

# **Distribution and Fate of Background and Bioavailable Metals in Oregon Agricultural Soils, and Plants**

## **FINAL REPORT**

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## EXECUTIVE SUMMARY

### **Distribution and Fate of Background and Bioavailable Metals in Agricultural Soils and Plants**

Concentrations of non-nutritive metals and metalloids in fertilizers, and agricultural amendments are subject to regulations by state governments. Oregon must adopt standards for arsenic, cadmium, lead, mercury and nickel in these products. The objective of this regulation is to protect human health and natural resources from toxicity of these metals/metalloids. In order to set these regulations considerations of cumulative change over decades will be necessary. In a review report prepared for ODA in 2002, Curtis and Smith found that there were limitations to the available information necessary for models that represent behavior of these metals in agricultural systems. Curtis and Smith also concluded that estimates of the soil metal concentration after 50 years (200 years for lead) dominantly determined the human health risk. Curtis and Smith, ran simulations and found that estimates of the metal distribution coefficients (soil to water concentration ratio) were critical determinants in the projections of soil metal accumulation with time. The large disparity between distribution ( $K_d$ ) estimates was found to be problematic and created a high degree of uncertainty.

The objectives of this study were:

- Determine the background concentrations of metals in agricultural systems in Oregon.
- Apply environmentally relevant treatment levels of a commercially available phosphate fertilizer over a three year period, using typical agricultural practices.
- Determine the metals/metalloids concentration in the edible portion of crops and the total, dissolved, and labile metal/metalloid concentrations.
- Estimate the correlation between bioavailable, soil and soil solution metal concentrations with the edible crop portion.
- Define the bioaccumulation potential from fertilizer input of metals/metalloids in agricultural systems over the three year study.
- Identify the rates of change for metal concentrations in distinct agricultural soils over time.

The background levels of arsenic, cadmium, lead, and mercury were found to be the same or lower than those reported by Holgrem *et al* and Boerngen and Shakette 20 years ago. This is consistent with current national trends that these metals are generally declining in the environment. The mean background level of arsenic, cadmium, lead, nickel and mercury are below the ODEQ soil screening levels for risk assessments for representative mammals. Metal concentration in irrigations waters from Hermiston and Klamath were below the fresh water quality limit for both the aquatic life and human health criteria.

No significant treatment effect was observed for arsenic, lead and nickel in soil. A significant treatment effect was observed for cadmium and mercury in soil at most sites. Cadmium and mercury were found in the edible portion of the potato and wheat crop. Nickel was found in potato. Arsenic and lead were not found in either crop for any of the trials. For some trials (site and crop -specific) cadmium, nickel and mercury were yearly and/or dose dependent.

The bioavailable metals were site specific and in general significant treatment and/or yearly effects were seen for cadmium, lead, and nickel. The distribution and bio-distribution coefficients were determined and generally found to be larger than those reported by Bates and Sharp, and typically smaller than those reported by Suave *et al*. The distribution coefficients were similar among the sites except for arsenic which was seen to vary significantly between the sites. There was a slight tendency for the bio-distribution coefficients to decrease with treatment and with yearly applications. If these tendencies were to continue with further studies, they may have long term implication for risk assessment.

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## INTRODUCTION

Many commercially available fertilizers contain variable levels of non-nutritive metals or metalloids such as arsenic (As), cadmium (Cd), lead (Pb), nickel (Ni), and mercury (Hg), arising from multiple sources including parent rock, or the use of waste products as fertilizer (1,2). Recycling of waste is encouraged by the EPA, to minimize output of toxins, including metals into the environment. Tailings can contain valuable plant nutrients such as zinc (Zn), phosphorus (P), and potassium (K) that can be packaged and sold as agricultural fertilizer. Consequently, metals can be present in concentrations greater than part per million levels and may pose a potential risk. The market share of waste derived fertilizer is unknown and has proven difficult to track. The United States ranks in the top five globally for fertilizer importation and an estimated 53 million tons were used in the U.S. in 2001-02 (3). In February 2000 a zinc fertilizer distributor in Washington upon inspection discovered 200,000 mg/kg cadmium in raw zinc sulfate material from China. Consequently, the company was forced to recall fertilizer from the market and closed for several months for facility clean up. Worker exposure was a major concern and the possibility remains that the Zn sulfate was deliberately contaminated (4). Investigations in to the long term effect of applying potentially toxic, metal rich fertilizer to soils have resulted in mixed and conflicting conclusions (5) making risk parameterization difficult.

Metal sorption by soil may be enhanced with the addition of phosphatic fertilizers, which have been found to decrease positive charge, but increase the cation exchange capacity (CEC) of soil (6). Soil pH can decline with the addition of fertilizer high in ammonium ( $\text{NH}_4^+$ ) (7). Notable differences between field and greenhouse or container

studies continue to exacerbate the difficult task for regulatory agencies to set maximum tolerable limits for non-nutritive metals/metalloids in soils. Previous studies have employed a one time use of highly contaminated soils to measure metals. This leaves unanswered questions about metal bioavailability in agricultural settings where metal concentrations are assumed to be considerably lower. Many studies used spiked soils, which have been shown to have consistently higher transfer rates to plants (8,9). In addition, physical and chemical properties may differ significantly in agricultural soils subjected to repetitive tilling and irrigation (10), potentially affecting metal bioavailability over time. Potential risks from metals in fertilizers have been outlined (11) and in development are soil screening criteria (USEPA) to estimate risk of soil metal contamination to biota. Although maximum allowable concentrations for metals in contaminated soils exist, limits in non-contaminated, agricultural soils have yet been defined (12). European nations observe critical limits of metals in both contaminated and non-contaminated soils (13). Potential risks of repeated input of non-nutritive or toxic constituents from fertilizer include the potential accumulation and increased bioavailability of metals in agricultural soils over time.

Bioavailability of metals is the accessibility for biological assimilation and possible toxicity. An increase in the bioavailability of metals may lead to enhanced plant assimilation including the potential for transport of metals into the edible portion of crops. Tolerable intake values of many toxic metals from foods have been recommended (14,15). Metals also leave agricultural systems via surficial waters and leaching and may negatively impact adjacent water systems, posing a potential risk to aquatic life and to drinking water quality. The majority of metal speciation studies assessing the

bioavailability of metals in soil utilize one-step extraction methods, or modeling programs such as the free ion activity model (FIAM)(16). Few studies have analyzed for the bioavailable fraction of metals in agricultural soils. One approach to capture the reported bioavailable fraction is the use of Diffusive Gradients in Thin Films (DGT), with which recent research has demonstrated both insight into the supply of metals from soils and the potential for use as physical surrogates for plant/organism uptake.

DGT is a passive sampling device developed and used for quantitative determination of labile metals *in situ* (17). Labile metal fractions are considered to be bioavailable from soil solution to biota. The focus of DGT is on the availability of metals in soil systems rather than on their mere presence. Prior studies have applied the use of DGT to measure labile metal in soils (18-20), and DGT measured labile metal has been shown to more accurately reflect metal availability to plants than measurement of ion activities alone (21). The chelex 100 resin layer used in the DGT device adsorbs mostly divalent and some monovalent cations (22). Binding affinities to the resin are metal specific and are dependent on the pH, ionic strength, and presence of other complex-forming species. Chelex 100 will not readily bind arsenic due to the trivalent and pentavalent states ( $As^{3+}$ ,  $As^{5+}$ ). Although chelex 100 has a high affinity for mercury in the presence of nitrate ions, other competing ions, such as chloride, lower its affinity to undetectable levels. We hypothesize that DGT captures the dose-dependent, fertilizer cadmium, nickel, and lead contribution in distinct agricultural systems. Secondly, DGT measured metal is an effective indicator of the fraction of metal available for crop uptake. The objectives of this three year field study were:

1. Determine the background concentrations of metals in distinct agricultural systems in Oregon.
2. Apply environmentally relevant treatment levels of a commercially available phosphate fertilizer to four experimental field plots over a three year period, using typical agricultural practices.
3. Determine the availability of metals/metalloids to the edible portion of wheat or potato crops and the total, dissolved, and labile metal/metalloid concentrations in soils.
4. Estimate the correlation between DGT measured labile metal and metal concentration in the edible portion of wheat and potato crop.
5. Define the bioaccumulation potential from fertilizer input of metals/metalloids in agricultural systems over the three year study.
6. Identify the rates of change for metal concentrations in distinct agricultural soils over time.

## **EXPERIMENTAL SECTION**

**Study area.** Soils were collected from four field locations in the state of Oregon, USA (**Figure 1**). Sampling locations represent distinct agricultural systems defined by differing climates, soil classifications, crop rotations, and agronomy practices. Selected characteristics of the soils used in the study are presented in **Table 1**. At each sampling location, an area of 1012 m<sup>2</sup> was allocated and divided into a 4x4 randomized grid consisting of four treatment (dose) levels (**Figure 2**).

