

Heavy Metal in Fertilizers:
Considerations for Setting Regulations
In Oregon

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TABLE OF CONTENTS

	Page
Executive Summary	1
Transport, Fate and Effects of Heavy Metals in Agricultural Soils	2-8
Figure 1 – Pathways for loss of heavy metals from a fertilizer application sites	3
Table 1 – Background concentrations for five heavy metals in Oregon soils and Oregon Department of Environmental Quality	6
Table 2 – Water quality criteria for five heavy metals in fresh-water	7
Toxicology and Environmental Chemistry of Arsenic, Cadmium, Lead, Mercury, and Nickel	8-12
Risk-based Models and Other Approaches for Regulating Heavy Metals Concentrations in Fertilizers and Related Materials	12-25
Figure 2 – Profound effect of K_d on the RBC for cadmium in the low range of estimated K_d values	15
Table 3 – Distribution Coefficients and Plant Transfer Coefficients for Heavy Metals in Agricultural Soils	16
Table 4 –Schematic of information collection in a risk assessment	17
Figure 3 – Profound effect of PUF on the RBC for cadmium in the low range of estimated PUF values	20
Figure 4 – Estimated K_d for cadmium strongly influences model simulation of accumulation of the metal in soil over time	22
Figure 5 – Demonstration that the relationship between half-life for cadmium in soil and RBC is essentially identical to the k_d /RBC relationship	23
Figure 6 – There is a linear relationship between the half-life and K_d for cadmium in soil	24
Conclusions and Recommendations	25-28
Figure 7 – Simulation of arsenic accumulation in soil over time after application of 75 grams of 20% phosphate product containing 260 mg/kg arsenic once a year	26
References	29-32
Appendix 1	33-35

Heavy Metals in Fertilizers: Considerations for Setting Regulations in Oregon

Executive Summary

Concentrations of heavy metals in fertilizers, agricultural minerals, agricultural amendments, and lime products are subject to regulation by state governments. Oregon Department of Agriculture must adopt standards for arsenic, cadmium, lead, mercury, and nickel concentrations in these products during 2002. The objective of this regulation is to protect human health and natural resources from toxicity of these heavy metals. Since use of fertilizers and related products is a repetitive practice, it is necessary to consider cumulative changes over decades of applications. There is a significant body of scientific literature on transport, fate and effects of arsenic, cadmium, lead, mercury, and nickel. Integration of this information into models that represent behavior of these heavy metals in agricultural systems provides a rational approach to establishing unacceptable concentrations in fertilizers and related products. This involves screening available information, and identification of areas in which data limitations create uncertainty.

Human health risk assessment integrates information on environmental chemistry and toxicology of the metals of interest with estimates of product application rates and human exposures. Evaluation of the structure and results of existing risk assessments for fertilizers and related products yields several conclusions. Existing risk assessments are of common structure and follow the United States Environmental Protection Agency guidelines. Farm families are the human population at most risk. Estimates of soil metal concentrations after 50 years (200 years for lead) of product application largely determines human health risk. Estimates of distribution coefficients (soil-to-water concentration ratios) for each metal largely determine projections of soil metal accumulation over time, and there is high uncertainty in these estimates. Addressing uncertainty will likely require new research and re-evaluation of standards when the data is available. Since heavy metal concentrations in the United States food supply are on a declining trajectory, a compromise within the range of existing risk assessment results is rational for setting standards in 2002.

Transport, Fate and Effects of Heavy Metals in Agricultural Soils

Physical processes are primary determinants of transport and fate of heavy metals applied to soil in fertilizers and related products (Fig.1). Erosion, leaching, export in harvested plants, and volatilization are major potential pathways for loss from soil at an application site. Since they are elements, heavy metals are not subject to chemical degradation that is critically important in fate of organic compounds. Chemical conditions in soil are important secondary determinants of heavy metal transport and fate, however. The importance of interactions between metals and solid phases of soils, soil water, and air within and above soil depends on a variety of chemical factors. Absorption of metals from soil water to soil particles is the most important chemical determinant that limits mobility in soils (Alloway, 1995a). There are four general classes of these interactions: specific adsorption, co-precipitation, cation exchange, and organic complexation. Specific adsorption involves partly covalent bonds of the heavy metal with lattice ions on soil particle surfaces. Co-precipitation involves formation of water insoluble precipitates from metal ions (cations) and anions such as carbonate, sulfide, or phosphate. Cation exchange is non-specific interaction of metals with negative surface charges on soils minerals, such as clay. Finally, soil organic matter (e.g., humus) adsorbs metals by forming chelate complexes, with carboxyl groups playing a predominant role. Given the chemical basis for each of the four general classes of metal absorption, it is clear that soil type is a fundamental determinant of heavy metal transport and fate.

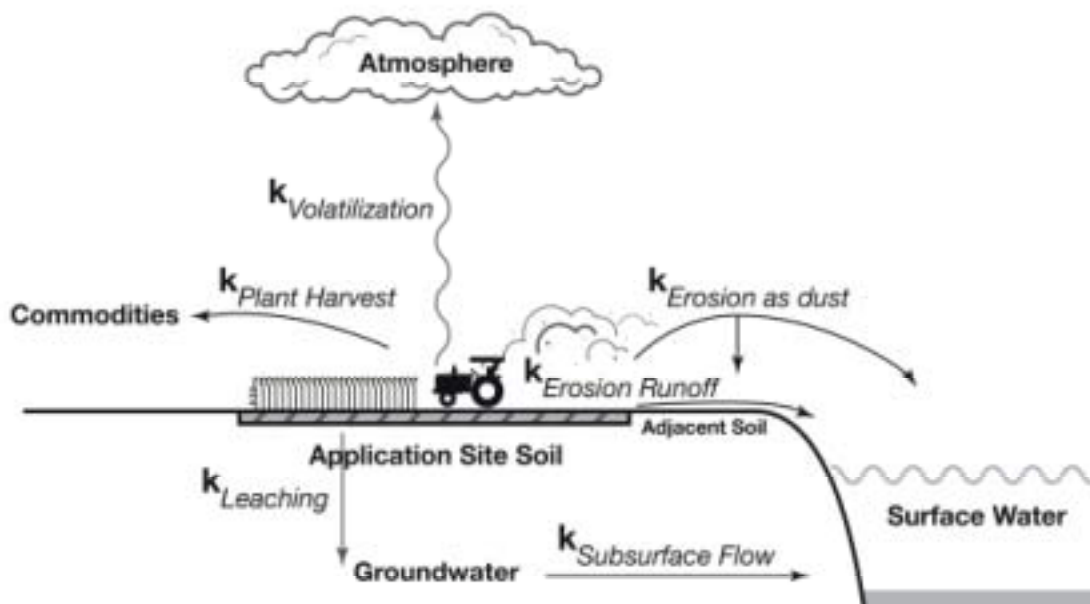


Figure 1. Pathways for loss of heavy metals from a fertilizer application site. For each pathway (arrows) a particular loss process occurs at some rate (K). The importance of each pathway and magnitude of each rate will vary substantially between arsenic, cadmium, lead, mercury, and nickel. For example, loss to the atmosphere by volatilization is probably often significant for mercury and perhaps arsenic, but not the other three metals. Alternatively, loss to commodities through plant harvest is probably important for cadmium and nickel but insignificant for lead.

