A Report on the Plant Uptake of Metals from Fertilizers

This report summarizes and makes recommendations based on the Washington State University report entitled:

Influence of Metal Rates and Forms on Crop Productivity and Metal Uptake in Some Washington Soils

Submitted to:

Washington State Legislature

Submitted by:

Lead Agency
Washington State Department of Agriculture

Cooperating Agencies
Washington State Department of Health
Washington State Department of Ecology
Washington State University

This report is mandated by the Fertilizer Regulation Act of 1998 (Chapter 36, Laws of 1998).

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Table of Contents

Acronyms and Symbols

DAP	Diammonium Phosphate
DTPA	Diethylenetriaminepentaacetic acid.
E DAP	Diammonium Phosphate from Eastern United States
PR	Phosphate Rock
Tc	Transfer Coefficient
TSP	Triple Superphosphate
W DAP	Diammonium Phosphate from Western United States
WSU	Washington State University

Glossary

For purposes of this report, the following definitions are used:

Diammonium phosphate – a product composed of ammonium phosphates, principally diammonium phosphate, resulting from the ammoniation of phoshoric acid. It may contain up to 2% non-ammoniacal nitrogen. An ingredient in commercial phosphate fertilizers.

Diethylenetriaminepentaacetic acid – a chelating agent for extracting cadmium, lead, zinc, and other heavy metals from soils.

Ironite – A fertilizer sold primarily in the home and garden market as a source of iron and zinc. It contains relatively high levels of arsenic and lead.

Lime – an agricultural product with calcium and magnesium compound that are used for the purpose of neutralizing soil acidity.

Phosphate rock - a natural rock containing one or more calcium phosphate minerals of sufficient purity and quantity to permit its use, either directly or after concentration, in the manufacture of phosphate fertilizers. About 84% of the US production of phosphate rock comes from North Carolina and Florida. The remaining is from Idaho, Montana, Utah, and Wyoming.

Sodium bicarbonate – a sodium salt for use in extracting arsenic from the soil.

Transfer coefficient - the ratio of the concentration of metal in a plant to the concentration of metal in soil. Transfer coefficients can be calculated based on the concentration of extractable metals in soil or based on the total concentration of metal in soil. A higher transfer coefficient indicates a greater transfer of metal from soil into plant.

Triple superphosphate - a product obtained when rock phosphate is treated with sulfuric acid, phosphoric acid, or a mixture of those acids. Refers to all grades containing 40% or more available phosphate, which are commonly made by acidulation of natural phosphatic material primarily with phosphoric acid. An ingredient in commercial phosphate fertilizers.

Zinc sulfate – a zinc salt of sulfuric acid for use as a zinc fertilizer.

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I. Executive Summary

The Fertilizer Regulation Act of 1998 directed the Department of Agriculture to conduct a comprehensive study evaluating plant uptake of metals from fertilizers. As mandated by the Act, this report, prepared by the Departments of Agriculture, Ecology, Health and Washington State University (WSU) summarizes and interprets the results of the study.

The WSU study was conducted to determine, in part, if the accumulation of arsenic, lead, and cadmium in soils and crops may occur from continual agricultural applications of fertilizers. The four crops used were lettuce, cucumber, wheat, and potato. The two soils utilized were a Sultan silt loam at the Puyallup site or Quincy-Hezel fine sandy loam at the Prosser site. Commercial fertilizers that contain relatively high levels of heavy metals were evaluated.

The results of the study indicate that cadmium is of greater concern than arsenic and lead in terms of crop uptake. Cadmium is commonly found in phosphate fertilizers used in agriculture. The WSU study also shows, that for the conditions tested, the amount of cadmium taken up by crops is greatly influenced by the source of the cadmium. Although crops take up some amount of cadmium from the soil, the WSU study indicates that cadmium could build up in soil over time due to continual fertilizer use. This is more likely to occur from using fertilizers that contain higher cadmium levels. Increases in soil cadmium concentrations are of concern since they may lead to increases in cadmium concentrations in crops. Cadmium levels in soils should be periodically monitored to ensure that levels do not become a concern in the future.

There are many factors that influence the uptake of metals into plants. They include soil pH, source of metals, soil type, existing or initial soil metal concentrations, and whether all plant material is removed before tilling and subsequent planting. Due to the many uncertainties associated with predicting the uptake of metals into plants and the limited number of conditions evaluated in this study, projections of metal concentrations in plants over time cannot be estimated with a high degree of certainty. This is because soils vary considerably in their ability to bind cadmium. Additionally, there may be major differences in cadmium availability between soil types even when they contain the same amount of cadmium. The study would need to be extended to other soil types before it could be applicable to a broad range of soil conditions.

Arsenic and lead levels in most agricultural fertilizers are very low. Occasionally, relatively high levels of lead can be found in some micronutrient fertilizers, but the application rate of those products is so low that it does not significantly contribute to lead soil levels. In addition, compared to cadmium, the transfer of arsenic and lead from soil to crop is minimal.

The study indicates the existing Washington State standards for arsenic, cadmium, and lead in fertilizer appear to be sufficiently protective at this time. However, the study also indicates there is a potential for the levels of these metals to increase in soil over time. This is especially true of cadmium, due to current applications of phosphate fertilizers containing relatively high levels of cadmium. The agencies involved in the development of this report make the following recommendations:

1) WSU should extend its study for a minimum of two years and focus on the development of a soil-to-plant transfer coefficient for cadmium that is independent of time. This would greatly improve the accuracy of predicting crop uptake of cadmium.
2) A long-term program should be developed to monitor soil levels of arsenic, cadmium, and lead over time to ensure that soil levels do not become a concern in the future.
3) A process should be initiated to attempt to develop a regional approach dealing with the issue of metals standards and labeling. This should initially include Washington, Oregon and Idaho, but could be expanded to include other western states.