**TABLE 1. Site specifications and selected properties of soils 2003-2006.**

Location	Soil classification <sup>a</sup>	pH <sup>b</sup>	% Organic Matter <sup>c</sup>	CEC <sup>d</sup> (cmol/kg)	P <sup>e</sup> (μg/g)	K <sup>f</sup> (μg/g)	NH <sub>4</sub> -N <sup>g</sup> (μg/g)	NO <sub>3</sub> -N <sup>h</sup> (μg/g)	Irrigation practices	Crop(s) grown
Klamath Basin	Poe fine sandy loam	5.9	0.9	13	9-33	48-91	3.1-56	5.7-53	irrigated	summer wheat/ potato
Hermiston	Adkins fine sandy loam	7.1	1.1	11	7.2-42	240-510	2.2-72	2.2-81	irrigated	winter wheat/ potato
Pendleton	Walla Walla silt loam	4.8	2.6	18	7.4-35	540-720	3.1-75	8.5-70	dry land	winter wheat
Willamette Basin	Woodburn silt loam	5.6	2.4	18	8-44	170-290	2.7-15	1.1-54	dry land	winter wheat

a Soil classification according to the NRCS.

b Measured using a saturated paste; electrode method (ASA 12-2.6).

c Dichromate/H<sub>2</sub>SO<sub>4</sub> colorimetric method.

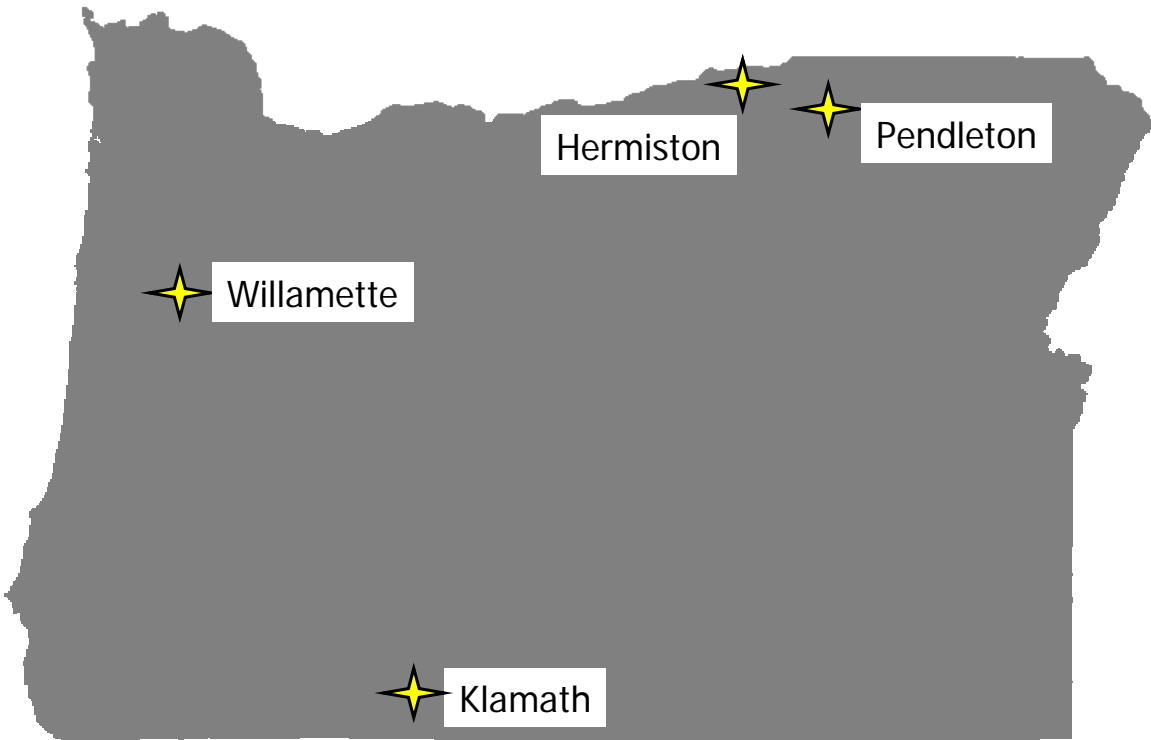
d CEC=cation exchange capacity, measured using ammonium acetate EPA method 9081.

e available P Colorimetric, ASA 24-3.4, Na acetate extraction

f available K AA, Na acetate extraction

g Nitrogen-Ammonia: Colorimetric, ASA 33-7.3KCl Extractable, ASA 33-3.2

h Nitrate-N + Nitrite-N Colorimetric, ASA 33-8.3, KCl extractable, ASA 33-3.2



**FIGURE 1. Oregon field sampling locations.**

**TABLE 2. Soil background concentrations for five metals in Oregon soils and Oregon Department of Environmental Quality (ODEQ) bird/mammal screening levels soil concentrations (mg metal / dry kg of soil). (Adapted from Curtis, L.R. and Smith, B.W., 2002, ODA report)**

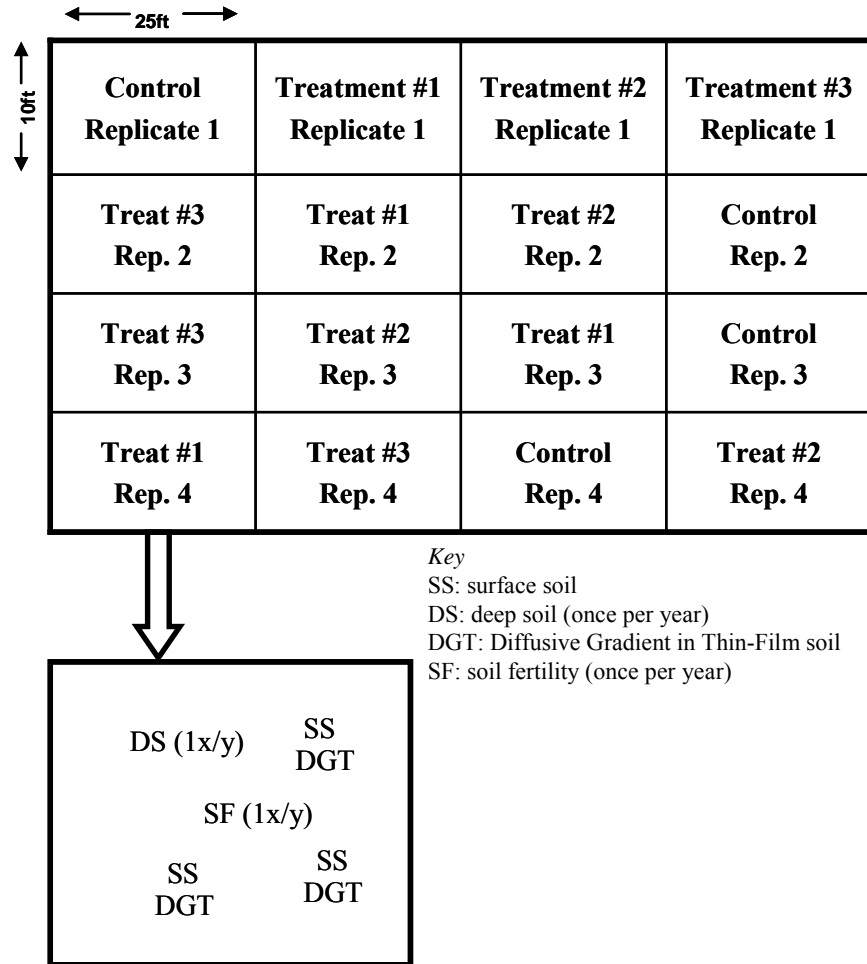
	Pérez and Anderson 2007, <i>in preparation</i> <sup>1</sup>	Holmgren <i>et al.</i> 1993 <sup>2</sup>	Boerngen and Shackette, 1981 <sup>3</sup>	ODEQ <sup>4</sup>
Arsenic	3.8 (1.6-6.5)	N/A	6.4 (4.3-10.3)	10/29
Cadmium	0.18 (0.10-0.23)	0.294	N/A	6/125
Lead	13.4 (4.8-20.3)	8.6	16 (10-20)	16/4000
Nickel	13.6 (10-18.4)	27.4	16 (7-30)	320/625
Mercury	0.013 (0.005-0.034)	N/A	0.11 (0.04-0.26)	1.5/73

N/A = not available.

1. Values are arithmetic means (range) for 16 background samples collected from fallow field sites at Oregon State University agricultural research stations Klamath, Hermiston, Columbia, and Hyslop.
2. The values are geometric means for 88 samples collected from northwestern, southcentral and southeastern Oregon.
3. 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.
4. ODEQ soil screening levels from risk assessments with rats (representative mammal) and robins (representative bird).