Soil pH is another chemical factor that influences heavy metal transport and fate, especially mobility in soil water (Alloway, 1995a). First, ionization of metals increases at low pH thereby increasing water solubility and mobility. Second, hydronium ions displace most other cations on negative surface charges. This reduces metal absorption by cation exchange and organic complexation.

The rates of metal absorption to (also called sorption) and desorption from (which leads to mobilization) soil particle surfaces differ, sometimes greatly (Strawn and Sparks, 2000; Ford et al., 2001). In fact, sorption includes initial fast reactions, followed by slow reactions. The four general classes of absorption interactions described above constitute fast reactions. The mechanistic basis for slow reactions involves at least two processes: (1) while sorption to soil particle surfaces is fast, diffusion into pores and subsequent sorption at these sites is time-dependent; (2) sorbed complexes may undergo subsequent reactions to form more stable structures. Desorption of metals deep in pores or complexed in stable “aged” structures is much slower than initial sorption. This at least partially explains the “irreversible” sorption that is often reported. For example, desorption of lead from three soils with different organic matter content in stirred-flow reactors varied from 32 to 76% (Strawn and Sparks, 2000). These data do not reflect truly irreversible sorption, however. Slow desorption is not resolved in the design of most experiments due to the short times of typical experiments. Lead continues to desorb from these soils as more water volume washes through it. There is a progressive decline in the percentage desorbed with cumulative washes. The slow reactions for desorption are much slower than the slow reactions for sorption. Classical chemical descriptions for chemical sorption/desorption assume equilibrium conditions. Distribution coefficient

(K_d) for partitioning of a metal between the solid phase of soil and soil water is an example. Heavy metal sorption and especially desorption reactions are usually, if not always, dynamic within the time frame of experiments that estimate K_d . This violates the assumption of equilibrium conditions. This is one major contribution to problems with application of K_d values to estimates of heavy metal transport and fate in soil.

Understanding transport and fate of arsenic, cadmium, lead, mercury, and nickel provides a basis for explaining their capacity to accumulate in agricultural soils and plants that grow on these soils. It is also useful for assessing the potential for these metals to move into groundwater and surface water. It is clearly necessary to avoid heavy metal concentrations in soils, plants, groundwater, and surface water that can produce adverse effects on human or ecological health. Results from human health risk assessments are available for application of arsenic, cadmium, lead, mercury, and nickel found in fertilizers applied to agricultural soils. These risk assessments draw two general conclusions: (1) farm family members are at highest potential risk; (2) consumption of soil itself and crops grown on soils with high metal concentrations is the dominant pathway contributing to risk. The final section of this report provides an in-depth evaluation of these risk assessments.

Ecological risk assessments for soil applications of heavy metals in fertilizers and related products are not available. Despite this, sensitivities of several sub-systems within agricultural systems and boundary ecosystems to arsenic, cadmium, lead, mercury, and nickel remain important considerations. If one assumes direct phytotoxicity to crops and soil quality are within the domain of production management, then regulatory concerns focus on terrestrial/wetland systems, and surface water quality (assuming

groundwater quality is a human health concern). Some data is available that provides reasonable insight into background concentrations of arsenic, cadmium, lead, mercury, and nickel in Oregon soils (Table 1). There are also screening levels for metal concentrations in soils set to protect wildlife (Table 1). Consideration of these standards can provide a starting point for evaluating potential impacts of metals in fertilizers on ecological health. Screening levels for arsenic and lead overlap the range for background soils concentrations in Oregon (Boerngen and Shackette, 1981). Mean background soil concentrations of cadmium, mercury, or nickel for arsenic and lead are significantly lower than these screening levels, however. The modeling work done in our examination of human health risk assessments does not suggest fertilizer applications increase background soil concentrations to screening levels.

Table 1. Background concentrations for five heavy metals in Oregon soils and Oregon Department of Environmental Quality (ODEQ) bird/mammal screening levels soil concentrations (mg metal/dry kg of soil).

	<u>Holmgren et al., 1993¹</u>	<u>Boerngen and Shackette, 1981²</u>	<u>ODEQ³</u>
Arsenic	N/A	6.4 (4.3-10.3)	10/29
Cadmium	0.294	N/A	6/125
Lead	8.6	16 (10-20)	16/4000
Mercury	N/A	0.11 (0.04-0.26)	1.5/73
Nickel	27.4	16 (7-30)	320/625

N/A= not available.

1. The values are geometric means for 88 samples collected from northwestern, southcentral and southeastern Oregon.
2. The values are arithmetic means and (ranges) for samples from Benton (1 site), Columbia (1 site), Lincoln (1 site), Marion (2 sites), Multnomah (1 site), and Tillamook (2 sites) counties.
3. ODEQ soil screening levels from risk assessments with rats (representative mammal) and robins (representative bird).

Standards exist for protection of aquatic life from metal toxicity in surface waters for Oregon (Table 2). There is good reason to expect that these criteria protect aquatic ecosystem health since water quality criteria development requires a substantial data base on toxicity of each metal to multiple species of fish, invertebrates and plants (USEPA, 1986). These criteria are federal recommendations to the states that regulate water quality through setting standards and monitoring surface waters to assure compliance. In Oregon, this regulatory authority resides with ODEQ. It is not apparent that application of fertilizers or related materials results in arsenic, cadmium, lead, mercury or nickel concentrations in surface waters that violate Oregon water quality standards. However, expansion of monitoring programs to focus on surface waters adjacent to application sites can confirm or refute this.

