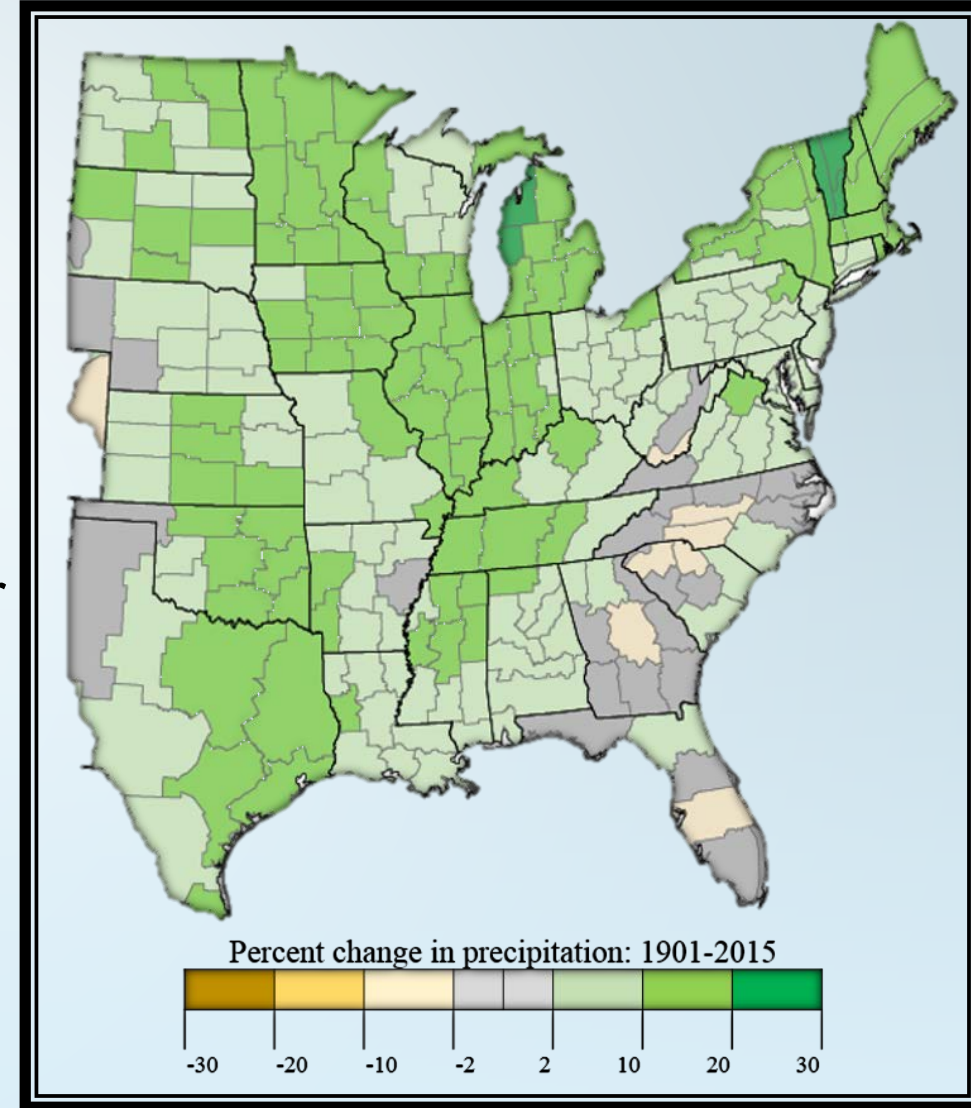


PHYTOREMEDIATION OF STORMWATER BY AQUATIC MACROPHYTES

MICHAEL P. NATTRASS, N. REBECCA MCGREW, JESSE I. MORRISON
AND BRIAN S. BALDWIN
MISSISSIPPI STATE UNIVERSITY

INTRODUCTION

- Water pollution degrades terrestrial and aquatic ecosystems
 - Agricultural and urban runoff
 - Fossil fuel combustion and petroleum refineries
 - Acid mine spoil and drainage
 - Industrial processing
- Runoff accumulates nutrients, trace minerals, and other chemical compounds
 - MS annual rainfall \sim 140 cm
 - By 2050, 9-13% increase (NOAA, 2016)
 - Seasonal variability
 - Impacts water budgets



Source: NOAA, 2016

INTRODUCTION

- Coal combustion residuals - 1.1 M Mt produced yearly
 - Sulfur/nitrogen oxides (SNO_x) and trace heavy metals adsorbed to alkaline reagents
 - Coal fly ash (57%), FGD byproducts (24%), bottom ash (16%), and boiler slag (3%)
 - Road bed for heavy mining equipment, soil amendment, concrete, and drywall
- Impoundments or retention ponds store residuals or runoff
 - Water quality standards (MDEQ, 2016)
 - TMDL - 11.8 $\mu\text{g Se L}^{-1}$ (ppb Se)
 - Monthly mean - 4.6 ppb Se
 - Compromised structural integrity from long term storage

