Potential Role of Nitrate in the Release and Attenuation of Selenium in Coal-Mine Environments

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MEND / NEDEM

Outline

- Background
- Objectives and Approach
- Nitrate “*the oxidant*”
- Nitrate “*the inhibitor*”
- Results
- Conclusions

Background

- There is evidence to suggest that NO_3 can potentially affect both the remobilization and attenuation of Se within waste rock environments:
  - Lab-based studies have demonstrated that NO_3 can effectively oxidize reduced Se in shale materials.
  - In agricultural settings, the oxidation of Se and pyrite has been shown to occur via denitrification (NO_3 as an oxidant).
  - In various laboratory and field settings (e.g., wetlands), selenate reduction has been shown to be inhibited by the presence of NO_3.

Background

- Active coal mine settings are nitrogen rich!
- The abundance of NO_3 relates to the leaching of residual blasting residues associated with the use of nitrogen-based explosives (e.g., ANFO).
- NO_3-N concentrations in the range of 10-100 mg/L are common in waste rock seepage.

Objectives

- Assess the potential links between explosive-derived nitrogen compounds with the remobilization and attenuation of Se in coal mine waste environments.

- Analysis has relevance with respect to several aspects of Se management, including:
    1) Source control (prevention);
    3) Environmental protection; and
    4) Treatment (passive and active).

Approach

- Literature review
- Compilation of data for coal mines in Western Canada.
  - Water quality data (seeps, sediment ponds).
  - Explosives information (powder factor, explosives type)
  - Mine waste materials information (volumes, age, geology, static test data, *etc*.)
- Analysis:
  - Relationships between Se, SO_4 and NO_3

Distinguishing O_2 versus NO_3^- Oxidation Mechanisms = Not Easy

- Contrasting sources: atmosphere *versus* blasting residues.
- Reaction products (SO_4, Ca, Mg, HCO_3, Se): largely the same.
- Non-conservative behaviour of oxidants and reaction products (e.g., gypsum precip. and N_2 degassing)
- Potential for "correlative artifacts"
  - i.e., We would expect to see positive correlations of NO_3 and Se irrespective of the role of NO_3, as both are highly soluble and flushed from waste rock surfaces.

Nitrate "The Oxidizer"

- Nitrate can take the place of oxygen in the oxidation of reduced sulphur and selenium species.

Pyrite Oxidation:

$$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 5Fe^{2+} + 10SO_4^{2-} + 7N_2 + 2H_2O$$

Selenide Oxidation:

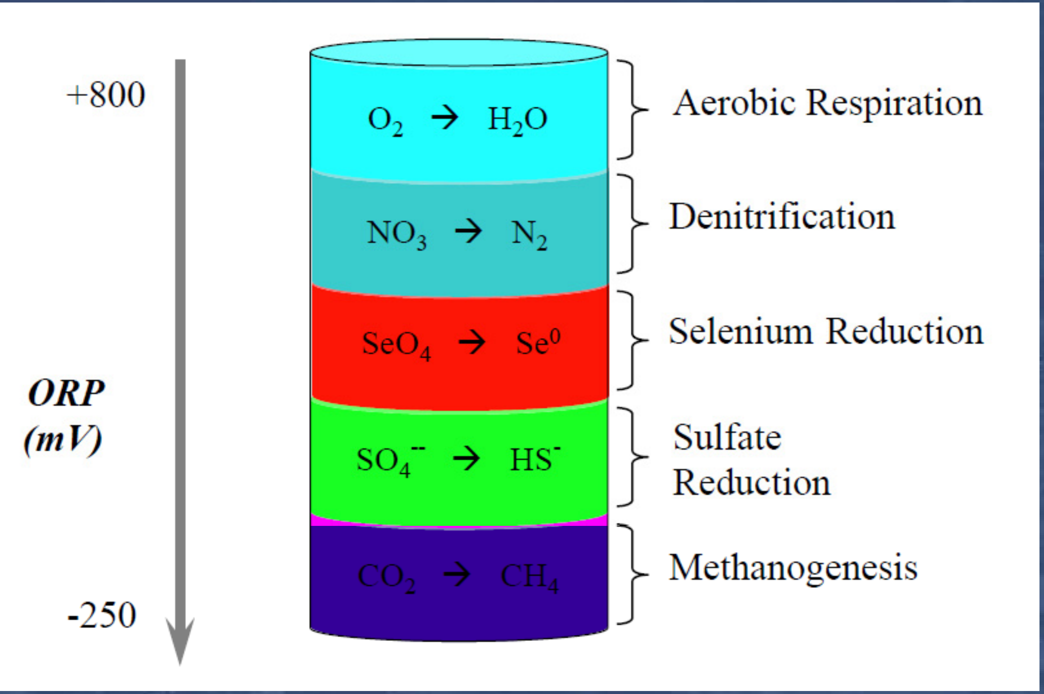
$$5FeSe_2 + 14NO_3^- + 4H^+ \rightarrow 5Fe^{2+} + 10SeO_4^{2-} + 7N_2 + 2H_2O$$

Nitrate "The Oxidizer"

- Although oxygen is a thermodynamically more favorable electron acceptor, NO_3 is second to oxygen in free energy yield.
- NO_3 is also much more soluble than oxygen.
  - Saturation of dissolved O_2= <15 mg/L
  - NO_3 concentrations in coal mine drainage typically ranges from 10 to 50 mg/L, and can exceed 100 mg/L.