Table 2. Water quality criteria for five heavy metals in fresh-water.¹ Exceeding these concentrations (µg/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

There are two general approaches to setting standards for concentrations of heavy metals in fertilizers and related products. They consider the same parameters but differ in the structure of formulas for calculations. The first approach considers the total mass of a metal applied to an area of soil per unit time. Canadian and State of Washington standards follow this approach. Canadian standards limit cumulative metal additions to soils over 45 years. The State of Washington divides the Canadian standards by 45 and expresses maximum pounds of metal added to soil per acre per year (Washington State Department of Agriculture, 2000). The standards are: arsenic, 0.297; cadmium, 0.079; lead, 1.981; mercury, 0.019; and nickel, 0.713. In order to determine metal additions one multiplies the pounds of product applied per acre times the concentration of metal in the product. The second approach is to base standards on the maximum concentration of a metal in the product. Since application rates vary substantially between types of products (i.e., micronutrient and phosphate fertilizers) it is necessary to set different standards for different products. Development of these standards requires estimating (modeling) soil concentration over time with cumulative product application. The advantage of this approach is that there is no need to calculate metal loading to soil for each product application.

Toxicology and Environmental Chemistry of Arsenic, Cadmium, Lead, Mercury, and Nickel

There are several potential pathways that determine transport and fate of heavy metals in soils (Fig.1). The relative importance of each pathway varies substantially between arsenic, cadmium, lead, mercury, and nickel. The potency and mode of toxic action also differs greatly between these heavy metals. This section briefly summarizes

the environmental chemistry and toxicology of arsenic, cadmium, lead, mercury, and nickel. Short term responses to large doses (acute toxicity) are not relevant to the risk assessments of interest here, so discussion focuses on long-term exposure to low concentrations (chronic toxicity).

The environmental chemistry of arsenic is similar to that of phosphorus, but more diverse (O'Neill, 1995). The natural forms of arsenic in soils are oxysalts and sulfur containing minerals. Arsenate (As V) composes about 90% of total oxysalts in aerobic soils. Arsenite (As III) is 60-85% of the total oxysalts in water-saturated anaerobic soils. Arsenate is more water soluble and mobile than arsenite. Microbial activity methylates arsenic to volatile compounds but the quantitative importance of loss via the atmospheric pathway remains unclear. Plant uptake of arsenic is usually low (plant uptake factors of 0.01-0.10) and phytotoxicity occurs at 40-200 mg/kg soil, depending on soil chemistry. The complex chemistry of arsenic leads to multiple chemical species that differ in toxicity (Goyer and Clarkson, 2001). Neurotoxicity, liver injury, cardiovascular disease, and skin cancer result from chronic exposure to inorganic arsenic. Arsenic in drinking water leading to exposures around 0.4 mg/kg/day can produce signs of toxicity in humans within six months to 3 years. Human health effects due to consumption of arsenic in crops is not evident.

Cadmium tends to be more mobile in soil systems and therefore more available to plants than many other heavy metals (Alloway, 1995b). Cd^{2+} is the principal species in soil solution. Accumulation of cadmium in food crops at soil concentrations that are not phytotoxic is a significant concern. Plant species differ widely in their tendency to accumulate cadmium. Lettuce, spinach, celery and cabbage avidly accumulate cadmium

while potato tubers, maize, french beans, and peas accumulate much less. Many studies show linear relationships between soil cadmium concentrations and wheat and barley grain, cabbage, and lettuce cadmium contents. Soil chemistry also influences cadmium mobility and uptake by plants. As with other metals, low pH increases mobility.

Absorption/desorption of cadmium is about 10-fold more rapid than for lead. Chronic cadmium exposures result in kidney damage, bone deformities, and cardiovascular problems (Goyer and Clarkson, 2001). A major human poisoning occurred in Japan during World War II due to industrial contamination of rice paddies. Since phosphate fertilizers can contain significant cadmium concentrations, cadmium can accumulate in crops, and human health problems can result from crop cadmium contamination; this metal received special scrutiny in our review of human health risk assessments.

Lead is especially prone to accumulation in surface horizons of soil because its low water solubility within an environmentally relevant pH range results in very low mobility (Davies, 1995). Soil water contains only about 0.05-0.13% of the total soil lead concentration. Lead speciation is rather simple and Pb^{2+} is the dominant soluble form. It forms a number of highly insoluble precipitates including $Pb(OH)_2$, $Pb_3(PO_4)_2$, and $PbCO_3$. Plant uptake factors for lead are low (0.01-0.1) due to very low water solubility. Due to past uses of lead in industrial processes and consumer products (e.g., paint, gasoline), urban soils often contain high lead concentrations, up to 1840 mg/kg. Neurologic problems, especially in children, are the principal concern for chronic lead exposure (Goyer and Clarkson, 2001). Past uses of lead solder in food and beverage cans lead to significant human exposures. Dietary intakes of 400 to 500 $\mu g/day$ dropped to

20 µg/day with elimination of this practice. Consumption of lead contaminated soil itself, rather than crop contamination, is a more likely exposure hazard.

Mercury solubility in soil water and hence mobility in soil systems is quite low (Steinnes, 1995). Plant accumulation (plant uptake factors of 0.01-0.1) and phytotoxicity are quite low. The most common chemical species in soils are Hg^0 and Hg^{2+} . Long-range atmospheric transport of mercury, in large part from coal combustion, can contribute up to 50% of total loading to humus-rich soils. Humic matter forms strong complexes with Hg^{2+} . In fact, transport of mercury in soil water is largely due to association with soluble humic matter. Chronic exposure due to consumption of methyl mercury in fish and other seafood with subsequent neurotoxicity is a human health concern (Goyer and Clarkson, 2001). Methyl mercury forms in anerobic sediments of aquatic ecosystems and biomagnifies through trophic transfer to fish. There is no evidence that this is a significant process in production of agricultural crops.

Nickel is moderately soluble in soil water and as is typically true for metals, increases at low pH (McGrath, 1995). The predominant soluble species in most agricultural soils is Ni^{2+} . Nickel sulfides likely control the Ni^{2+} concentration in soil solution. The nickel concentrations in plants generally reflect that of their soils and plant transfer coefficients range from 0.1 to 1.0. Inhalation of nickel during refining of ore produces respiratory tract cancer, and allergic contact dermatitis to nickel alloys is common (Goyer and Clarkson, 2001). Aside from these problems, nickel toxicity appears quite low. It is a nutritionally essential metal for some plants, microbes, and invertebrates. There is no known biochemical function for nickel in humans. Crop

contamination with nickel in fertilizers and related products seems an unlikely human health problem.

Risk-based Models and Other Approaches for Regulating Heavy Metal Concentrations in Fertilizers and Related Materials.