**Soil treatment.** Commercially available fertilizers known to contain more elevated concentrations of As, Cd, Pb, Ni, and Hg were used for field dosing. All phosphate fertilizers used in this study were purchased by the Oregon Department of Agriculture and were assumed to be representative of phosphate fertilizers currently on the market. Application levels were assigned based on crop and irrigation practice (23,24). Treatment levels were control, using a 1x typical agronomical application of a commercially available, non-metal rich fertilizer (21-0-0-24/N-P-K-S); treatment level 1,

using a 1x application of a commercially available fertilizer with elevated metal concentrations (16-20-0/N-P-K); treatment level 2, using a 2x application of a metal rich fertilizer; and treatment level 3 using 3x application of a metal rich fertilizer (Table 3).



**FIGURE 2. Soil sampling scheme from each of the four field sites. The control indicates a 1x application with a non-metal rich fertilizer. Treatment indicates either a 1x, 2x, or 3x application with a metal rich fertilizer. Within each replicate 3 sub-samples of surface soil and DGT soil were taken. Deep soil, also a composite of three sub-samples, and soil fertility were sampled once a year at harvest.**

**TABLE 3. Measured metal concentrations in fertilizers 2003-2006**

n=5 N-P-K-(S) mg/kg	2003/2004		2004/2005		2005/2006	
	21-0-0-24 Control	16-21-0 Treat	21-0-0-24 Control	16-20-0 Treat	21-0-0-24 Control	16-20-0 Treat
As	0.2	0.8	<0.014	7.7	0.7	6.3
Cd	0.1	20	<.00012	49	0.3	52
Pb	3.0	0.6	0.1	1.5	0.9	2.3
Ni	4.5	131	23	112	16	118
Hg (µg/kg)	110	3.9	1.4	2.5	40.4	5.1

**SAMPLE COLLECTION**

Soils were collected twice annually, post fertilizer application allowing  $\geq 60$  days incorporation, and again at crop harvest approximately 5-10 months post fertilizer application.

**Surface soils.** Surface soils were collected from the rhizosphere (0-22 cm) using stainless steel soil probes (AMS inc., American Falls, ID, USA), which sample an intact core. Within each treatment replicate, a composite of three cores were collected from distinct spots within the treatment plot area. This was done to capture field heterogeneity within each treatment plot (**Figure 2**). Overall, 16 surface soil samples were taken back to the laboratory, each of the 16 samples was a composite of 3 sub-samples.

**Deep soils.** Deep soils were collected once a year using a gas powered auger to drill a core of 3 m in depth. Only the control replicate 1, treatment 1 replicate 1, treatment 2 replicate 1, and treatment 3 replicate 1 were sampled. These correspond to one row of each field plot at all four sites (**Figure 2**). In 2003, a deep soil core was made 1' over, 1' in from the top left corner of each of the replicate 1 grids from the field plot. To prevent repeated sampling from the same deep core location in 2004, the core drilling spot was shifted 2' over, 2' in, followed by a 3' by 3' in 2005, and a 4' by 4' in 2006. Stainless

steel probes were used to sample soil in triplicate from the 3 m hole. Deep soil samples were placed in clean bags for transport and further processing.

**Diffusive Gradient in Thin Film soils.** DGT soils were collected from the surface horizon and the rhizosphere (0-22 cm). A composite of three sub-samples were taken from each treatment replicate to account for soil heterogeneity. Soils were kept intact (not dried or ground) to preserve the natural biota of the soil. Rhizosphere microbial communities are thought to contribute  $\geq 65\%$  of the total organic acids from both plant and microbial contributions (25) making their role critical in our efforts to realistically determine the bioavailability of metals. DGT soils were placed in clean plastic bags, and stored in a  $< -20$  °C freezer until further analysis. Side-by-side aliquots were removed from the DGT soil to simultaneously test for DGT measured and soil solution metal concentrations.

**Plant.** Sixteen plant samples were collected once a year at harvest from each of the sites. In 2005, Pendleton was fallow and no plant samples were taken. Wheat samples were harvested using a mini-combine. By using the mini-combine, we were able to sample each individual replicate from all of the treatments. Aliquots were taken from each of the 16 grain bags and placed in plastic bags for transport and analysis. Potatoes were sampled using a small potato harvesting machine. Potatoes were pulled from the ground by the harvester and moved up a slotted conveyor belt to help shake off debris. Twelve potatoes were randomly sampled from each treatment and each replicate, for a total of 192 (12 \* 16) potatoes from one field site. Potatoes were stored in mesh bags for transport to the laboratory.

## **CHEMICAL ANALYSIS**

**Reagents.** Concentrated nitric ( $\text{HNO}_3$ ) and hydrochloric ( $\text{HCl}$ ) acid, trace metal grade (Fisher Optima, Pittsburgh, PA); elemental stock standard solutions (Alfa Aesar Specpure, Ward Hill, MA); and 18  $\text{M}\Omega$  cm water (Barnstead, Dubuque, IA, USA) were used.

Certified reference materials (CRMs) were purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Soil CRMs included 2710 Montana Highly elevated soil, 2711 Montana Moderately elevated soil, and 2709 San Joaquin soil. For DGT and soil solution analysis, CRM 1640 Natural Waters was utilized. Plant CRMs included 1515 apple leaf, and 1573a tomato leaf.

**Methods.** Surface soils were dried at 75 °C for 24 h, and homogenized using coffee grinders (Toastmaster corp., Menominee, MI, USA) with stainless steel blades. Soil moisture content was determined for each site during the drying process. Total recoverable metal concentration of surface soils and plant samples was determined using an acid digestion. An aliquot of  $0.25 \pm 0.01$  g of dried and homogenized soil or plant matrix was weighed out in to graduated kimax digestion tubes (Kimble/Kontes, Vineland, New Jersey, USA). A measurement of 2 mL of concentrated  $\text{HNO}_3$  was immediately added to begin the digestion process. The soil or plant matrix digested at room temperature for approximately 24 h in a fume hood. After 24 h, 1 mL of concentrated  $\text{HNO}_3$  and 1 mL of concentrated  $\text{HCl}$  were added to each digestion tube. Tubes were placed on a digest block and refluxed at increasing temperatures (40, 60, 100 up to 150 C) until orange  $\text{NO}_x$  gases no longer formed. Typical digest times were 10 h for soils and 5 h for plants. Following the digestion, the tubes were cooled to room temperature, then diluted to a 10 mL final volume using 18  $\text{M}\Omega$  cm water. All digest tubes were vortexed and filtered using a 0.45 $\mu\text{m}$  PVDF (polyvinylidene difluoride) (Pall Corporation, East

Hills, New York, USA) filter. Samples were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) (PQ ExCell, Thermo Elemental, Waltham, MA, USA) as adapted from EPA methods 3050B and 7020 (26). Soil sub-samples, collected from the rhizosphere with stainless steel probes, were sent to the University of Idaho Analytical Sciences Laboratory (Moscow, ID, USA) and analyzed for moisture content and general fertility including pH, P, K, percent organic matter (% O.M.), nitrate ( $\text{NO}_3\text{-N}$ ), ammonium ( $\text{NH}_4\text{-N}$ ), and CEC. A summary of these data are shown in **Table 1**.

**DGT deployment and sample analysis.** DGT soils were brought to room temperature (21 °C) prior to use. An aliquot of each soil (~50 g) was weighed in duplicate and placed in individual acid washed plastic containers. Appropriate quantities of 18 M $\Omega$  cm water were added to achieve a 115% moisture level. Soils were stirred with glass rods, followed by a 24 h equilibration prior to DGT deployment. Diffusive and chelex gels were purchased (DGT Research Ltd., Lancaster, Lancashire, UK) and assembled according to Zhang and Davison (27,28) (**Figure 3-4**). DGT units were deployed into the saturated soil slurry by pushing them below the soil solution surface at an angle to prevent air bubbles and into the soil as previously described (29). Containers were covered and maintained at room temperature for 72 h. Previous experiments were conducted in lab to determine the deployment duration. We found that 72 h provided ample time for the chelex resin to concentrate enough metal to be detected using ICP-MS (**Equation 1**). To alleviate any concern about potential depletion of metal from the soil within the 50 g sample cups, time trials were also conducted, where DGT units were deployed for fixed times 24, 36, 48, 72 h. It was found that the time integrated

concentration of DGT measured metal, was identical for all deployment times (**Equation 2**). This information demonstrates that at each agricultural field site, metals in the soil systems are constantly resupplied from soil solids, or bound states, in to soil solution. DGT units were retrieved from the soil and rinsed with 18 MΩ cm water to remove any soil particulates that remained on the filter membrane. The resin gel was removed and placed into an acid cleaned plastic vial along with 1 mL of 1 N HNO<sub>3</sub> for 24 h. Samples were diluted 10-fold and analyzed by ICP-MS. The amount of metal accumulated on the resin gel per unit area was calculated as:

