Passive Treatment Systems for the Removal of Selenium: Selenium Removal Mechanisms with Biochemical Reactor Substrate

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CH2MHILL®

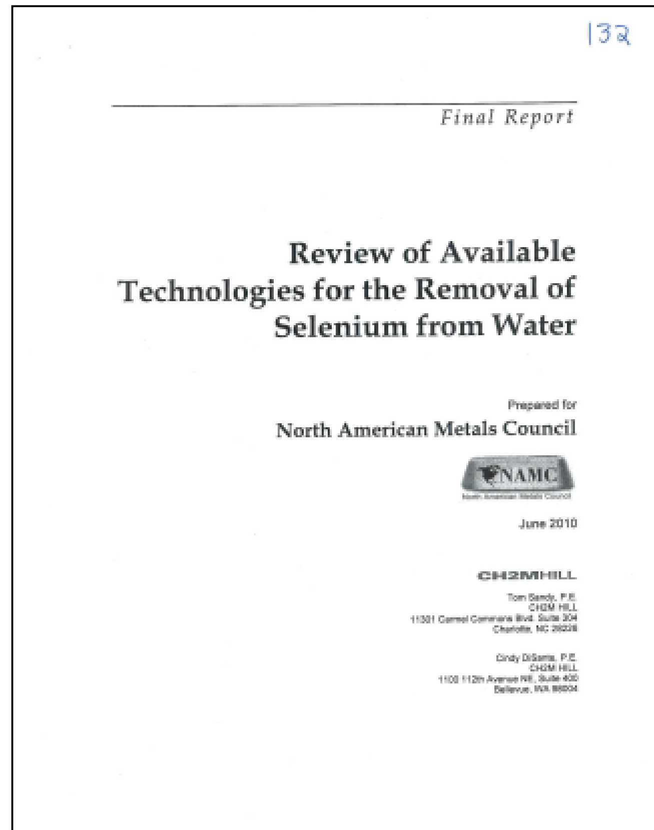
June 3 2013

Overview of Presentation

Outline

- Barrel-Study Overview
- Aqueous Results
- Volumetric/Aerial Loading Rates
- Substrate Se Removal
- Volatilization
- Substrate Se Speciation
- Modeling Calibration/Removal Rate Development
- Secondary Parameters
- Conclusions

NAMC Selenium Report 2010



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Final Report

Review of Available Technologies for the Removal of Selenium from Water

Prepared for

North American Metals Council

NAMC

June 2010

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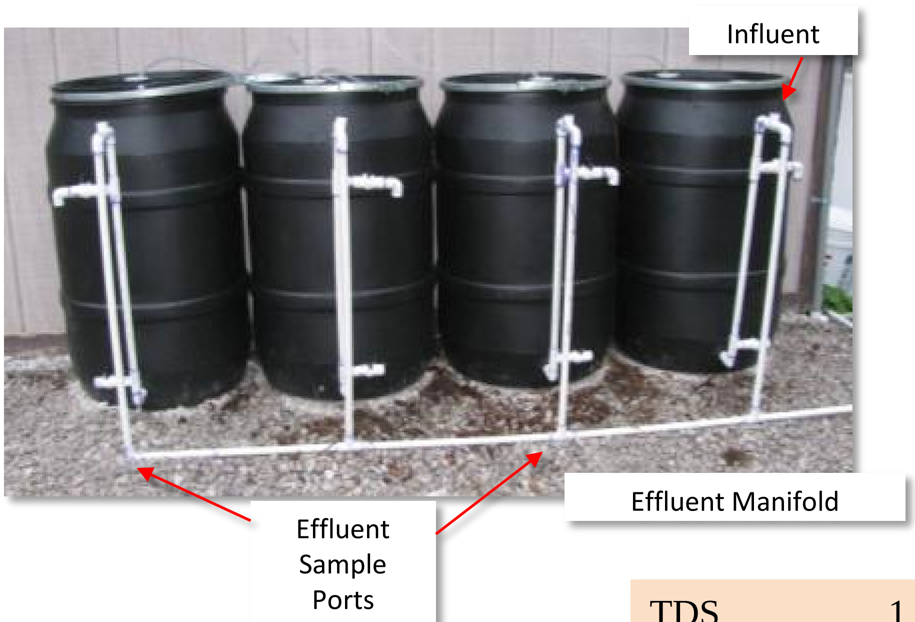
http://www.namc.org/docs/00062756.PDF