Application of risk assessment to setting standards for concentrations of potentially toxic chemicals in food and other sources of environmental exposure emerged over 20 years ago (Calkins et al., 1980; NRC, 1983). Faustman and Omenn (2001) summarized the current process of human health risk assessment. The probability of an adverse health effect was termed risk. A hazard was defined as a substance with intrinsic toxic properties, which presented risk. Risk assessment was defined as “the systematic scientific characterization of potential adverse health effects resulting from human exposures to hazardous agents or situations.” The conduct of a risk assessment included four steps: (1) Hazard identification indicated whether an agent caused adverse effects. (2) Dose-response assessment determined the relationship between dose and an adverse effect. (3) Exposure assessment estimated concentrations and durations of exposure to the agent. (4) Risk characterization estimated incidence of the adverse effect in a population, evaluated strength of evidence used underlying the analysis, and defined the degree of certainty for the analysis. Risk management involved development of regulatory options based on the outcome of the risk assessment. Stakeholder engagement was viewed as a critical element for selection of specific options in policy decisions and actions.

Risk assessments that focused on protection of human health were conducted by two groups of consultants (Foster Wheeler, 1998; Weinberg Group, 2000). Recent

analyses adopted procedures developed in a USEPA (1999) risk assessment for heavy metals in fertilizers (Weinberg, 2001). Final calculations for concentrations of heavy metals in fertilizers that presented a particular risk were not included in the USEPA (1999) work. Both the Foster Wheeler (1998) and Weinberg Group (2000) risk assessments generated maximum concentrations of metals in fertilizers that should not be exceeded (risk-based concentrations). Foster Wheeler conducted the risk assessment for arsenic, cadmium, and lead. The Weinberg Group expanded the risk assessment to 12 metals, including arsenic, cadmium, lead, mercury, and nickel. Estimates for the two critical parameters, plant uptake factors for each metal and metal concentrations in soil after 50 years of applications (200 years for lead), were necessary to conduct these risk assessments. Several limitations in modeling transport and fate of heavy metals in agricultural soils forced application of simplifying assumptions: (1) For any site, fertilizer application rates and schedules may vary within and between years. (2) Rainfall and irrigation rates can greatly influence metal mobility and these vary over time within site and often to an even greater extent between sites. (3) Soil type and management practices influence metal mobility and vary within and between sites. (4) Uptake of each of the metals differs between species of plants.

All of the human health risk assessments assume leaching of the metal from soil is the predominant pathway of loss from the application site. In order for metal uptake across the plant root to occur the metal must be in soil water solution (Alloway, 1995a). Therefore, metal solubility in soil water is a key determinant of metal accumulation in soil (concentration in soil after some series of applications) and plant uptake factor (for any particular plant and metal). In the human health risk assessments, the ratio of metal

concentration in soil-to-metal concentration in soil water (K_d) estimates solubility. Application of this estimate is an attempt to compensate for the capacity of soils to absorb metals. Under equilibrium conditions, the K_d remains constant for a given soil unless absorption sites saturate. Functions like Langmuir absorption isotherms consider concentration-dependent changes (Alloway, 1995a). The human health risk assessments assume estimates of K_d as constants.

The risk assessment model for heavy metals in fertilizers is extremely sensitive to K_d . The relationship between risk-based concentrations (RBC) for cadmium in soil and a range of theoretical K_d values for cadmium clearly illustrates this (Figure 2). The RBC is extremely sensitive to slight changes in K_d at low to moderate values, while RBCs become asymptotic at high K_d values. The short duration of laboratory studies that estimate K_d are typically inadequate for establishing equilibrium conditions because sorption/desorption kinetics involve fast and slow reactions (Ford et al., 2001; Strawn and Sparks, 2000). Please refer the first section of this report for a more complete explanation. Risk assessments use two sets of estimates for K_d values that are derived from modeling data from the literature (Baes and Sharp, 1983; Sauve et al., 2000). The magnitude of differences in K_d value estimates between these two reviews is very large (Table 3). In the cases of arsenic, cadmium, and lead the differences are a factor of 1000, 100, and 20 respectively. This is clearly a major problem, and is a great contributor to uncertainty for any risk assessment.

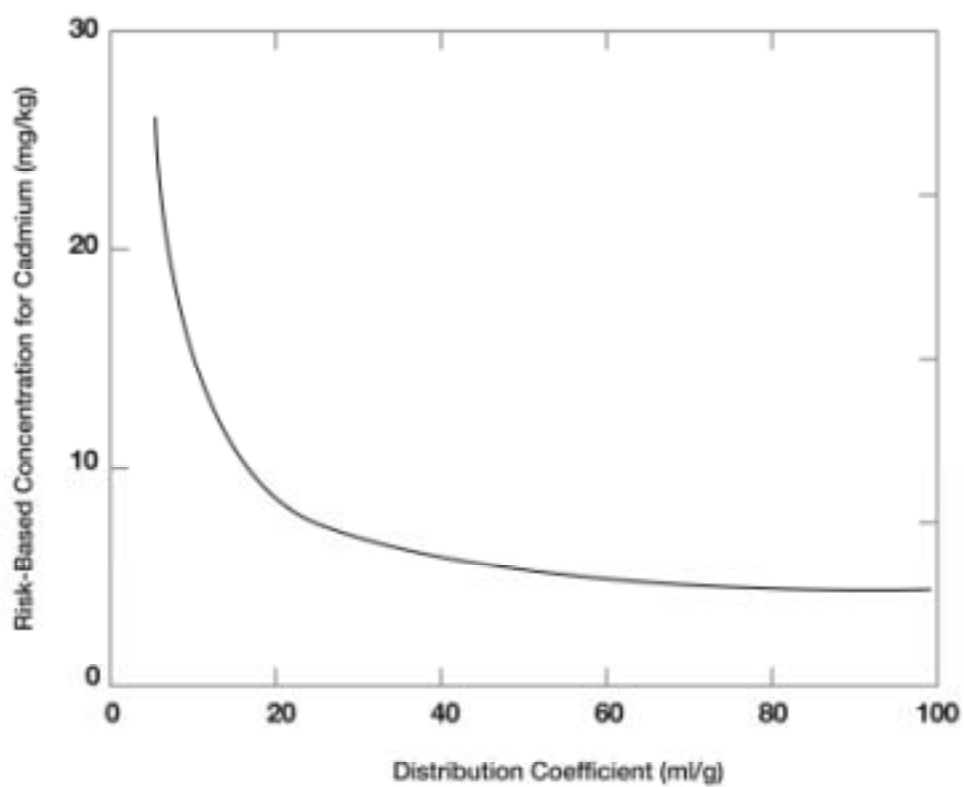


Figure 2. Profound effect of K_d on the RBC for cadmium in the low range of estimated K_d values. Note asymptotic behavior as K_d exceeds 40.