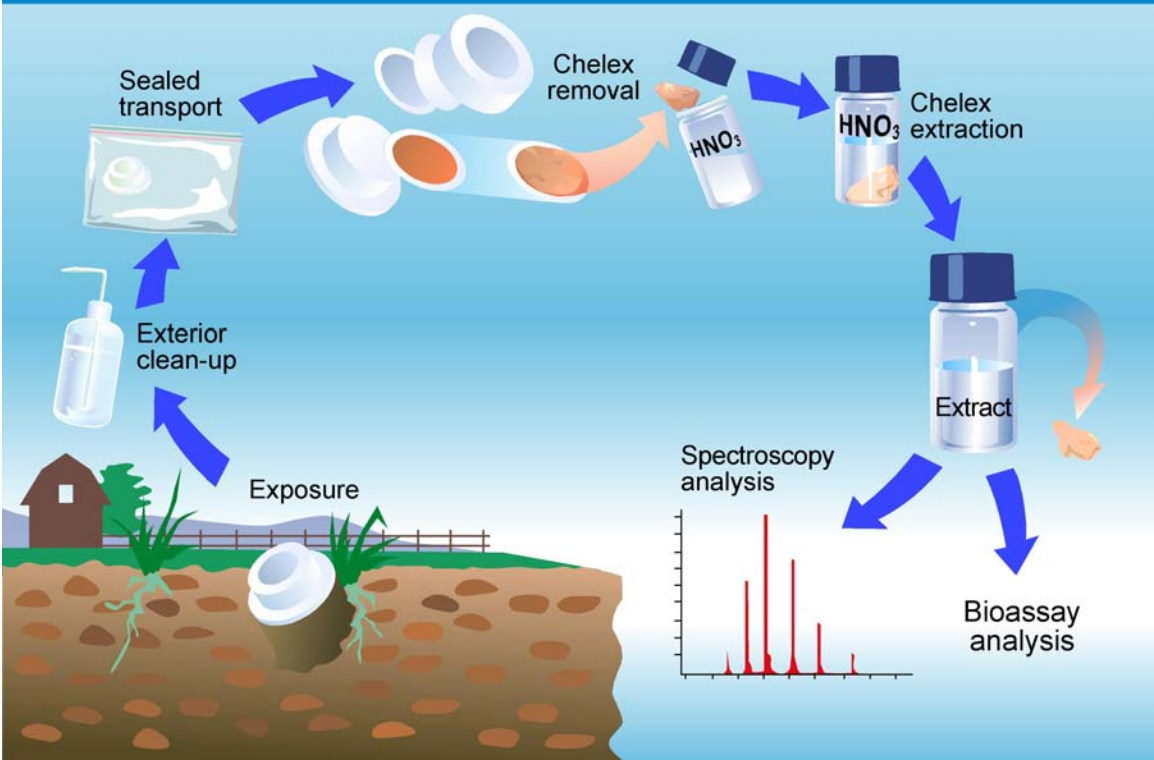
$$M = C_{\text{eluent}} (V_{\text{HNO}_3} + V_{\text{gel}}) / f_e \quad (1)$$

Where  $C_{\text{eluent}}$  is the eluent concentration in μg/L,  $V_{\text{HNO}_3}$  is the volume of 1N nitric acid used to extract metal from the resin,  $V_{\text{gel}}$  is the volume of the gel,  $f_e$  is the elution factor. To calculate the time integrated metal concentration in the DGT device ( $C_{\text{DGT}}$ ), the following equation is used:

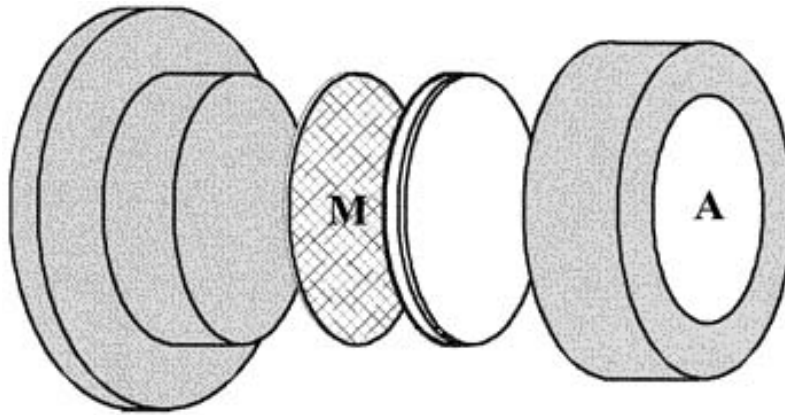
$$C_{\text{DGT}} = M \Delta g / (D t A) \quad (2)$$

Where  $M$  is the mass of metal accumulated on the resin layer;  $\Delta g$  is 0.093 cm, or the thickness of the diffusive gel layer (~0.8mm) plus the filter (~0.13mm);  $D$  is the diffusion coefficient for each metal at 22 °C from "Practical Guide to using DGT for Metal" (30);  $t$  is the deployment time, and  $A$  is the exposure area of the chelex resin (3.14 cm<sup>2</sup>).

# Diffusive Gradients Thinfilm (DGT) Processing



**FIGURE 3. Diffusive Gradients Thinfilm (DGT) Processing from field to laboratory analysis.**



**FIGURE 4. Diffusive Gradient in Thin Film (DGT) deployed in soil solution. The majority of metal in soil is bound to a solid, with variable rates of release. The fraction of metal that is released into solution, or labile metal, diffuses through the diffusive gel layer and is bound to the chelex resin. (adapted from Ernstberger *et al.*, ES&T, 2002)**

**Quality Control.** Quality control (QC) consisted of both field and laboratory components. QC samples comprise at least 15% of each analytical run. The field QC was comprised of trip blanks, field blanks, and rinsate blanks. Rinsate blanks were taken at each sampling event from each soil sampling tool utilized, including the trowel and soil probes, as well as the aluminum pans used for soil drying and coffee grinders used for soil homogenization. The method detection limits for metals/metalloids in quality control field water samples are as follows: arsenic 0.35, cadmium 0.084, lead 0.53, nickel 3.7  $\mu\text{g/L}$ . Field QC waters were not analyzed for mercury. Trip blanks and rinsate blanks were below detection limits for all metals/metalloids 2003-2006. Field blanks were below detection limits for all metals except lead. Only the Hermiston site had detectable lead concentrations in the field blanks. The average lead concentration in

Hermiston field blanks was 3.81  $\mu\text{g/L}$  (2003 BDL, 2004 BDL, 2005  $4.63 \pm 0.29$ , 2006  $2.98 \pm 2.67 \mu\text{g/L}$ ). Laboratory QC consists of blanks, rinsate blanks of lab equipment, check standards, spikes, and certified reference materials. No blank samples of 1%  $\text{HNO}_3$  solution were above detection limits ( $n=104$ ), nor were the rinsate blanks of laboratory equipment used to process samples ( $n=4$ ). The average percent recovery for all check standards was 96% ( $n= 63$ ; As 95%, Cd 97%, Pb 97%, Ni 96%). Average spike recoveries were  $\geq 90\%$  ( $n= 10$ ). The average percent recovery for all certified reference materials shown in **Table 4** was 101% ( $n= 40$ ; CRMs: 2711, 107%; 2709, 96%; 1515, 100%; 1573a, 100%; 1640, 101%). In house reference soil was collected at the beginning of the project. Large quantities were dried and ground for use in each analytical batch to track concentrations over time. The average concentrations of metals in the in house reference soil were: As  $3.8 \pm 0.85$ , Cd  $0.12 \pm 0.02$ , Pb  $6.6 \pm 0.69$ , Ni  $40.9 \pm 4.21 \text{ mg/kg}$  ( $n=16$ ), Hg  $15.0 \pm 5.3 \mu\text{g/kg}$ . Irrigation waters were sampled from sprinkler heads and outdoor hoses from Klamath and Hermiston sites ( $n=22/\text{site total}$ ). Average concentrations of irrigation water are shown in **Table 5**.

**TABLE 4. Average percent recovery of check standards, spikes and certified reference materials.**

<i>n</i>	% recovery						
	check		certified reference material				
	standards	spikes	2709	2711	1515	1573a	1640
	<i>63</i>	<i>10</i>	<i>13</i>	<i>6</i>	<i>8</i>	<i>8</i>	<i>12</i>
As	95	90	97	104	nd	nd	91
Cd	97	84	97	99	nd	100	100
Pb	97	94	93	125	100	nd	117
Ni	96	91	95	100	nd	121	96
Hg	-	-	100	101	96	91	-

\* Hg n values: (CRM 2709, n=61; 2711, n=16; 1515, n=35; 1573a, n=16)

**TABLE 5. Metal concentrations in irrigation waters from Hermiston and Klamath field sites 2003-2006.**

	Hermiston			Klamath		
	μg/L	SD	n	μg/L	SD	n
			above MDL			above MDL
As	0.87	0.37	7	5.2	1.4	21
Cd	0.10	0.017	3	0.092		1
Pb	4.0	3.1	18	0.33	0.19	6
Ni	2.1	-	1	-	-	0