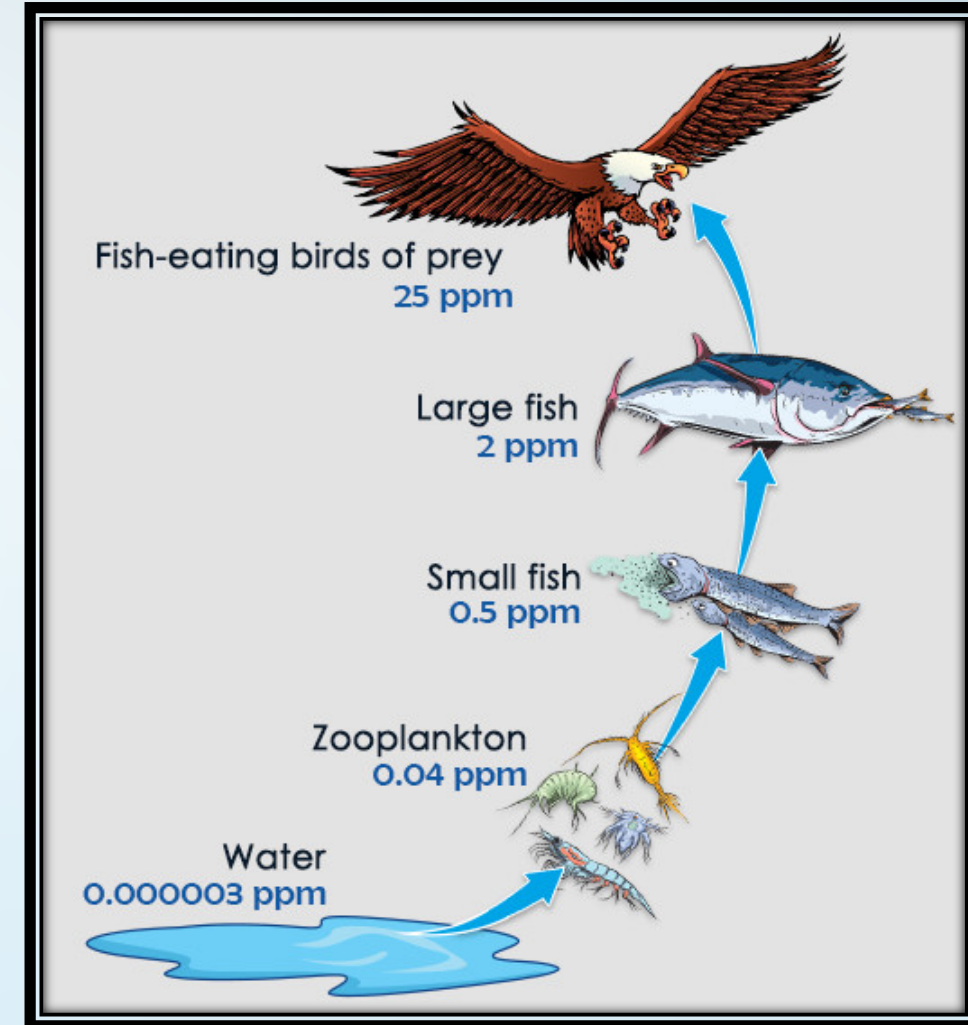
NOTABLE U.S. SELENIUM CONTAMINATION EVENTS



Lemly and Skorupa, 2012

ENVIRONMENTAL AND ECONOMIC IMPACT

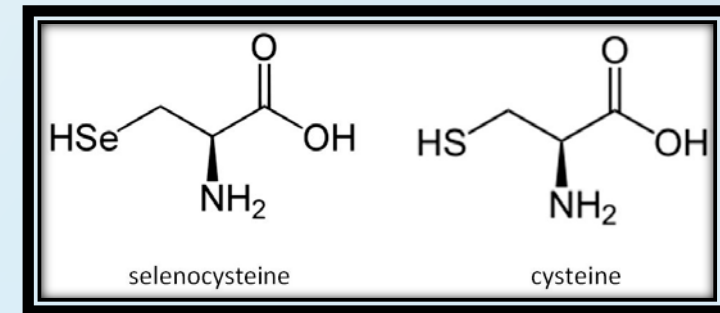
- Bioaccumulation of Se up trophic levels
 - 35,000x greater than aqueous Se (Hamilton, 2004)
 - Reproductive deformities (Ohlendorf, 1988; Lemly, 1997)
- Site-specific toxicity thresholds
 - Species, food web models, ecosystem
- Environmental cleanup and lost revenue
 - Kingston, TN - \$3.3 billion (Matthews et al., 2014)
 - North Carolina - \$169 billion (Lemly, 2014)



SELENIUM CYCLING

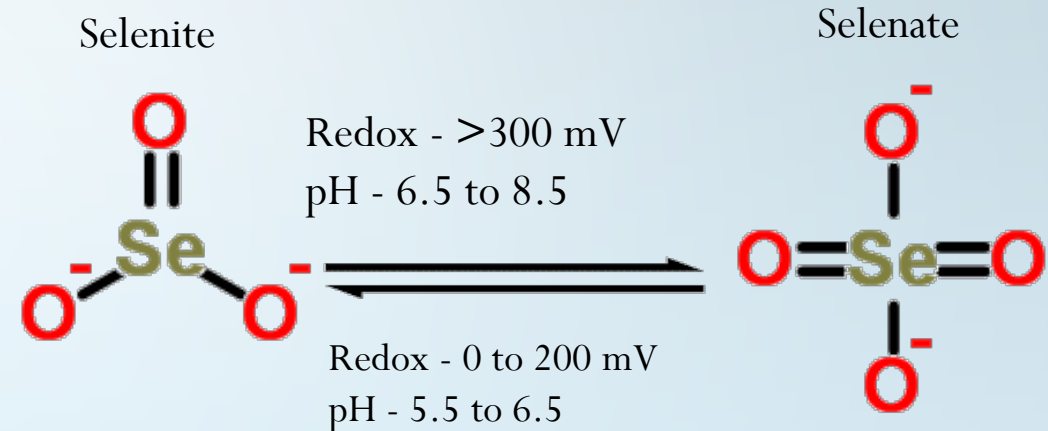
- Soil Se concentrations range from 0.01 to 2 ppm (Fordyce, 2005)
 - Salton Sea – 100 ppm Se
 - Deficient in regions of China and Africa
- Essential micronutrient for humans and livestock
 - Important for thyroid hormone production, bone metabolism, enhanced immune system (Rayman, 2000)
 - Range between deficiency and toxicity (40 to 400 $\mu\text{g d}^{-1}$)
 - Biofortification in Se-deficient regions

16
8
O
Oxygen
16
S
Sulfur
34
Se
Selenium
52
Te
Tellurium
84
Po
Polonium



BIOGEOCHEMICAL INFLUENCE ON SELENIUM CYCLING

- Inorganic Se exists in four oxidation states
 - Immobile - Selenide (-II) and Se (0)
 - Bioavailable - Selenite (IV) and selenate (VI)
- Temperature (Allen, 1991; Kedlec and Reddy, 2001)
 - Enhances microbial decomposition of OM
 - Reduces dissolved O₂ supply, releases CO₂
- Redox potential and pH (Masscheleynn et al., 1991)
 - Speciation is a function of redox potential
 - Adsorption to Al/Fe oxy-hydroxides, OM