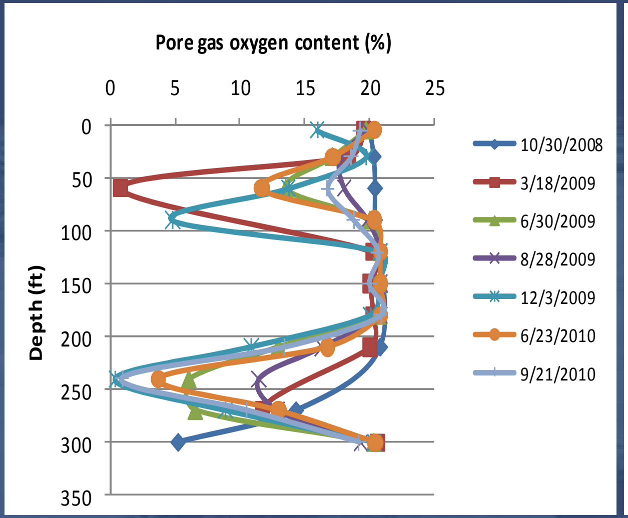
Nitrate "The Inhibitor"

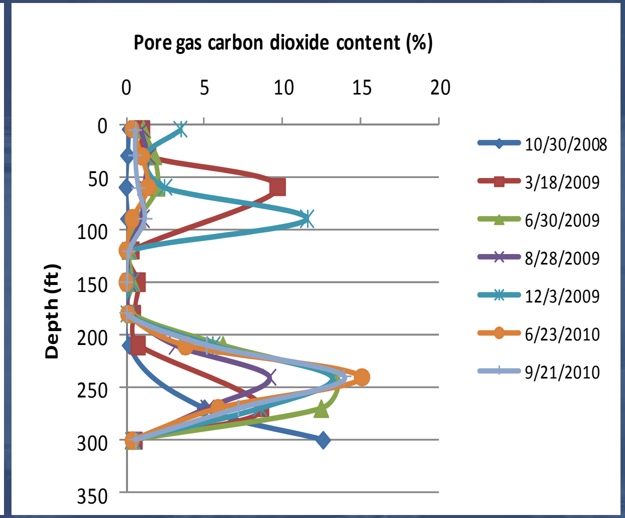
- Selenium reduction inhibited by NO_3
- Accordingly, NO_3 removal (denitrification) is required for effective Se attenuation
- Applies to passive bioremediation or active treatment.
- Potential for Se attenuation is implicitly linked to NO_3.



Conceptual Model for Nitrate

- The importance of NO_3 arises under oxygen limited conditions
  - Potential oxidant of reduced Se (e.g., selenide) and sulfur,
  - Limit attenuation of dissolved Se by inhibiting SeO_4 reduction.
- At macro-scale, suboxic conditions can develop naturally within localized areas in the interior of waste rock dumps.





Reproduced from SRK (2010)

Database Overview

- Dataset:
  - 9 coal mines in western Canada
  - Three geologic formations
  - Similar Se abundance in coal seams