Table 3. 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

It is necessary to consider some of the technical details relating to mathematical risk models. A mathematical risk model for fertilizer application ('fertilizer risk model') has three principle components: 1) a description of metal accumulation in soil, 2) a description of exposure pathways to humans, and 3) a description of toxicity risk associated with exposure (Table 4). Each part of the model represents an approximation of what might happen in an actual agricultural setting. The selection of model parameters is always intended to over-estimate the actual potential risk to human health, reflecting an overall posture of maximal health protectiveness. Given a prescribed acceptable risk-level, there will be a corresponding maximum 'safe' threshold concentration of a heavy

metal in a fertilizer product. Concentrations higher than this threshold will result in risk levels higher than those deemed to be acceptable. This threshold concentration is the RBC. A fertilizer risk model can be organized into a formula that generates an RBC in terms of other model parameters including the acceptable risk level. For convenience fertilizer risk models can also be standardized in terms of a fixed percentage of active ingredient. For example, for much of this report we focus on phosphate based fertilizers. Standardized RBCs have been developed for phosphate fertilizers products assuming these products contain 1% phosphate. An RBC for an actual product that contains some other percentage of phosphate can be converted to reflect the actual percentage of phosphate in the product by multiplying the standardized RBC by the actual proportion.

Table 4. Schematic of information collection in a risk assessment.

<p>1. Metal Accumulation</p> <ul style="list-style-type: none"> - metal concentration in product - application rate - metal level in soil after 50-100 years 	<p>2. Exposures Pathways to Humans</p> <ul style="list-style-type: none"> - metal uptake in plants - food and soil ingestion rates 	<p>3. Toxicity Risk</p> <ul style="list-style-type: none"> - established acceptable metal level in diet
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It is helpful to summarize recent efforts to develop fertilizer models to generate RBCs. The California Department of Food and Agriculture (CDFA), contracted with Foster Wheeler Consultants for a human health risk assessment that included an RBC model equation (Foster Wheeler, 1998). A probabilistic method called Monte Carlo simulation was applied which takes into account the underlying variability in the model parameters. In a Monte Carlo simulation, an RBC is calculated many times. Each time an RBC is calculated, the parameter values are chosen randomly from their respective distributions. Overall then, extreme values for a particular parameter occur much less frequently than values close to the mode. If an RBC is calculated 10,000 times for

example, a listing of all of these 10,000 values forms a frequency distribution. For an RBC value such that 9,000 are above this value and the remaining 1,000 are below this value, then this RBC value should be health protective in approximately 90 percent of cases where fertilizers are being applied. This value defines the 90th percentile for the RBC frequency distribution. Other percentiles can be determined in a similar fashion. Using the resulting inferred distribution for the RBCs, CDFA set RBC values for three metals corresponding to the 90th percentile for each metal.

In 2000 The Fertilizer Institute (TFI) contracted with the Weinberg Group to develop RBCs for twelve metals . The RBC model equation was essentially the same as that used by CDFA, but, instead of a probabilistic approach, TFI used a deterministic approach, using ‘high-end’ point estimates for the model parameters. The point estimates used were upper 95% confidence limits for the means of the model parameters. The idea was to ensure that the resulting RBCs would be health protective in many cases where the model parameters are higher than average. The two methods (probabilistic and deterministic) yielded RBC values similar to one another for the three metals examined in the CDFA report.

In 2001, TFI and CDFA consultants collaborated and refined the RBCs for twelve metals. For this effort the important K_d and plant uptake factor (PUF) data were revised. RBC values were very sensitive to changes in K_d (Fig. 2) and PUF (Fig. 3) values. For this new effort they used recent data from the U.S. Environmental Protection Agency (USEPA 1999), thought to be more broadly representative of agricultural settings than those drawn from the previous data set. The K_d and PUF values were negatively correlated. That is, high K_d values tend to be associated with low PUF values and vice-

versa. RBCs were generated using the probabilistic Monte Carlo simulation process described above. The negative correlation between K_d and PUF values was considered in that they were treated as pairs (as opposed to being randomly selected individually and independently) during the Monte Carlo simulation process.

RBC values derived from the original data and revised paired data can be determined for any specified percentile. The Weinberg Group (2001) compared RBCs calculated using the Foster Wheeler (1998) and USEPA (1999) data. The Foster Wheeler (1998) data defined upper bound conditions and the USEPA (1999) data defined lower bound conditions for the relationship between RBC and risk percentile. They suggested the mid-point between the upper and lower bound conditions as a basis for setting standards.

A number of simulations were performed with point estimates for risk assessment model parameters. As discussed at the beginning of this section, fertilizer risk models are highly sensitive to K_d (Fig. 2) and plant uptake factor PUF values (Fig. 3). In both cases the values not being varied are fixed at 'high end' point estimates. There is a high degree of variability in the K_d and PUF data, and hence a large degree of uncertainty about what is actually happening in 'real life' agricultural settings.

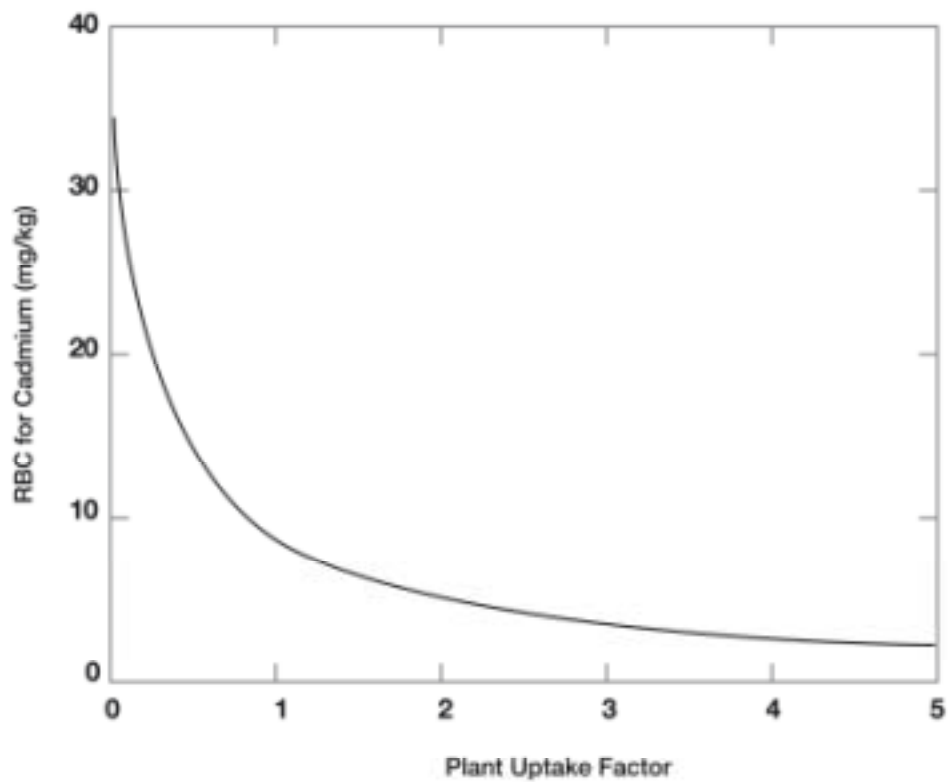


Figure 3. Profound effect of PUF on the RBC for cadmium in the low range of estimated PUF values. Note asymptotic behavior as PUF exceeds 3.