CHALLENGES TO SELENIUM REMOVAL

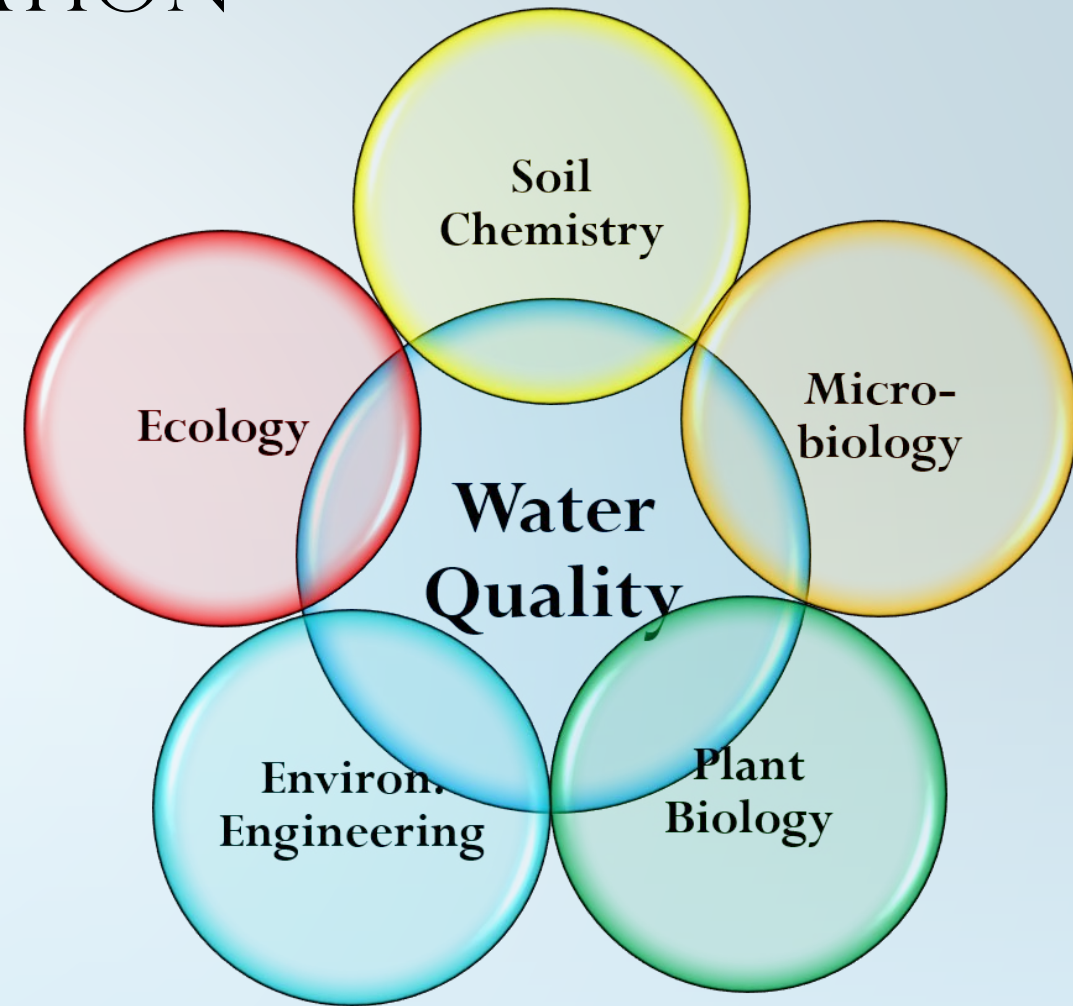
- Active treatment – physical/chemical
 - Large energy inputs, low treatment volumes
 - Environmentally toxic byproducts
 - Interference from other anions and cations
- Need for rapid treatment of large volumes of stormwater runoff
- Phytoremediation using constructed wetlands for improving water quality

Treatment System	Selenium Removal (%)	Cost (\$ m ⁻³)
Ferrihydrite (A)	85-90	3.97
Nanofiltration (A)	>90	0.71
Reverse osmosis (A)	>95	0.75
Algal-bacteria removal (P)	97	0.21
Constructed wetlands (P)	96	0.26

(A) Active, (P) Passive

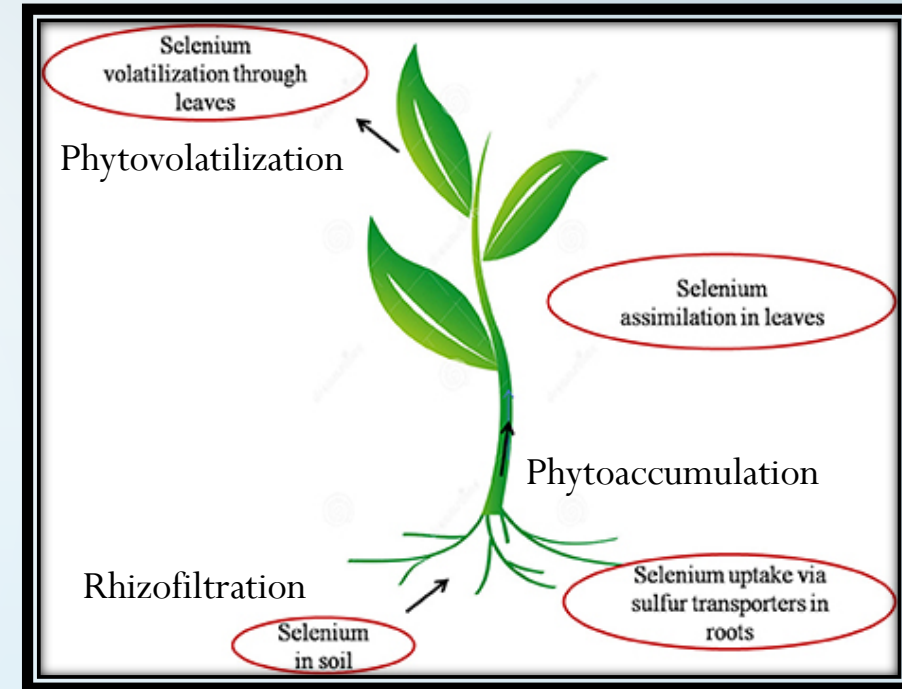
PHYTOREMEDIATION

- Phytoremediation – “green” technology
 - Plant metabolic processes remove contaminants
 - Terrestrial and aquatic applications
 - Gained popularity during Kesterson restoration
- Constructed wetlands - natural application of biogeochemical processes
 - Eco-friendly, inexpensive, low maintenance
 - Sustainable energy source, renewable resources
 - Large treatment capacity for multiple contaminants
 - Marchand et al., 2010; Rezania et al., 2016