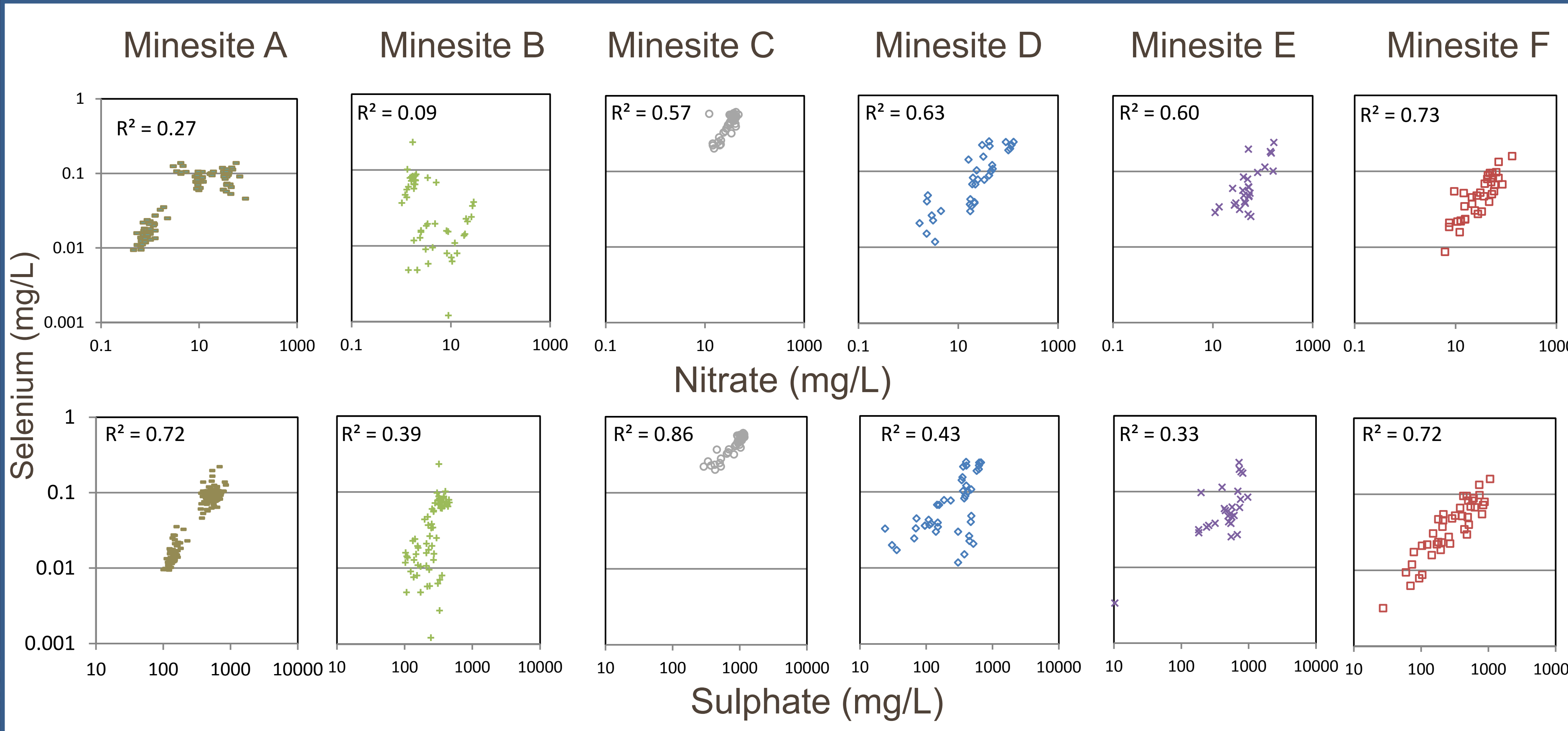
Coal Bearing Formation	Age	Mean Se in coal
Misty Mt. Fm.	Lower Cretaceous	1.6 ppm
Gates Fm.	Jur/Cret	1.5 ppm
Gething Fm.	Jur/Cret	1.4 ppm

Database – Water Types

Sample Type	Number of Sites	Number of D-Se samples
Background surface waters	34	747
Receiving Watercourses	57	1102
Groundwater	48	348
Settling Ponds	18	969
Seeps	26	402
Other	18	254
Total	196	3822

- Focus of analysis is settling ponds and seeps.