Under current modeling assumptions leaching is the principle dissipation mechanism for metals in soils and the degree of leaching is controlled by the K_d parameter. The metal loss parameter K_s , appearing in the exponent in fertilizer risk models is a function of the K_d parameter. Thus the K_d parameter is a critical component of the part of the model that describes metal accumulation in the soil. Given a fixed application rate and soil density, Figure 4 demonstrates the concentration of cadmium in soil versus time for a K_d value of 50 and a K_d value of 6.7. There is a dramatic effect of K_d on metal concentration in soils.

In Appendix 1 the metal accumulation part of the model is developed from basic principles and assumptions. This development confirms that the K_s value is the loss constant associated with first order exponential dissipation. In this case there is an elementary mathematical relationship between K_s and the half-life, T_{half} , of a metal in the root zone of the soil. Namely, $T_{half} * K_s = -\ln(0.5)$. The relationship between half-life and RBC (Fig. 5) approximates that for K_d and RBC (Fig. 2). In effect then, K_d values model the half-life of a metal in the root-zone. Under present modeling assumptions, there is linear relationship between K_d and half-life (Fig. 6). If the extremely large ranges of K_d values are assumed to be correct, and the model is assumed to be accurate, this implies that half-lives of metals in agricultural settings can vary dramatically, by several orders of magnitude also. Unfortunately there is not adequate data on half-life of metals in soils in verify or refute this implication.

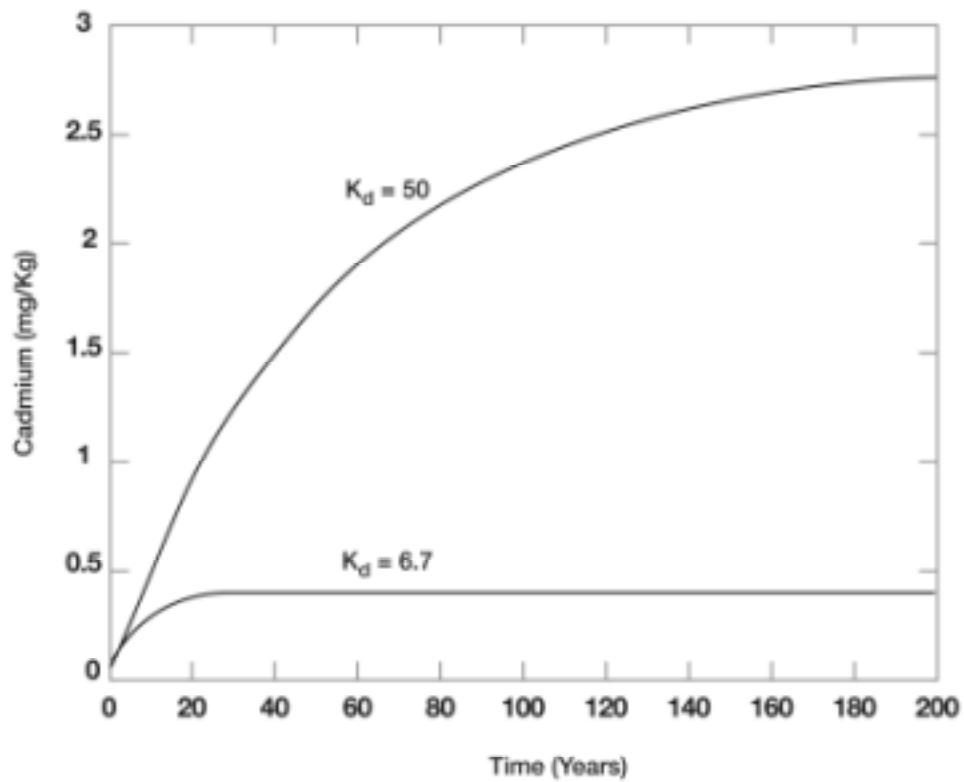


Figure 4. The estimated K_d for cadmium strongly influences model simulation of accumulation of the metal in soil over time. This assumes application of 75 grams per m^2 of a 20% phosphate product containing 210 mg/kg cadmium once a year.

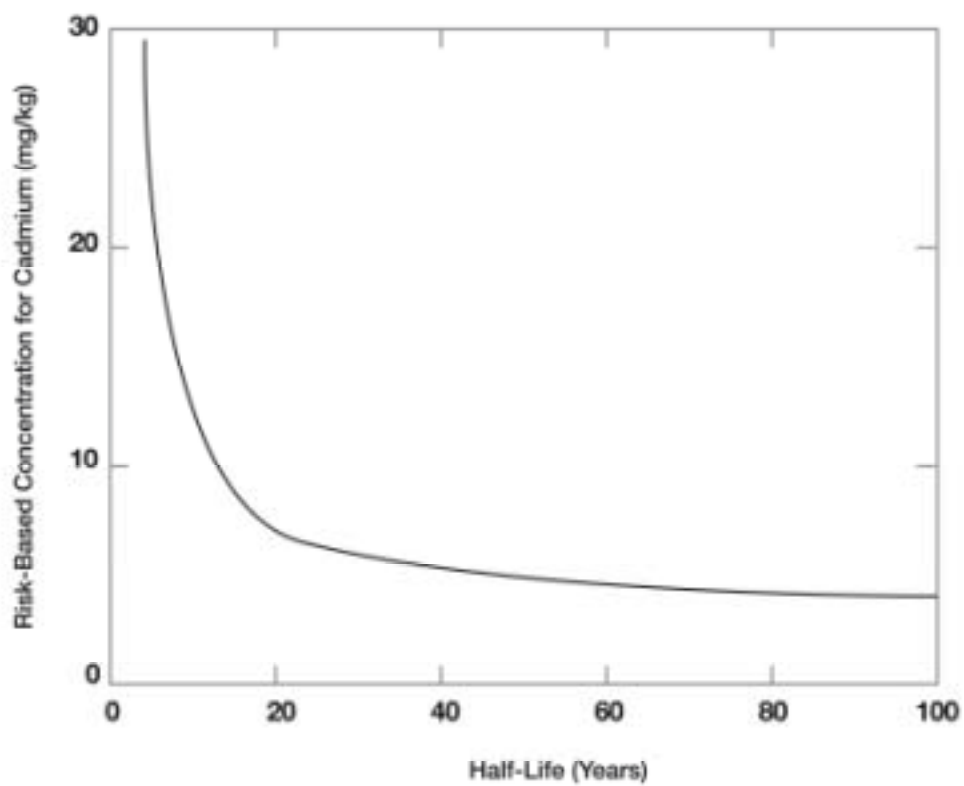


Figure 5. Demonstration that the relationship between half-life for cadmium in soil and RBC is essentially identical to the K_d /RBC relationship.