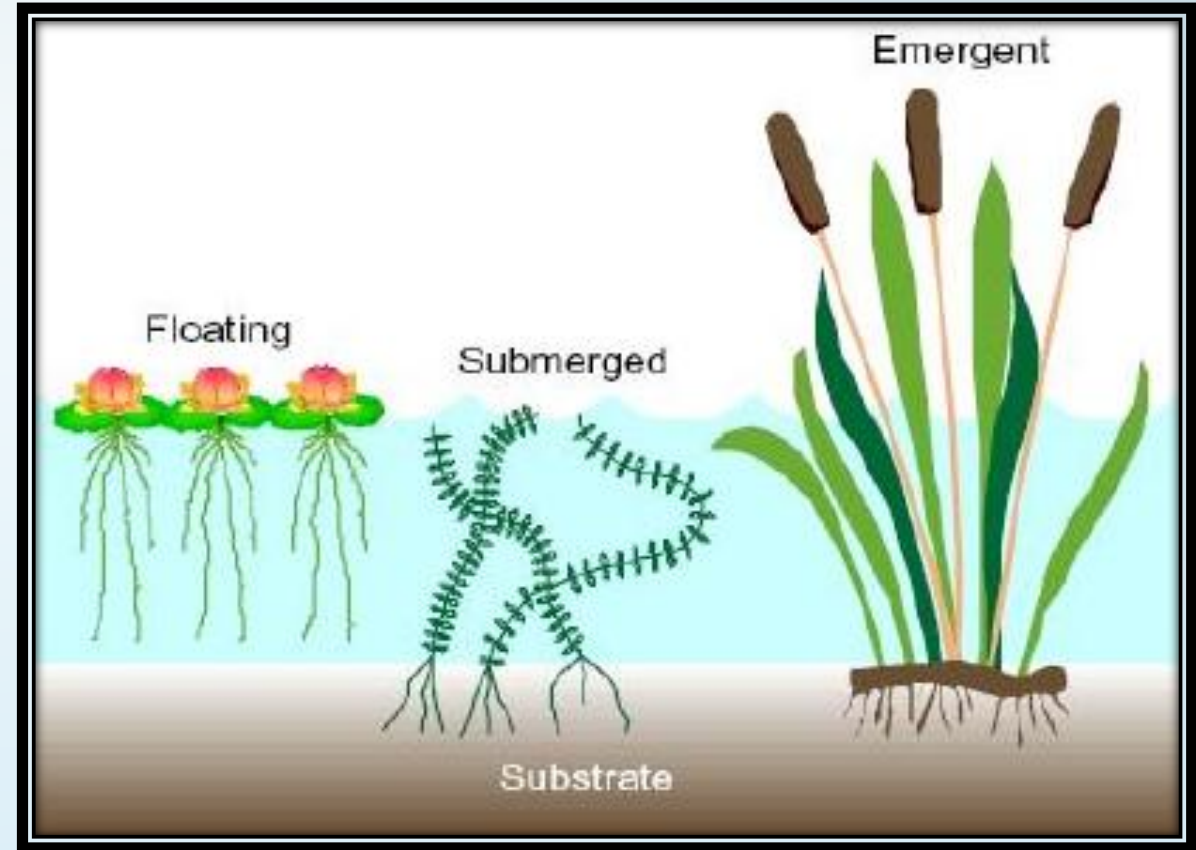
SELENIUM ELIMINATION PATHWAYS

- Rhizofiltration - concentrates Se near the root zone
 - Microbial-root interactions, redox, pH
- Phytoaccumulation - plant uptake
 - Sulfur assimilatory pathway
 - Sulfate inhibits selenate uptake (Zayed et al., 1998)
- Phytovolatilization – inorganic Se to organic Se
 - Selenite \longrightarrow Dimethylselenide (DMSE)
 - Selenate \longrightarrow Dimethyldiselenide (DMDSE)
 - 600x less toxic compared to inorganic Se (Wilbur, 1980)



AQUATIC PLANT SELECTION

- Desirable characteristics
 - Se tolerance
 - Fast-growing, large biomass production
 - Harvestability, potential cash crop
- Growth Habit
 - Floating, submerged, emergent
 - Native vs. exotic vs. invasive
 - Habitat and food source for aquatic biota



FLOATING

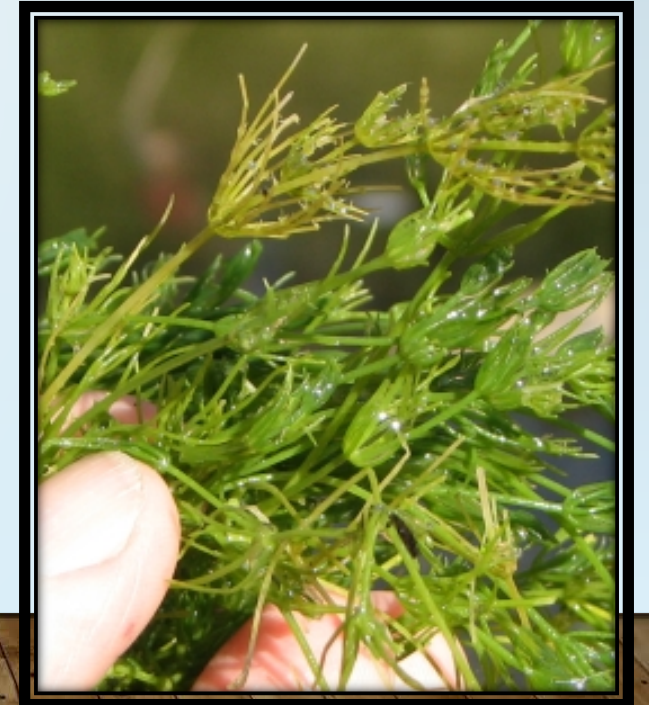
- Duckweed (*Lemna minor* L.)
 - Rapid vegetative reproduction
 - Bioconcentration of Se (Allen, 1991; Zayed et al., 1998)
 - 55 to 99% removal (Carvalho and Martin, 2001; Miranda et al., 2014)
 - Potential feed supplement and biofuel feedstock
 - Complete surface coverage can deplete O₂



SUBMERGED

- Fanwort (*Cabomba caroliniana* A. Gray)
 - Native to Southeast
 - High tolerance to anaerobic, alkaline conditions

- Muskgrass (MG; *Chara* sp. Desv. & Lois.)
 - Macroalga and known sulfur accumulator
 - Selenite - 70 to 75% Se removal
 - Selenate - 51% Se removal (Lin et al., 2002; Lin and Terry, 2002)