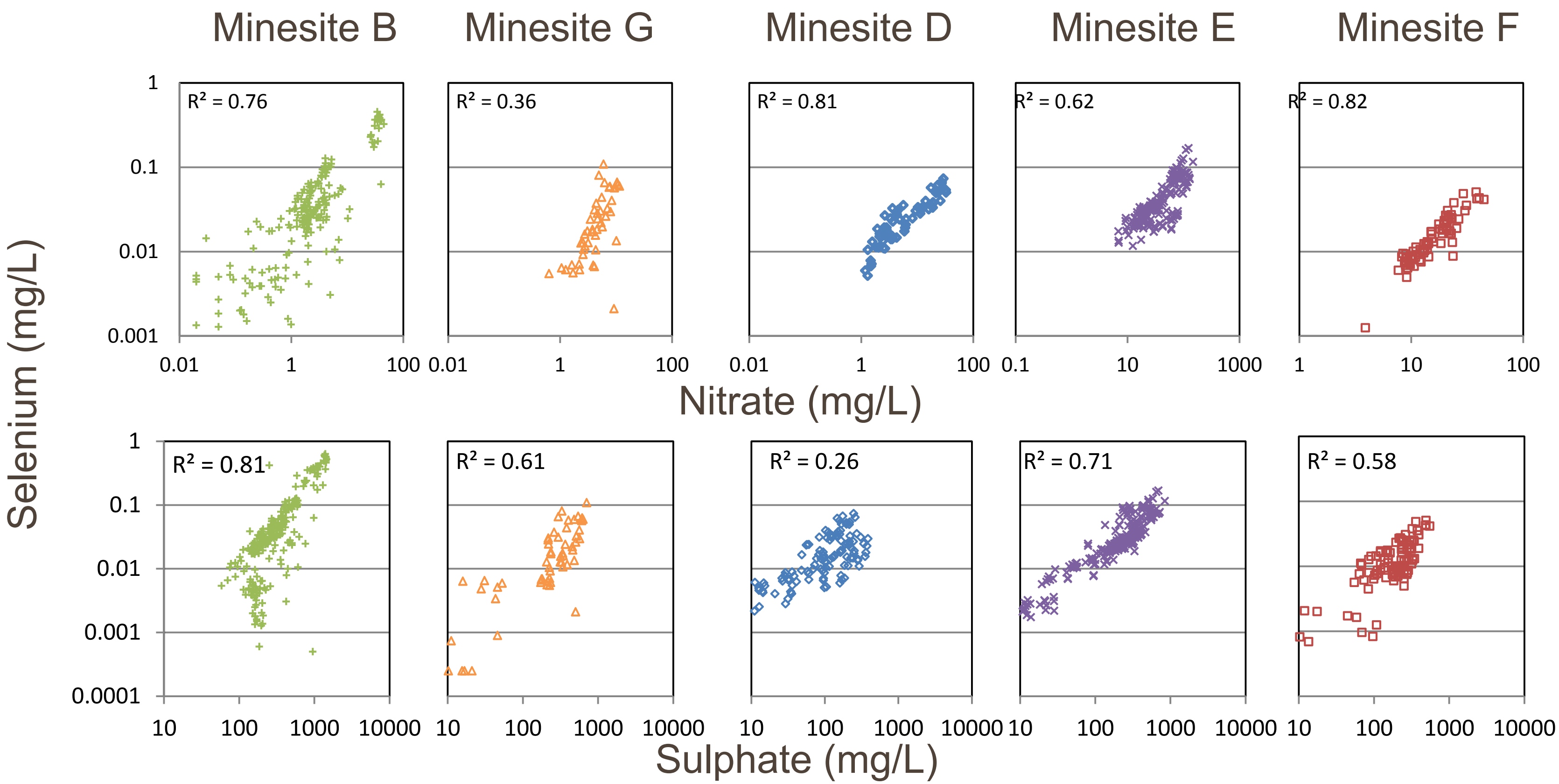
Results – Correlations in Seep Data



	Minesite A	Minesite B	Minesite C	Minesite D	Minesite E	Minesite F
Se/NO_3 R^2	0.27	0.09	0.57	**0.63**	**0.60**	**0.73**
Se/SO_4 R^2	**0.72**	**0.39**	**0.86**	0.43	0.33	**0.72**

- Selenium correlates with NO_3 and SO_4 more closely than with any other parameters in the database.

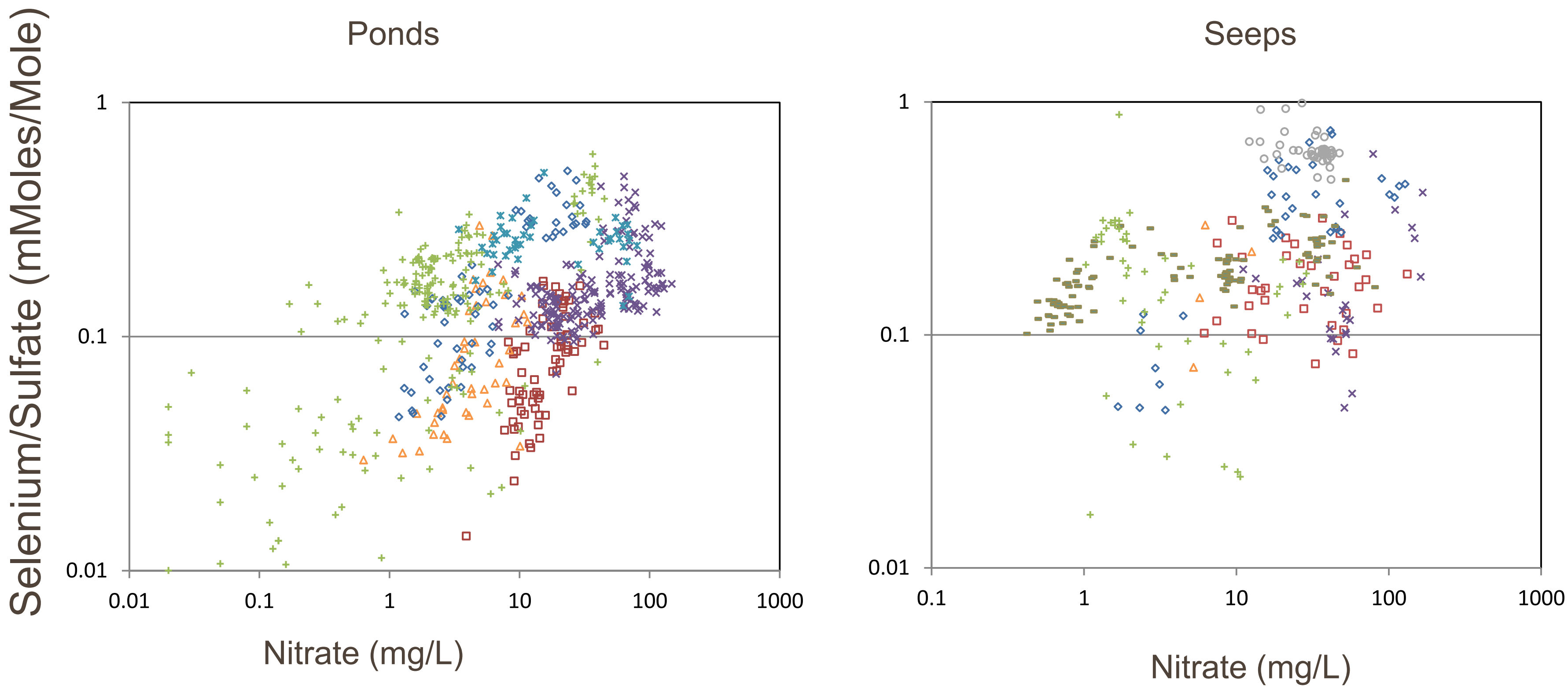
Results – Correlations in Sediment Ponds



	Minesite B	Minesite G	Minesite D	Minesite E	Minesite F
NO_3 R^2	**0.76**	0.36	**0.81**	**0.62**	**0.82**
SO_4 R^2	**0.81**	**0.61**	0.26	**0.71**	0.58

- Selenium generally occurs as a replacement for S.
- The reason for the strong correlation between NO_3 and Se is less clear.