Case History (2011-2012)
Two Concurrent BCR Pilot Studies for Coal Mine Drainage

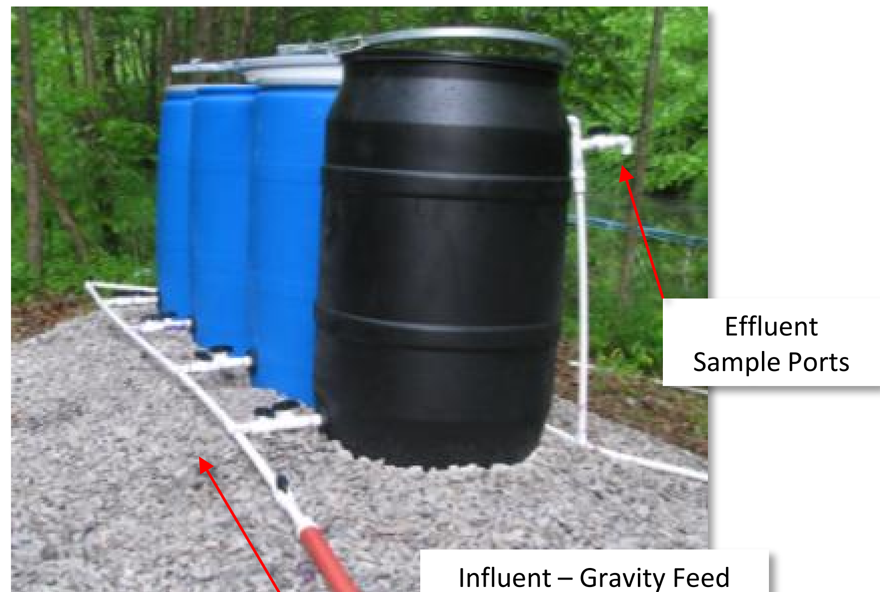
Outlet A: 389 days

Pumped Inflow



Outlet B: 180 days

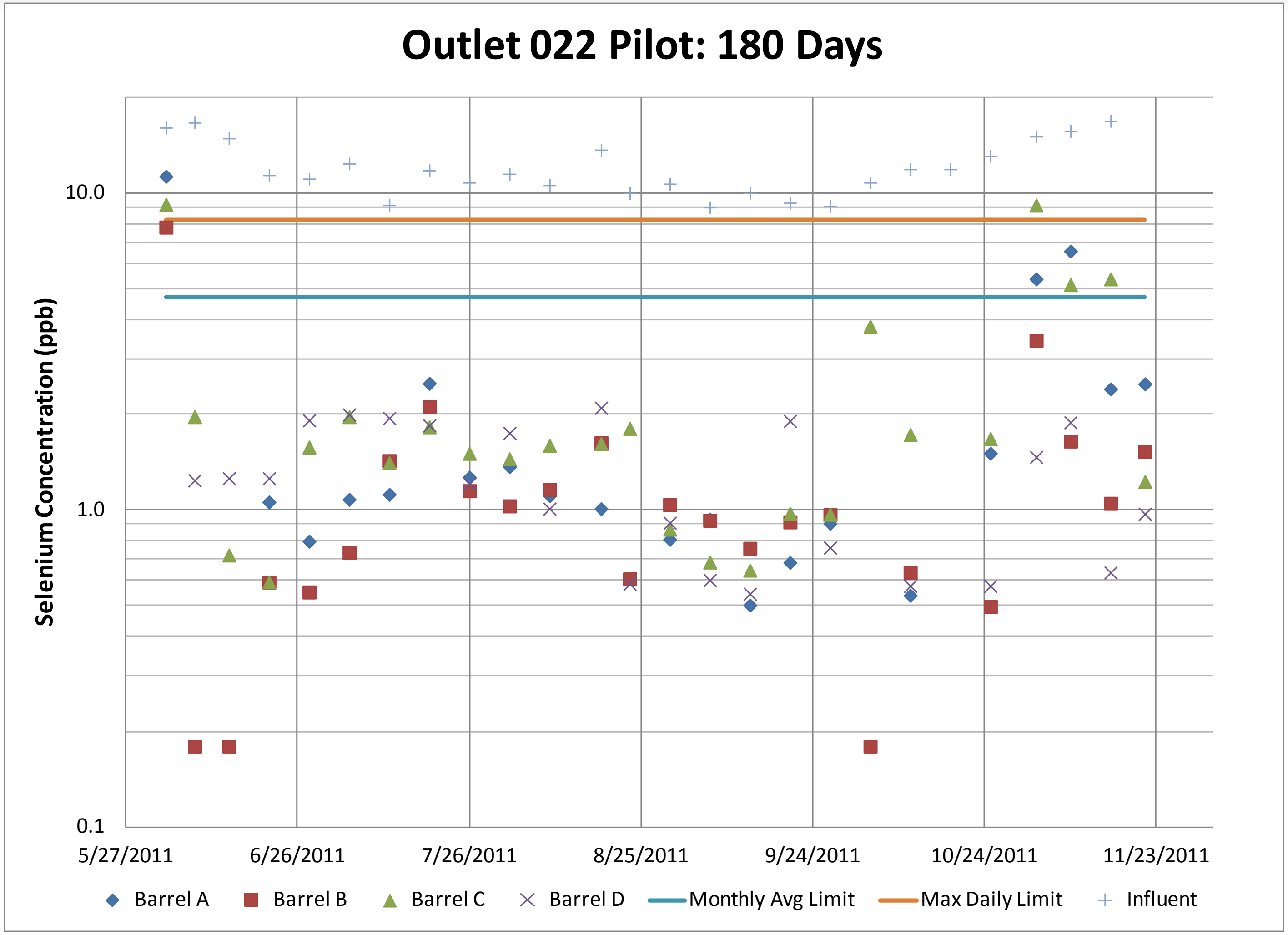
Gravity Inflow



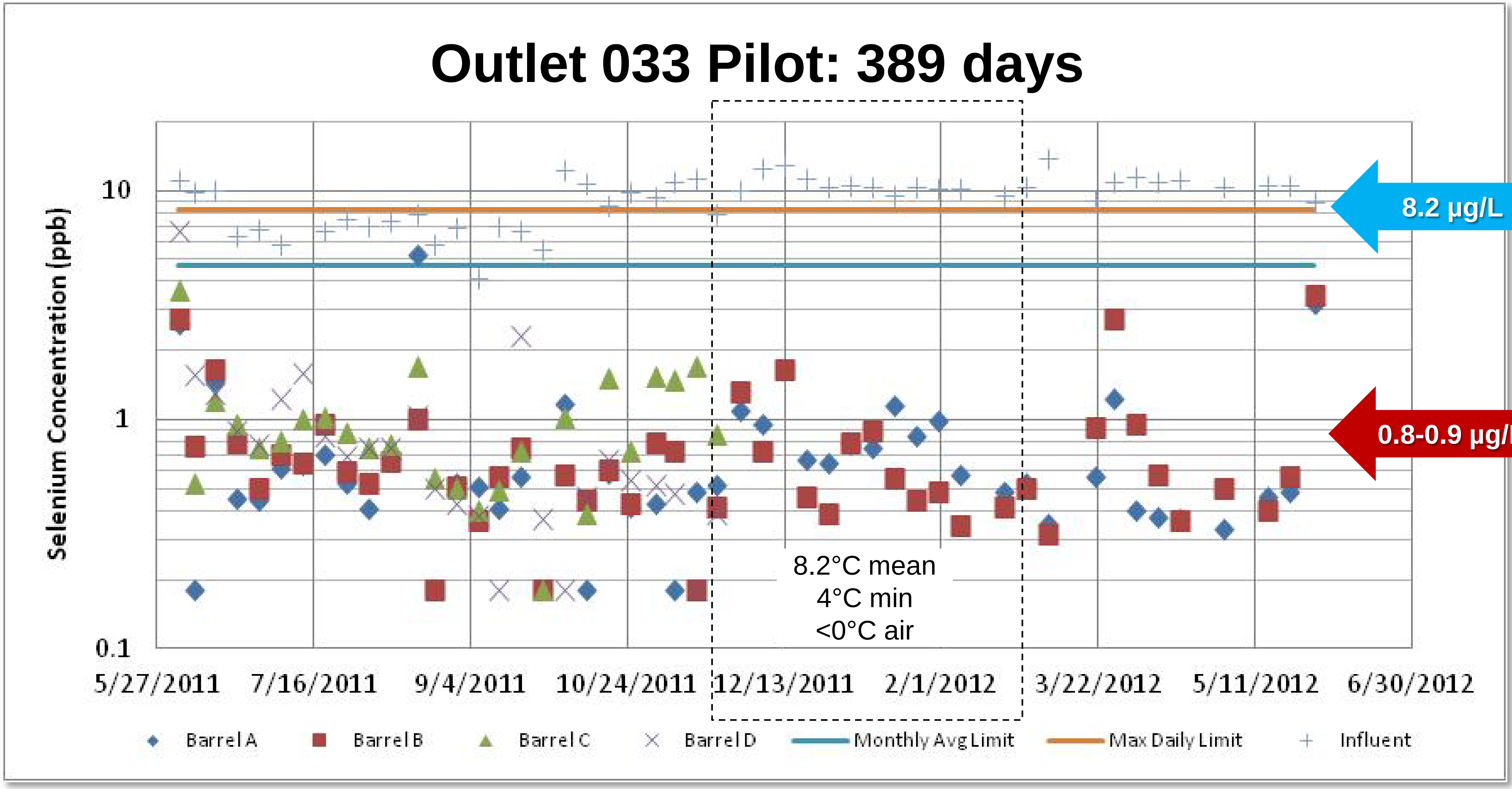
TDS	1	g/L
Se in	6–17	µg/L
NO3-N	0.47	mg/L
TP	0.071	mg/L

Source:
R. Thomas (2011)

Outlet 022: Variable Flow and Limited Flow Control Resulting in Variable Se Reduction

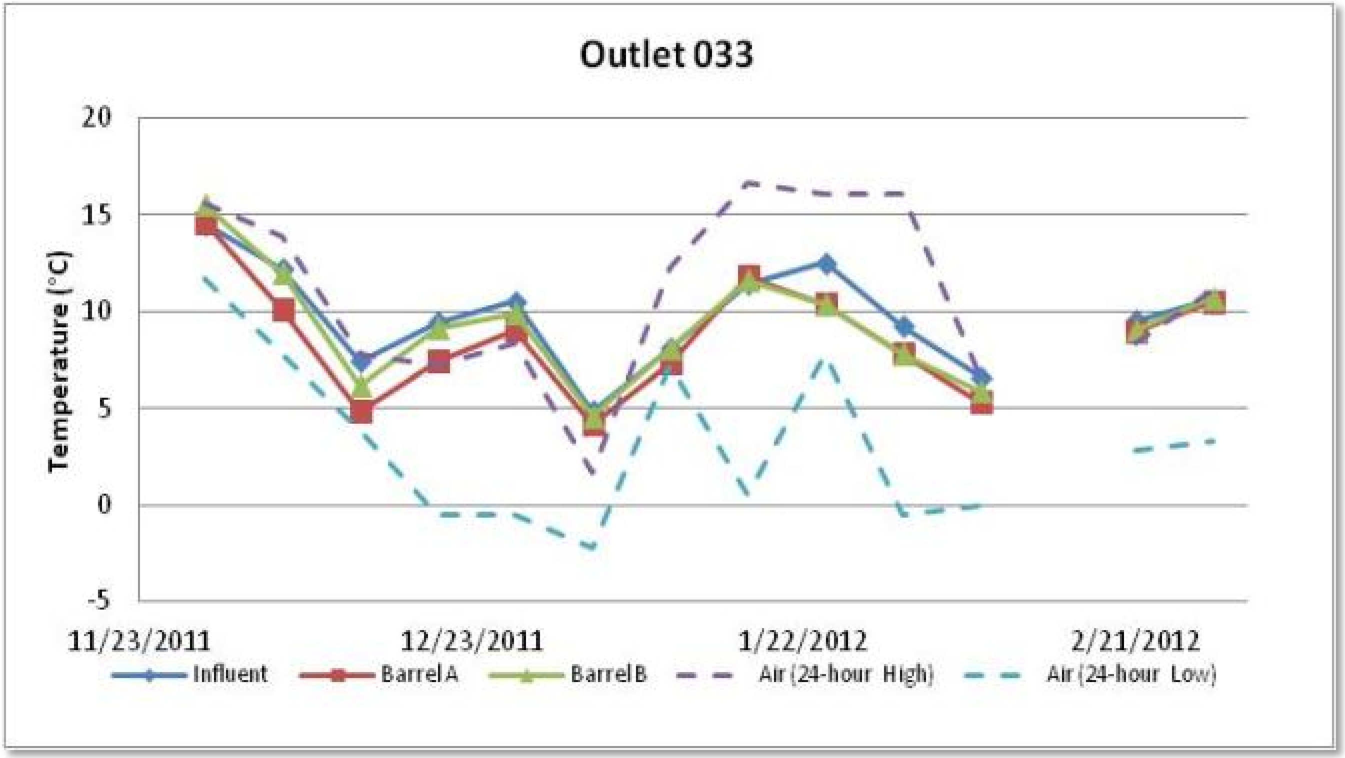


Outlet 033: Consistent Se Reduction Through Winter



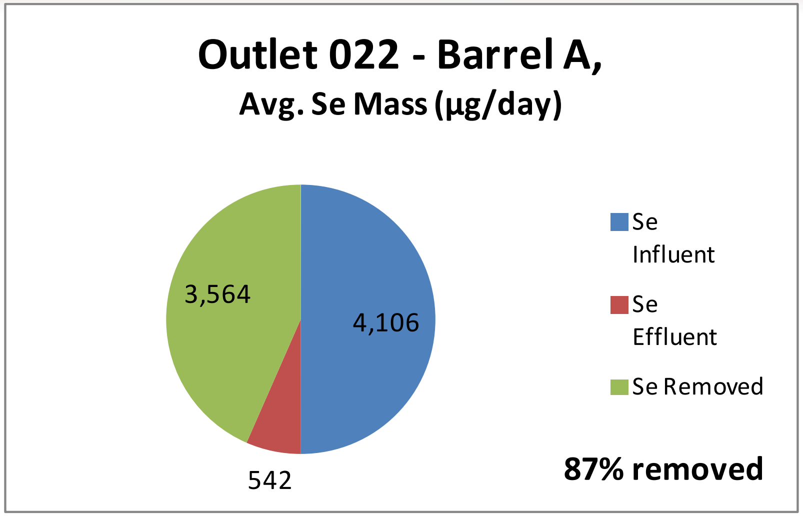
Source:
CH2MHILL (2012)

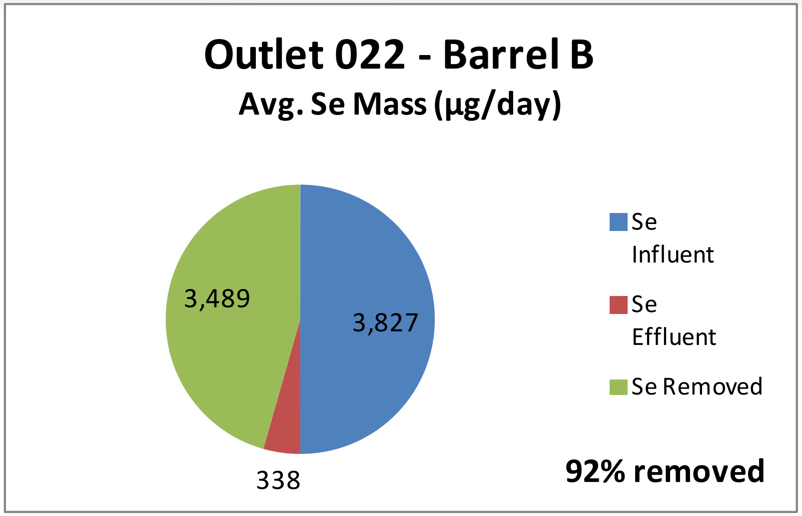
Focus on Winter
Water Minimum Temperature 4°C