EMERGENT

- Cattail (*Typha sp. L.*)
 - *T. angustifolia* - 89% Se removal as selenite (Hansen et al., 1989)
 - *T. latifolia* - 46% Se removal as selenate (Shardendu et al., 2002)
 - 2 mg Se m⁻² d⁻¹ volatilized as selenite or selenate (Pilon-Smits et. al, 1999)
- Softrush (*Juncus effusus L.*)
 - Abundant in Southeast wetland environments
 - Less invasive than cattail
- Aerenchyma tissue supplies soil microbes with oxygen



OBJECTIVES

- Assess the potential of aquatic plants to improve water quality of selenium-impacted stormwater
- Evaluate the influence of selenium chemical form and concentration on plant uptake

EXPERIMENTAL PREPARATION

- Plants collected locally, rinsed of debris, and translocated into 115-L microcosms
 - Five CT plants and five SR clusters (3 culms)
 - CAB, DWD, and MG - 250 g (fresh wt.)
- Catalpa silty clay loam (fine, smectitic, thermic Fluvaquentic Hapludolls)
 - OM - 3.2%; pH - 6.1; CEC - 16 $\text{cmol}_c \text{kg}^{-1}$
 - 286 ppb Se
- Acclimation period of 14-d in 26 L 0.1 M Hoagland's solution in tap water



EXPERIMENTAL DESIGN

- 2 X 2 nested within a split-split plot design
 - Main plot: selenite and selenate
 - Sub-plot: 500 and 1000 ppb Se
 - Zero Se control
 - Sub-subplot: Aquatic plants
 - Cabomba (CAB)
 - Cattail (CT)
 - Duckweed (DWD)
 - Muskgrass (MG)
 - Softrush (SR)
 - Unplanted (UNP)
- Repeated in time: Sep, Oct, Nov

Selenite				Selenate				Control	
500 ppb		1000 ppb		1000 ppb		500 ppb		0 ppb	
CAB	MG	MG	DWD	SR	CT	MG	CAB	CT	UNP
UNP	CT	UNP	SR	DWD	CAB	CT	DWD	SR	MG
SR	DWD	CAB	CT	UNP	MG	SR	UNP	CAB	DWD

DATA COLLECTION AND ANALYSIS

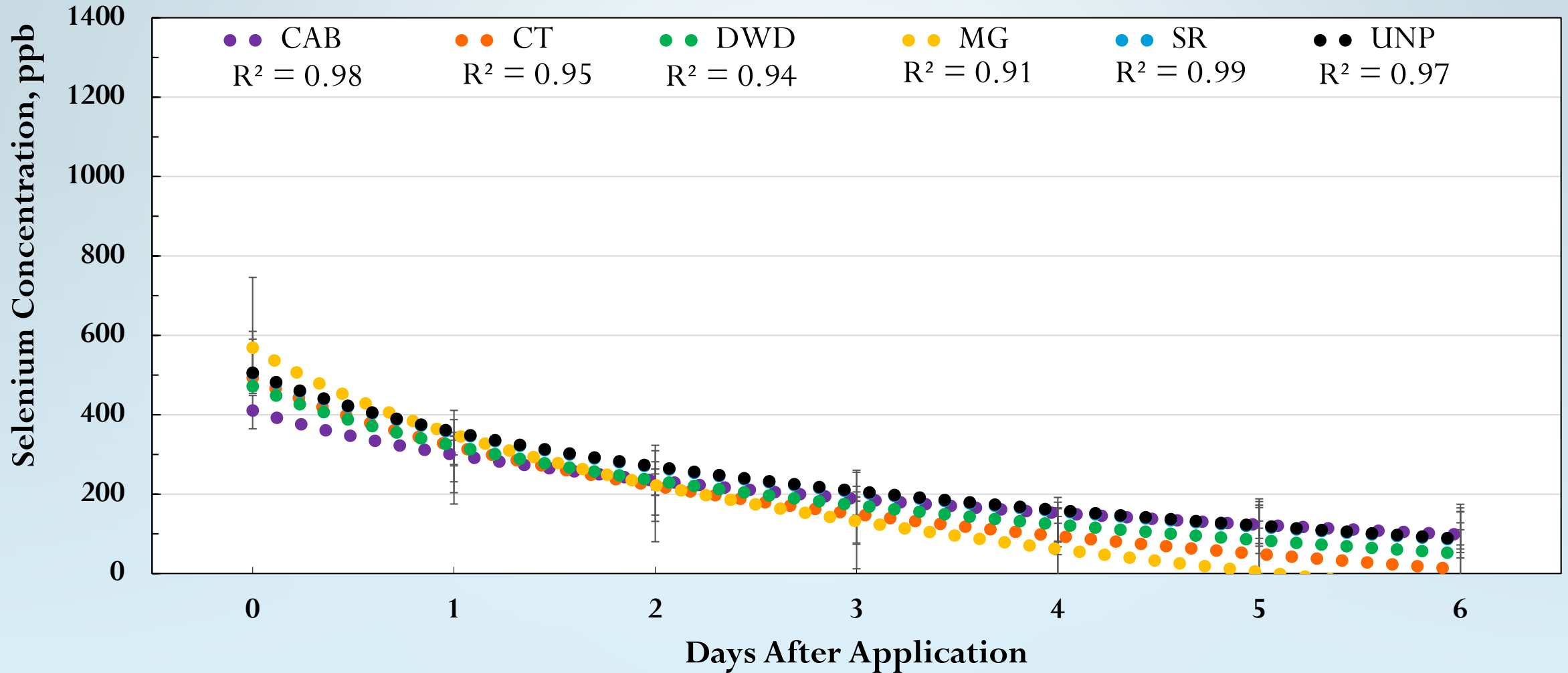
- Water samples were collected daily for six days
- Plant and soil samples collected at three and six days after Se application (DAA)
- Total Se Analysis
 - Water (EPA Method 200.8); Plant and soil (EPA Method 6020)
 - Inductively coupled plasma-mass spectrometry (ICP-MS)
 - Waypoint Analytical, Inc. (Memphis, TN)
- PROC GLM ($\alpha = 0.05$)
 - MANOVA using repeated measures