Results – Nitrogen as an Oxidant?

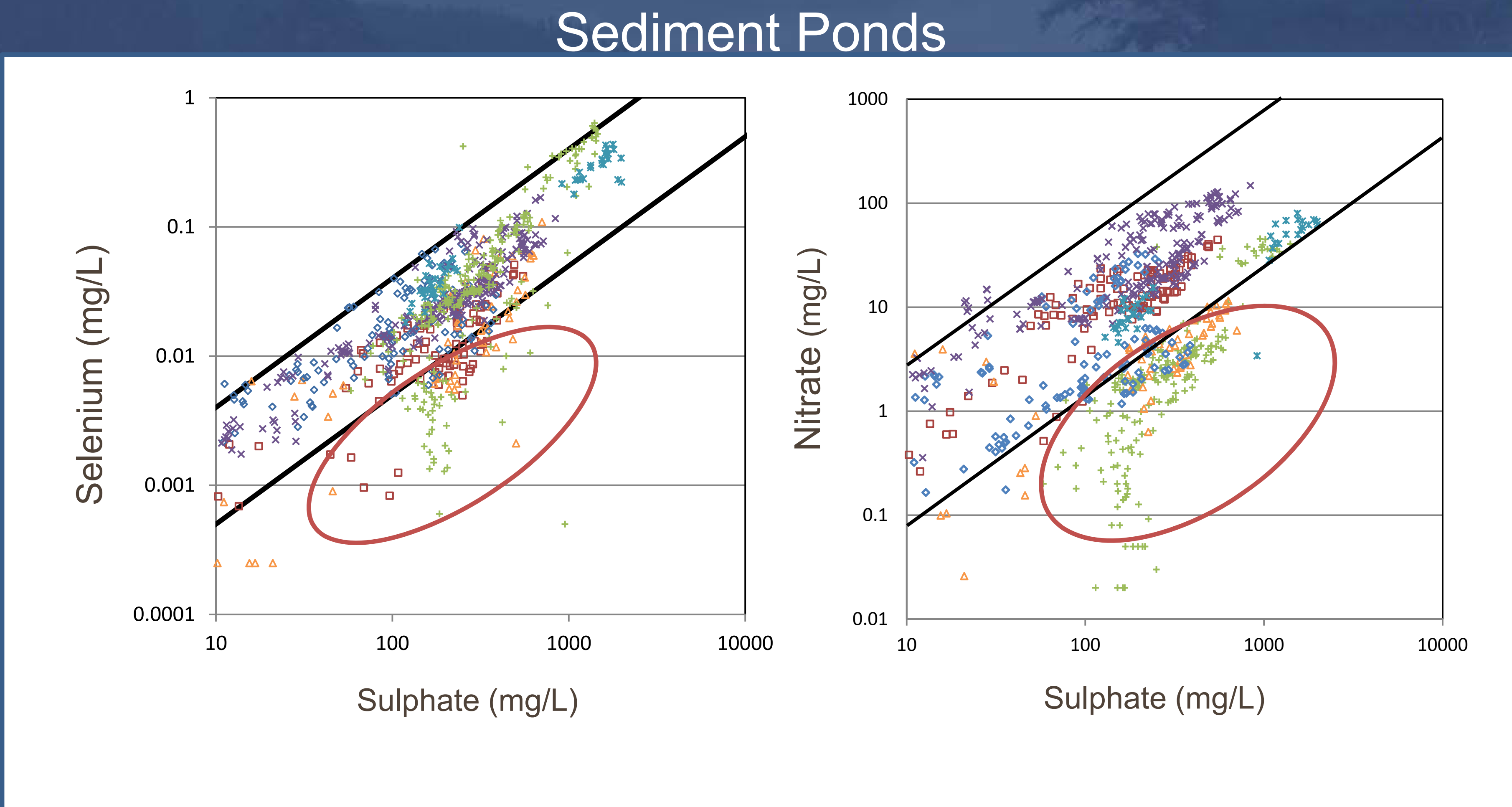


- Seeps and Ponds with higher NO_3 values tend to have higher ratios of selenium to sulfate.
- This result suggests that high NO_3 concentrations may promote elevated levels of selenium in coal mine drainages.
- This may relate to either the ability of NO_3 to promote selenium solubility, or the ability of NO_3 to actively oxidize reduced forms of Se.

