

Proposal submitted to
Agricultural Research Foundation
For
Pesticide Division of ODA

Lawrence R. Curtis
Environmental & Molecular Toxicology Department
Oregon State University
Corvallis, OR 97331

Principal Investigator: Lawrence R. Curtis
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Of Metals in Fertilizers
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Lawrence R. Curtis
Telephone: 541-737-1764
Email: lawrence.curtis@orst.edu

Date

Peggy S. Lowry, Director of Sponsored Programs
Telephone: 541-737-3437
Email: Sponsored.Programs@orst.edu

Date

Validating Modeling Parameters for Risk Assessment Of Metals In Fertilizers

Background and Rationale

The Oregon Department of Agriculture (ODA) set standards for arsenic, cadmium, lead, mercury, and nickel concentrations in fertilizers and related products in 2003. Development of these standards was largely based on critical evaluation of previously-conducted human health risk assessments (Foster-Wheeler, 1998; USEPA, 1999; Weinberg Group, 2000; Weinberg Group, 2001). These risk assessments evaluated multiple exposure pathways for farm workers and farm families, including children. These groups were considered as those with highest exposure potential and therefore at most risk. Accumulation of metals in crops consumed in high quantities by farm families and direct consumption of soil were identified as pathways for maximum potential exposures. Estimated soil concentrations of arsenic, cadmium, lead, mercury, and nickel after 50 years of product applications and soil lead concentration after 200 years of product applications were used for exposure pathway analyses. Therefore, estimated soil accumulation rates for these metals over time were critical determinants of outcomes for exposure modeling.

Aside from amount applied, estimated tendencies of metals to leach from soils to groundwater and or surface water were major determinants of outcomes for soil accumulation modeling. The ratio of metal concentration in soil particles divided by that in soil water (distribution coefficient, K_d) was the modeling parameter that represented tendency for leaching of each metal. K_d values employed for risk assessments were derived from two literatures reviews (Baes and Sharp, 1983; Sauve et al., 2000). The work reviewed in these studies clearly demonstrated K_d s for metals were not constants but varied greatly depending on soil chemistry, especially pH and organic matter content. Metals were consistently more water soluble and prone to leaching in acid soils (lower K_d). Increased organic matter content elevated the number of metal binding sites in soil and increased K_d . The K_d for a given metal in a soil was also dependent the total metal concentration. As metal binding sites saturated, K_d decreased. Since K_d values were determined in the laboratory differences in methods employed also contributed to variability. K_d s were most often estimated with soil columns or stirred flow reactors. Strawn and Sparks (2000) demonstrated equilibrium conditions assumed for such methods were not achieved under standard laboratory conditions. Taken together, complex environmental chemistry and methodological limitations were expected to produce uncertainty in K_d estimates. The great disparity between K_d estimates was problematic (Table 1). Estimates for arsenic varied about 1000-fold, those for cadmium at least 100-fold, and those for lead at least 20-fold. Selection for K_d s for risk assessment was therefore a huge source of uncertainty and controversy. The major goal of this project is to “ground truth” estimates of metal accumulation rates in agricultural soils with the K_d estimates incorporated into risk assessment modeling. This involves data analyses for arsenic, cadmium, lead, mercury, and nickel concentrations in Oregon soils

collected in other projects ODA funds in response to the “2003 Ground and Surface Water Research Grants.” Specifically, proposals that determine soil metal concentrations over time with or without fertilizer applications are of special value for validation of K_d s. Measurements in ground and surface waters provide additional insight into metal leaching/mobility and potential impacts on freshwater resources. Determinations of metal concentrations in crops grown in soils of known metal concentrations provide a means for “grounding truthing” plant uptake factor (PUF) estimates. It is important to recognize that substantial dilution of metals in fertilizers occurs when they are dispersed in the tilled layer of agricultural soils. Years of monitoring after the current funding cycle is clearly necessary. Major objectives of the work we propose are to establish a firm background for this monitoring program and provide ODA the computer software necessary to appropriately analyze data deriving from it.

Table 1. Distribution Coefficients and Plant Transfer Coefficients for Heavy Metals in Agricultural Soils

	Arsenic	Cadmium	Lead	Mercury	Nickel
Baes and Sharp K_d	1-18	1.3-26.8	4.5-7640	NA	NA
Sauve et al. K_d	13,119	2869	171,214	8946	16,761
Plant Transfer coefficients	0.01-0.10	1-10	0.01-0.10	0.01-0.10	0.1-1.0

NA= not available

Ranges for Baes and Sharp (1983) are for a range of pH 4.5 to 9.0

Sauve (et al. 2000) specify their K_d values do not consider desorption potential or bioavailability of different metal species

The potential for crops to accumulate arsenic, cadmium, lead, mercury or nickel from soils were represented by PUFs in risk assessment modeling. Measurements for PUFs varied about 10-fold for a particular metal (Table 1). Much of this was due to differences in metal accumulation for different plant species. The impact of uncertainty about PUFs was much less problematic for risk assessment than uncertainty over K_d s. None-the-less a secondary goal of this project is to validate PUFs for crops grown on agricultural soils with known fertilizer product applications.