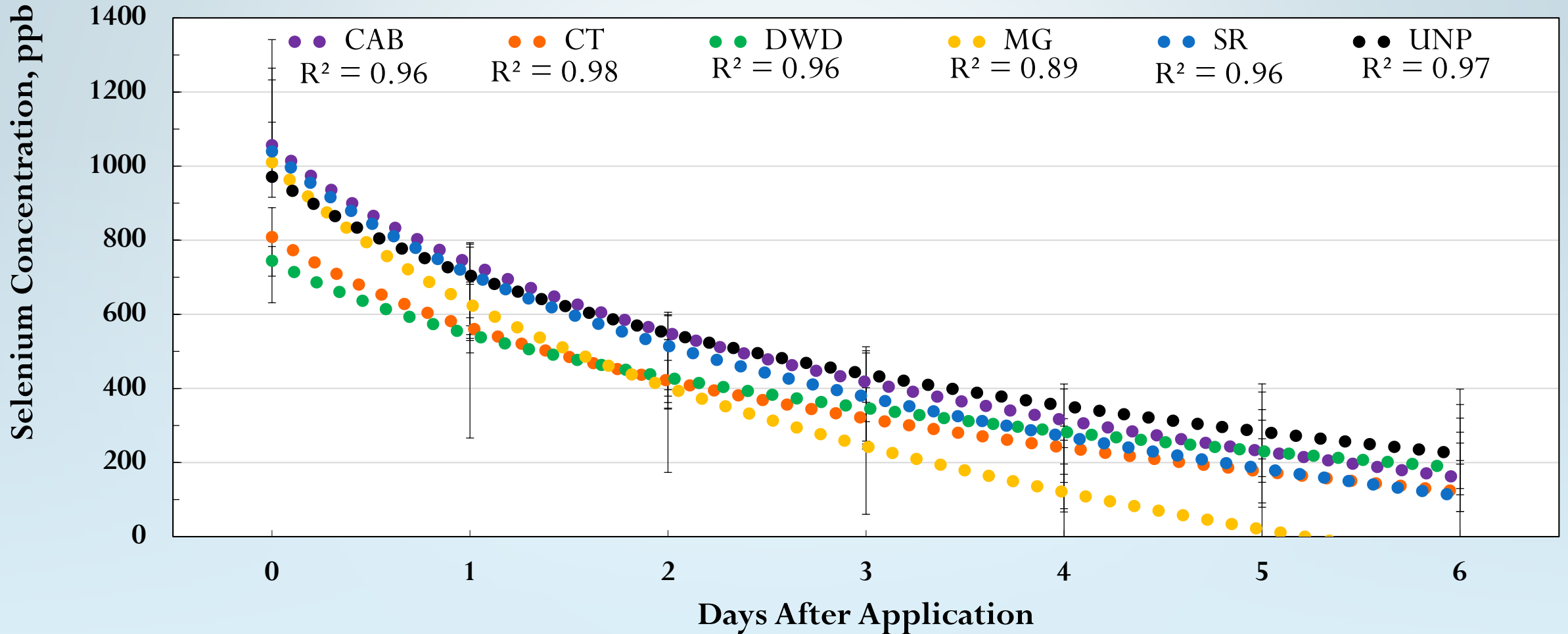
AQUEOUS SELENIUM RESULTS

Source	Aqueous Selenium
Rep (R)	<0.001
Oxidation (O)	<0.001
Concentration (C)	<0.001
O * C	<0.001
R * C	<0.001
Plant (P)	0.04