Results – Correlation Summary

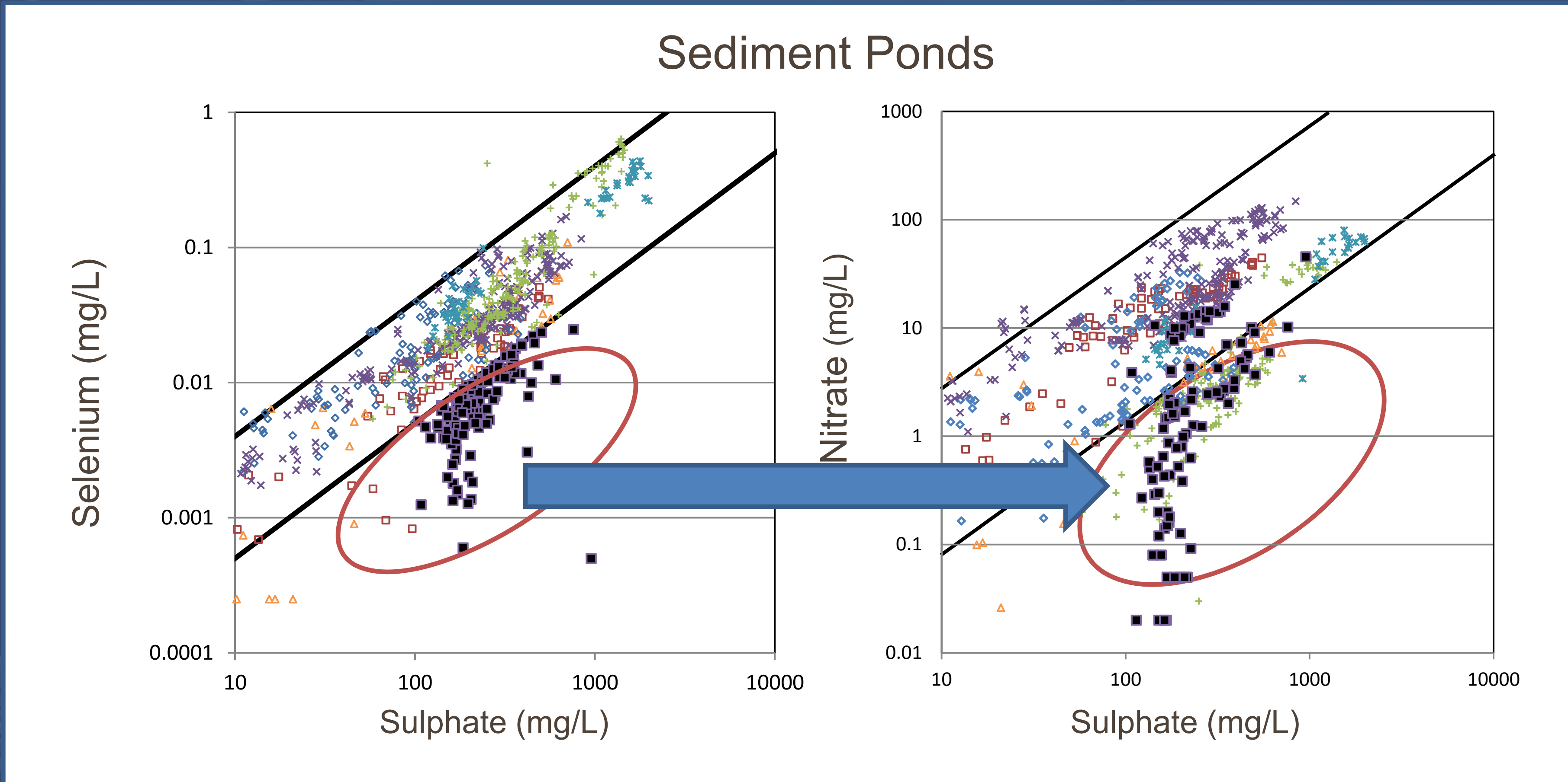
- Selenium correlates with NO_3 and SO_4 more closely than with any other major ion (Ca, Mg, HCO_3^-) or trace metal.
- The correlation between SO_4 and Se is expected, as Se typically occurs as a replacement for S (e.g. pyrite).
- The fact that the correlation of Se with NO_3 is similar in magnitude to the correlation with SO_4 suggests that it represents more than a coincidental relationship (*i.e.*, not just an auto correlative effect).
- In general, higher Se:SO_4 ratios are observed at higher NO_3 concentrations. This may potentially be related to NO_3 as an oxidant of solid phase Se, or its ability to inhibit Se attenuation.

Results – Nitrate the "Inhibitor" (Sed Ponds)