\* Hg not tested

M.D.L. = method detection limit

## DATA ANALYSIS

For graphical representations, SigmaPlot 2003 for Windows, Version 8.0 (SPSS Inc., Chicago IL, USA) was used. Several statistical analysis methods were applied to the data. Multiple comparisons analysis of variance (ANOVA) was used in treatment analysis by Sigma Stat for Windows, Version 3.1 (Systat Software, Inc., San Jose, CA, USA). Yearly effects and multivariate modeling were addressed using multiple linear regression (MLR) with Sigma Stat. For a simplistic modeling approach, correlations between metal/metalloid concentrations in surface soil, DGT, soil solution and plant were observed. The soil fertility parameters were also included in the correlation analysis. All

correlations were analyzed using a Pearson product moment correlation program by Sigma Stat. In order to take in to account the effect of multiple parameters on the metal/metalloid concentration response, a rich model was developed using multiple linear regression (MLR). Using MLR provides data that can help answer the question of whether continuous metal input from fertilizer increased, decreased or had no effect on the concentration of metal in the soil, soil solution or the labile fraction as measured by DGT over the three year study period. By using MLR, other variables that potentially may alter concentrations of metal, particularly the bioavailable fraction, could be accounted for in the model. These variables included P, K, NO<sub>3</sub>-N, NH<sub>4</sub>-N, pH, % O.M., CEC, irrigation practices, and the fertilizer loads to the soil each year. Fertilizer loads were calculated using the fertilizer application rate, the volume of the plot using a 12" till depth, which accounted for the dilution of the fertilizer. The fertilizer application rates were derived from Oregon State University's "Fertilizer Guide" and are specific for individual crops, soils, and irrigation practices. From the dilution, a total metal load was calculated using the measured metal concentrations in the fertilizers for each year of the study. The load (g/ha/y) is used as the treatment value and is always included in the MLR model (**Figure 5-6**). With this information about the loads, we can determine if a change in metal concentration over time is a result of the input of fertilizer or is a product of another soil chemistry interaction. If yearly effects were present, slope factors from the MLR model were investigated to determine the rates of change of metal concentrations in soils over time. Significance levels for all statistical analyses were set at  $P < 0.05$ .

Distribution coefficients were also determined for metals in Oregon agricultural soils. Traditional K<sub>d</sub> values were calculated using the total recoverable metal concentration in surface soil divided by the concentration measured in soil solution from rhizosphere soil sample (**equation 3**).

$$\text{Total recoverable [Me]} / \text{soil solution [Me]} \quad (3)$$

Bio-distribution coefficients (K<sub>d</sub>-dgt) were calculated as detailed in **equation 4**.

$$\text{Total recoverable [Me]} / \text{DGT measured [Me]} \quad (4)$$

The bio-distribution coefficients are another method to evaluate the potential for metal uptake into crops, or offsite movement of metal. One of the many benefits of utilizing bio-distribution coefficients is that only the fraction that is truly in solution, or that which is reported to be more representative of crop uptake, is measured. The K<sub>d</sub>-dgt values reported in this study also provide real system data, sampled at circumneutral pH levels, at active agricultural sites. Traditional K<sub>d</sub> values range orders of magnitude, are often determined in laboratory settings, and later extrapolated to real systems. With this data we offer not only a point of comparison to a massive body of traditional K<sub>d</sub> literature, but also a much sought after bioavailable fraction represented as a distribution coefficient. A comparison of both K<sub>d</sub> and K<sub>d</sub>-dgt values for this study are listed in **Table 6** along with those measured by Bates and Sharp (34), and Sauve *et al.* (35).

**TABLE 6. Distribution coefficients (log, 10) for metals in agricultural soils.**

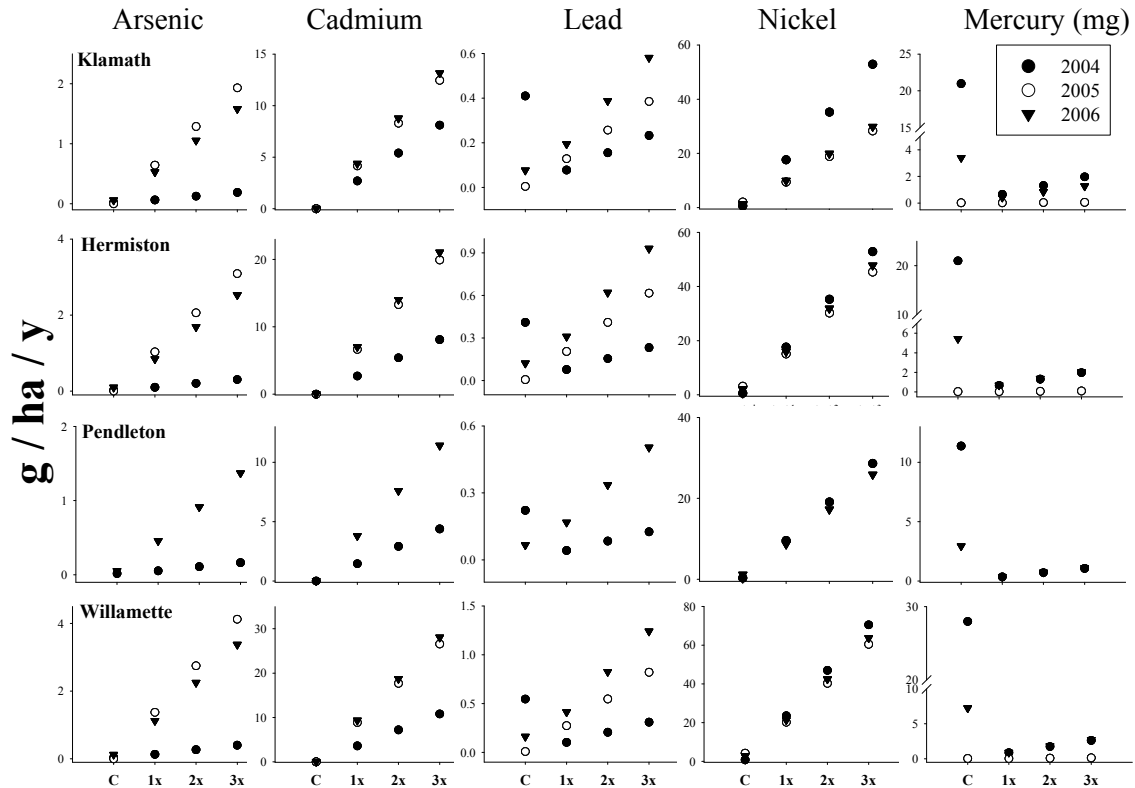
		Arsenic	Cadmium	Lead	Nickel	Mercury
Perez and Anderson <sup>1</sup>						
Klamath	K <sub>d-dgt</sub>	N/A	2.3-3.4	3.4-4.5	2.9-3.8	N/A
	K <sub>d</sub>	2.4-3.3	2.0-3.8	3.8-4.5	2.7-3.5	
Hermiston	K <sub>d-dgt</sub>	2.6-3.1	2.6-3.6	3.8-4.8	3.6-4.2	N/A
	K <sub>d</sub>	2.9-3.3	2.5-3.9	3.5-4.7	3.1-3.6	
Pendleton	K <sub>d-dgt</sub>	3.5-3.8	2.4-3.7	3.7-4.8	3.6-3.9	N/A
	K <sub>d</sub>	3.5-3.8	2.8-4.0	3.7-5.0	3.0-3.4	
Willamette	K <sub>d-dgt</sub>	3.5-4.4	2.8-3.9	3.7-4.6	4.0-4.8	N/A
	K <sub>d</sub>	3.5-4.3	2.8-4.0	3.9-5.2	3.7-4.7	
Bates and Sharp <sup>2</sup>						
	K <sub>d</sub>	0-1.3	0.1-1.4	0.7-3.9	N/A	N/A
Sauve <i>et al.</i> <sup>3</sup>						
	K <sub>d</sub>	4.1	3.5	5.2	4.0	4.2

N/A = not available

1. Ranges for Perez and Anderson (2007), *in preparation* are for a range of pH (4.3 to 7. and include a control, treatment level 1x, 2x, and 3x measured at four agricultural sites in Oregon 2003-2006. Classical K<sub>d</sub> values are calculated using a total recoverable surface soil [Me]/soil solution [Me]. K<sub>d-dgt</sub> values for Cd, Pb, and Ni are calculated using total recoverable surface soil [Me]/Diffusive Gradient in Thin-Film [Me].

