



Assessing best management practices for remediation of selenium loading in groundwater to streams in an irrigated region



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SUMMARY

Selenium (Se) contamination in groundwater and surface water in numerous river basins worldwide has become a critical issue in recent decades. An essential micro-nutrient, Se can prove harmful to fish, water fowl, livestock, and even humans at elevated concentrations. In an overall effort to curb Se contamination in environmental systems, this study aims to identify best-management practices (BMPs) that can assist in remediating Se contamination in irrigated river basins. Using multi-decadal simulations of a calibrated and tested groundwater flow model (MODFLOW-UZF) and Se chemical reactive transport model (UZF-RT3D), the impact of water- and land-management strategies in reducing Se contamination are explored for a 500 km² study region in the Lower Arkansas River Valley (LARV) in southeastern Colorado. The effectiveness of reduced applied irrigation volumes, sealing of earthen irrigation canals, rotational fallowing of cultivated land, reduced fertilizer loading, and enhanced riparian buffer zones, implemented individually as well as concurrently in various combinations, is explored. Results indicate that significant (>10%) decreases in Se mass loading to the Arkansas River system (main stem and tributaries) can be achieved when individual BMPs are implemented, with land fallowing, reduced irrigation, and enhanced riparian buffer zones providing the best results (13–14% load reduction). Even greater impacts (20–50% Se load reduction) can be achieved with 3 or 4 BMPs implemented concurrently. Results demonstrate that Se remediation can potentially be achieved within the LARV, and also can serve as a guide for other Se-affected river basins within the western United States and throughout the world.

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1. Introduction

Elevated concentrations of Selenium (Se) in river basins throughout the western United States and in many regions worldwide (Seiler, 1997; Afzal et al., 2000; Mizutani et al., 2001; Zhang et al., 2008) has become a serious environmental issue in recent decades. An essential micro-nutrient for humans and animals (Combs et al., 1986; Aro et al., 1998), moderate concentrations can cause deformities and even death among water fowl and fish populations (Flury et al., 1997; Hamilton, 1998; Skorupa, 1998), and as such the chronic freshwater ambient water quality criteria for Se has been set to 4.6 µg/L. Elevated Se concentrations typically occur in alluvial, irrigated river valleys underlain by marine shale, wherein residual Se contained in the shale (Bye and Lund, 1982; Logan et al., 1987) can be oxidized in the presence of dissolved oxygen (O₂) and nitrate (NO₃) (Wright, 1999; Fernández-Martínez and Charlet, 2009; Stillings and Amacher, 2010; Bailey

et al., 2012), resulting in drainage water containing toxic concentrations of Se (Seiler, 1995). Once in the dissolved phase, the chemical reduction of toxic Se species also is inhibited by the presence of O₂ and NO₃ (Oremland et al., 1989; Weres et al., 1990; White et al., 1991; Zhang and Moore, 1997).

In response to this issue, it has become increasingly important to identify water- and land-management practices that could assist in first, remediating Se-contaminated stream systems and the aquifer systems that discharge groundwater to these systems in alluvial river valleys; and second, inhibiting further Se contamination from occurring. Several studies (Gao et al., 2000, 2003; Lin and Terry, 2003) report the use of a small-scale constructed flow-through wetland (10 compartments, with each compartment 15 m by 77 m) in Tulare Lake Drainage District in Central California to remove Se from agricultural subsurface drainage water. The field studies evaluated Se speciation and transformation, and found that dissolved-Se concentrations in the effluent water were significantly lower than in the influent water, and that Se accumulated in wetland surface sediments via chemical reduction and also within plant tissues. A follow-up study (Chow et al., 2004) developed a mathematical model to simulate the fate and transport of