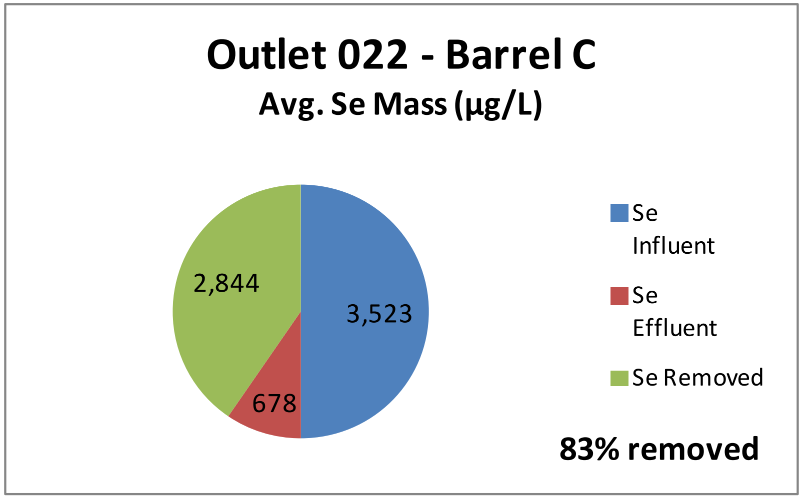


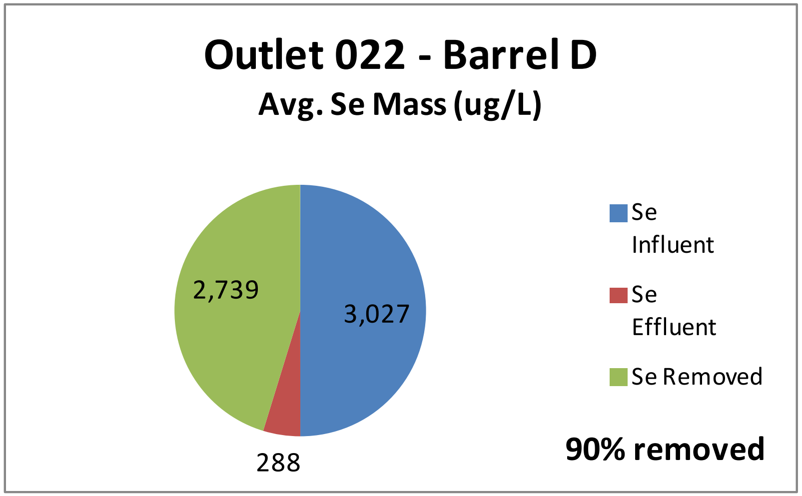
Avg Water Temp 8.2°C
Avg Min Air Temp 4.2°C