II. Introduction

The Fertilizer Regulation Act of 1998 directed the Department of Agriculture to conduct a comprehensive study evaluating plant uptake of metals from fertilizers. As mandated by the Act, this report, prepared by the Departments of Agriculture, Ecology, Health and Washington State University (WSU), summarizes and interprets the results of the study conducted by WSU regarding potential impacts to public and environmental health from metals in fertilizers.

History

The issue of heavy metals in fertilizers arose in Washington State when a small group of citizens living in and around Quincy, Washington became concerned about recycling hazardous wastes into fertilizers. Several 1997 articles in *The Seattle Times* addressed these concerns and brought the issue to national attention.

The state agencies recognized recycling of waste materials as a valid way to conserve limited natural resources; and that the use of recycled material in fertilizer had grown in concert with increased industrialization, advancement in technologies, population growth, and increased costs of production. It was also recognized that fertilizers could contain contaminants such as heavy metals at varying concentrations, regardless of whether the fertilizer was waste-derived or not.

In August 1997, the Departments of Agriculture, Ecology, and Health proposed a ten-point plan to ensure that fertilizers used in Washington did not pose a risk to human health or the environment. As part of this plan, an advisory group was established which included representatives from the fertilizer industry, agricultural commodity producers and processors, environmental interests, county health agencies, the departments of Agriculture, Ecology, Health, and Labor and Industries and the Governor's Office. A primary task of the group was to advise the agencies in developing legislation that would authorize the Department of Agriculture to adopt standards for heavy metals content for all fertilizer products.

The advisory group met a number of times in late 1997 and, in January 1998, the agencies proposed legislation to significantly revise the state's fertilizer law. On March 18, 1998, the Fertilizer Regulation Act was signed into law and Washington became the first state in the country to adopt metals standards for fertilizers.

The Act adopted the Canadian standards for maximum acceptable heavy metals additions to soil. The standards limit the levels of nine heavy metals in fertilizers – arsenic, cadmium, cobalt, mercury, molybdenum, nickel, lead, selenium, and zinc. The following table converts the Canadian standards (expressed in kilograms/hectare/year) to Washington standards (expressed in pounds/acre/year).

Table 1. Washington standards for metal additions to soils.		
Metals	**lbs/acre/yr**	**kg/ha/yr**
Arsenic	**0.297**	**0.333**
Cadmium	**0.079**	**0.089**
Cobalt	**0.594**	**0.667**
Mercury	**0.019**	**0.022**
Molybdenum	**0.079**	**0.089**
Nickel	**0.713**	**0.800**
Lead	**1.981**	**2.222**
Selenium	**0.055**	**0.062**
Zinc	**7.329**	**8.222**

III. Study Summaries

This Summary Report is based on the Washington State University (WSU) study entitled, "Influence of Metal Rates and Forms on Crop Productivity and Metal Uptake in some Washington Soils". The WSU study was designed to evaluate the various effects that heavy metals from fertilizers might have on the production of four crops produced in Washington State soils at two sites. The four crops used were lettuce, cucumber, wheat, and potato. The two soils utilized were a Sultan silt loam at the Puyallup site or Quincy-Hezel fine sandy loam at the Prosser site. Commercial fertilizers that contain relatively high levels of heavy metals were used in this study. The materials used in the production of commercial phosphate fertilizers such as phosphate rock (PR), triple superphosphate (TSP), and diammonium phosphate (DAP) were evaluated. For the purpose of comparison, the effects of soluble metal salts were also determined. Soluble metal salts are not commercial fertilizers but represent a readily available source of heavy metals to crops. Treatments containing soluble metal salts were compared with those with commercial fertilizers. Liming treatments were also evaluated. Liming is the act of adding lime to the soil for the purpose of neutralizing soil acidity (increasing soil pH). The availability of metals in soils is dependent on the acidity of the soil. For a full understanding of the WSU research effort, reviewers of this Summary Report are encouraged to consult the original study.

The WSU Study consisted of four parts: 1) a greenhouse study conducted in Puyallup, 2) a field study conducted in Puyallup, 3) a field study conducted in Prosser, and 4) an incubation study conducted in Pullman. Each part of the study was conducted under different conditions, and, in most cases, different parameters were measured. The four parts of the WSU Study are summarized as follows.

Part 1: Plant Yield and Uptake of Heavy Metals from Fertilizers and Soluble Metal Salts by Greenhouse-Grown Lettuce - Puyallup Site

Purpose:

The purpose of the study was to see if fertilizers applied to a Sultan silt loam at rates up to 40 times the Washington fertilizer standard (or Canadian standard) for arsenic, cadmium and lead could cause phytotoxicity in lettuce grown in pots in the greenhouse. Phytotoxicity was measured by lettuce dry and wet yields. In addition, the study evaluated the uptake of metals by lettuce grown in the greenhouse with varying application rates of three fertilizers (PR, granular zinc and Ironite) and soluble metal salts. Fertilizers and soluble metal salts were applied up to 40 times the Washington fertilizer standard for arsenic (0.333 kg/ha/yr), cadmium (0.089 kg/ha/yr), and lead (2.222 kg/ha/yr). The study evaluated if the uptake of metals into lettuce differs between fertilizers and soluble metal salts. Concentrations of total and extractable metals in soils were measured to determine which most closely correlated with plant metal concentrations. Extractable metals reflect the amount of metal in soil that is in a form available for plant uptake (i.e. plant availability or bioavailability). Soil metal and plant metal concentrations were used to develop soil-to-plant transfer coefficient (Tc). A Tc is the ratio of the concentration of metal in a plant to the concentration of metal in soil. A higher Tc indicates a greater transfer of metal from the soil into the plant. The study also evaluated the effect of liming on plant uptake of metals. Greenhouse study results were compared with the results from the field study.