Risk assessments for arsenic, cadmium, lead, mercury, and nickel require assembly of data sets on the toxicology of these metals in addition to environmental chemistry used for exposure assessment. The project’s final goal is to review recent literature on environmental chemistry, general toxicology, and ecotoxicology of these metals. This provides valuable context for examining assumptions inherent to risk assessment. It also provides a basis for evaluation of groundwater and surface water data for sites associated

with fertilizer product applications. There are allowable levels for these metals in drinking water for human health and surface water for protection of aquatic life (Table 2). These provide context necessary for interpretation new data collected over the next three years. If metal concentrations in sediments from surface waters adjacent to fertilized agricultural land are provided by other projects, these will be compared to available USEPA sediment quality criteria.

Table 2. Water quality criteria for five heavy metals in fresh-water.¹ Exceeding these concentrations ($\mu\text{g/L}$) is unacceptable for protection of natural resources and human health.

	<u>Aquatic Life</u>		<u>Human Health</u>
	Acute ²	Chronic ³	MCL ⁴
Arsenic	NA ⁵	NA	50
Cadmium	3.9	1.1	10
Lead	8.2	3.2	50
Mercury	2.4	0.012	2
Nickel	1400	160	N/A

1. These concentrations were derived by the United States Environmental Protection Agency (USEPA, 1986).
2. Short-term exposures, four days or less.
3. Long-term exposures, whole lifetime.
4. Maximum contaminant level.
5. N/A = not available

Specific Aims

- Task 1: Review critically, evaluate, and summarize recent peer reviewed literature on environmental chemistry, general toxicology, and ecotoxicology of arsenic, cadmium, lead, mercury, and nickel. The literature review is due 12 months after funding of the project.
- Task 2: Review progress and integrate results of ongoing field research on transport and fate arsenic, cadmium, lead, mercury, and nickel in Oregon, Washington, and California. This will focus on information necessary for validating critical risk assessment parameters; specifically, to assure coordination of field work with risk assessment modeling. A preliminary report is due 24 months after funding.

Project Design and Methods

Task 1: Human health risk assessments for arsenic, cadmium, lead, mercury, and nickel were completed between 1998 and 2001 (Foster-Wheeler, 1998; USEPA, 1999; Weinberg Group, 2000; Weinberg Group, 2001). Scientific research on environmental chemistry, general toxicology, and ecotoxicology of these metals continued after these reports were released. A comprehensive literature review in these areas will focus on peer-reviewed work published between 1999 and 2003. An extensive data base assembled through the American Chemical Society (SciFinder Scholar 2002) will be searched for each metal and the topic phrases environmental chemistry and toxicology. For example, searching cadmium and environmental chemistry yields 1049 references. Titles are screened for potential relevance, date of publication, and journal reputation. Abstracts for papers of interest are available on-line. Papers are selected for acquisition through the Oregon State University Library after confirming relevance by reading the abstract. The literature review will emphasize mobility and speciation in soil and freshwater systems, human epidemiology and mechanistic toxicology, and toxicology studies in freshwater organisms and wildlife. The chemical forms (metal speciation) present in soils and freshwater systems are of special interest as they relate to PUF, mobility (K_d), and toxicity.

Task 2. Several projects in Oregon funded through the “2003 Ground and Surface Water Research Grants” should provide important new data useful for validating critical risk assessment parameters. Soil and crop arsenic, cadmium, lead, mercury, and nickel concentration data are of great value in validation of K_d and PUF values incorporated in risk assessment modeling. It is also important to obtain data generated in ongoing studies in California and Washington. An Oregon State University proposal by Dr. Kim Anderson is the major source of soil and crop data. Surface and groundwater data from Anderson are of additional value for considering potential inputs on aquatic life. As stated above: integration and analysis of data for metals in soils, crops, surface and ground waters with intent of validation of risk assessment requires a long-term commitment by ODA. The work described herein provides a foundation for validation of estimates of metal accumulation rates in soils that largely determine outcomes of risk

assessment modeling. Future monitoring is essential. Empirical validation of critical risk assessment parameters is possible and assures protection of human health and the environment.

References

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