 190.2	Ir 192.2	Pt 195.1	Au 197	Hg 200.5	Tl 204.4	Pb 207.2	Bi 209	Po (210)	At (210)	Rn (222)	
7	Fr (223)	Ra (226)	Ac (227)	Rf (257)	Db (260)	Sg (263)	Bh (262)	Hs (265)	Mt (266)	Ds (271)	Rg (272)	Uub (285)	Uut (284)	Uuq (289)	Uup (288)	Uuh (292)	Uus 0	Uuo 0	
6				58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (147)	62 Sm 150.4	63 Eu 152	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173	71 Lu 175		
7				90 Th 232	91 Pa (231)	92 U (238)	93 Np (237)	94 Pu (242)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (249)	99 Es (254)	100 Fm (253)	101 Md (256)	102 No (254)	103 Lr (257)		

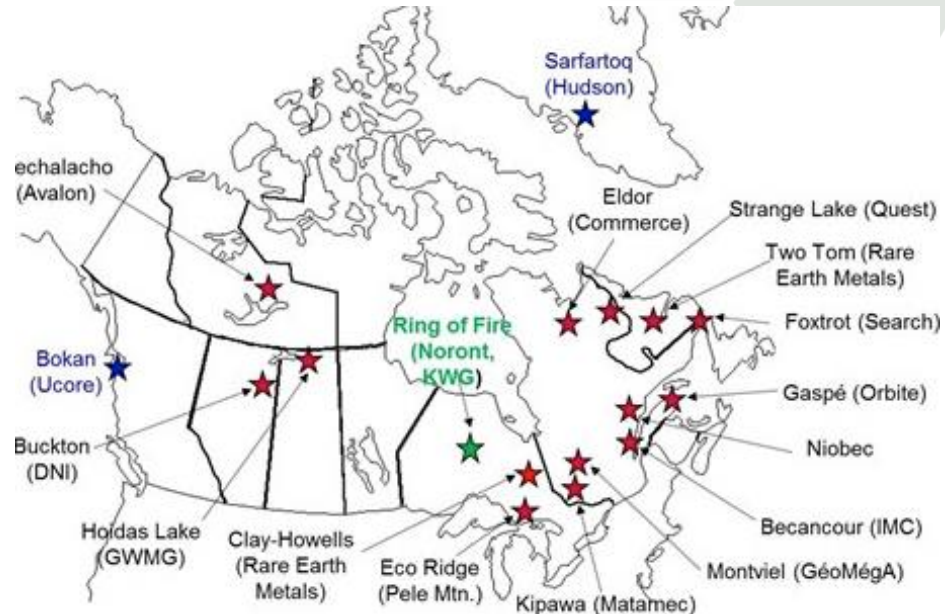
- Nonmetals
- Alkali metals
- Alkaline Earth metals
- Transition elements
- Other metals
- Metalloids
- Halogenes
- Noble gases
- Lanthanides
- Actinides

1. INTRODUCTION: PREVALENCE

- In North America, REE's are primarily found in the western US and throughout Canada.
- Historical lab data shows REEs are found in mining samples, in addition to landfills and industrial wastewater.