Methods:

- Crop: lettuce
- Soil: Sultan silt loam
- Application Rates: 0, 1X, 2X, 4X and 8X, repeated after 3-month incubation of the treated soil for a total of 5 times to reach a maximum application of 40X. 1X is based on maximum allowable metal addition to soil from the Washington fertilizer standard (WAC 16-200-7064). Product application rates at 1X: 97.1 kg granular zinc/ha, 2493 kg western PR/ha, 76.5 kg Ironite/ha. Metals addition at 1X rate for soluble metal salts: 0.09 kg cadmium /ha, 0.33 kg arsenic /ha, 2.2 kg lead/ha.
- Fertilizers and soluble metal salts applied and metals measured: granular zinc (cadmium and lead), PR (cadmium), Ironite (arsenic and cadmium), and soluble metal salts (arsenic, cadmium and lead).

Main Results:

Cadmium

- Application of cadmium to a Sultan silt loam up to 40 times the Washington fertilizer standard had no effect on fresh or dry weight lettuce yield, i.e. phytotoxicity was not observed at any application rate.
- Lettuce cadmium concentrations were higher from soluble metal salt application than from application of any of the three fertilizers. Lettuce uptake of cadmium from

different sources was observed in the following order: PR < granular zinc < soluble metal salts. Ironite did not contribute significant cadmium to lettuce.

- Cadmium added to the soil from soluble metal salts was more extractable compared to the fertilizers. The extractability increased in the order of PR < granular zinc < soluble metal salts.
- Lettuce cadmium concentrations correlated better with soil extractable cadmium than with total cadmium soil concentrations.
- Tc's based on soil extractable cadmium provided a more accurate prediction of uptake of cadmium by lettuce than Tc's based on the total cadmium concentration in the soil.
- Cadmium soil-lettuce Tc's were higher for soluble cadmium salt than for the fertilizers. The average soil-plant Tc for cadmium for PR and granular zinc was 4.17.
- Soil cadmium extractability decreased with increasing lime rates. Liming had the greatest effect on the extractability of cadmium from PR. Cadmium plant concentrations decreased with increasing rates of lime.
- Lettuce cadmium concentrations and cadmium soil-lettuce Tc's were lower in the greenhouse study than in the field study.

Arsenic

- Application of arsenic to a Sultan silt loam up to 40 times the Washington fertilizer standard had no effect on fresh or dry weight lettuce yield, i.e. phytotoxicity was not observed at any application rate.
- Lettuce arsenic concentrations increased with increasing application rates of Ironite.
- Less arsenic accumulated in soil than would be expected from arsenic soil additions.
- Liming did not affect arsenic uptake into lettuce.
- Extractability of soil arsenic increased with increasing lime rates.
- Soil extractable arsenic was similar between Ironite and soluble metal salts at an application rate 40 times that allowed by the Washington State standards.
- The average Tc was small (0.012); indicating a low potential for plant uptake of arsenic.

Lead

- Application of lead to a Sultan silt loam up to 40 times the Washington fertilizer standard had no effect on fresh or dry weight lettuce yield, i.e. phytotoxicity was not observed at any application rate.
- Lettuce lead concentrations increased with increasing application rates of granular zinc.
- Liming did not affect lead uptake by lettuce.
- Soil extractable lead was lower in soil treated with granular zinc than with soluble lead salt.
- The average Tc was small (0.005); indicating a low potential for plant uptake of lead.

Main Conclusions: (Part 1 continued, Greenhouse study, Puyallup Site)

- Application of metals to a Sultan silt loam up to 40 times the Washington fertilizer standard had no effect on fresh or dry weight lettuce yield, i.e. phytotoxicity was not observed at any application rate.
- The amount of metals taken up by lettuce depends on whether the metal was added to a Sultan silt loam soil as fertilizer or as soluble metal salt. Cadmium is more available to lettuce in the form of soluble metal salts than from the fertilizers.
- Lettuce accumulated more cadmium than arsenic or lead.

Part 2: Plant Yield and Uptake of Heavy Metals from Fertilizers and Soluble Metal Salts in Field-Grown Lettuce and Cucumbers- Puyallup Site

Purpose:

The purpose of this study was to determine the amount of metals taken up by lettuce and cucumbers grown in the field on a Sultan silt-loam with varying application rates of three fertilizers (TSP, PR, and Ironite) and with varying application rates of cadmium and arsenic in soluble metal salts. Ironite and soluble metal salts were applied to the field up to 16 times the Washington fertilizer standard for arsenic and cadmium additions to soil (WAC 16-200-7064). TSP and PR were applied up to 16 times their maximum product application rate as defined by in WAC 16-200-7063.

The study evaluated whether uptake of arsenic and cadmium by lettuce and cucumbers differs between fertilizers and soluble metal salts and whether uptake of metals changed over the 2-year study period. Concentrations of total and extractable metals in soils were measured to determine which most closely correlated with plant metal concentrations. Soil metal (total and extractable) and plant metal concentrations were used to develop Tc's. The study also evaluated the effect of liming on plant uptake of arsenic and cadmium from fertilizers and soluble cadmium and arsenic salts. The study also measured the effect of different application rates of fertilizers and liming on fresh and dry weight lettuce yields. The amount of the metals removed from the soil due to plant uptake was calculated to determine the amount of the metals that remains in the soil after crop harvest to address possible metal accumulation in soil over time. The result for the field study was compared with that of the greenhouse study.

Methods:

- Crop: lettuce and cucumber
- Soil: Sultan silt loam
- Application rates: 1X, 2X, 4X and 8X for the 1^{st} year; 2X, 4X, 8X and 16X cumulative rates for the 2^{nd} year. 1X rate for Ironite = maximum arsenic addition per Washington fertilizer standard (WAC 16-200-7064), 1X for soluble metal salts = maximum arsenic and =cadmium addition per WA fertilizer standard (WAC 16-200-7064), 1X rate for TSP and PR = maximum recommended screening product

application per WAC 16-200-7063. Product application rates at 1X rate: 430 kg TSP/ha, 645 kg western PR/ha, 100 kg Ironite/ha. Metals addition at 1X rate for soluble metal salts: 0.09 kg cadmium/ha, 0.33 kg arsenic/ha.
- Fertilizers and soluble metal salts applied and metals measured: TSP (cadmium), PR (cadmium), Ironite (arsenic and cadmium), and soluble metal salts (arsenic and cadmium).