2. Ranges for Bates and Sharp (1983) are for a range of pH 4.5 to 9.0

3. Sauve (*et al.* 2000) specify their K<sub>d</sub> values do not consider desorption potential or bioavailability of different metal species



**FIGURE 5. Fertilizer loads (g/ha/y) for arsenic, cadmium, lead, nickel and mercury (mg) at four field sites in Oregon.**

E03-02 Bioavailable Metals Project-Oregon State University  
**Klamath Fertilizer Application Rates-Potatoes- Metal loading calculations**

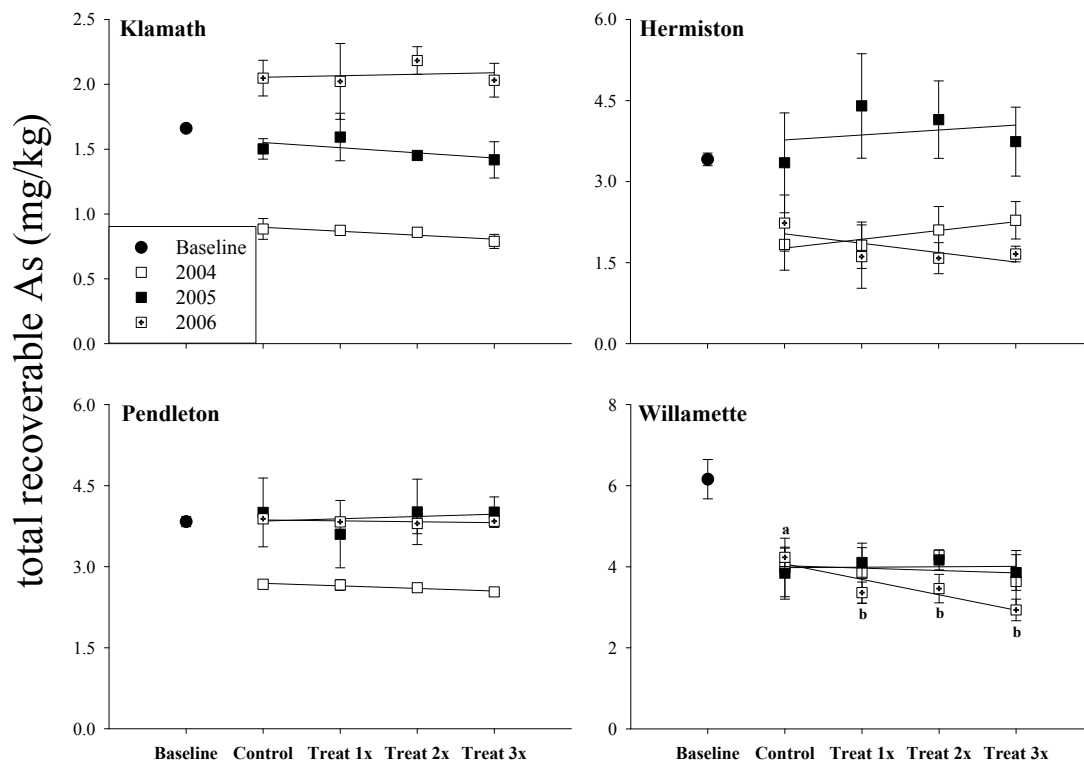
Klamath / Irrigated Spring Potato	Plot Width	Plot Length	Total Plot Square Feet - 4 Reps	Pounds of N needed per acre	Pounds of fertilizer applied per plot (lbs N/43560ft <sup>2</sup> *1000/1 plot ft <sup>2</sup> )	Pounds of N applied per plot (lbs N app./0.21; 0.16)	Pounds of P applied per plot (lbs P applied per plot (lbs P app./0; 0.21)	plot volume (till depth 1ft) (ft <sup>3</sup> )	Dilution to fertilizer (lbs/ft <sup>3</sup> )	Metal per application (mg)	Metal loads (mg/ft <sup>3</sup> )	Metal loads (mg/m <sup>3</sup> )	Metal loads (g/ha)	
Control - Rep 1	10.7	25	267.5	120	0.74	3.51	267.5	0.0131	0.1	0.00	0.02	0.01	Cd	
Treat 1X - Rep 1	10.7	25	267.5	120	0.74	4.61	3.51	267.5	0.0172	42.0	0.16	5.54		3
Treat 2X - Rep 1	10.7	25	267.5	240	1.47	9.21	7.02	267.5	0.0344	84.0	0.31	11.08		5
Treat 3X - Rep 1	10.7	25	267.5	360	2.21	13.82	10.53	267.5	0.0517	125.9	0.47	16.63		8
<b>Fertilizer Concentrations</b>														
n=5	2003/2004		2004/2005		2005/2006									
NPK(S)	21-0-0-24	16-21-0	21-0-0-24	16-20-0	21-0-0-24	16-20-0								
mg/kg	Control	Treat	Control	Treat	Control	Treat								
As	0.2	0.8	<0.014	7.7	0.7	6.3								
Cd	0.1	20	<0.00012	49	0.3	52								
Pb	3.0	0.6	0.1	1.5	0.9	2.3								
Ni	4.5	131	23	112	16	118								
Hg (ug/kg)	110	3.9	1.4	2.5	40.4	5.1								
<b>Key:</b> 1 lb= 453.59237 g      1 acre = 43560 ft <sup>2</sup> 1 acre= 4046.8564 m <sup>2</sup> 1 ft <sup>2</sup> = 0.02831685 m <sup>2</sup> 1 plot = 0.006140955 ft <sup>2</sup> 1 lb= 453.59237 g 1 hectare = 2.471054 acres      1 m <sup>2</sup> = 10.7639104 ft <sup>2</sup> 1 ft <sup>3</sup> = 0.0283168 m <sup>3</sup>														
Hg results are 1000x lower										7.2	0.03	0.95	0.61	Ni
										273.8	1.02	36.15	18	
										547.6	2.05	72.29	35	
										821.4	3.07	108.44	53	
										4.9	0.02	0.64	0.41	Pb
										1.2	0.00	0.16	0.08	
										2.4	0.01	0.32	0.16	
										3.6	0.01	0.48	0.23	
										0.4	0.00	0.05	0.03	As
										1.6	0.01	0.21	0.10	
										3.1	0.01	0.41	0.20	
										4.7	0.02	0.62	0.30	
										175.1	0.65	23.11	14.80	Hg
										8.1	0.03	1.08	0.5	
										16.3	0.06	2.15	1.0	
										24.4	0.09	3.23	1.6	

**FIGURE 6. Dilution to fertilizer in agricultural soil example calculations spreadsheet for Klamath Falls experiment station based on soil type and crop grown.**

## RESULTS and DISCUSSION

### Arsenic

*Arsenic in surface soil.* The mean baseline As concentration in surface soil at all four sites was 3.77 mg/kg (Klamath  $1.66 \pm 0.02$ , Hermiston  $3.41 \pm 0.12$ , Pendleton  $3.83 \pm 0.10$ , Willamette  $6.16 \pm 0.49$ ). The average method detection limit for As in surface soil was 0.37 mg/kg (average of 5 sample runs). Arsenic is largely immobile in agricultural soils and tends to remain in the upper O and A soil horizons (31). In general, no treatment effects were observed at all four sites during the study. At the Klamath, Hermiston, and Pendleton experimental plots, no significant treatment effect was observed for surface soil during the harvest field sampling events in 2004, 2005, and 2006 based on a one way analysis of variance ( $P > 0.05$ , 11 d.f.) (Figure 7). At Willamette, arsenic concentrations for the 2004 and 2005 events were not significantly different between treatments. A significant treatment effect was observed for the 2006 harvest sampling event at Willamette where treatments 1x, 2x, and 3x were significantly lower than the control samples by 0.87, 0.77, 1.3 mg/kg less respectively (All pairwise multiple comparison procedures (Holm-Sidak method;  $P < 0.001$ ). On average, the treatment samples at Willamette in 2006 contained 0.98 mg/kg less As than the control samples. One factor to consider is that the pH at Willamette in 2005 fell to less than 5 (4.7-5) and in response, as per typical agronomy practice, the field was limed prior to the 2006 growing season. The lime samples were below detection limits for all metals except Pb, which had an average of  $1.6 \pm 0.07$  mg/kg.