Bastnasite



1. INTRODUCTION: APPLICATIONS

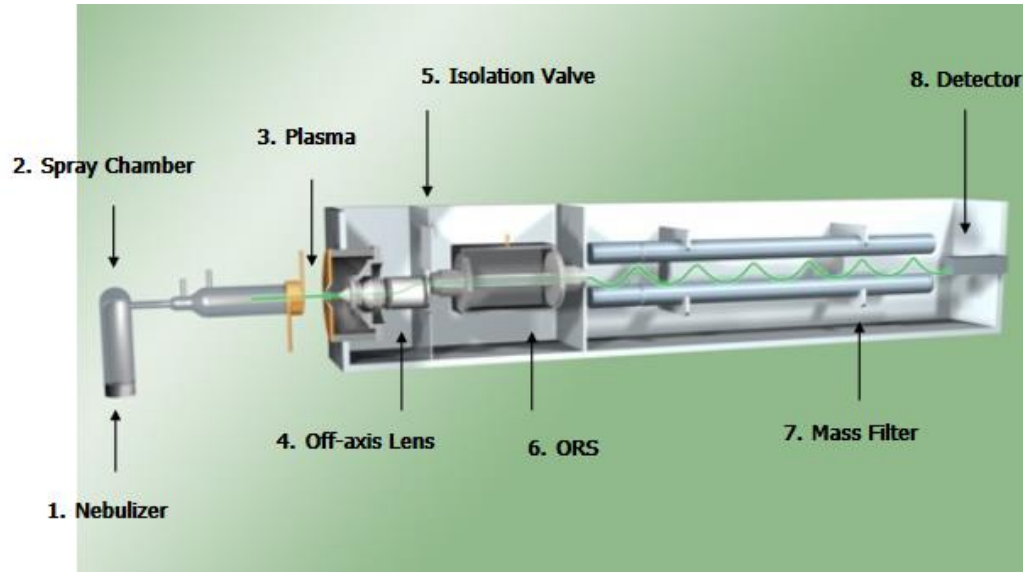
Rare Earth Elements

End Use	Percentage
Metallurgical applications and alloys	29%
Electronics	18%
Chemical catalysts	14%
Rare earth phosphors for computer monitors, lighting, radar, televisions, and X-ray-intensifying film	12%
Automotive catalytic converters	9%
Glass polishing and ceramics	6%
Permanent magnets	5%
Petroleum refining catalysts	4%
Other	3%

Source: US DOI/USGS 2010

2. ANALYTICAL CHALLENGE

ICP-MS is the preferred instrumentation for trace metals analysis in environmental samples for its high throughput and low detection limits (ppt).



Ions are separated based on their mass to charge ratio.

2. ANALYTICAL CHALLENGE

Technology advances have led to a variety of operation modes (ex. He or H₂).

1. Helium Collision mode – considered universal
 - inert so no new interferences form
 - simpler and more consistent in operation
2. Hydrogen Reaction mode – situationally specific benefits
 - substantially better accuracy for metals like Se and As.

Expertise is required to select the right mode to optimize the analysis.

2. ANALYTICAL CHALLENGE

Rare Earth Elements

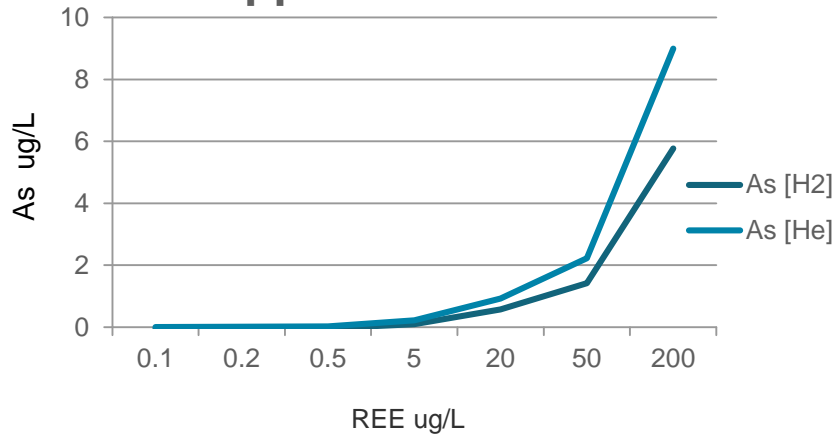
<u>As and Se isotope</u>			<u>Interference</u>
<u>Element</u>	<u>Mass</u>	<u>Abundance (%)</u>	<u>Doubly charged</u>
As	75	100	$^{150}\text{Sm}^{++}$, $^{150}\text{Nd}^{++}$
Se	77	7.63	$^{154}\text{Sm}^{++}$, $^{154}\text{Gd}^{++}$
	78	23.77	$^{156}\text{Gd}^{++}$, $^{156}\text{Dy}^{++}$
	80	49.61	$^{160}\text{Gd}^{++}$, $^{160}\text{Dy}^{++}$,
	82	8.73	$^{164}\text{Dy}^{++}$, $^{164}\text{Er}^{++}$

Doubly charged atoms will give positive bias for arsenic and selenium in the mass spectrum.