Average Se Mass Removed Per Day – 022

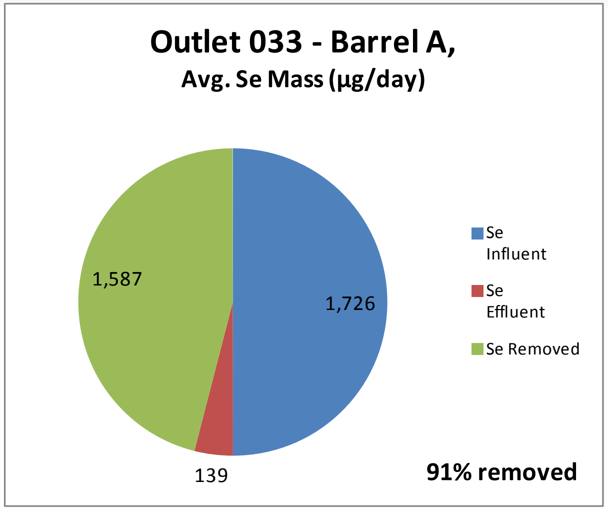


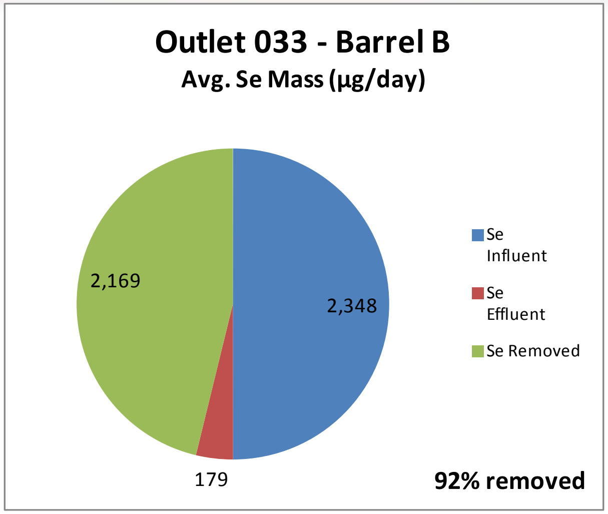


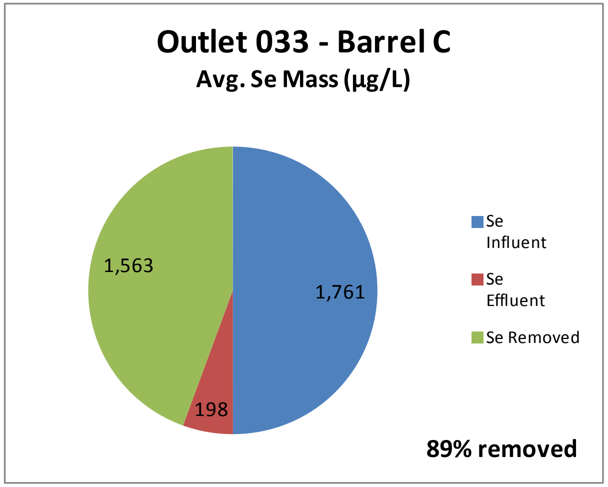


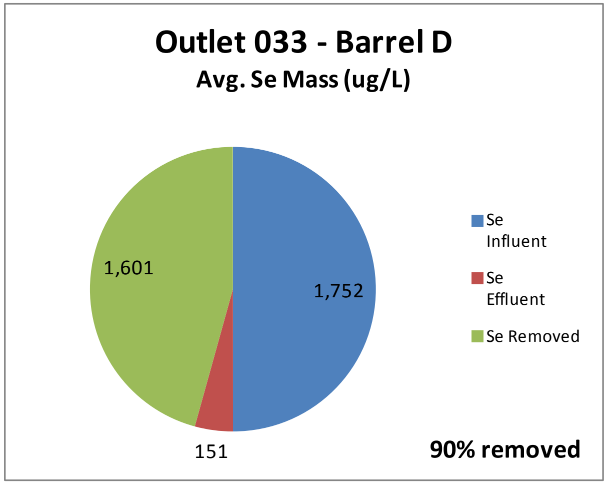


Average Se Mass Removed Per Day – 033

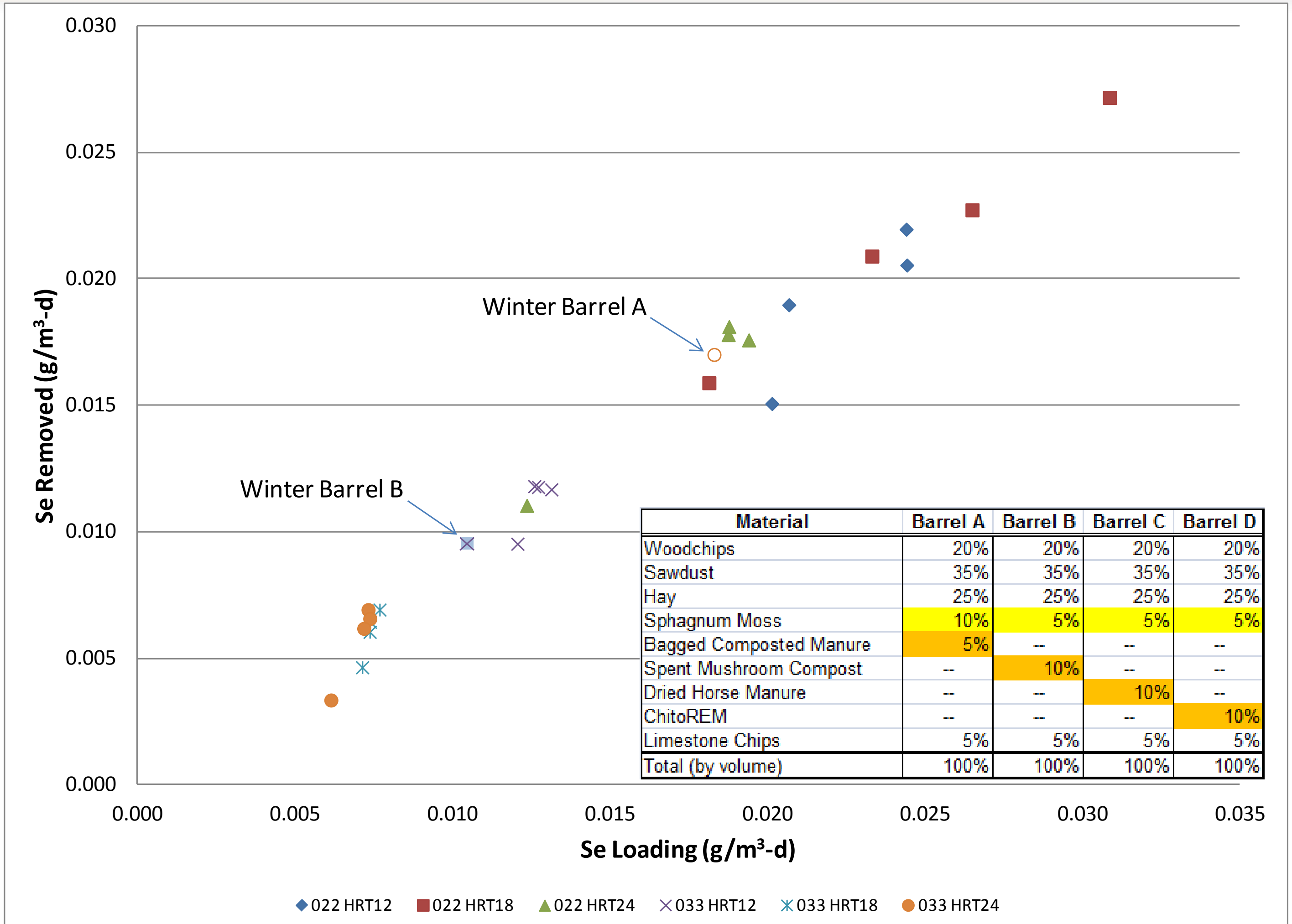








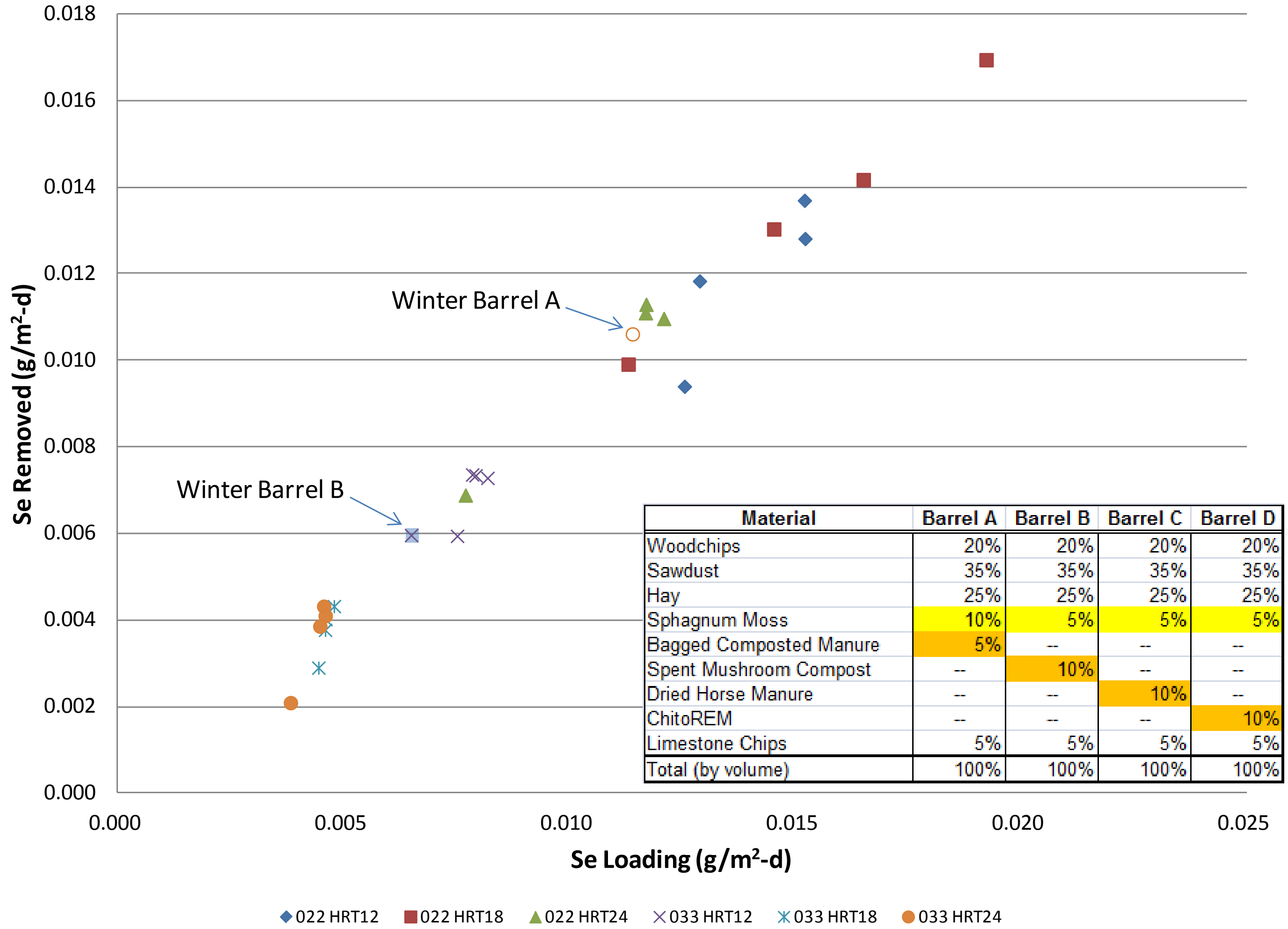
Se Mass Removed vs Volumetric Loading



Material	Barrel A	Barrel B	Barrel C	Barrel D
Woodchips	20%	20%	20%	20%
Sawdust	35%	35%	35%	35%
Hay	25%	25%	25%	25%
Sphagnum Moss	10%	5%	5%	5%
Bagged Composted Manure	5%	--	--	--
Spent Mushroom Compost	--	10%	--	--
Dried Horse Manure	--	--	10%	--