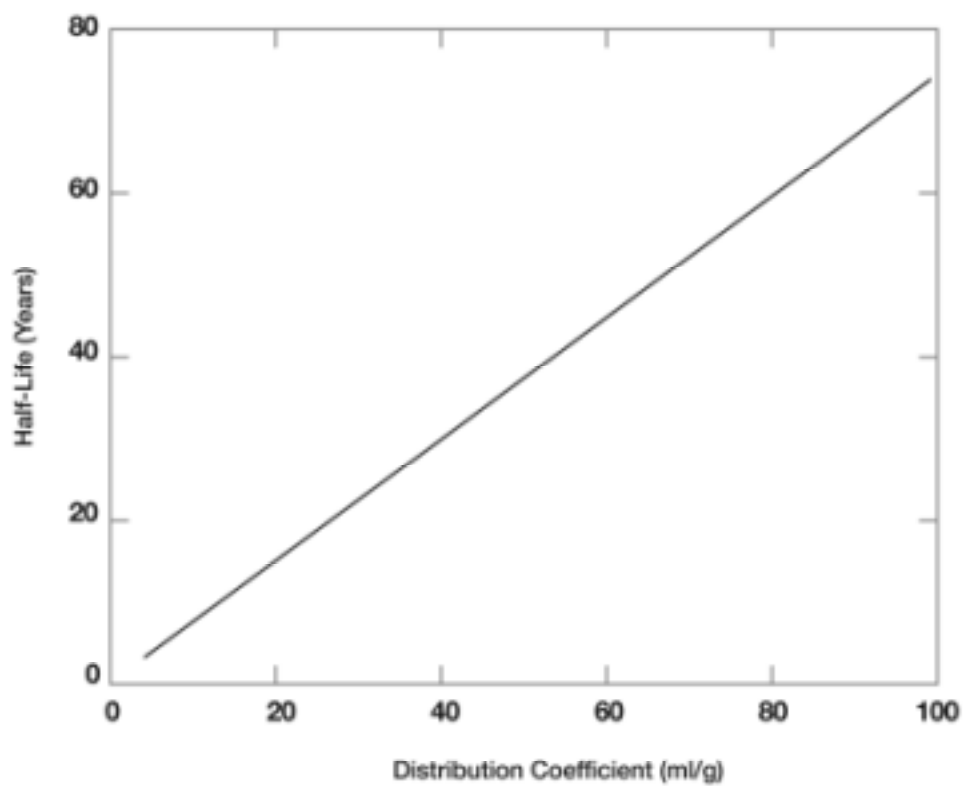


Figure 6. There is a linear relationship between the half-life and K_d for cadmium in soil.

The human health risk assessment available for metals in fertilizers yield RBCs that do not allow more than one-in-one hundred thousand (10^5) excess risk for exposures to arsenic, cadmium, lead, mercury, and nickel in soils. Of these metals, arsenic is unique in that it presents cancer risk for exposure pathways relevant to soil. The excess risk allowable for carcinogens is typically one-in-one million (10^6). Adjustment of the risk assessment for arsenic to the 10^6 excess risk level reduces the RBC by a factor of 10. The Weinberg (2001) work proposes a RBC for arsenic at 10^5 excess risk and allows 260 mg/kg arsenic in a 20% phosphate product. Application of the 10^6 excess risk factor reduces this to 26 mg/kg arsenic for the 20% phosphate product. Soils in Oregon contain a significant amount (background) of arsenic without fertilizer addition (Table 1). The interaction of background arsenic concentration with addition of arsenic from fertilizer, or any other source, determines soil accumulation over time (Fig. 7). Annual arsenic additions to a background soil arsenic concentration near the average for Oregon (Fig.7, upper curve) or well below the average (Fig. 7, lower curve) yield similar steady state concentrations after 200 years. The contribution from fertilizer application is an important determinant of this concentration. However, the background concentration determines the long-term trend for reducing or increasing soil arsenic concentration. This assumes exponential decay for arsenic (consistent with other modeling herein) and does not consider inputs from other sources.

Conclusions and Recommendations

Wide variability in estimates in K_d for arsenic, cadmium, and lead introduce much uncertainty into human health risk assessments. This raises two questions: Is this degree

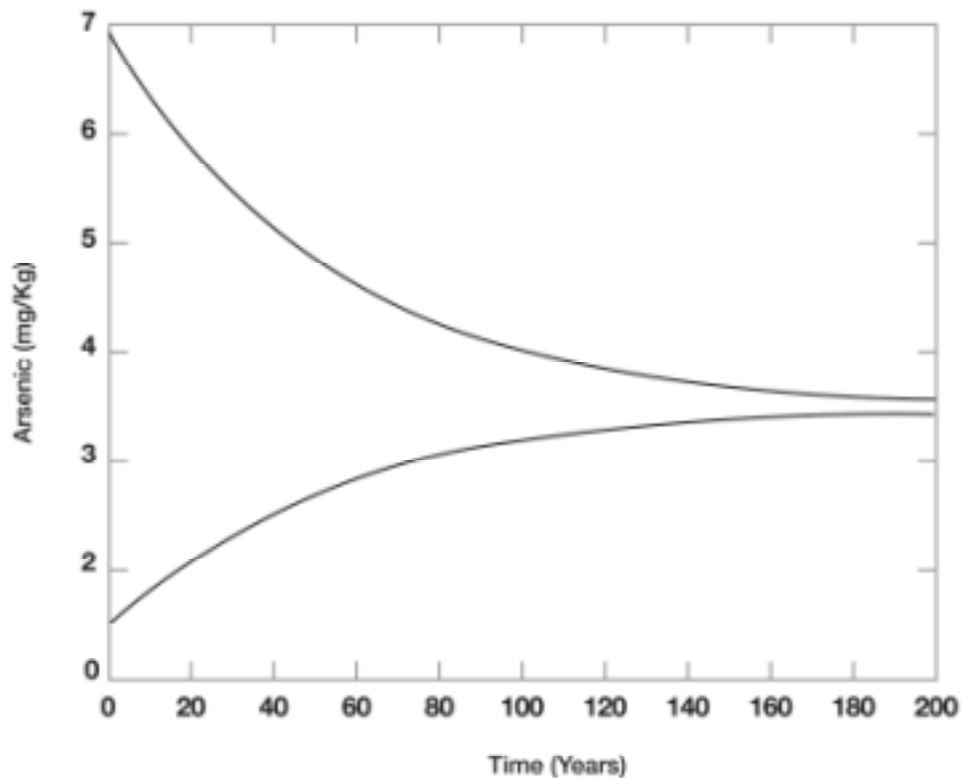


Figure 7. Simulation of arsenic accumulation in soil over time after application of 75 grams of 20% phosphate product containing 260 mg/kg arsenic once a year. The simulations assume a K_d of 50 for arsenic. The upper curve assumes an initial (background) soil arsenic concentration of 7 mg/kg. The lower curve assumes an initial (background) soil arsenic concentration 1.5 mg/kg. Note that the curves converge on the same asymptote.