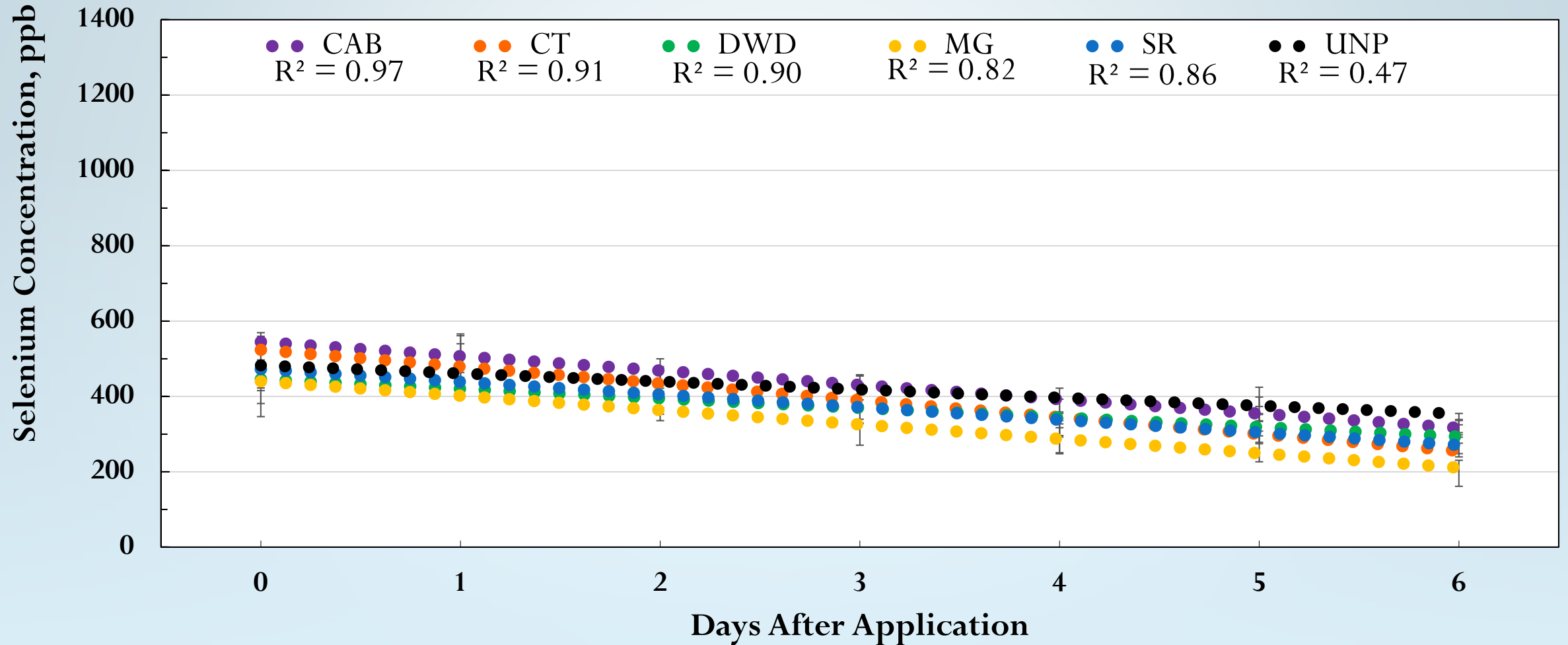
AQUEOUS SELENIUM CONCENTRATIONS IN MICROCOSMS TREATED WITH 500 PPB AS SELENITE



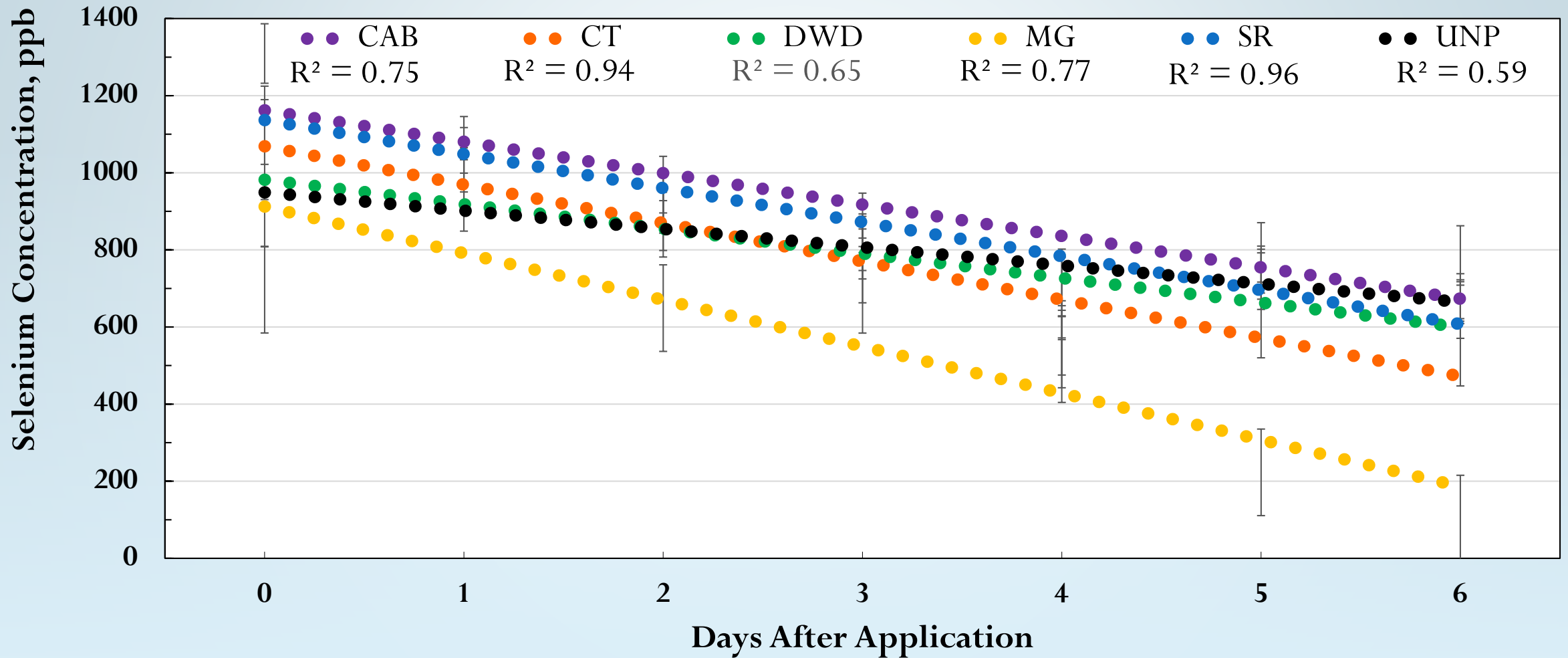
AQUEOUS TOTAL SELENIUM CONCENTRATIONS IN MICROCOSMS TREATED WITH 1000 PPB AS SELENITE