Main Results:

Cadmium
- The concentrations of cadmium in lettuce were higher than in cucumber (i.e. lettuce took up more cadmium from fertilizers and soluble salt added to a Sultan silt loam than did cucumber at the same rate of cadmium). The concentration of cadmium was higher in the cucumber vine than in the fruit.
- In the first year of the study, the availability of cadmium to lettuce increased in the following order: PR < TSP < soluble cadmium salt. During the second year of the study, the availability of cadmium from soluble salt remained high. In the second year, however, the availability of cadmium to lettuce from TSP decreased while the availability of cadmium from PR increased.
- Soil cadmium extractability increased in the following order: PR < TSP < soluble salt.
- The concentration of cadmium in lettuce correlated better with the level of cadmium extracted from soil than with the total level of cadmium in the soil. Conversely, the concentration of cadmium in cucumber correlated better with the total level of cadmium in the soil.
- The two-year average Tc, for cadmium in lettuce, based on the total level of cadmium in the soil was 16.9. Although, the Tc value of 16.9 appears high, this estimate is not a reflection of commercial fertilizers only as this number also includes the Tc's for commercial fertilizers and soluble metal salts. The average Tc for only fertilizers was 6.2. The average Tc for cadmium for cucumber fruit was 0.68.
- Generally, liming caused a decrease in the extractability of cadmium from soil. Liming decreased the uptake of cadmium from fertilizers by lettuce and had no effect on the uptake of cadmium by cucumber.
- Application of fertilizers within the rates used did not decrease crop yields. Lettuce yield increased with increasing TSP rates.
- Lettuce and cucumber accumulated less than 3% of the total cadmium added to soil.
- Tc's for cadmium in lettuce and lettuce cadmium concentrations were higher for field than for greenhouse for the phosphate fertilizers.

Arsenic
- Lettuce and cucumber accumulated less than 0.001%[*] of the total arsenic added to soil. The lower accumulation of arsenic compared to cadmium may be attributed to differential sorption mechanisms of both cucumber and lettuce for these two elements.

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[*] Originally reported incorrectly as 0.1%.

- There was no difference between extractable soil arsenic and total soil arsenic for predicting the concentration of arsenic in lettuce.
- The Tc averaged 0.021 for lettuce and 0.011 for cucumber fruit.

Main Conclusions:

- There were significant year and source effects, as well as lime effects, in regard to the concentrations of cadmium found in lettuce. Due to differences in plant uptake of cadmium from different fertilizers added to a Sultan silt loam, extrapolation of plant uptake from one fertilizer source to other fertilizer sources should not be done without qualification.
- Soil-to-lettuce Tc's based on extractable soil cadmium concentrations are more responsive to factors that influence plant uptake of cadmium. Consequently, this Tc provides a more accurate prediction of potential food chain exposures in human health risk assessments than Tc's based on the total level of cadmium in the soil.
- The Tc's for cadmium in lettuce or cucumber are higher than those used in EPA's biosolids (leafy = 0.6, fruits = 0.11) and fertilizer (lettuce 0.05-1.56) risk assessments.
- The recovery of cadmium in lettuce from any of the added cadmium sources was very low (3%) from a mass balance point of view. This indicates that increased cadmium accumulation in soil over time should be expected unless the concentration of cadmium in the fertilizers is reduced.
- The recovery of arsenic in plants is low (< 0.1%). Consequently, one would predict an accumulation of arsenic in soil over time.

Part 3: Uptake of Heavy Metals from Fertilizer and a Soluble Metal Salt in Field-Grown Potatoes and Winter Wheat- Prosser Site

Purpose:

The purpose of this study was to determine the amount of metals taken up by potatoes and winter wheat grown in the field in a Quincy-Hezel fine sandy loam with varying application rates of five fertilizers. The five fertilizers used were TSP, PR, DAP from Idaho (Western DAP), DAP from Florida (Eastern DAP), and zinc sulfate. TSP and DAP are derived from PR. The phosphate fertilizers manufactured from Florida rock phosphate deposits are typically low in cadmium (3 to 15 ppm). Conversely, fertilizers from western phosphate rock contain cadmium levels several times higher than that of PR deposits in Florida. Washington soils have a greater potential for cadmium accumulation because western PR has become the material currently utilized in the production of most commercial phosphate fertilizers used in Washington State. Fertilizers were applied up to 16 times their maximum product application rate as defined in WAC 16-200-7063. The crop uptake of cadmium from a soluble cadmium salt was included for comparison. The study also evaluated if there were differences in cadmium concentrations between peeled and unpeeled potatoes at selected application rates. The quantity of extractable metals in soils was measured for each application rate for each fertilizer. The study also measured the effect of different application rates of fertilizers on crop yields. In addition, this study also determined the concentration of extractable metal in soil for each fertilizer to a depth of 0-15 and 15-30 cm. The amount of metal removed from the soil due to plant uptake was calculated to determine the amount of metal remaining in the soil after crop harvest to address possible metal accumulation in soil over time. This study was conducted over a 2-year period. Lime treatments were not included in this study.