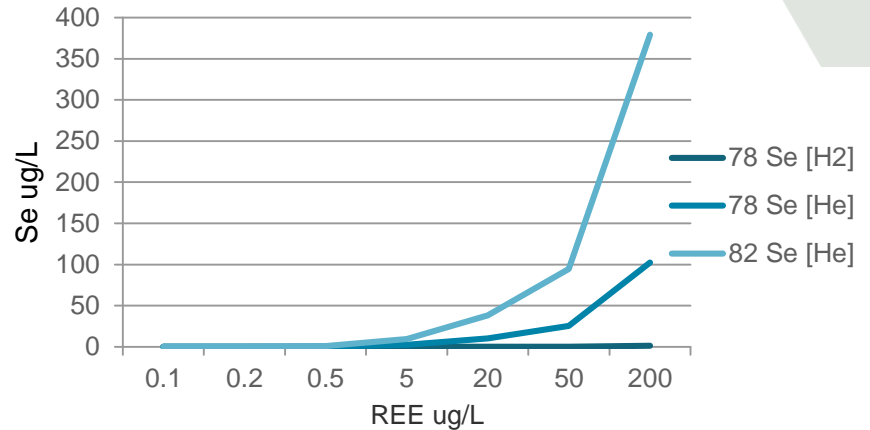
2. ANALYTICAL CHALLENGE

Lab prepared samples of REE standards at varying concentrations.

Apparent Arsenic



Apparent Selenium



Samples analyzed on a Agilent 7900 ICP-MS operating in either helium [He] collision cell or hydrogen [H2] reaction mode.

2. ANALYTICAL CHALLENGE



Summary of Analytical Challenges:

- A detailed understanding of the sample matrix is critical to properly report contaminants of concern.
- It is important to know the specific method used when interpreting historical data.



3. APPLICATION



Water samples collected from a site in BC:

Sample	Selenium [He] (ug/L)	Gd (ug/L)	Dy (ug/L)	Selenium [H2] (ug/L)
1	84.9	159.43	129.86	0.56
2	75.2	143.46	116.86	1
3	88.2	159.62	136.72	1.23
4	74.7	136.72	110.02	0.89
5	78.2	136.27	109.32	1.42

Selenium standard under BC CSR for aquatic water is 20 ug/L .

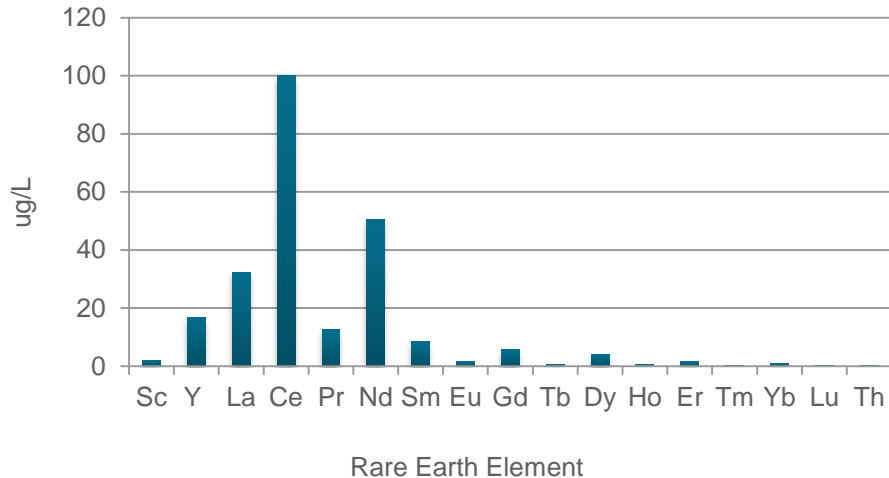
Selenium standard under Alberta Tier 2 for aquatic life is 1 ug/L .