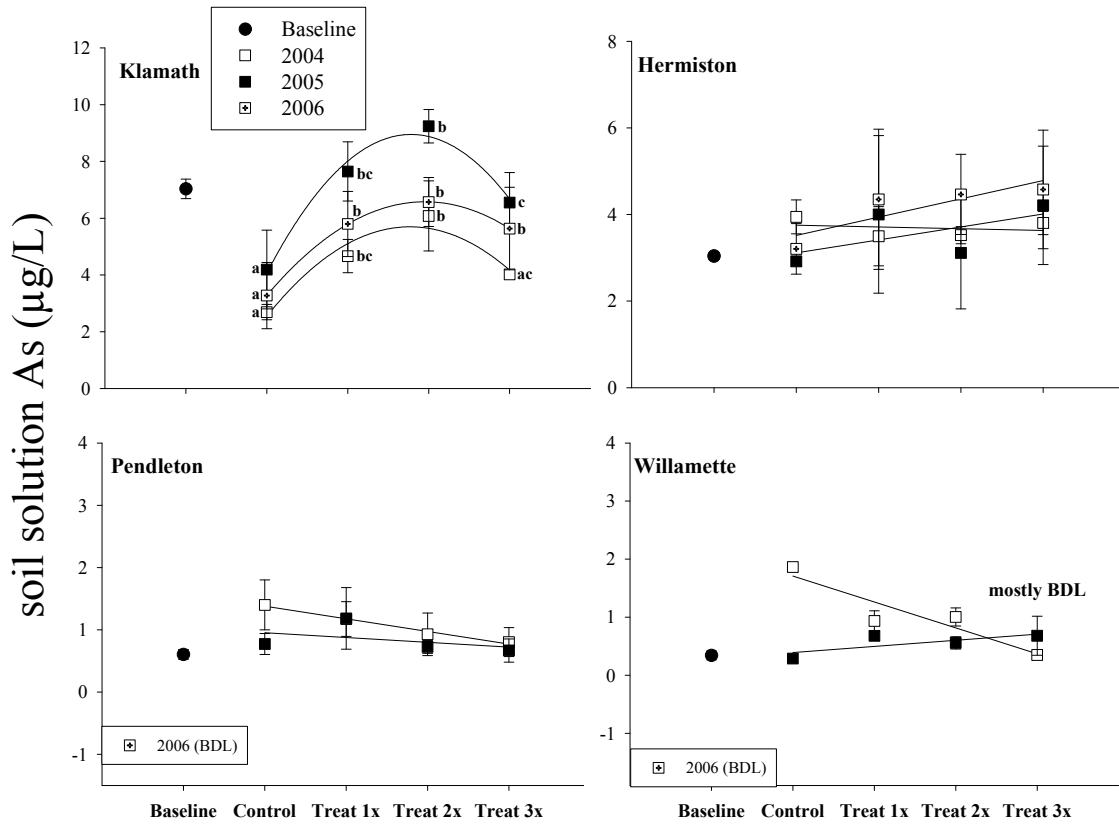


**FIGURE 7. Arsenic concentrations (mg/kg) in surface soil sampled at harvest from four field sites in Oregon (n=4).**

Arsenic concentrations in surface soil at Klamath, Hermiston, and Willamette, did not correlate significantly with As concentrations in soil solution or plant. The only exception was at Pendleton in 2005, where surface soil As did show a negative correlation with soil solution As (Pearson Product moment test,  $r^2 = -0.573$ ,  $P = 0.02$ ). Using backward stepwise regression, the following variables were determined to be the most predictive of the surface soil As concentration: pH,  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$ , K, irrigation practice, and year ( $P < 0.001$  all factors). To determine whether As concentration increased in surface soil each year, all sites and treatments were held constant in the MLR model. The adjusted  $r^2$  for the model was 0.71 with a standard error of estimate 0.12. A yearly increase of surface soil As was seen at Klamath, but no other site. In 2004 and 2006, surface soil As was not significantly different from the baseline As concentration ( $P = 0.68, 0.07$  respectively,  $n=200$ ). In 2005, surface soil As concentrations were significantly greater than those of baseline ( $P = 0.01$ ,  $n=200$ ). In 2004, As was significantly lower than 2005 and 2006 ( $P = 0.002, 0.004$  respectively,  $n=200$ ). Surface soil As in 2005 was not significantly different from 2006 ( $P = 0.65$ ). The As concentrations in the fertilizer for 2005 were also the highest of the study. Using MLR, it was determined that after taking into account multiple other field variables, the increase in As surface soil concentrations both at Klamath all years, and in 2005 at all other sites, could be attributed to the addition of fertilizer. These results were anticipated as the As loads from the treatment fertilizer in 2005 were a factor of 10 greater than those in 2004. The 2005 As loads from the treatment fertilizer were 120% those from 2006.

*Arsenic in soil solution.* The mean baseline As concentration in soil solution at all four sites was  $2.76 \mu\text{g/L}$  (Klamath  $7.03 \pm 0.34$ , Hermiston  $3.04 \pm 0.08$ , Pendleton  $0.61 \pm 0.08$ ,

Willamette BDL). The average method detection limit for As in soil solution was 0.80 µg/L soil solution (average of 8 sample runs). Soil solution As showed no significant treatment effect at all sites except Klamath. A significant treatment effect was observed in 2004, 2005, and 2006 at the Klamath experimental plots. Three years data resulted in quadratic curves each year, which cannot be dismissed as chance (**Figure 8**). By fitting a quadratic equation,  $r^2$  values of 0.93, 0.98, 0.99 were achieved for 2004-2006 respectively. One explanation is that phosphate effectively competes with As for adsorption sites in soil (32,33). Excess P may have resulted in the release of soluble As species and subsequent off site movement at the highest treatment level. No significant treatment effect was observed at the Hermiston, Pendleton, nor Willamette field sites 2004-2006. Willamette soil solution samples from 2004 and 2005 were below the method detection limit (BDL), while all soil solution samples from Pendleton and Willamette 2006 were BDL. The best predictor of As in soil solution was a linear combination of the variables CEC,  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$ , K, and irrigation practice ( $r^2 = 0.85 \pm 0.17$ ; N=150). No significant yearly increases were seen in soil solution As. Soil solution measurements of As in 2004 and 2006 were not significantly different from baseline. In 2005, As soil solution concentrations were marginally less than the baseline concentration by  $1.5 \pm 1.1$  µg/L ( $P = 0.05$ ). In 2004-2006, no significant differences of soil solution As were seen between years.

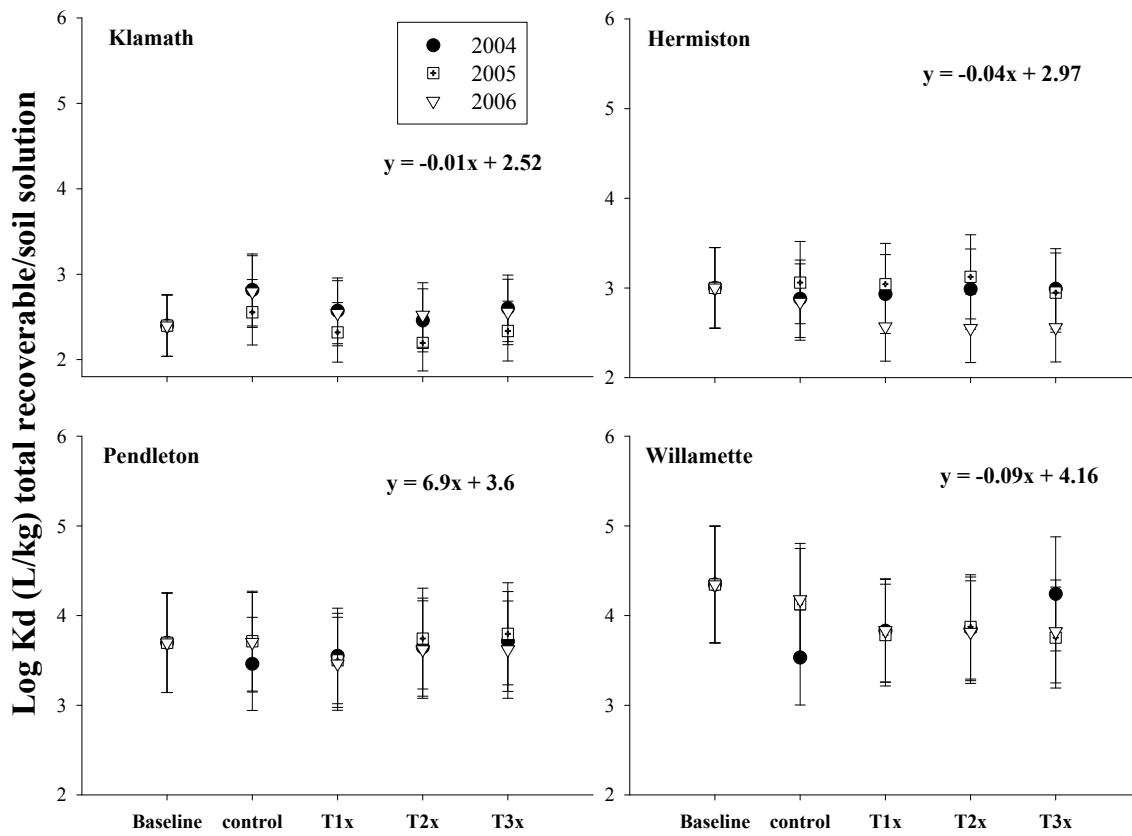


**FIGURE 8. Arsenic concentrations ( $\mu\text{g/L}$ ) in soil solution sampled at harvest from four Oregon field sites ( $n=4$ ).**