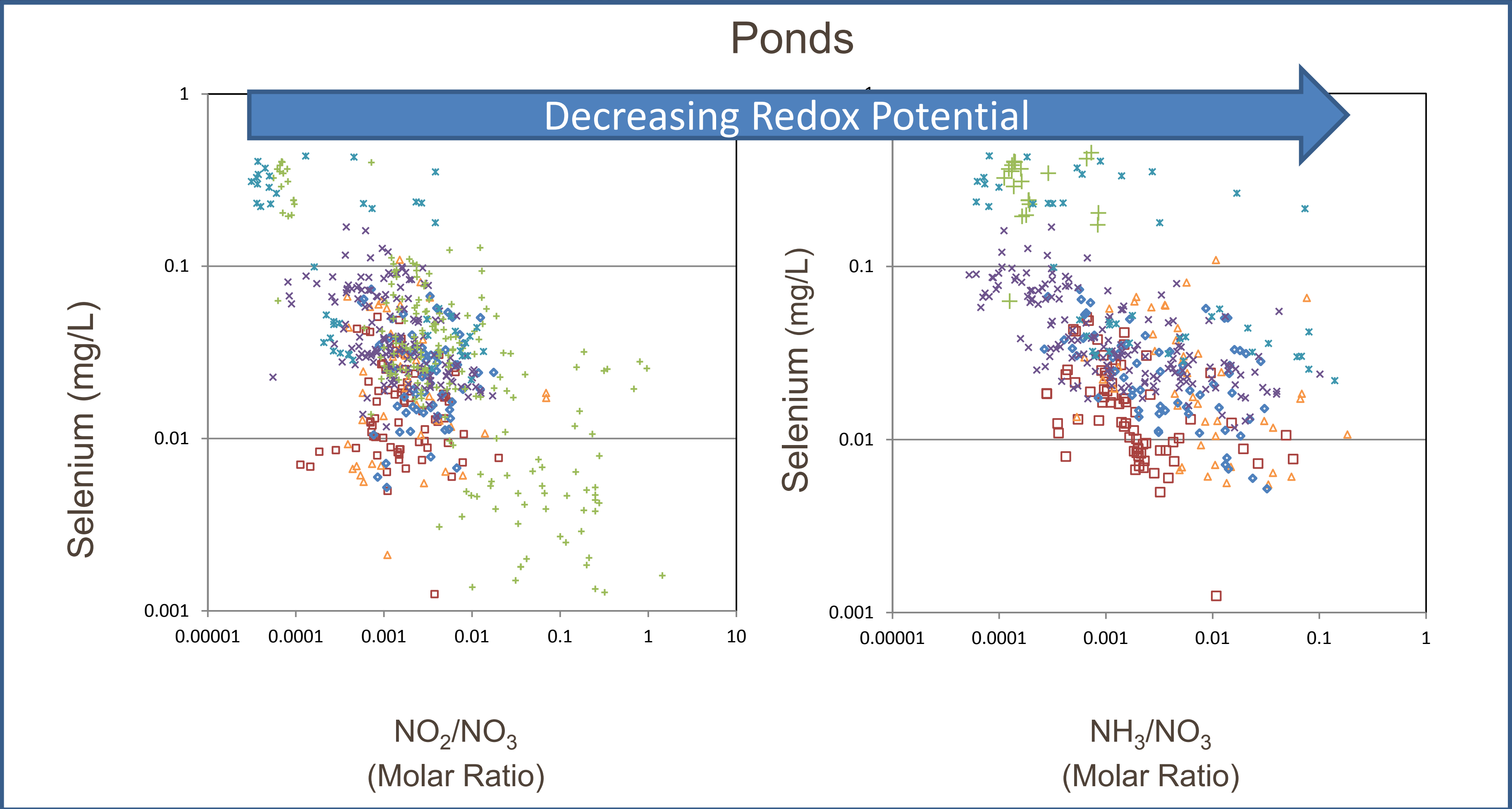
- A number of deviations from the linear relationship between sulfate and selenium are evident.
- The same sample group that deviates from the Se/SO_4 linear relationship also deviates from the NO_3/SO_4 linear relationship.

Results – Nitrate the "Inhibitor" (Sed Ponds)