ChitoREM	--	--	--	10%
Limestone Chips	5%	5%	5%	5%
Total (by volume)	100%	100%	100%	100%

Reaction Fronts in BCR Substrates Over Time

Se Mass Removed vs Surface Aerial Loading



Material	Barrel A	Barrel B	Barrel C	Barrel D
Woodchips	20%	20%	20%	20%
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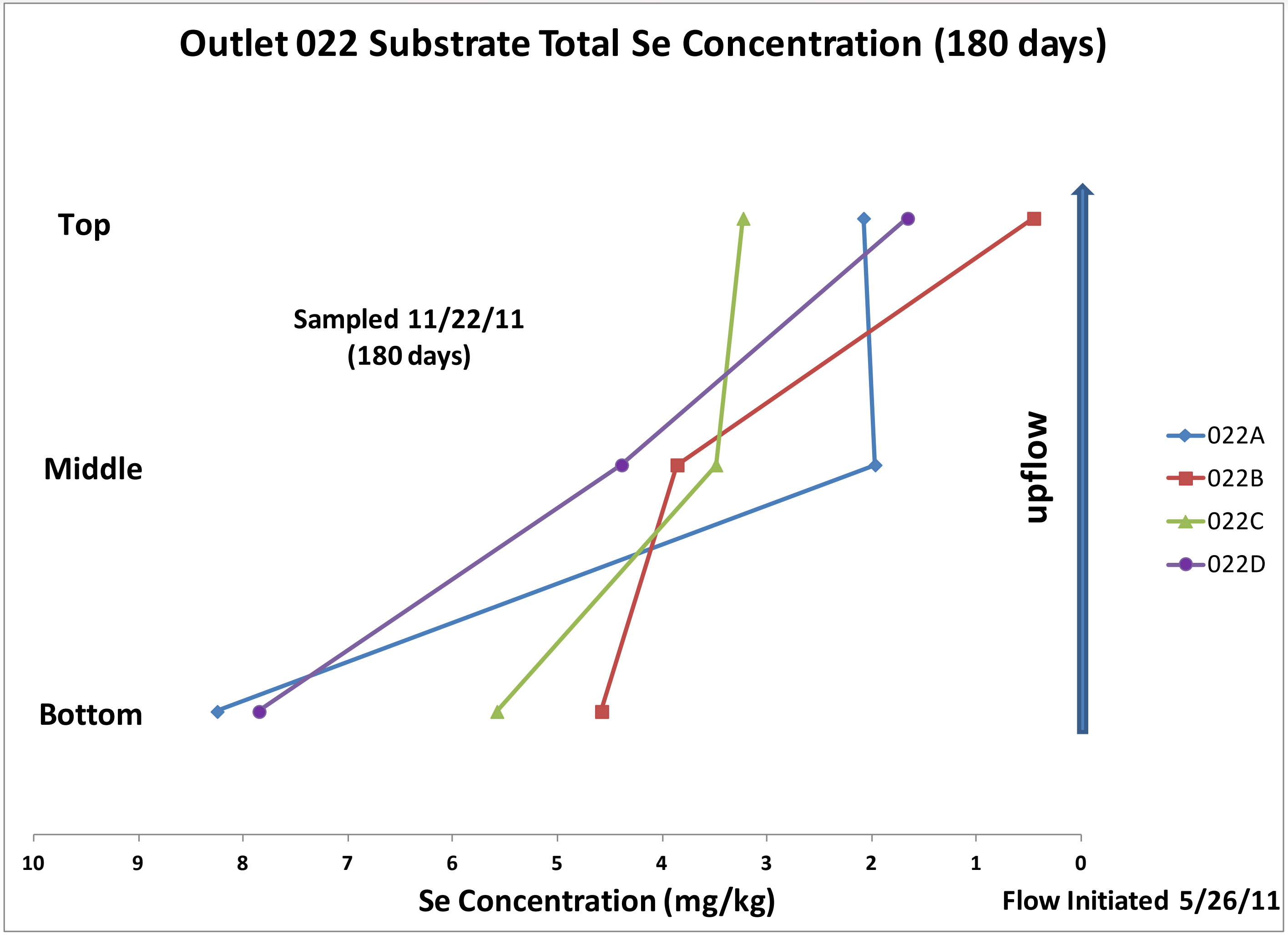
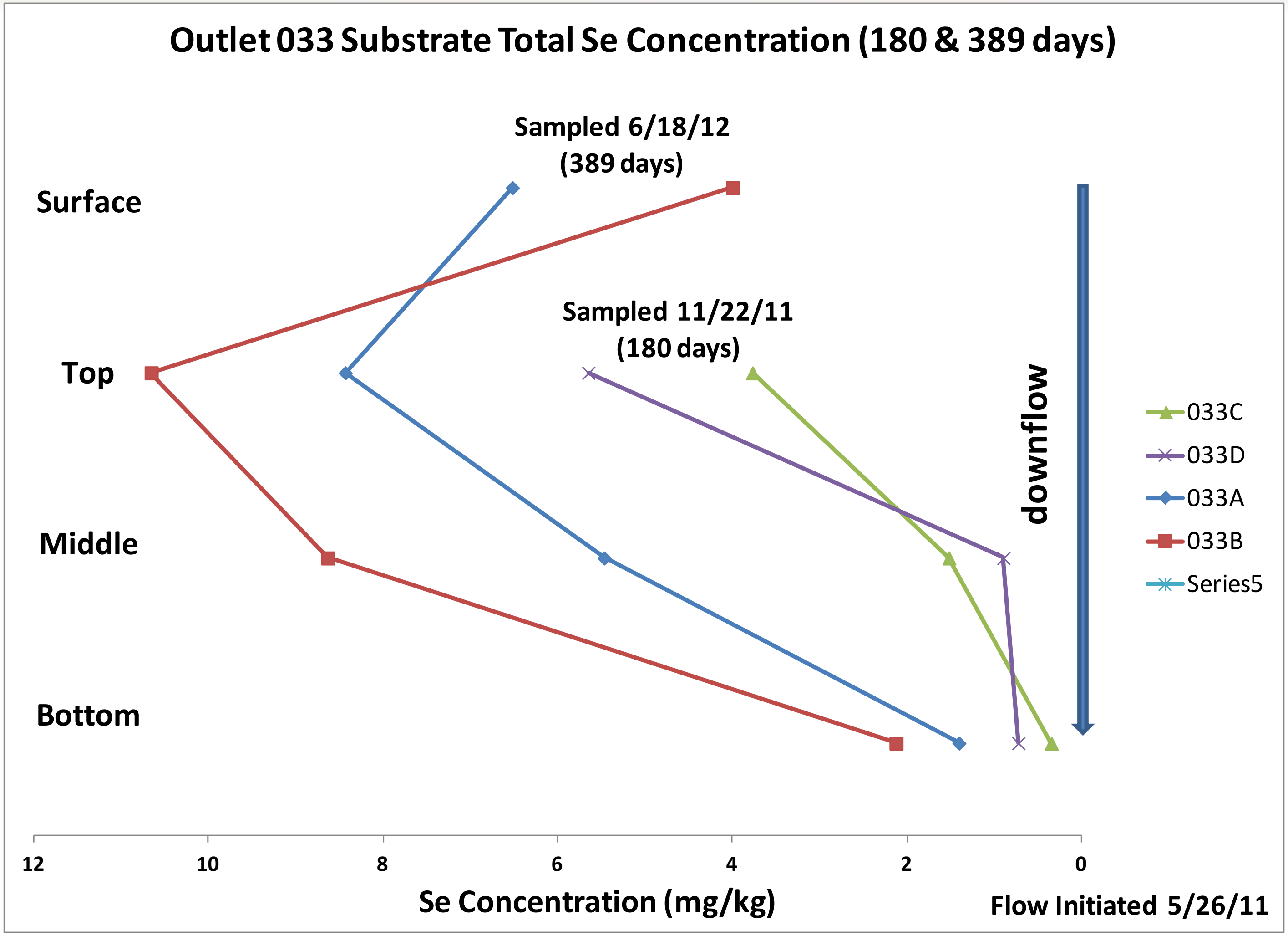
Hay	25%	25%	25%	25%
Sphagnum Moss	10%	5%	5%	5%
Bagged Composted Manure	5%	--	--	--
Spent Mushroom Compost	--	10%	--	--
Dried Horse Manure	--	--	10%	--
ChitoREM	--	--	--	10%
Limestone Chips	5%	5%	5%	5%
Total (by volume)	100%	100%	100%	100%