Methods:

- Crop: winter wheat and potato (tuber only)
- Soil: Quincy-Hezel fine sandy loam
- Application rates: 1X, 2X, 4X and 8X for the 1st year; 2X, 4X, 8X and 16X accumulative for the 2nd year for TSP, PR and zinc sulfate. 1X, 2X 1st year; 2X and 4X 2nd year for W DAP and E DAP. 1X for all fertilizers = maximum recommended product screening application per WAC 16-200-7063. 1X for soluble cadmium salt (cadmium chloride) = maximum cadmium addition per Washington fertilizer standard (WAC 16-200-7064). Product application rates at 1X: 435 kg TSP/ha, 653 kg PR/ha, 426 kg W DAP/ha, 426 kg E DAP/ha, and 48.3 kg zinc sulfate/ha. Metals addition at 1X for soluble metal salts: 0.09 kg cadmium/ha.
- Fertilizers and soluble metal salts applied and metals measured: TSP, PR, DAP (W DAP, from Idaho), DAP (E DAP, from Florida), and zinc sulfate. Products, soils at all treatments and crops at all treatments were analyzed for both cadmium and lead. DTPA extractable cadmium and lead in soils were measured at 0-15 and 15-30 cm depths. Total metals in soils were only measured at the beginning of the study and were not measured for treatment groups.

Main Results:

Cadmium

- Wheat stover had higher cadmium concentrations than wheat grain. Stover is the dried stalks and leaves of a cereal crop, used as bedding or incorporated into the soil as residue after the grain has been harvested.
- TSP added the most cadmium to the Quincy-Hezel fine sandy loam of any fertilizer in this study. Cadmium potato tuber concentrations increased at the higher TSP application rate of 8 and 16X in the 2nd year.
- In the 1st year of the study (1999), the average cadmium concentration in peeled potato tuber was significantly lower than in unpeeled tubers. For those treatments analyzed in the 2nd year of the study (2000), the average cadmium concentration, in unpeeled and peeled tuber was not significantly different. Additional analysis of the 2000 data is being conducted to verify this inconclusive result.
- For all treatments, the cadmium concentrations in wheat grain and potato tuber correlated with the levels of cadmium extracted from soil to a depth of 0-15 cm. This indicates that soil extractability is good predictor of cadmium uptake in these crops.
- In 1999, there was a lower grain yield with PR compared to other phosphate fertilizers. The wheat grain yield in 2000, however, was not significantly affected by fertilizer source or rate. Potato tuber yield was unaffected by fertilizer source or rate for both 1st and 2nd years of study.

- It was estimated that 1% of total soil cadmium was recovered in wheat, indicating that most cadmium remains in the soil.
- The plot design in this study did not allow the differences in cadmium availability to be sorted out between years. Since crops were rotated between plots; the year effect and plot effect could not be separated from the variability in yearly uptake. Increasing the application rate in the second year increased uptake of Cd in both crops.
- The Tc's obtained at Prosser were much smaller than those obtained in Puyallup. This could be explained by differences in the crops and soils used at both locations.
- The Tc's based on total soil cadmium in Prosser were as follows: The Tc for wheat grain in 1999 was 0.34. The Tc for wheat grain in 2000 was 0.24. The Tc for potato tubers in 1999 was 0.35. The Tc for potato tubers in 2000 was 0.5.

Lead

- The rate and type of fertilizer had little effect on the level of lead found in grain or potato tuber. Concentrations in both grain and tubers were very low.

Main Conclusions from Prosser study

- The Quincy-Hezel fine sandy loam data indicates that even with rototilling and digging of potatoes, most of the cadmium remained in the top 0-15 cm soil layer.
- As expected, most of the cadmium uptake was related to the upper part of the soil profile where soil cadmium levels had increased.

Part 4: Laboratory Analysis of the Availability of Heavy Metals in Soils Supplemented with Fertilizers and Soluble Metal Salts- Pullman Site

Laboratory experiments determined the capacity of the two soils used in the field studies to retain zinc, lead, and cadmium from soluble metal salts of these metals. The Sultan silt loam had a higher capacity for all metals than the Quincy-Hezel fine sandy loam, but the retained metals were easier to extract by dilute salt solutions, water, and DTPA from the Sultan soil. The difference in extractability of metals was also determined by comparing the incremental addition of fertilizers to both soils versus an “all-at-once” addition of each soluble metal salt to both soils. The DTPA extractability for cadmium even after 45 additions was similar to cadmium added all at one time. For both lead and zinc, the metals were much less extractable after 30 and 45 additions than the one-time applications. This observation suggests that metal addition over time in a cropping situation could render lead and zinc less available than a single application of the same amount of metal.

Soil samples taken from the field sites in Puyallup (Sultan) and Prosser (Quincy-Hezel) were also amended with fertilizers in the laboratory. Soils fortified with fertilizers up to 50X an estimated agronomic rate, were incubated at field moisture content for up to one year. Over the first 30 weeks of incubation, the DTPA-extractability of metal was erratic with time. In the following 20 weeks, there was a general decrease in extractability with time, but many samples did not reach a steady state. These results imply that the availability of lead, zinc, and cadmium to crops decrease over time.

IV. Implications

A. Accumulation of Metals in Soil Over Time

The WSU study was conducted to determine, in part, the accumulation of arsenic, lead, and cadmium in soils and crops that may occur from continual agricultural applications of fertilizers. The predictions and comparisons presented in the following sections focus on cadmium. The results of the study indicate that cadmium is of greater concern than arsenic and lead in terms of soil accumulation and crop uptake. The WSU study also shows, that for the conditions tested, the amount of cadmium taken up by crops is greatly influenced by the source of the cadmium. Although crops take up some amount of cadmium from the soil, the WSU study indicate that cadmium could build up in soil over time due to continual fertilizer use. This is more likely to occur from using fertilizers that contain higher cadmium levels. Western PR which is used to produce a majority of the phosphate fertilizers used in Washington agriculture, has considerably higher levels of cadmium that eastern PR. Increases in soil cadmium concentrations are of concern since they may lead to increases in cadmium concentrations in crops.

Arsenic and lead levels in most agricultural fertilizers are very low. Occasionally, relatively high levels of lead can be found in some micronutrient fertilizers, but the application rate of those products is so low that it does not significantly contribute to lead soil levels. In addition, compared to cadmium, the transfer of arsenic and lead from soil to crop is minimal.