of uncertainty “real” in that it reflects variability in soil chemistry that determines sorption/desorption kinetics? Is this degree of uncertainty an artifact and problematic due to limitations in estimation of K_d with a variety of different methods? We recommend implementation of a monitoring program for metals in agricultural soil, surface waters, and harvested crops. The heavy metal analyses of soil over a five year period can provide estimates of half-lives that can directly address problems inherent to use of K_d . Analyses of surface waters directly determines compliance with water quality standards. Measurements in crops assess validity of plant uptake factors, an important component of the human health risk assessments.

While Oregon Department of Agriculture can generate new data for assuring protection of human health and natural resources other valuable information is under development. Dr. Andrew Chang of University of California at Riverside is conducting a major study of mass balance of heavy metals in agricultural soils. No data is currently available. However, initial results will be available within a year. These field-based studies will provide valuable estimates of accumulation and loss pathways for heavy metals in high intensity agricultural systems, and very low management natural lands and forage systems. This design of these studies is consistent with the half-life work proposed above, and should be considered in conjunction with work done in Oregon.

The Oregon Department of Agriculture is responsible for setting standards for arsenic, cadmium, lead, mercury, and nickel in fertilizers and related products in 2002.

Decision making is necessary before data from the two recommendations above are available. There is an important line of evidence that provides guidance for development of standards using the risk assessments currently available. First, the heavy metal concentrations in our food supply is not increasing. Human dietary intake of arsenic, cadmium, and lead is on a declining trajectory for 1976-1991 (Johnson et al., 1984a,b; Podebarac et al., 1984a,b; Gundersun, 1995). For example, the estimate for daily adult intake of arsenic for 1977 is 75 $\mu\text{g}/\text{day}$ and that for 1986-1991 is 25 $\mu\text{g}/\text{day}$. In the case of cadmium, the 1977 estimate is about 36 $\mu\text{g}/\text{day}$ and the estimate for 1986-1991 is about 13 $\mu\text{g}/\text{day}$. This does not support the contention that increasing soil and crop heavy metal concentrations present immediate human health risk that requires strict regulatory action. While an immediate problem is not evident, reliable estimates of heavy metal input and output fluxes are necessary to accurately estimate sustainability of agricultural soil quality after repeated fertilizer applications. Recent results for Swiss agricultural soils identify sources and losses that contribute to regional net fluxes for cadmium and zinc (Keller et al., 2002). In the Sundgau region of Switzerland about 18% of total cadmium input is from commercial fertilizers, while 67% of input is atmospheric. The remaining inputs are from applications of manure and biosolids. The estimate of total annual output (in crops plus leaching) is 58% of total input. This is more output than risk assessment using high range K_d estimates predict. It is unlikely that sources of heavy metals for Oregon soils closely approximate those of the Sundgau region. None-the-less, the results of this work reinforce the value of actual field data in understanding heavy metal accumulation in agricultural soils. Until such information is available, it is

reasonable to adopt standards that are a compromise between RBCs generated with high and low K_d estimates.

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APPENDIX 1

We derive an expression for the amount, A (weight), of some material accumulated on a parcel of land as a function of the annual application rate, AR (weight of the applied material per year), and the number of years, T , that the material has been applied. We assume that the material is deposited uniformly over this parcel of land with each application. Note that an expression for concentration could be obtained by simply dividing A by the weight of the affected soil. Suppose there are n equal sized applications per year, equally spaced throughout the year. If the material were applied monthly, for example, n would be equal to twelve. Then the amount material applied with each application is $\frac{AR}{n}$, and, assuming a first order exponential loss with loss constant k , the amount of accumulated material immediately after the second application will be,

$$A = \frac{AR}{n} * \exp\left(-\frac{k}{n}\right) + \frac{AR}{n} . \quad (1)$$

Note that the first term on the right-hand side of (1) describes the amount of material that remains from the initial (first) application and the second term describes the amount of material just deposited by the second application.

In order to make the following development easier to follow, we define $B = \frac{AR}{n}$, and

$a = \exp\left(-\frac{k}{n}\right)$. The expression in (1) above can now be written more compactly as,

$$A = a * B + B$$

$$= B *(a + 1) .$$

Similarly, just after the third application the amount of accumulated material is,

$$A = a *(a * B + B) + B$$

$$= B *(a^2 + a + 1)$$

This pattern continues for subsequent applications so that just after the $(m + 1)^{th}$ application, the amount of accumulated material is,

$$A = B *(a^m + a^{m-1} + \dots + a + 1) \quad (2)$$

$$= B * \left(\frac{a^{m+1} - 1}{a - 1} \right) .$$

The last equality arises from fact that the right-hand side of (2) is a geometric series.

After T years there will have been $T * n$ applications, so letting $m = T * n$ in the above

expression, and, using the full expressions for B and a , we obtain an expression for A that depends on T , n , AR , and k ,

$$A = \frac{AR}{n} * \frac{\exp(-k * T - k/n) - 1}{\exp(-k/n) - 1} . \quad (3)$$

The expression in (3) can be simplified by making the assumption that the material is continuously applied, which corresponds to letting n approach infinity. Letting n approach infinity and applying limit rules from calculus we obtain,

$$A = \frac{AR * (1 - \exp(-k * T))}{k} \quad (4)$$

The right-hand side of (4) is a familiar expression in the formulas for risk-based concentrations that appear in the reports cited in this report. The important structural observation is that the loss constant k corresponds to the loss constant K_5 appearing in the exponent in the formulas for risk-based concentrations. Then, as discussed in the main body of this report, we can make direct connection between the half-life of a given material and the value of K_s , and thus infer a connection between half-life and K_d (dissociation constant) values for the metals discussed in this report.