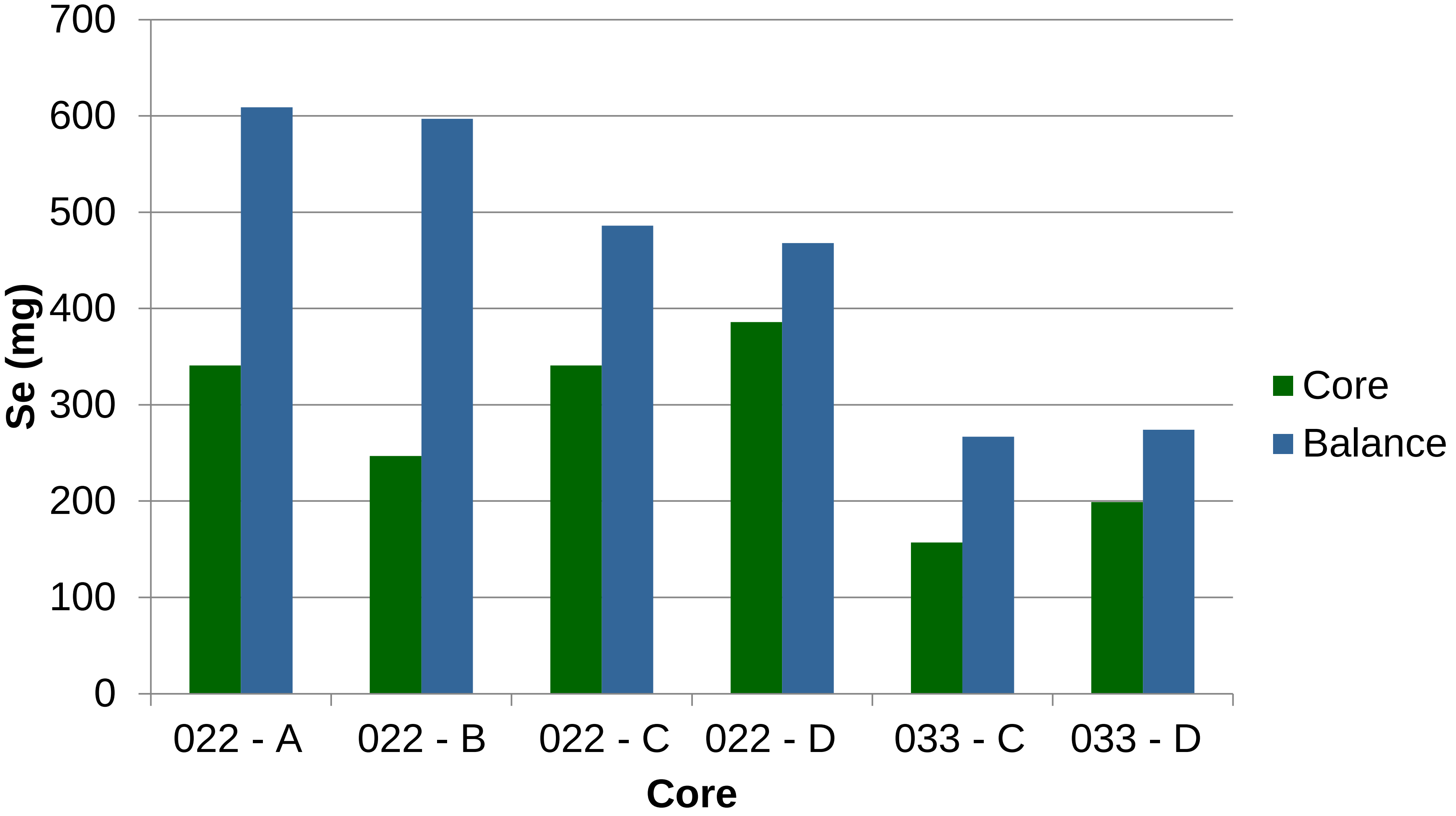
Barrel Selenium Profile



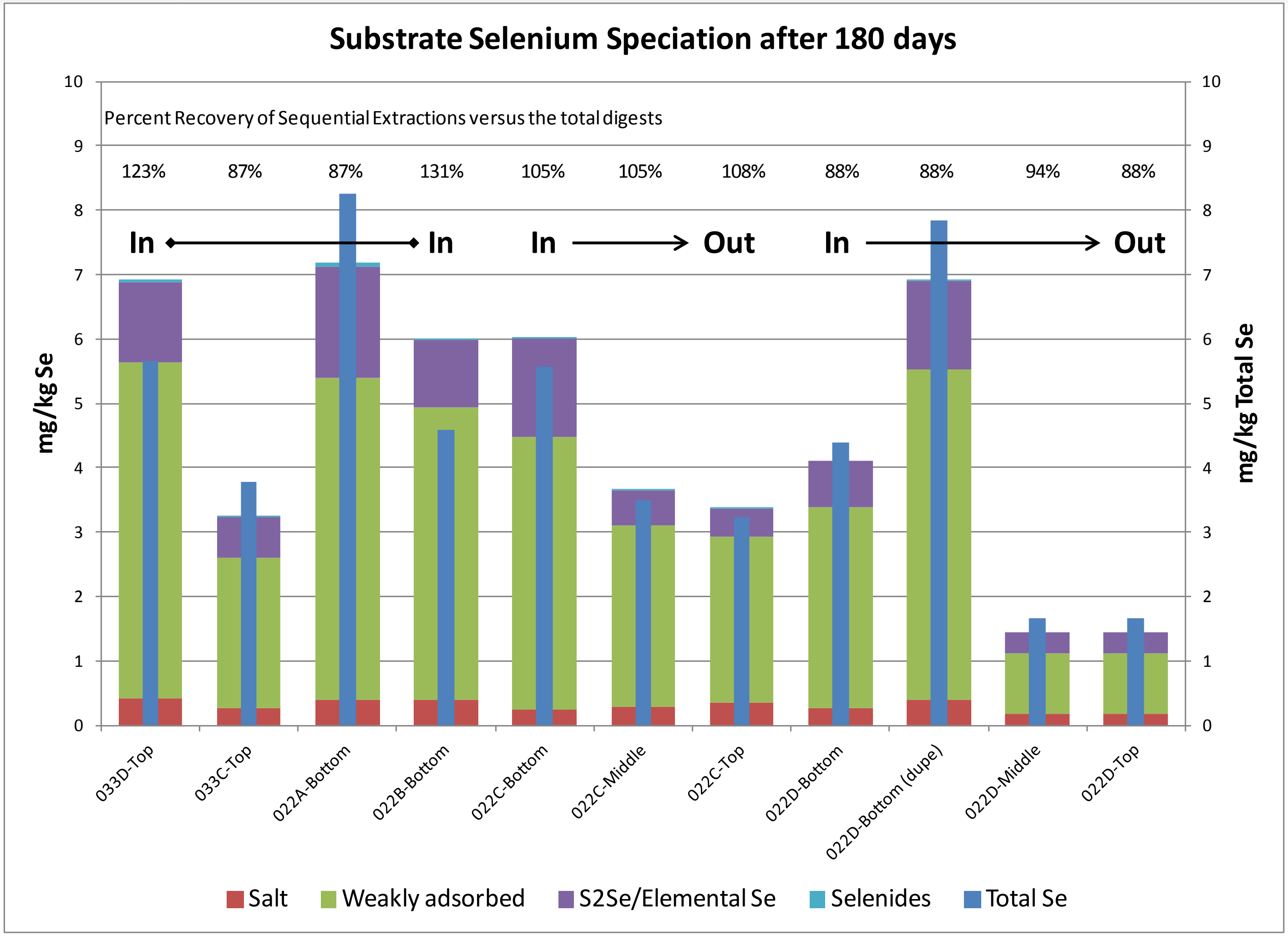
Barrel Selenium Profile



Selenium Mass Balance vs Sediment Core: Gap Suggests Volatilization Loss

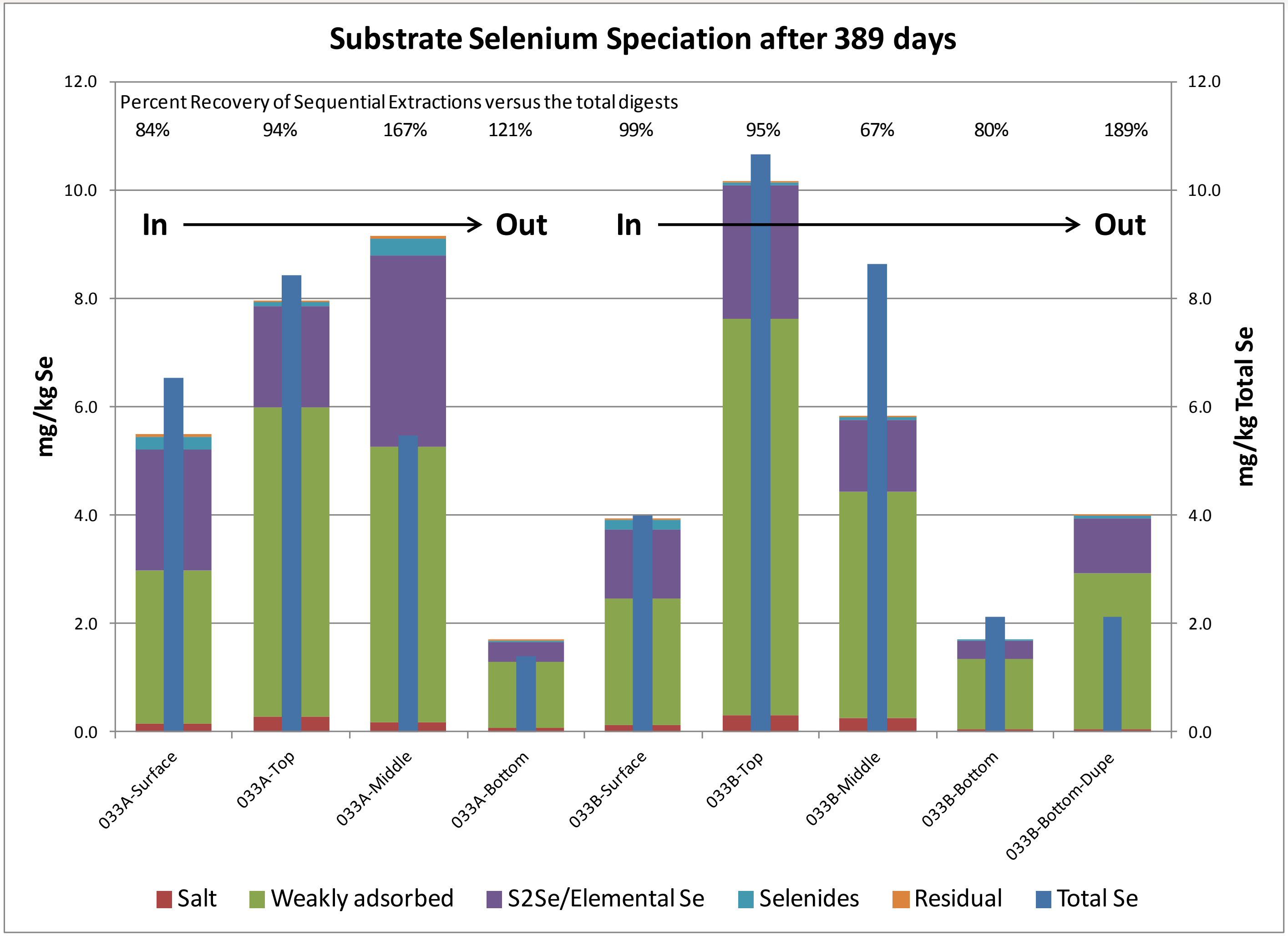


Vertical Distribution and Speciation of Selenium: Reduction, Sorption, Volatilization



Source:
CH2MHILL (2012)

Vertical Distribution and Speciation of Selenium: Reduction, Sorption, Volatilization



Source:
CH2MHILL (2012)

Model Rate Constant Calibration

- Empirical data from barrel studies used to calibrate treatment rates in the development of a sizing model for a full-scale treatment system
- General terms of mass conservation for a plug flow system are used while maintaining the first order model as the basis
- Empirical data was modeled using first order area-based treatment wetland model of Kadlec & Knight (1996) & Kadlec & Wallace (2009)
- Model estimates the potential BCR effluent concentration for a given flow rate and concentration for a given BCR area, as adjusted for temperature

$$J = k(Ci - Ce)$$

where:

J = zero-order contaminant removal rate [g/m²/yr])

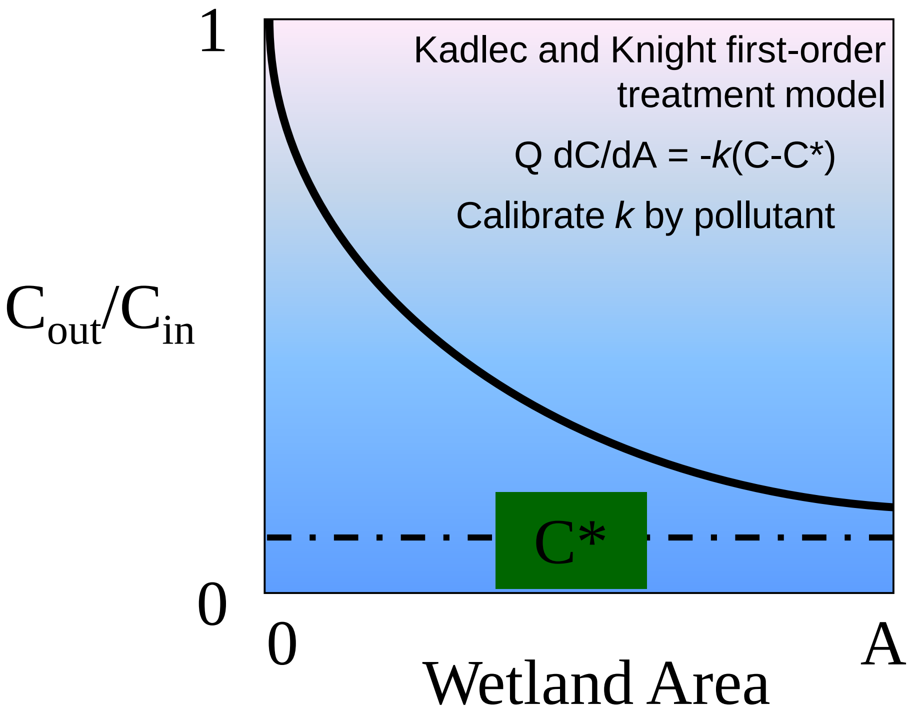
k = first-order, area-based rate constant (m/yr)

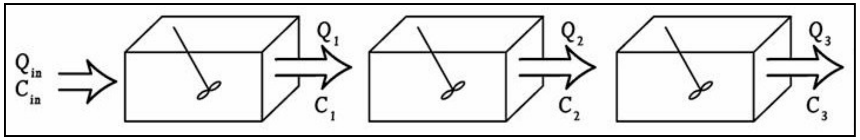
C_i = influent concentration (g/m³)

C_e = effluent concentration (g/m³)

First-order Area-based Treatment Model

First-order treatment model was expanded to the P-k-C* model, which is solved by relating: 1) hydraulic loading, 2) removal rate, 3) concentration terms, and 4) hydraulic mixing