Although the study indicates cadmium may increase over time due to the application of cadmium-containing fertilizer, the prediction of future concentrations of cadmium in the soils depends on the annual input of cadmium and how much cadmium is removed via the harvested plant part. Because not all soils have the same initial cadmium concentration or contribute the same amount of cadmium to crops, the rate of increase in the total level of cadmium in soil from the applications of fertilizers will vary with soils. The number of years it will take to double the concentration of cadmium initially in the soil from continuous applications of the fertilizers is estimated with the following assumptions:

1. The same crops are grown and the yields of the crops are the same throughout the entire period of this prediction;
2. Plant materials other than the top growth of the lettuce, cucumber fruit, potato tuber, and wheat grain are left in the same field;
3. Tillage depth is less than15 cm;
4. No loss of cadmium occurs other than that removed in the harvested plant material and there is no addition of cadmium into the soils happens other than the amount of cadmium added from the phosphate fertilizers;
5. The same soil conditions and same phosphorus fertilizers are used; and

6. The soil-to-plant Tc's calculated based on the total level of cadmium in the soil for each crop are the same throughout the entire period of this prediction and are considered satisfactory as a measure of the transfer of soil cadmium to the plants.

In most instances, the above assumptions would result in an estimate that is higher than the actual levels of metal in soils. This is because monocropping systems are not what always occurs in Washington. For instance, potatoes require the highest levels of phosphate fertilizers and are normally grown on a three-year rotation. Because the total level of cadmium in soils was not determined for the field experiment in eastern Washington that involved potato and winter wheat, it was estimated from the amount of cadmium applied.

The following section provides an estimate of the time it may take for the soil to double the level of cadmium for each of the four crops based on average fertilizer application rates. This estimate is referred to as the doubling time. The doubling time is based on the concentrations of cadmium in soil, in fertilizer, as well as the amount of cadmium removed in the harvested plant parts. The average fertilizer rates are rough estimates. They were determined by consulting a variety of experts that included WSU personnel and fertilizer distributors. Growers are strongly encouraged to perform an annual soil test for each field and modify their use of fertilizer accordingly.

Doubling Time of Cadmium in Soil Cropped to Leaf Lettuce:

Initially, the Sultan soil contained 0.44 ppm cadmium. The estimated number of years for total cadmium in this soil to double its initial level at the average application rate (248 kg/ha for TSP and 339 kg/ha for PR) will be 38 years for the TSP and more than 100 years for the PR.

Doubling Time of Cadmium in Soil Cropped to Cucumber:

At the average application rate, the total cadmium present in the Sultan soil will double from its initial value in about 38 years for TSP and about 98 years for the PR.

Doubling Time of Cadmium in Soil Cropped to Potato:

The initial cadmium concentration for the Quincy fine sandy loam was 0.1 ppm. The number of years for the Quincy fine sandy loam to double its initial total cadmium concentration will be 17 and 36 years for the TSP and PR, respectively, at their average application rates (373 kg/ha for TSP and 509 kg/ha for PR).

Doubling Time of Cadmium in Soil Cropped to Winter Wheat:

The estimated number of years for the Quincy fine sandy loam to double its initial cadmium concentration will be 46 and more than 100 years for the TSP and PR, respectively, if applied at their average application rates (50 kg/ha for TSP and 68 kg/ha for PR).

The observations in the WSU study are consistent with the findings of a report entitled, "Final Report, Screening Survey for Metal and Dioxins in Fertilizer Products and Soils in Washington State, April 1999, Washington State Department of Ecology Publication No. 99-309". The findings in Ecology Publication No. 99-309, include:

- Agricultural practices over the last 50 years may have increased cadmium concentrations to a small degree over background levels in the Columbia Basin, although further investigation is necessary to confirm this.
- The increased cadmium soil concentrations in the agricultural fields sampled suggest no potential soil quality impairment because the values detected are within the lower range of background comparison studies.
- Increased agricultural cadmium levels over background levels indicate a need to periodically monitor cadmium concentrations in soils to determine if any rate of increase is occurring and to ensure levels do not become a concern in the future.

B. Plant Uptake of Metals from Soil Treated with Fertilizer

There are many factors that influence the uptake of metals into plants. They include soil pH, source of metals, soil type, existing or initial soil metal concentrations, and whether all harvested plant material is removed before tilling and subsequent planting. Due to the many uncertainties associated with predicting the uptake of metals into plants and the limited number of conditions evaluated in this study, projections of metal concentrations in plants over time cannot be estimated with a high degree of certainty. However, there are some comparisons that can be made with the data generated from the present study with other recent studies.

C. Relevance to Other Studies

Since the time the WSU study was initiated, three fertilizer risk assessments have been completed (California Department of Food & Agriculture, 1998; US EPA, 1999; and The Fertilizer Institute, 2000). Each of these assessments evaluated possible human exposures, primarily to metals, in fertilizers.

Risk assessment is a process used to evaluate potential health risks associated with contaminants in the environment. Human health risk assessments estimate how much people may be exposed to the contaminants of interest via different possible pathways, such as breathing dust or drinking water containing contaminants. Exposure estimates are combined with information on the toxicity of the contaminants to calculate health risks. Risk assessment can be used to develop risk-based environmental standards, set environmental cleanup levels at hazardous waste sites, and provide general or comparative information on health risks associated with contaminants in the environment.

The fertilizer risk assessments evaluated several ways in which people might be exposed to metals from fertilizers, including estimating human exposures through the food chain via crops grown using different fertilizers. A significant component of this analysis includes estimating crop uptake of metals using Tc's. Tc is the ratio of the concentration of metal in a plant to the concentration of metal in soil. A higher Tc indicates a greater transfer of metal from the soil into the plant. The three risk assessments that have evaluated health risks associated with fertilizer use are briefly summarized.