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Nomenclature

ADR	advection–dispersion–reaction	LF	lease following BMP
<i>auto</i>	autotrophic chemical reduction	<i>min</i>	mineralization
BMP	best management practice	N_{up}	seasonal crop uptake of nitrogen
C	solute concentration	OC	organic carbon
C_f	solute concentration of the source or sink	P_{Rt}	application rate of root mass
CN_{RT}	carbon–nitrogen ratio in root mass	P_{St}	application rate of after-harvest stover mass
CN_{ST}	carbon–nitrogen ratio in stover mass	q_f	volumetric flux of water representing sources and sinks
CS	canal sealing BMP	R	retardation factor
D_{ij}	hydrodynamic dispersion coefficient (tensor with index notation)	RF	reduced fertilizer BMP
<i>dec</i>	organic matter decomposition	RI	reduced irrigation BMP
$d_{rt,max}$	maximum rooting depth	r_f	rate of all reactions that occur in the dissolved-phase
E	environmental reduction factor	r_s	rate of all reactions that occur in the solid phase
ERB	enhanced riparian buffer zone BMP	Se_{up}	seasonal crop uptake of selenium
f_e	synthesis efficiency	T	temperature
f_h	humification factor	TDS	total dissolved solids
F	inorganic fertilizer application rate	U	potential uptake rate
H	humus pool	USR	upstream study region
$H_{C/N}$	carbon–nitrogen ratio in humus pool	α_{Rt}	portion of root mass
$B_{C/N}$	carbon–nitrogen ratio in microbial population	α_{St}	portion of stover mass
<i>het</i>	heterotrophic chemical reduction	ε	volumetric solid content
<i>imm</i>	immobilization	ξ	S:Se shale mass ratio
I_{O_2}	O_2 chemical reduction inhibition term	θ	volumetric water content
I_{NO_3}	NO_3 chemical reduction inhibition term	λ	base reaction rate constant
K	Monod half-saturation constant	ρ_b	bulk density of the porous media
K_d	partition coefficient	ϕ	porosity
L	litter pool	v	pore velocity
LARV	lower Arkansas river valley	γ_{up}	SeO_4 – SeO_3 crop uptake ratio

Se species within and between the 10 wetland compartments, with complete mixing assumed within each compartment. Physical processes simulated include water movement, leaf litter drop, and physical material breakdown. Chemical processes simulated include chemical reduction of Se species and volatilization, assumed to follow first-order kinetics. Once tested, the model could be used to determine which wetland cell characteristics (e.g., water inflow rate, water depth, lateral dimensions of cells) govern Se removal, and hence assist in optimally designing a constructed flow-through wetland for Se removal.

More recently, a study along a 48-km reach of the Colorado River near Grand Junction, CO (Bureau of Reclamation, 2007) has identified possible cost-effective solutions to meet Se water quality standards using economic appraisal methods. These solutions include diluting high-priority tributaries and drains in the river valley by importing water from small storage reservoirs or canal diversions, improving habitat within these tributaries and drains by increasing sinuosity, reducing sediment load and increasing the amount of woody debris, and also treating Se-contaminated groundwater drainage using bioreactors or other methods. Myers (2013) used a groundwater flow and Se contaminant transport model to explore the effect of remediation scenarios in the Blackfoot watershed in Idaho, USA, wherein phosphate mining has led to elevated Se concentrations in the river in recent decades. The study treated Se as a conservative solute and used 400-year hypothetical simulations to investigate the impact of remediating waste rock from mines as compared to a baseline (no-remediation) scenario.

Numerous studies have used field and numerical modeling techniques to explore and identify remediation BMPs for other chemical species, particularly for nutrients such as nitrogen (N) and phosphorus (P). For agricultural watersheds, typically the reduction in loadings of N and P from the aquifer to the stream is used as an indicator of improvement and remediation. Specific BMPs analyzed

include reduction in applied irrigation water (Buchleiter et al., 1995; Ma et al., 1998; Rong and Xuefeng, 2011) and fertilizer loading (Molénat and Gascuel-Oudoux, 2002; Chaplot et al., 2004; Almasri and Kaluarachchi, 2007; Lee et al., 2010; Zhang et al., 2012), and implementing or enhancing riparian buffer zones due to the increased source of organic carbon (OC) and associated increased chemical reaction rates for denitrification (Heathwaite et al., 1998; Hefting and de Klein, 1998; Spruill, 2000; Vaché et al., 2002; Sahu and Gu, 2009). For reduction in fertilizer loading, rates of decrease used in the studies typically range between 20% and 40% (Ledoux et al., 2007; Almasri and Kaluarachchi, 2007; Lee et al., 2010). These values of decrease are consistent with the reports of Babcock and Blackmer (1992) and Trachtenberg and Ogg (1994), who report that farmers apply a fertilizer loading that is generally 24–38% higher than the demand of the crop.

Also, in recognition that several years to decades may be required for these best-management practices (BMPs) to provide a change in loadings to streams due to the long travel time of groundwater, model simulations exploring alternative management scenarios typically are run for one or more decades using system inputs (e.g., rainfall, climate variables, irrigation application, etc.) that are both reflective of watershed conditions and that also capture the temporal variability of climate. For example, Garcet et al. (2002) and El-Sadek et al. (2001) used simulation runs of 30 years in their field-scale studies, Kurtzman et al. (2013) used simulation runs of 25 years to predict the change in NO_3 flux to groundwater, and Conan et al. (2003), Chaplot et al. (2004) and Ledoux et al. (2007) used 15-year, 32-year, and 45-year forecast simulations, respectively.

Although decreasing application of Se-laden irrigation water and enhancing riparian buffer zones are appealing remediation strategies for Se-contaminated stream-aquifer systems, with the latter enhancing the potential for Se chemical reduction before

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