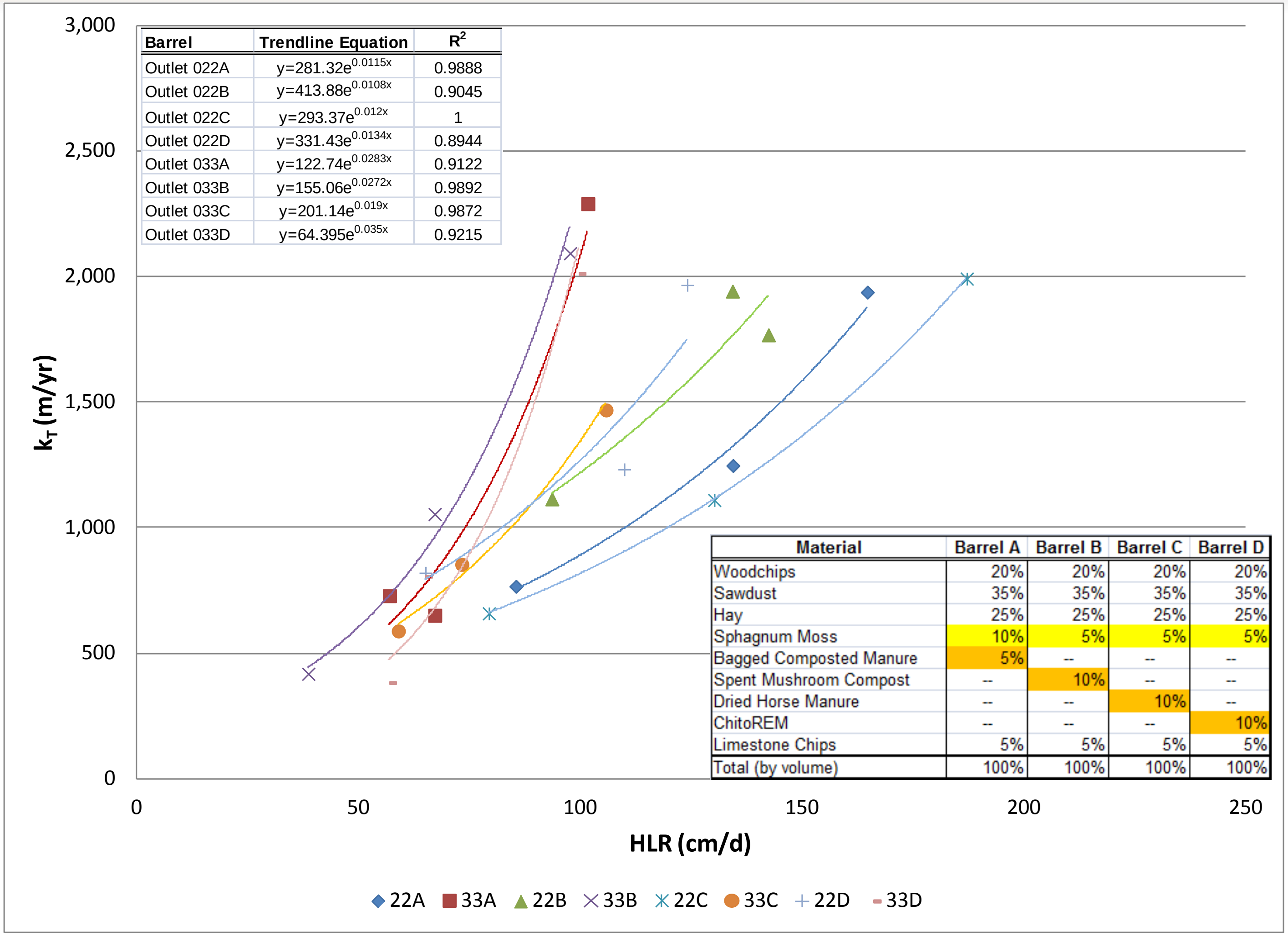




$$\left(\frac{C - C^*}{C_i - C^*}\right) = \frac{1}{(1 + k/Pq)^P}$$

?
?
?

Rate Constant vs Hydraulic Loading Rate



Barrel	Trendline Equation	R^2
Outlet 022A	$y=281.32e^{0.0115x}$	0.9888
Outlet 022B	$y=413.88e^{0.0108x}$	0.9045
Outlet 022C	$y=293.37e^{0.012x}$	1
Outlet 022D	$y=331.43e^{0.0134x}$	0.8944
Outlet 033A	$y=122.74e^{0.0283x}$	0.9122
Outlet 033B	$y=155.06e^{0.0272x}$	0.9892
Outlet 033C	$y=201.14e^{0.019x}$	0.9872
Outlet 033D	$y=64.395e^{0.035x}$	0.9215

Material	Barrel A	Barrel B	Barrel C	Barrel D
Woodchips	20%	20%	20%	20%
Sawdust	35%	35%	35%	35%
Hay	25%	25%	25%	25%
Sphagnum Moss	10%	5%	5%	5%
Bagged Composted Manure	5%	--	--	--
Spent Mushroom Compost	--	10%	--	--
Dried Horse Manure	--	--	10%	--
ChitoREM	--	--	--	10%
Limestone Chips	5%	5%	5%	5%
Total (by volume)	100%	100%	100%	100%

First-Order, Area-Based Tanks-in Series Rate Constant Modeling Results

- Passive Treatment Systems rarely operate as plug-flow reactors
  - Heterogeneous substrate, preferential flow
- Passive Treatment Systems are better characterized hydraulically as a series of well-mixed tanks (3 – 6 in series for VFW)
- Barrel-study data was configured in a three tank series using the P-k-C* model to assess the variable hydraulic characteristics on overall performance

First-Order, Area-Based Tanks-in Series Rate Constant Modeling Results

	1st-order, Area Based, Rate Constants (m/y)			
Barrel	**Outlet 022[a]**	**Outlet 033[a]**	**Outlet 033[b]**	**Outlet 033[c]**
A	1,379	1,498	675	675
B	1,744	1,671	1,177	1,177
C	1,246	1,180	—	—
D	1,547	1,115	—	—

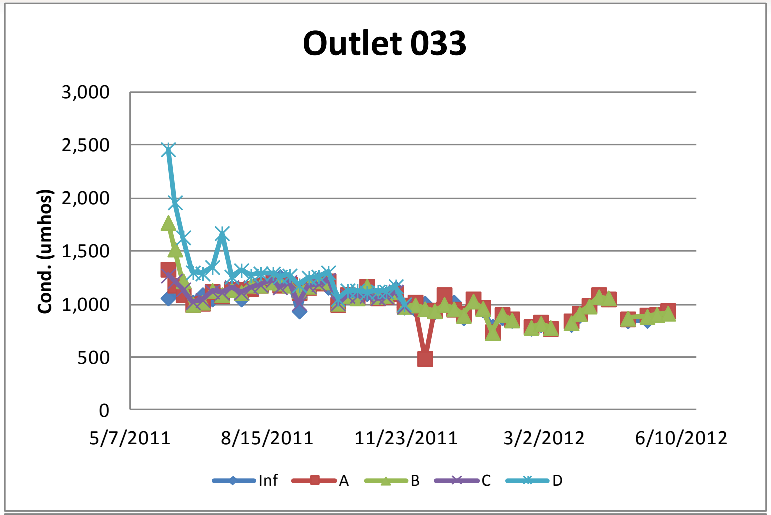
Note: Target effluent concentration was set at 4 µg/L.

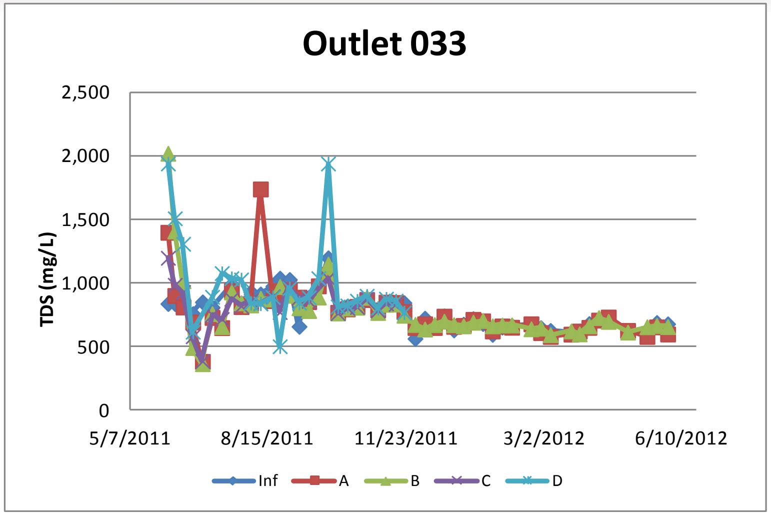
[a] Influent temperatures monitored during the summer and fall operations used in model (θ set at 1).

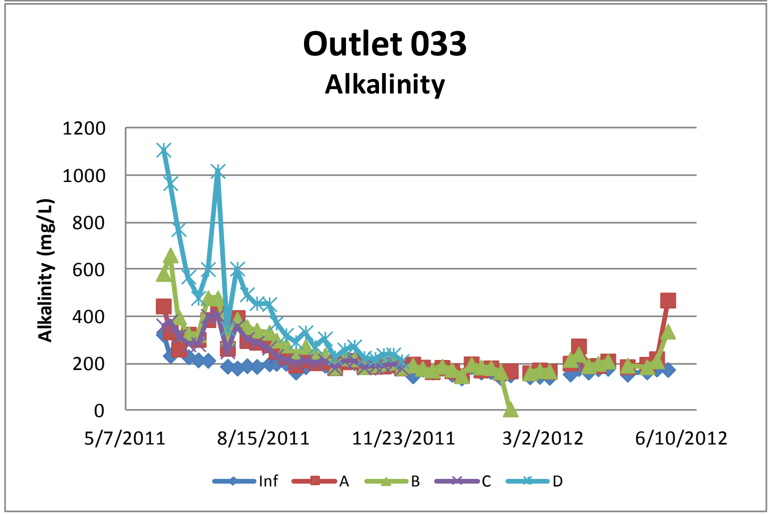
[b] Influent temperatures monitored during the winter operations used in model (10.5°C) (θ determined to be 0.95).

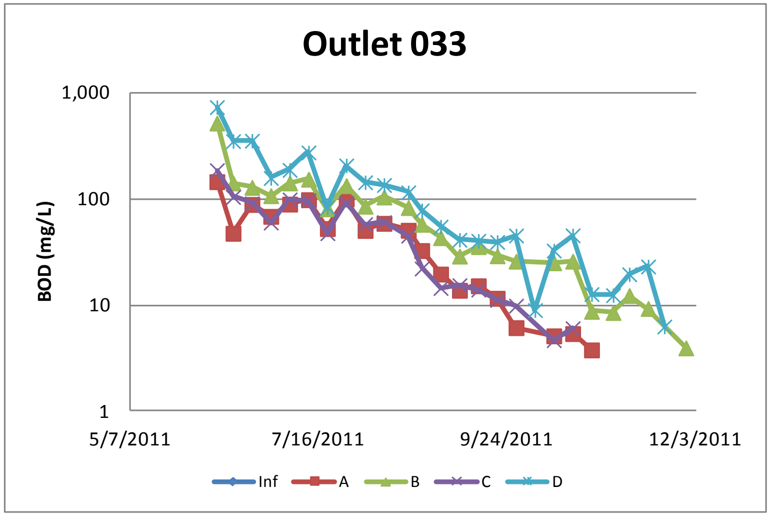
[c] Influent temperature set at 9°C in model (θ determined to be 0.96).

