

ENVIRONMENTAL SELENIUM AND LAND DISTURBANCE: SOIL, VEGETATION, WATER AND ANIMALS¹

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Abstract. Selenium (Se), an element of interest and concern, is recognized for its environmental impact to soils, plants, and waters in native and disturbed ecosystems in western U.S. because of its natural occurrence and potential toxicity to wildlife and livestock (Vance & Schuman 1996). This presentation will address issues related to Se analysis and levels in soils, plants, waters, and wildlife. Information presented will be based on several Se-related research projects conducted by the author that examined analytical methods for Se analysis; methods of sampling; Se analytical procedures for soil, overburden, backfill, vegetation, and water; identification of Se levels in native and disturbed environments; and organism Se concentrations. Objectives of this research were to identify: 1) what extraction procedures are better indicators of "soluble" (plant available) soil or backfill Se; 2) what forms of Se are present in seleniferous soil and backfill materials, and how are these related to plant Se uptake; 3) what impacts do chemical, physical and biological soil characteristics have on plant Se uptake; 4) how does Se content of native and reclaimed plant species vary; 5) what effect does soil depth have on plant uptake of Se; and 6) what Se suitability limits should be recommended for reclaimed topsoil and vegetation?

Additional Key Words: Selenite; Selenate; Extractable Se; Hot water Se; AB-DTPA Se; Phosphate Se; Saturated paste Se; Bioavailable Se; Soil-plant Relationships; Site Characteristics; Standard Operating Procedures; Statistical Analysis; Atomic Absorption Spectroscopy; Hydride Generation; Ion Chromatography; Sediments; Vegetation Life-forms; Grasses; Forbs; Shrubs

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Methods for Se Analysis

The solubility and availability of Se depends on the relative concentration of Se species present in solution, which subsequently can govern Se deficiency or biotoxicity. Numerous analytical methods have been used to determine Se in waters, soils, overburden, and plants (Reddy & Vance 1995, Reddy et al. 1995b, Sharmasarkar et al. 1998). Studies have included suitable instrumentation for Se analysis (ion chromatography (IC) and atomic absorption spectrophotometry (AAS) with hydride generation) (Sharmasarkar et al. 1996b); solution Se speciation (water, hot water (CaCl₂), AB-DTPA, and phosphate extracts) (Sharmasarkar et al. 1998); Se extraction methods (phosphate, AB-DTPA, hot water, saturated paste) (Vance & Pasch 1995); solid Se speciation (0.25M KCl, 1M KH₂PO₄, 4N HCl, KClO + 12 N HCl, concentrated HNO₃+HClO₄+HF) (Sharmasarkar & Vance 1994, 1995a); adsorption/desorption studies (Blaylock et al. 1995, See et al. 1995, Sharmasarkar et al. 1992, 1995, Sharmasarkar & Vance 2002a, Vance et al. 1995, 1998, You et al. 2001); precipitation/dissolution studies (Sharmasarkar et al. 1996a), plant Se characterization (Sharmasarkar & Vance 2002b); and soil chemical and pedological characterization (Sharmasarkar & Vance 1995c, 1997b). Whereas AAS-HG is capable of analyzing very low Se level, IC is capable of speciating aqueous Se directly; AAS-HG can determine total Se and selenite, but in separate runs. The IC method quantifies both SeO₃²⁻ and SeO₄²⁻ in solution (Reddy et al. 1995c) without the need for sample pretreatment or HCl reduction, which is required for AAS-HG analysis (Sharmasarkar et al. 1996b, 1998).

Se in Soil, Backfill and Overburden Materials

During disturbance activities, exposure of Se-containing materials to oxidizing environments can result in elevated levels of mobile and plant-available Se that impacts the post-disturbance land use (i.e., grazing land, pastureland and/or fish, and wildlife habitats) (Reddy et al. 1995a, Sharmasarkar & Vance 1997a). Plant, soil, backfill, and overburden samples were collected from abandoned, reclaimed, and native sites at numerous surface coal mines (Carroll et al. 1993, Fadlemawla et al. 1992, 1994, Reddy et al. 1995a, Spackman et al. 1995), a phosphate mine