3. APPLICATION



Leachate samples collected from a site in BC:

TCLP



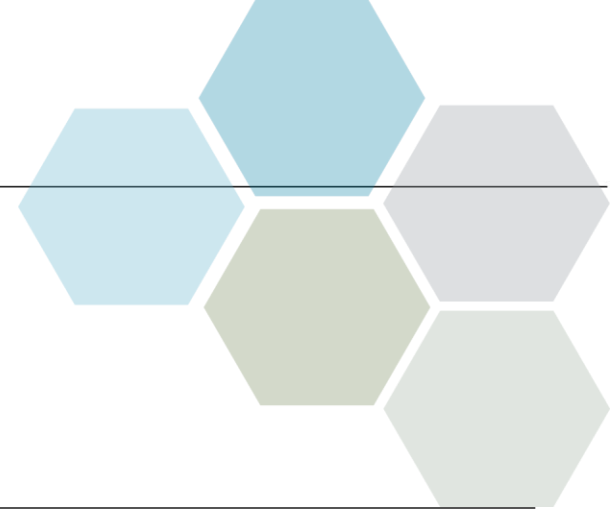
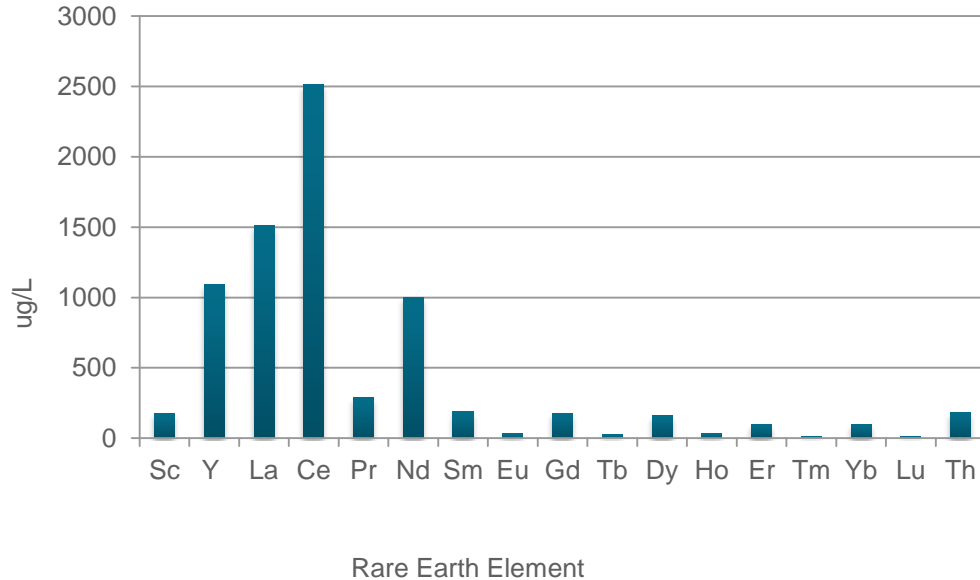
Arsenic [H2] (ug/L)	Nd (ug/L)	Sm (ug/L)	Arsenic [H2] (ug/L) corrected
13.1	50.62	8.54	11.5

CCME guideline for Arsenic in marine water is 12.5 ug/L.

3. APPLICATION

Industrial Process Water:

Organic Extract



Selenium [He] (ug/L)	Gd (ug/L)	Dy (ug/L)	Selenium [H2] (ug/L)
260.5	177.14	160.19	111.5

Organic material is known to accumulate REEs.

3. APPLICATION

Peat & Muskeg:

- High organic content of peat samples as a leading indicator of high levels of REE's
- Analysis as a soil vs a water is a significant factor in determining effect of REE's