Secondary Parameters (Salts & Labile C): Conductivity, TDS, Alkalinity, BOD

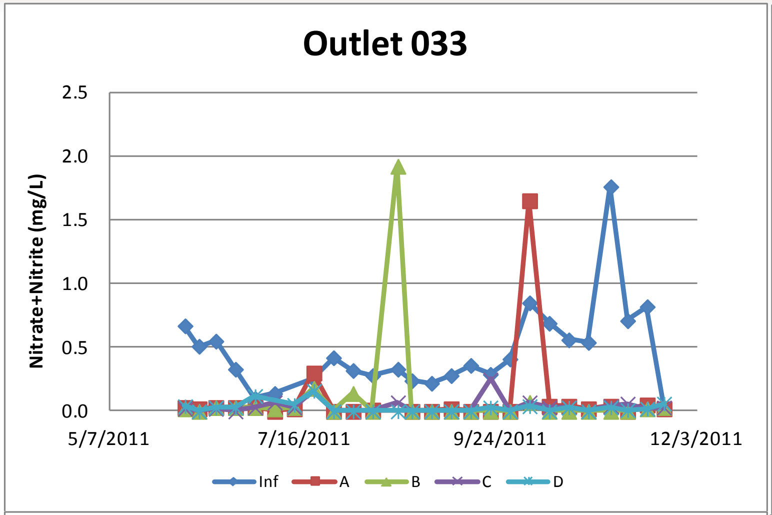


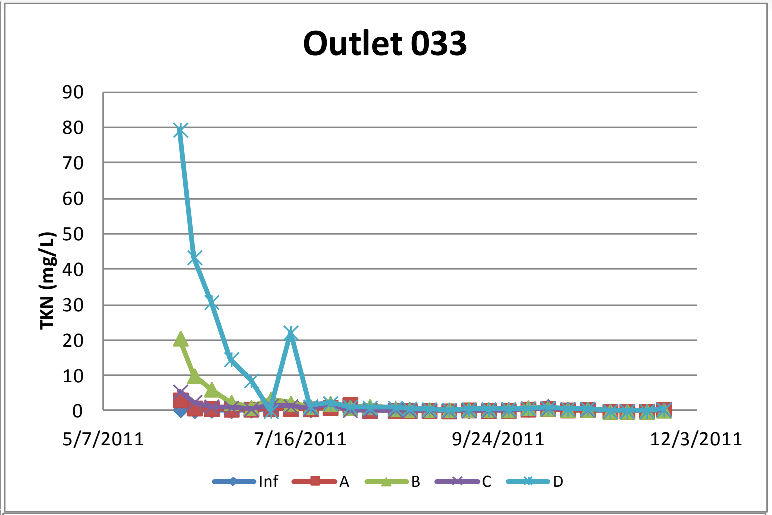


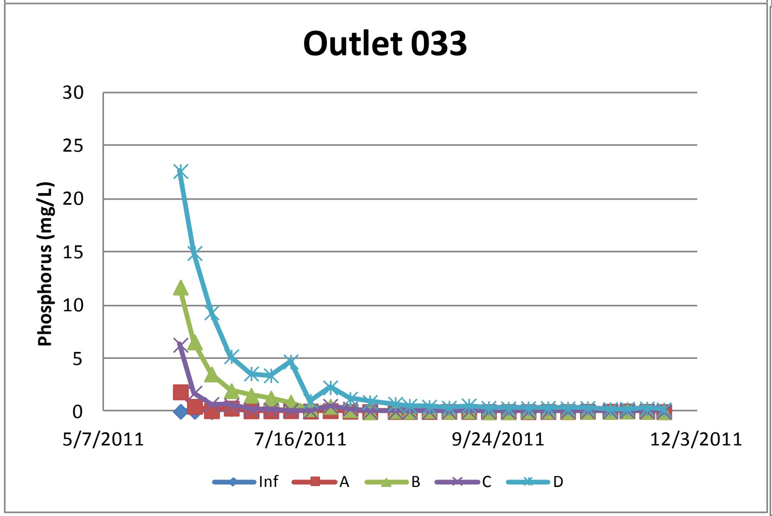


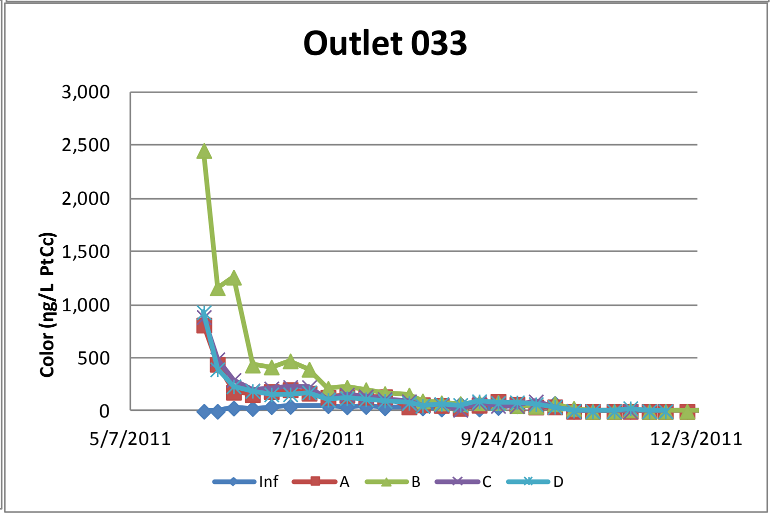


Secondary Parameters: Nutrients and Color

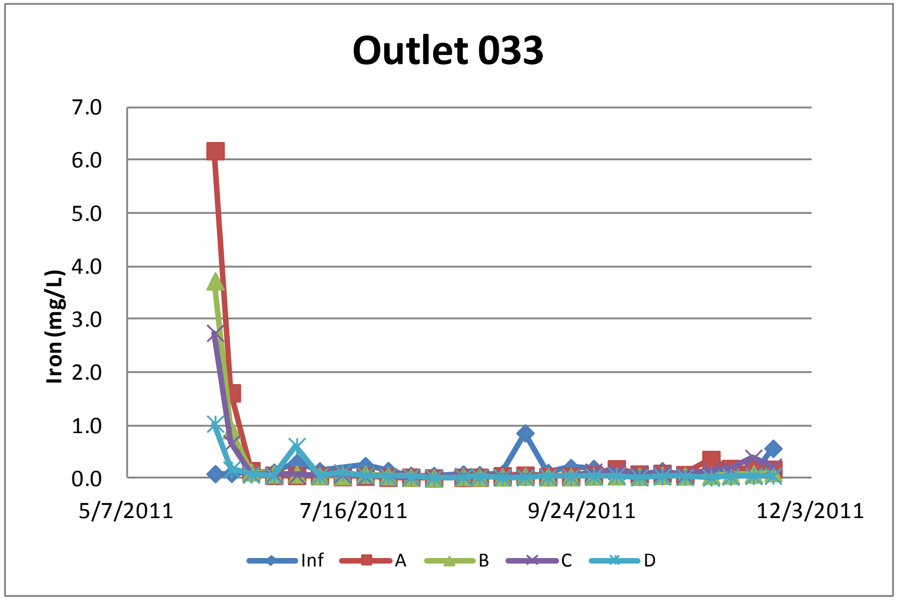


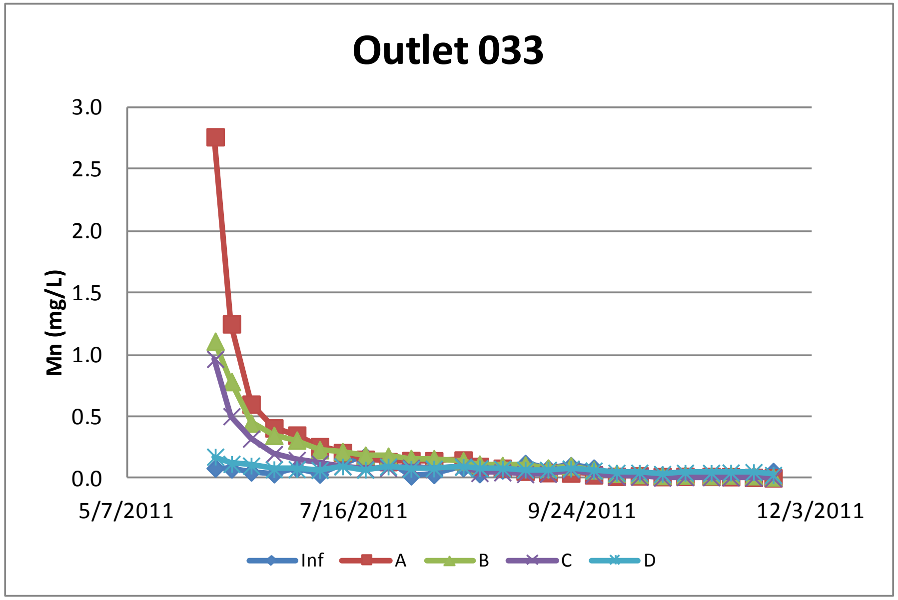






Secondary Parameters: Metals





Conclusions

- Selenium was effectively reduced by ~90% on average in all barrels.
- Selenium removal was effective at all HRTs tested (12 to 24 hours).
- Cold temperatures (below freezing) did not affect selenium removal rates significantly, and effluent selenium concentrations remained below discharge limits following startup.
- The organic substrates tested could generate secondary byproducts:
  - short-term increase in conductivity from the flushing of excess salts from the substrate during startup
  - elevated oxygen demand from excess labile carbon in the effluent
  - suspended solids (mainly fine particulate organic matter)
  - excess nutrients in the substrate mixture
  - release of regulated metals such as iron and manganese, which might also occur in small amounts in the substrate mixture.

Conclusions

- Se removal occurs at the influent water-substrate interface
  - consistent with first-order processes
  - extent of selenium distribution within the substrate is dependent on the selenium load.
- Substrate Se speciation indicates:
  - dominant mechanism is reduction of selenate to reduced forms of selenium that are weakly adsorbed to the substrate during early stages of selenium removal
  - approximately >50% weakly adsorbed Se attributable to selenite
  - Highly immobile elemental selenium or selenosulfide account for about a quarter of the total selenium retained
  - very little metal selenide was found.
- Both substrate coring and water-balance mass-balance evaluation methods show selenium retention
  - higher water balance method suggests a higher overall selenium retention than that observed in the substrate cores, suggesting loss to volatilization.
- Barrel media type B appeared to balance high treatment performance with moderate production of byproducts.
- Selenium treatment BCRs have been shown to treat mine site discharges effectively in order to achieve selenium compliance limits.

Acknowledgements

- Thanks to Alpha Natural Resources
- Thanks to supporting engineering and science staff at CH2M HILL

Questions