

Physical-Chemical Nature of Sediment Selenium with Implications for Bioavailability

(Funded 2001-2002)

Principal Investigators:

Richard M. Higashi

Crocker Nuclear Laboratory

UC Davis

(530) 752-1450

rmhigashi@ucdavis.edu

Robert G. Flocchini

Crocker Nuclear Laboratory

UC Davis

(530) 752-1460

flocchini@crocker.usdavis.edu

Executive Summary:

Overview

The project proposed here is one part of a larger, Joint Research effort proposed for selenium (Se) ecotoxicity remediation in evaporation basins. Our focus on evaporation basins has several major endorsements: (a) it is a proven, economical means by which to dispose of waste agricultural water and contain the salt; (b) it is a "no discharge" technology for the disposal of water since it is terminal, thus capable of avoiding almost all aspects of the Total Maximum Daily Load (TMDL) regulations; (c) historically, its principal detracting feature has been Se toxicity to migratory waterfowl, yet in recent years, basin management schemes have significantly reduced this risk; (d) most recently, we have obtained field-scale evidence that remediation through a combination of foodchain breakage with natural volatilization may be possible. This last is the topic of the Joint Research project.

In the San Joaquin Valley agricultural drainage waters, the only known issue with selenium is toxicity to top predators such as aquatic birds, which receive their selenium primarily through their diet, such as aquatic invertebrates and fish. The research shows that waterborne selenium concentration is not always a reliable predictor of selenium content in aquatic organisms (Skorupa and Ohlendorf, 1991; Bowie et al., 1996) or observed toxicity (e.g. Reash et al., 1997). It is now clear that selenium "biogeochemistry" - that is, how selenium chemically transforms both inside and out of organisms - plays a pivotal role in determining the ecotoxic risk at particular sites (EPA Office of Water, 1998). Consequently, there has been scientific consensus that tissue or protein-bound selenium concentrations are possibly better markers of ecotoxic risk (EPA Office of Water, 1998). There is additional scientific consensus that sediments harbor key pools of Se for ecotoxic effects (EPA Office of Water, 1998).

Thus, selenium biogeochemistry is where the solution must be sought for the best chance at selenium remediation. These processes must be evaluated for any remediation effort and may even be exploited to mitigate Se ecotoxic problems. These concepts form the foundation of the proposed projects at the Tulare Lake Drainage District (TLDD) evaporation basin and at the Lost Hills Water District's (LHWD) evaporation basin site. This is in contrast to most projects in the San Joaquin Valley, which keyed on simple, but unfortunately unreliable, indicators such as waterborne Se concentration.

The overarching objectives of the joint project, "Mitigating Selenium Ecotoxic Risk by Combining Foodchain Breakage with Natural Remediation", which involves the PIs listed above in separate but linked projects, plus cooperators at Novalek, DWR, TLDD, and LHWD, are keyed around the foodchain system in TLDD and LHWD evaporation ponds, which include:

- Evaluating the efficacy of reducing Se risk resulting from intensive commercial harvest of brine shrimp (*Artemia franciscana*) and other macroinvertebrates in TLDD and LHWD basins.
- Assessing effects of fertilizer inputs on algal dynamics for optimizing the harvest of brine shrimp and other macroinvertebrates as well as Se volatilization so that total and bioavailable Se are reduced in TLDD and LHWD basins.
- Evaluating ecotoxic status in different basins of widely varying salinity and other conditions, so that general factors leading to reduced ecotoxic risk can be discerned.

Objectives

The biogeochemistry of Se must be at the core of design and implementation of remediation on Se ecotoxic impact. Part of the biogeochemistry is trophic transfer of Se, which is being examined by Salinity/Drainage investigators (Fan and Fry). However, the chemical basis of bioavailability - that is, the molecular mechanisms of lower trophic level entry of Se into the foodchain - remains largely unknown and unstudied. There is only a general consensus that organic forms are much more bioavailable than inorganic forms of Se (e.g. Rosetta and Knight, 1995), yet such impressions have already worked their way into the regulatory arena for water (EPA, 1996; EPA, 1997). Moreover, the sediment is the major Se sink, yet it is essentially uninvestigated (EPA Office of Water, 1998).

The specific objectives of this proposal key on newly-deposited sediment (0-3 months old, using a sediment trap), from both in situ test enclosures (proposed by the Rejmankova and Fan projects) and existing evaporation basins at TLDD and Lost Hills Water District (LHWD). These two represent "low" (10-20 ppb) (Fan, Higashi, and Lane, 1998), "low-harvested", and "high" (300 ppb) (Nixon, 1996) waterborne Se sites, respectively. The objectives are to probe the:

- i. Microphysical basis for bioavailability of Se in sediments, by determining gaseous, "mobile" (waterborne), and "immobile" (solid) states of Se;
- ii. Chemical basis for bioavailability, by analyzing mobile and immobile states for several known and hypothesized organo-Se structures, such as proteinaceous Se;
- iii. Physico-chemical basis of bioavailability, by extraction of the organic matter ("humic") from the immobile Se state, and coarse size fractionation of the mobile Se into particulate-detrital and colloidal-soluble fractions, followed by (ii).

Approach for Objective (i). The physical state of organic Se forms defines the limits of exposure, and therefore the bioavailability. Three physical states will be separated from sediments, gaseous, mobile (e.g. waterborne), and immobile (e.g. solid).

Approach for Objective (ii). In conjunction with physical state, the chemical form is a key factor in bioavailability of any element, including Se. The gaseous Se will be "extracted" by freeze-drying whole sediment, then analyzed by gas chromatography/mass spectrometry (GC/MS). For the other fractions, we will probe for free and proteinaceous selenoamino acids as well as selenoniuml structures.

Approach for Objective (iii). The mobile state will be further separated on the basis of size (particulate/detrital vs. colloidal/soluble), while the immobile state will be extracted to yield the humic material. These will be subject to the battery of chemical analyses in (ii).

We will also study diagenesis of organic Se structures from (ii), by comparing recently sedimented material with the more aged sediment cores that will be investigated by the project of Drs. Gao and Dahlgren.