AQUEOUS TOTAL SELENIUM CONCENTRATIONS IN MICROCOSMS TREATED WITH 500 PPB AS SELENATE



AQUEOUS TOTAL SELENIUM CONCENTRATIONS IN MICROCOSMS TREATED WITH 1000 PPB AS SELENATE



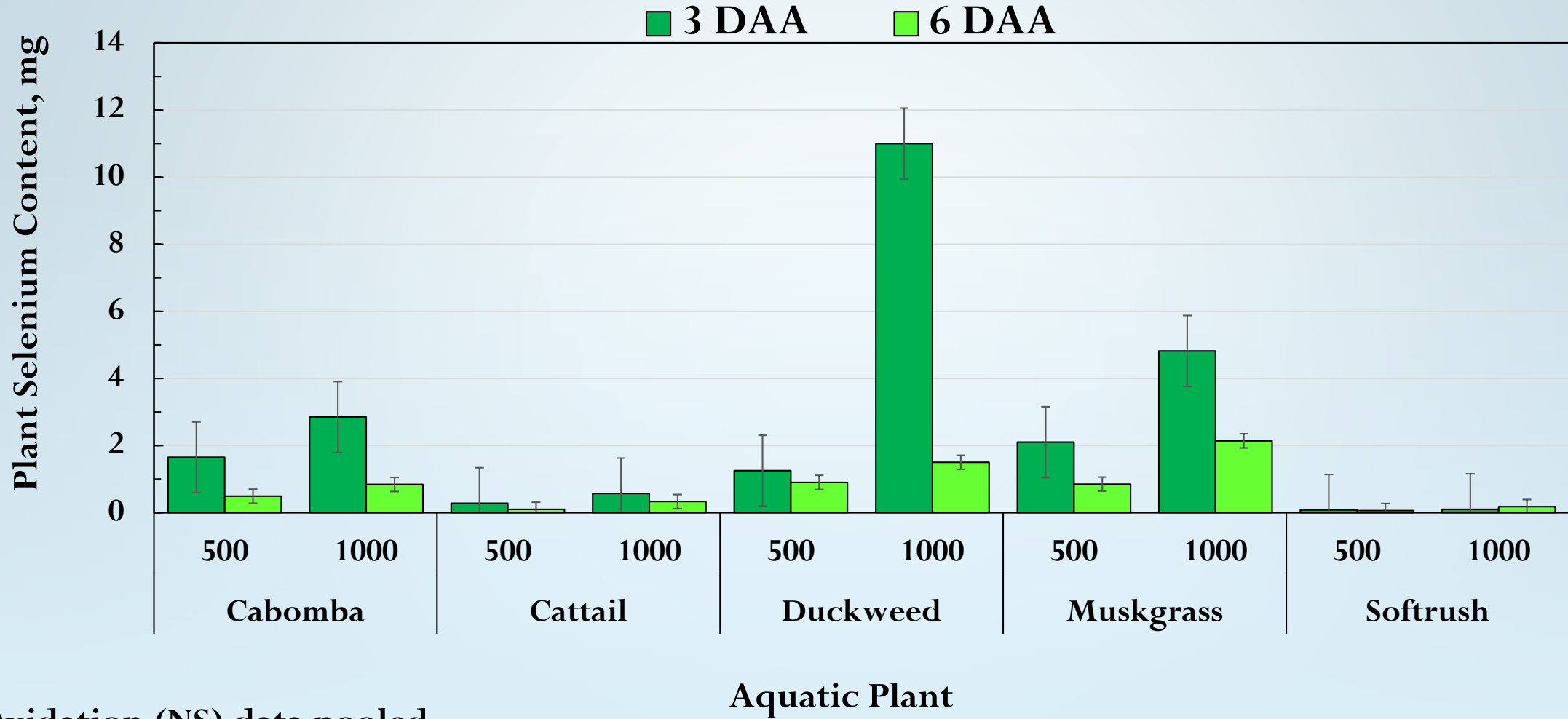
AQUEOUS SELENIUM RESULTS

- Selenite (83.6% of applied Se removed)
 - At 500 ppb Se, mean aqueous [Se] in MG-planted microcosm less than UNP at 3 DAA
 - At 1000 ppb Se, mean aqueous [Se] in CT and MG-planted microcosms less than UNP at 3 DAA
 - Cattail (87%) and MG (91%) reduced aqueous [Se] compared to UNP (81%)
 - Previous studies (Hansen et al., 1989; Lin et al., 2002) support our results
- Selenate (48.5% of applied Se removed)
 - At 500 ppb Se, no significant reduction in aqueous [Se] observed
 - At 1000 ppb Se, mean aqueous [Se] in MG-planted microcosms less than UNP after day 5

PLANT SELENIUM RESULTS

Source	Plant
Rep (R)	<0.001
Oxidation (O)	NS
Concentration (C)	0.0075
O * C	NS
R * C	NS
Plant (P)	<0.001

PLANT TISSUE ACCUMULATION WHEN SUPPLIED WITH 500 AND 1000 PPB SELENIUM



Oxidation (NS) data pooled

Aquatic Plant

PLANT SELENIUM

- Duckweed greatest Se accumulation (p-value < 0.001)
 - Dilution from vegetative growth, less aqueous Se available for uptake
- At 1000 ppb Se, CAB and MG greater Se accumulation compared to CT and SR (p-value = 0.01)
- Lower tissue Se content in CT and MG compared to DWD, but greater aqueous Se reduction, suggest possibility of phytovolatilization (Hansen et al., 1989; Lin et al., 2002)

SELENIUM MASS BALANCE

Treatment	Plant	Aqueous Selenium Removal	Plant Selenium Content	Missing Selenium
ppb Se		mg		
500	CAB	12.7	2.1	10.6
	CT	14.1	0.3	13.8
	DWD	10.4	5.1	5.3
	MG	12.9	2.8	10.1
	SR	10.9	0.1	10.8
	UNP	11.5	0.0	11.5
1000	CAB	22.4	3.6	18.8
	CT	19.5	0.9	18.6
	DWD	14.5	12.5	2.0
	MG	26.5	6.9	19.6
	SR	21.6	0.2	21.4
	UNP	17.4	0.0	17.4

SELENIUM MASS BALANCE

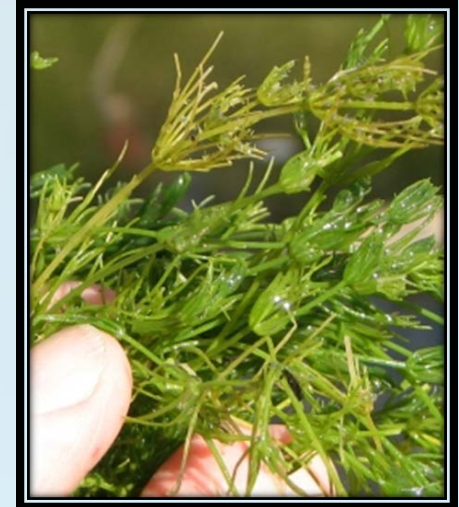
Treatment	Plant	Aqueous Selenium Removal	Plant Selenium Content	Missing Selenium
ppb Se		mg		
500	CAB	12.7	2.1	10.6
	CT	14.1	0.3	13.8
	DWD	10.4	5.1	5.3
	MG	12.9	2.8	10.1
	SR	10.9	0.1	10.8
	UNP	11.5	0.0	11.5
1000	CAB	22.4	3.6	18.8
	CT	19.5	0.9	18.6
	DWD	14.5	12.5	2.0
	MG	26.5	6.9	19.6
	SR	21.6	0.2	21.4
	UNP	17.4	0.0	17.4

SELENIUM MASS BALANCE

Treatment	Plant	Aqueous Selenium Removal	Plant Selenium Content	Missing Selenium
ppb Se		mg		
500	CAB	12.7	2.1	10.6
	CT	14.1	0.3	13.8
	DWD	10.4	5.1	5.3
	MG	12.9	2.8	10.1
	SR	10.9	0.1	10.8
	UNP	11.5	0.0	11.5
1000	CAB	22.4	3.6	18.8
	CT	22.8	0.9	21.9
	DWD	14.5	12.5	2.0
	MG	26.5	6.9	19.6
	SR	21.6	0.2	21.4
	UNP	17.4	0.0	17.4

CONCLUSIONS

- Results from this study indicate cattail and muskgrass can improve water quality of selenium impacted stormwater compared to unplanted constructed wetland systems
- Plant selenium accumulation was greater at 1000 ppb Se, regardless of selenium chemical form
- Phytovolatilization is a suspected elimination pathway



FUTURE RESEARCH

- Ephemeral dosing with ultra-low concentrations of selenate
 - Selenium removal and plant uptake
 - Seasonal replications
 - April, July, October, and January
- Phytovolatilization
 - Unaccounted for Se in CT and MG mass balance

ACKNOWLEDGEMENTS



Interdependence is of greater value than independence.

QUESTIONS?



mpn25@msstate.edu