(Vance 2000), a uranium mine (Sharmasarkar & Vance 2002b) and a military base (Skinner & Vance 2001, 2002). Data indicated the order of Se extractability was: phosphate > AB-DTPA > hot water > saturated paste; phosphate and AB-DTPA extractable Se were found to be strongly correlated (Vance & Pasch 1995). Five methods (Spackman et al. 1994) used to determine soil Se (i.e., total Se and the four extraction methods) were also compared among cores sampled in native and reclaimed sites at 3 to 5 depths. A large range in the coefficient of variation (CV) was noted (0 to 153%); however, the larger CV's tended to be grouped at specific sites and depths. Average CV's for mine type and ecological system (i.e., native versus reclaimed) were approximately 25%. Overall, total Se varied the least among the five Se variables followed by KH_2PO_4 < AB-DTPA < hot water = SPE Se. From inter-laboratory comparisons, AB-DTPA, hot water, and phosphate extractable Se were highly correlated ($R^2 = 0.95$) (Vance & Pasch 1995).

Vegetation Se Concentrations

Native and reclaimed disturbed areas were evaluate to determine the association between plant Se levels (Steward et al. 1994) to Se concentrations in soil, backfill, and overburden materials based on environmental variables at each site, vegetation surveys, and vegetation sampling by life-forms (Johnson et al. 1994, Schladweiler et al. 1992, 1993, 1995, Sharmasarkar & Vance 1995b, Vance & Pierzynski 2001, Wanek et al. 1995). Results suggest that there is: 1) a slight, but distinct, tendency for Se to be greater in reclaimed disturbed sites than native vegetation, 2) reclaimed vegetation Se concentrations decrease with time, 3) sites can be selected with elevated levels of Se in vegetation based on non-vegetative site characteristics, 4) Se levels in grasses are consistently lower than those in forbs and shrubs, and warm season grasses are lower than cool season grasses, 5) moisture availability may play an meaningful role in modifying Se uptake, 6) and geographic location may be more important than any other factor in the elevation of Se levels in vegetation (Skinner & Vance 2002, Vicklund et al. 1995). The relationship between soil/backfill Se levels (determined from four different extraction methods and total Se) and plant Se levels (three different life forms-grass, forb, shrub, and a composite grass) indicated plant Se levels varied widely from location to location; however, several plants had Se concentrations

above the suggested toxicity limit of 5 mg/kg (Sharmasarkar and Vance 1995b, 2002b, Wanek et al. 1999). Plants sampled in different years from the same sampling sites showed considerable changes in total Se content (Skinner & Vance 2002, Vicklund et al. 1995).

Se in Streams and Wetlands

Leachates from Se-bearing shale wastes derived from the mining of phosphate rock have contributed to the dispersion of Se in downstream environments (Vance 2000). Surface waters and sediments contained elevated levels of Se above the background levels of local non-contaminated streams and soils. Stream sediments (e.g., muck samples) were extremely high, with Se concentrations between 6.0 and 7.2 mg/kg. Transects placed across a stream flowing through pastures were sampled to examine Se concentrations in upland (e.g., native), midslope, and low-lying areas that were impacted by the Se-contaminated waters. Upland and midslope sites that were unaffected by the waste shale leachates had bioavailable Se concentrations that were approximately 0.05 mg/kg soil, whereas low-lying sites had levels ranging from 0.5 to 2.6 mg/kg soil. Selenium contents of vegetation within the contaminated sites were also high - ranges included 20 to 170 mg/kg for grasses and 40 to 210 mg/kg for forbs (Vance 2000). Results provide information for addressing three important aspects of Se distribution in the environment: 1) comparisons between Se concentrations in terrestrial and wetland soils, sediments, and plants; 2) relationships between Se contents in wetland plants, sediments, and waters; 3) effectiveness of various wetland-riparian vegetation species in Se uptake compared to plants traditionally studied for this purpose (Skinner & Vance 2002). Aqueous plant extracts can be speciated into inorganic and organic Se fractions (Sharmasarkar & Vance 1995b).

Animal Se Impacts

Effects of Se in forage and feed materials on select organisms were investigated (Raisbeck et al. 1995). The primary goal was to ascertain the environmental levels (e.g., land disturbance) at which Se toxicity effects correlate to dietary intake with target organisms. Organisms are

expected to provide information that will assist in the development of regulations for proper handling of Se in the post-mining environments. The target organism study provided information that assisted in developing new regulations for proper handling of Se in the post-mining environment. In addition, Se levels that are well above the concentrations recommended as suitable for soils (0.4 mg/kg) and plants (5 mg/kg) have been shown to contribute to long-term consequences of Se in phosphate mining areas, and the fact that horses were pastured in these Se-contaminated sites resulted in selenosis, i.e., Se poisoning (Vance 2000).

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