Just Add Water And The Peat Pellet Will Expand To This Size 



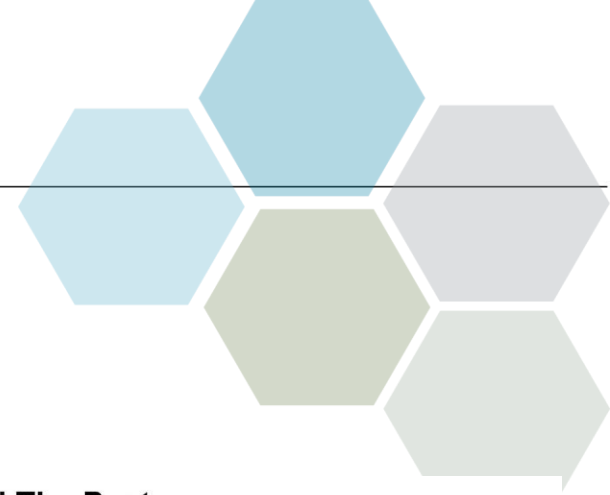
36 mm



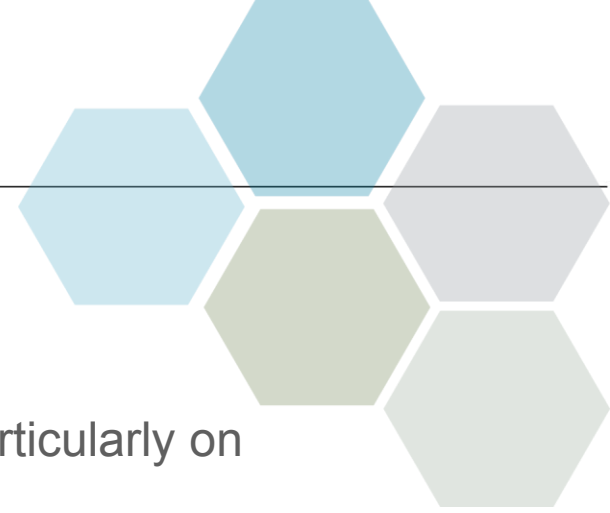
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3. APPLICATION



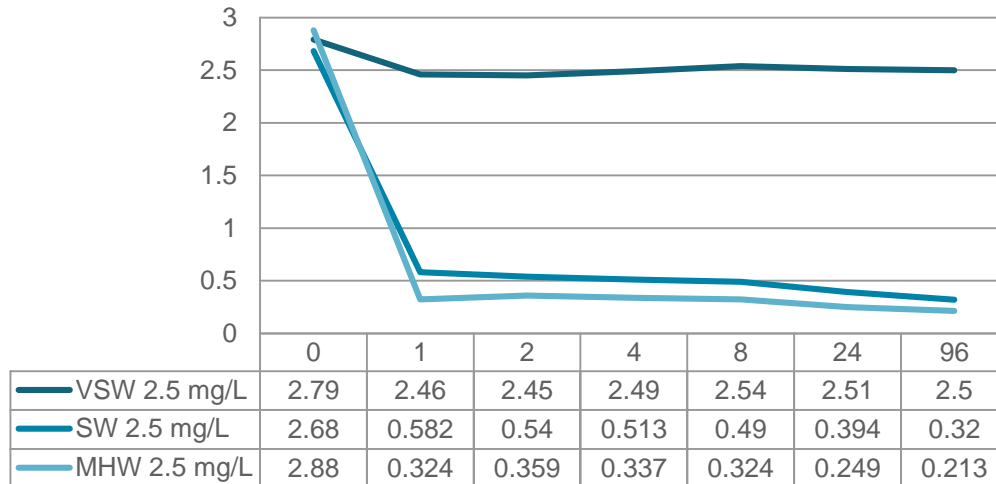
Summary of Applications:

- REE's can occur in water samples as well as soil, particularly on active mining sites
- High organic content materials have been shown to accumulate REEs
- Indications that further investigation into peat and muskeg matrix types would be valuable

4. SOLUBILITY

REEs will typically oxidize to form metal oxides in water which show limited solubility.

Dissolved Nd Conc. vs time (hr)