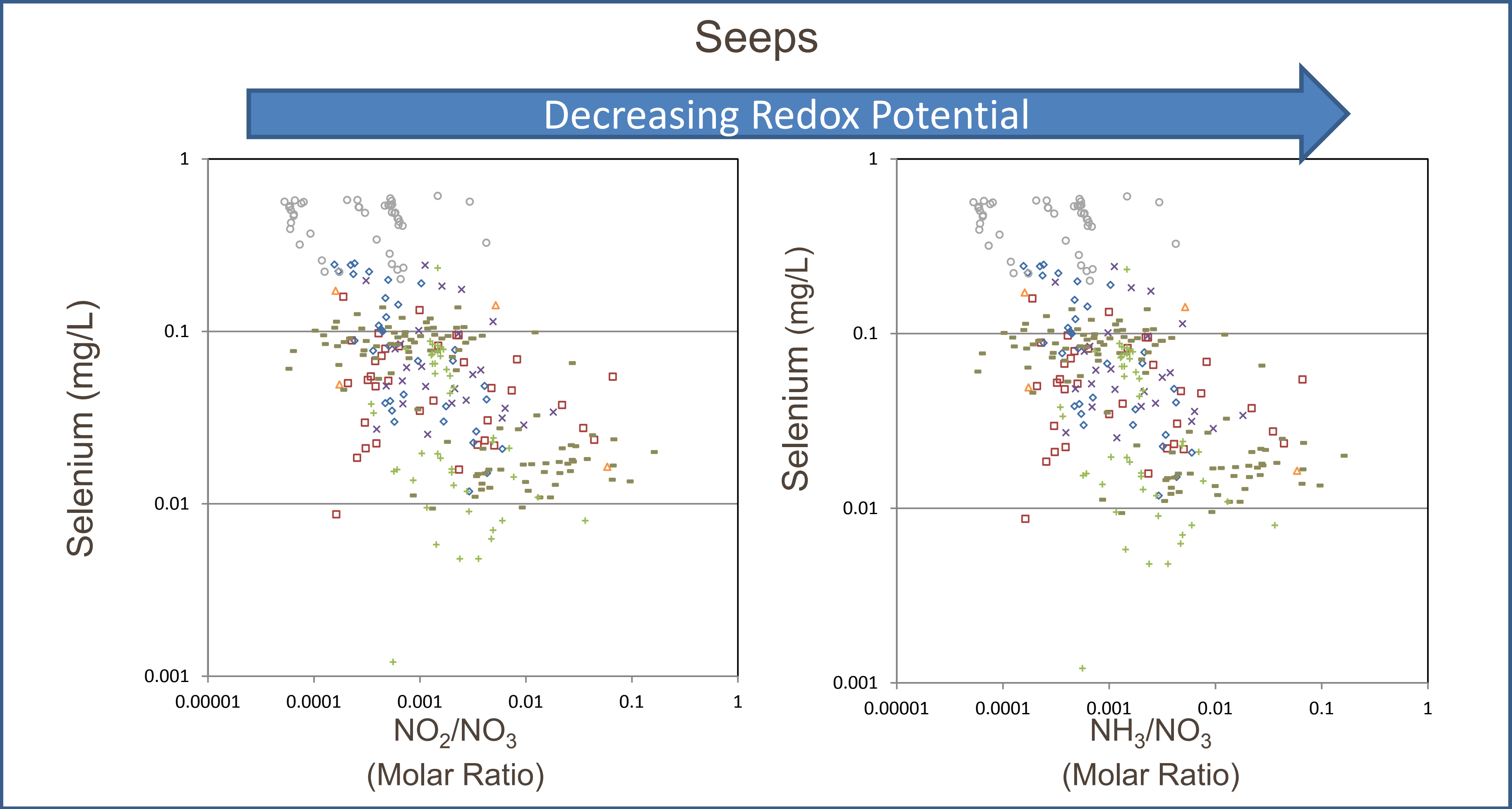
- Selenium has a linear relationship with sulphate while NO_3 is abundant. In low NO_3 systems, lower levels of selenium are observed when compared to sulphate.
- Lab-based studies show that selenate reduction is inhibited when concentrations of NO_3 are greater than 1 to 5 mg/L.

Results – Nitrate the "Inhibitor": Nitrogen Speciation (Sed Ponds)



- Nitrogen redox couples provide an indication of the redox potential of mine drainage.
- When reduced nitrogen species become even slightly prevalent, selenium concentrations decline.

Results – Nitrate the “Inhibitor”: Nitrogen Speciation (Seeps)



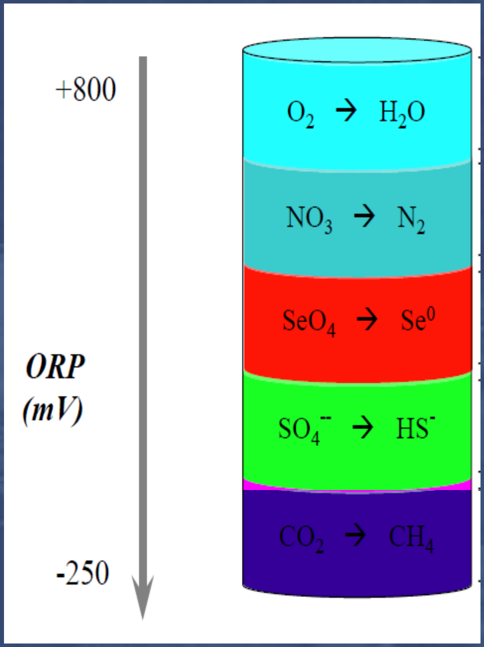
- A similar result is seen in seeps and rock drains.
- Provides evidence that Se attenuation is occurring in mildly suboxic settings.

Conclusions

- Explosive use is directly linked to NO_3 abundance in mine waste.
- SO_4, NO_3 and Se typically show linear correlations in mine waste drainages. The linear relationship between SO_4 and Se breaks down in systems with low NO_3. In these low NO_3 systems, Se concentrations are relatively low compared to SO_4. This may be due to suboxic conditions forming in the interior of the dumps, attenuating both NO_3 and selenium.
- Se release is sensitive to the speciation of nitrogen, which reflects redox conditions in waste environments. When reduced nitrogen species become even slightly prevalent, Se concentrations are generally low. This suggests that Se release is inhibited by mildly reducing conditions that can develop in waste rock environments.
- There is some evidence for NO_3 as a potential oxidant of Se. However, the relative importance of this mechanism is still uncertain.

Conclusions cont.

- There is a body of evidence to indicate that NO_3 enhances Se release from coal waste environments.
- Managing explosive use to minimize N abundance in mine waste should be considered an aspect of water management planning not only for NO_3 control, but also for Se management.
- The management of NO_3 has direct relevance to the costing of both active and passive treatment systems for Se.
- Take home message: to effectively manage Se you have to manage NO_3.



Thank you! Questions?

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