In the following section, the Tc's used in each of these risk assessments are compared to Tc's derived in the WSU study. Plant uptake of cadmium is of most concern because plants take it up to a greater extent than arsenic or lead. Therefore, the Tc values discussed in the following section are primarily for cadmium. Tc's are reported on a dry weight basis.

(1) California Department of Food and Agriculture, 1998. Development of Risk-Based Concentrations for Arsenic, Cadmium, and Lead in Inorganic Commercial Fertilizers.

California's risk assessment evaluated possible human exposures to arsenic, cadmium and lead from fertilizer use. Three pathways of human exposure were evaluated in the final tier of the risk assessment: ingestion of fertilizer-amended soil, dermal contact with fertilizer-amended soil, and ingestion of plant crops grown using fertilizers. The risk assessment indicated that the crop ingestion pathway contributed the most of any pathway to total risk. The results of this risk assessment were used to generate allowable levels of the three metals in fertilizers on a per nutrient basis for phosphate and micronutrient fertilizers. California has finalized standards for arsenic, cadmium and lead in fertilizer based, in part, on the results of this risk assessment.

California's risk assessment evaluated soil-to-crop uptake for three groups of crops: root crops (which includes potatoes), vegetable crops (which includes lettuce and cucumbers) and grains (which includes wheat). A range of Tc's were used for predicting crop uptake for each of these groups for each metal. For the California assessment, the Tc's were based on available Tc's in the literature compiled for this risk assessment and included data from fertilizer and non-fertilizer sources of metals and data primarily from greenhouse pot-studies and some field studies.

The Tc for cadmium for lettuce based on total soil cadmium in the WSU field study averaged 6.2 for two phosphate fertilizers. This is within the range of Tc's used for the vegetable group (including lettuce) in California's risk assessment. The Tc increased to 16.9 with the inclusion of soluble cadmium salt, which implies that the source of cadmium is also a major factor affecting the Tc for cadmium. The Tc for cadmium for cucumber averaged 0.68 in the WSU study, which is within the range of Tc's for the vegetable group in the California risk assessment.

It is not apparent how using the Tc's derived from the WSU study would impact the final results of California's risk assessment. This is because California's risk assessment relies on using ranges of Tc's as well as ranges of other exposure parameters (such as crop ingestion rates and bodyweights) in calculating risks in a process called probabilistic risk assessment. Therefore, including a Tc value of 16.9 into the risk assessment does not necessarily mean that the final calculated risk will be higher, and there is no easy way to predict if including this Tc value would have any appreciable effect on the risk calculation.

(2) U.S. EPA, 1999. Estimating Risk from Contaminants Contained in Agricultural Fertilizers.

EPA's fertilizer risk assessment evaluated human exposures to nine metals, including arsenic, cadmium and lead, as well as dioxins. Five exposure pathways were evaluated: direct ingestion of fertilizer products during application, ingestion of fertilizer-amended soil, inhalation of particles and vapors associated with fertilizer application, ingestion of plant crops and animal products produced on soil amended with fertilizers, and ingestion of fish from streams located adjacent to fertilizer-amended fields. As with the California risk assessment, exposures through the food chain were found to be one of the main contributors to the total (albeit small) risks. However, the EPA concluded from their risk assessment that for most fertilizers "hazardous constituents in fertilizers generally do not pose harm to human health or the environment."

EPA's risk assessment evaluated five categories of crops: grains, forage, fruit, herbage, and roots. EPA also collected and compiled a database of Tc values specifically for their risk assessment. The Tc database used was based on field data only for most metals and included data from fertilizer and non-fertilizer sources. A range of Tc's were used for predicting crop uptake for each metal for each category of crops. The Tc range used for cadmium in lettuce is 0.05-1.56. This range is lower than the average lettuce Tc for the WSU study of 16.9 (based on total soil metals) for all sources and 6.2 for fertilizer sources only. Because EPA calculated risks using a probabilistic approach, as did the California risk assessment, it is unclear what impact including a Tc value of 16.9 or 6.2 would have on the final risk results.

(3) The Fertilizer Institute (TFI), 2000. Health Risk Evaluation of Select Metals in Inorganic Fertilizers Post Application.

The TFI risk assessment evaluated possible human exposures to twelve metals associated with fertilizer use, including arsenic, cadmium and lead, and radium 226, a radionuclide. Three routes of human exposures were evaluated: ingestion of fertilizer-amended soil, dermal contact with fertilizer-amended soil, and ingestion of crops grown with fertilizers. Again, the crop ingestion pathway contributed the greatest amount of risk to the total risk levels. The risk assessment calculated allowable levels of metals in fertilizers based on acceptable risk levels, similar to the California risk assessment. The Association of American Plant Food Control Officials, made up of state fertilizer regulators, has tentatively adopted the allowable metals levels developed in TFI's risk assessment as national fertilizer guidelines.

TFI's risk assessment evaluated three groups of crops: vegetable, root, and grain crops. Tc values for the crop groups evaluated in the risk assessment were derived from studies using fertilizer and non-inorganic fertilizer sources (such as biosolids) and include data from field studies and a limited number of greenhouse(pot)-studies. The Tc values used in TFI's risk assessment for cadmium are 1.7, 0.93 and 0.12 (dry weight) for vegetable, root and grain, respectively. These Tc values are the 90% upper confidence limit of the geometric mean of the Tc values determined for each metal and each crop group. These values are lower than the average Tc of 6.2 for cadmium in lettuce across the other fertilizer treatments. The impact of adding these values to the Tc database used in the TFI risk assessment on the final allowable metals levels calculated for fertilizers cannot be easily calculated.

(4) Use of the Tc’s from WSU Study

Although the Tc's developed in the study cannot be directly applied to the existing risk assessments, they contribute to the database of Tc's that can be used in human health risk assessments. The Tc's developed in this study more accurately reflect potential crop uptake of metals from fertilizers since they are based on fertilizer data and were derived from field data.