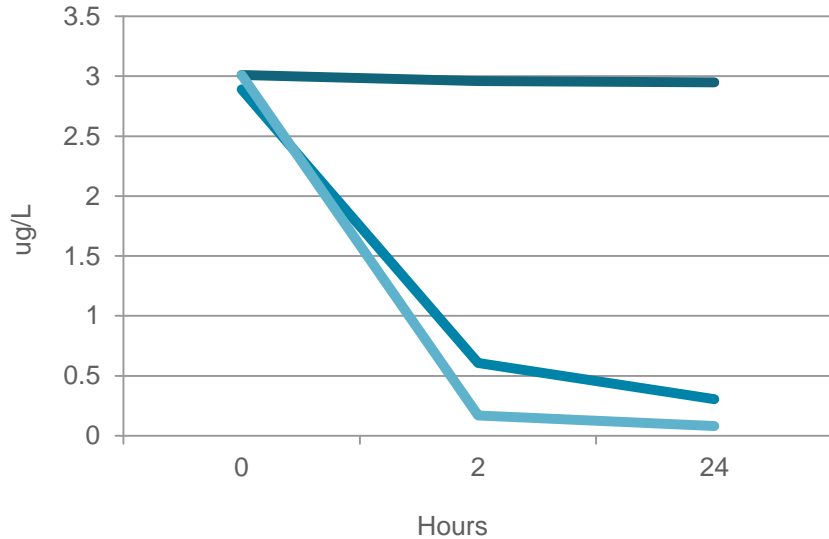
Very soft water

Soft water

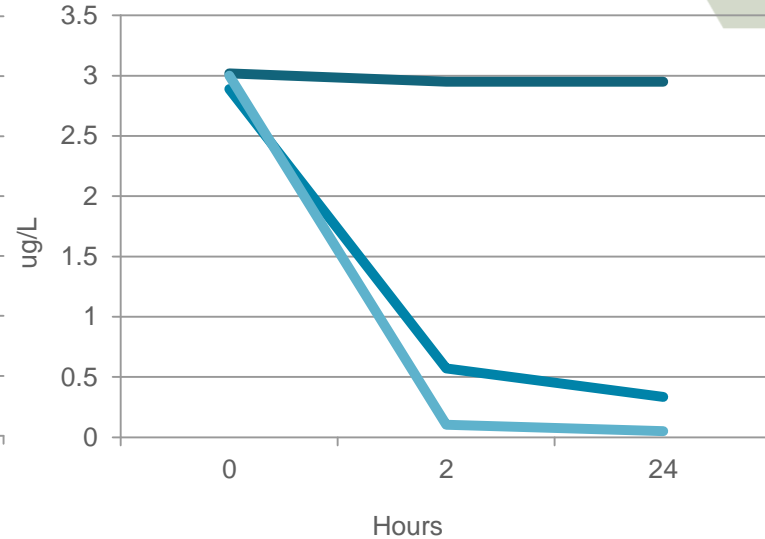
Moderately hard water

4. SOLUBILITY

Cerium Conc. Vs. Time



Lanthanum Conc. Vs. Time



- VSW
- SW
- MHW

Yttrium shows good solubility across all 3 water types.

4. SOLUBILITY



Solubility Takeaways:

- Limited solubility has a direct effect on bioavailability/toxicity.
- It is important to take into consideration the hardness of the water when considering potential REE solubility and resulting impact on analytical data.
- Further study is underway to look at the potential toxicity of these elements.

4. SOLUBILITY & REMEDIATION

Given their solubility properties, filtration systems will provide good results for the reduction of REE concentrations.

Increasing pH also decreases solubility through the formation of metal hydroxides.

Although, recovery may be the better strategy...



4. SOLUBILITY & RECOVERY

From the organic material shown previously:

Metal	Concentration (mg/L)	Value (\$/kg)	\$/1000 m3
La	1.510	7	\$10.57
Ce	2.510	7	\$17.57
Pr	0.289	85	\$24.57
Nd	0.995	60	\$59.70
Sm	0.186	7	\$1.30
Eu	0.029	200	\$5.80
Gd	0.177	55	\$9.74
Tb	0.023	550	\$12.65
Dy	0.160	350	\$56.00
Er	0.099	95	\$9.41

Scanning water samples for routine monitoring can be a good indicator of possible REE containing minerals.

U.S. Department of Energy recently announced \$17.4 million for REE recovery systems.

5. CONCLUSIONS

- Rare earth elements will become increasingly relevant as they become a bigger component of commercial products.
- The impact of rare earth elements on standard metal analysis must be considered when looking at historical data.
- Understanding solubility in different water types indicates the potential bioavailability and opportunities for recovery of REEs.
- When looking at any data it's important to consider interference effects in the decision making process, call the lab!





ACKNOWLEDGEMENTS

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Nautilus Environmental.



EMAof**BC**

Environmental Managers Association
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