The WSU study evaluated the uptake of metals into four crops (lettuce, cucumber, wheat, and potato) grown using a limited number of fertilizers on two different soil types. People generally eat a variety of vegetables grown in many different locations either from commercial farms or from home gardens. Therefore, it would not be realistic to predict how much a person would be exposed to if their only source of vegetables came from the locations and conditions tested in this study.

D. Comparison of Concentrations of Metals in Crops to FDA's Market Basket Survey Results

The U.S. Food and Drug Administration (FDA) conducts routine sampling of food for various pesticides, contaminants, and nutrients as part of their Market Basket Study. The main purpose of the Market Basked Study is to estimate intakes of these substances in representative diets for the U.S. population. Testing of different crops for arsenic, cadmium and lead is included in the Market Basket Study and these data can be used to compare to the results of the WSU study.

In general, the concentrations of cadmium measured in the four crop of the WSU study fall within the ranges of cadmium concentrations reported in FDA Market Basket data. However, some cadmium concentrations in lettuce in the WSU study at the higher fertilizer application rates are higher than values reported in the FDA data. This is expected since the higher fertilizer application rates of the WSU study are much greater than the normal fertilizer application rates used on a per year basis. The concentrations of arsenic and lead measured in crops in the WSU study are all within concentration ranges reported in FDA data.

V. Conclusions

The WSU study was conducted to determine, in part, if the accumulation of arsenic, lead, and cadmium in soils and crops may occur from continual agricultural applications of fertilizers. The results of the study indicate that cadmium is of greater concern than arsenic and lead in terms of soil accumulation and crop uptake. The WSU study also shows, that for the conditions tested, the amount of cadmium taken up by crops is greatly influenced by the source of the cadmium. Although crops take up some amount of cadmium from the soil, the WSU study indicate that cadmium could build up in soil over time due to continual fertilizer use. This is more likely to occur from using fertilizers that contain higher cadmium levels. Western PR which is used to produce a majority of the phosphate fertilizers used in Washington agriculture, has considerably higher levels of cadmium that eastern PR. Increases in soil cadmium concentrations are of concern since they may lead to increases in cadmium concentrations in crops.

Arsenic and lead levels in most agricultural fertilizers are very low. Occasionally, relatively high levels of lead can be found in some micronutrient fertilizers, but the application rate of those products is so low that it does not significantly contribute to lead soil levels. In addition, compared to cadmium, the transfer of arsenic and lead from soil to crop is minimal. Other pathways are important for arsenic and lead, therefore, the state standards for these metals must remain in effect.

The relatively high availability of naturally occurring cadmium and cadmium from the phosphate fertilizers used in the study led to relatively high accumulation of cadmium in the lettuce and wheat crops grown, respectively, in the Sultan and Quincy-Hezel soil types. While the results indicate a need to monitor soil cadmium levels to prevent excess soil cadmium accumulation, the extrapolation of the results to other soil types cannot be made with any degree of certainty. This is because soils vary considerably in their ability to bind cadmium. Additionally, there may be major differences in cadmium availability between soil types even when they contain the same amount of cadmium. The study would need to be extended to other soil types before it could be applicable to a broad range of soil conditions.

There are other important issues that have to be resolved in order to improve the accuracy of predicting the impact of continuous inputs of cadmium to soil from the application of the phosphate fertilizers. First, a soil-to-plant Tc is needed that is independent of time. The availability of cadmium from the TSP decreased in the 2^{nd} year of the study, whereas the availability of cadmium from the PR increased. This indicates that within the two-year period of this investigation, the Tc's changed with time. An extension of this research for two more years would be very useful in determining a Tc value after enough time has elapsed to allow the majority of the cadmium from fertilizer to be well equilibrated with the soils. Secondly, the model developed based on the first two years of the field research needs to be validated. Confidence in making long-term predictions regarding soil loading and plant uptake will be strengthened by such validation and a two year extension of this research would make that possible.

The current Washington metal standards established by the legislature in 1998, which limits the input of cadmium and other metals from fertilizers or other soil amendments to agricultural soils, should be sustained until after Tc values for crops have been further refined. If the input of cadmium to the soil far exceeds what is removed by the crop then future increases in the level of cadmium in Washington State soils are inevitable. Given the high availability of this metal to the vegetable and grain crops in the soils, allowing the level of cadmium in Washington State soils to rise much higher than their background level is not justified.

VI. Recommendations

The existing Washington State standards that govern the levels of heavy metals in fertilizers appear to be sufficiently protective at this time. Future levels of heavy metals in soils, especially cadmium, may be of concern due to the recent use of phosphate fertilizers with relatively high levels of cadmium. Cadmium levels in soils should be periodically monitored to ensure that levels do not become a concern in the future. Additional studies are necessary to refine the Tc values derived from this study. Additional data are also required to determine the heavy metal loading in other Washington soils. Finally, the existing model needs to be validated with a second two-year study.

The study indicates the existing Washington State standards for arsenic, cadmium, and lead in fertilizer appear to be sufficiently protective at this time. However, the study also indicates there is a potential for the levels of these metals to increase in soil over time. This is especially true of cadmium, due to current applications of phosphate fertilizers containing relatively high levels of cadmium. The agencies involved in the development of this report make the following recommendations:

1. WSU should extend its study for a minimum of two years and focus on the development of a soil-to-plant Tc for cadmium that is independent of time. This would greatly improve the accuracy of predicting crop uptake of cadmium.

2. A long-term program should be developed to monitor soil levels of arsenic, cadmium, and lead over time to ensure that soil levels do not become a concern in the future.

3. A process should be initiated to attempt to develop a regional approach dealing with the issue of metals standards and labeling. This should initially include Washington, Oregon and Idaho, but may be expanded to include other western states.