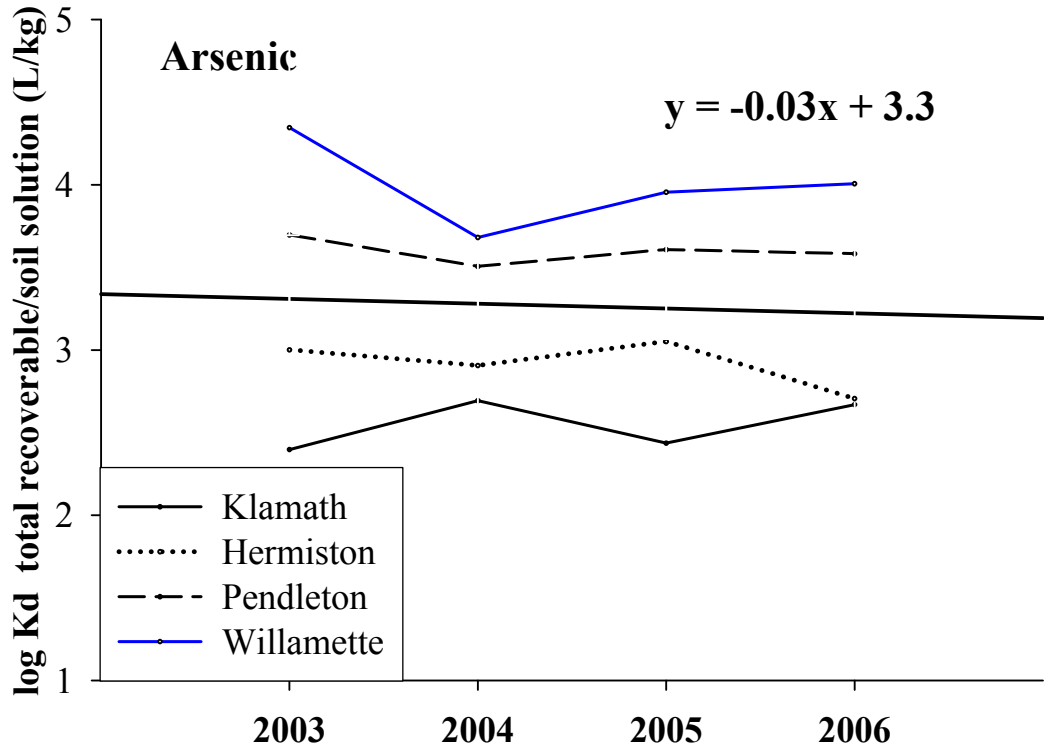
*Arsenic in plant.* The average method detection limit for As in plant was 0.48 mg/kg (average of 3 sample runs). The edible portion of all crops at all sites in 2004, 2005, and 2006 were below detection limits for As. The Pendleton site was fallow in 2005. Arsenic could not be measured using DGT. In general, As in phosphatic fertilizers applied at relevant application levels was largely unavailable in agricultural field trials for uptake into wheat and potato crop.

To define the bioaccumulation potential of As in agricultural soils in Oregon, Kd values were assessed. The Kd that is defined for As is the ratio between total recoverable As in surface soil and As in soil solution. Kd-dgt was not determined for As. First, Kd values were plotted by treatment levels (**Figure 9**). The log Kd values for As at all sites ranged from 2.2-4.4 L/kg. Trends showed negative slopes at Hermiston and Willamette, where Kd decreased with increasing treatment level, however no significant differences were observed between treatment levels or between years. To determine an overall Kd trend for Oregon agricultural soils, only the control and treatment level 1x were composited (**Figure 10**). This was done to capture the most realistic value for the distribution coefficient for As in Oregon soils, as 2x and 3x applications of fertilizer are rarely reported. The slope factor, or rate of change for As between surface soil and soil solution over time is -0.03 L/kg. A negative slope indicates that the ratio between the total recoverable [Me] and the soil solution [Me] is becoming smaller over time. In other words, the fraction of As in solution is increasing over time, barring no significant changes in surface soil As concentrations. This result suggests that under the current field management practices and based on the current model, a Kd projected out 50 years

would be considerably smaller than the Kds observed 2003-2006 and may result in more  
As in solution, available for uptake into crops and/or available for offsite movement.



**FIGURE 9. Log Kd values for As at four Oregon agricultural field sites based on ratios between total recoverable As in surface soil and As in soil solution (n=4).**



**FIGURE 10. Log Kd measured at four Oregon field sites. Each year represents a composite of control and treatment 1x samples only. Treatment 2x, and 3x were omitted.**

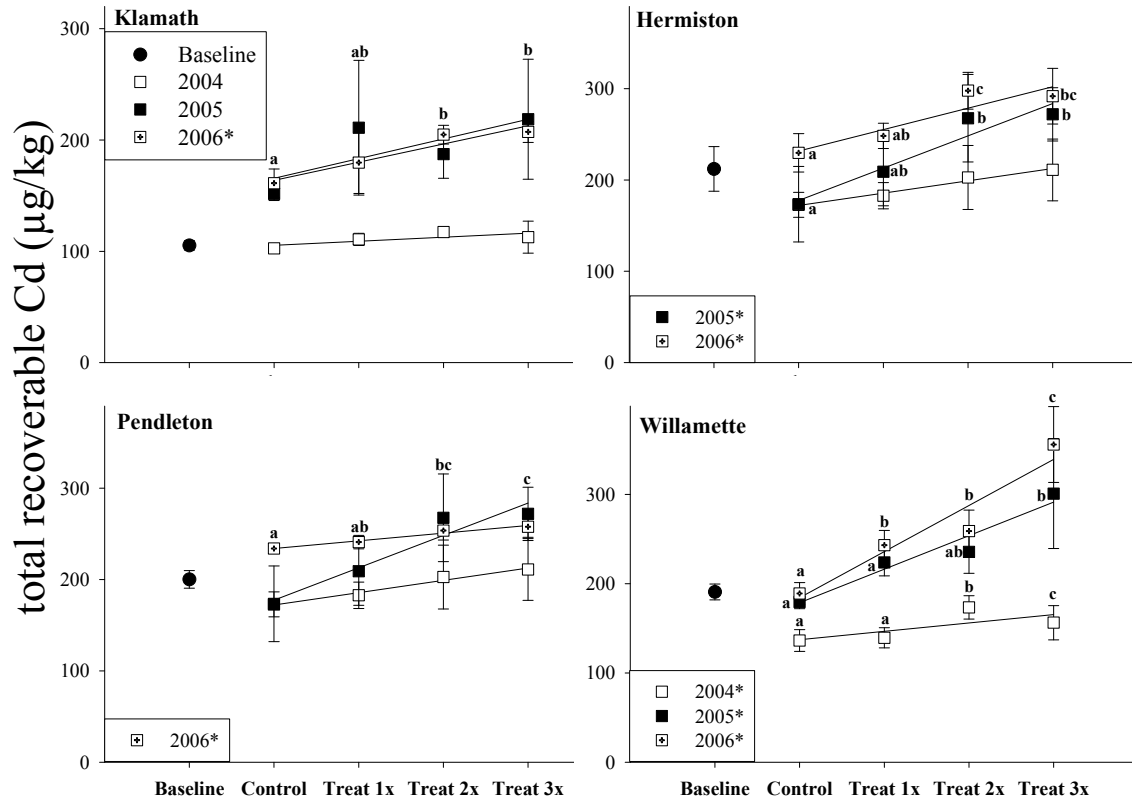
## Cadmium

*Cadmium in surface soil.* The mean baseline Cd concentration in surface soil at all four sites was 0.177 mg/kg (Klamath  $0.11 \pm 0.004$ , Hermiston  $0.21 \pm 0.02$ , Pendleton  $0.20 \pm 0.009$ , Willamette  $0.19 \pm 0.008$  mg/kg). The average method detection limit for Cd in surface soil was 0.06 mg/kg. Surface soil Cd showed significant treatment effect at all sites, in particular, at two sites in 2005, and at all sites in 2006. At Klamath field site there was a significant treatment effect for 2006, but no effect was observed in 2004 or 2005 (**Figure 11**). Treatment levels 3x and 2x had 0.046 and 0.044 mg/kg more Cd than the control respectively ( $P = 0.002, 0.003$  respectively). There was no significant treatment effect at Hermiston in 2004, but 2005-06 showed that treats 3x and 2x were significantly greater than the control. Hermiston 2005 treat 2x and 3x were 0.094 and 0.098 mg/kg greater than the control ( $P = 0.004, 0.006$  respectively). In 2006, treat 3x and 2x were 0.062 and 0.068 mg/kg greater than the control ( $P = 0.002, 0.001$ ), while treat 2x was also significantly larger than treat 1x by 0.049 mg/kg ( $P = 0.008$ ). Pendleton surface soil Cd showed no significant increases in 2004 and 2005. In 2006, treat 3x and 2x were significantly greater than the control by 0.024, and 0.020 mg/kg ( $P = 0.002, 0.008$ ). Surface soil samples from Willamette 2004-06 showed a significant Cd treatment effect. In 2004, treat 2x had an average of 0.041 mg/kg more Cd than the control ( $P = 0.02$ ). In 2005, treat 3x was significantly greater than treat 1x and the control by 0.12 and 0.077 mg/kg ( $P < 0.008$ ). In 2006, treats 3x, 2x, and 1x were all significantly greater than the control by 0.167, 0.70, and 0.064 mg/kg respectively ( $P < 0.005$ ). Treat 3x was also significantly larger than treats 2x and 1x by 0.097, 0.103 mg/kg ( $P < 0.0002$ ).

These results suggest that Cd is being retained in the soils, rather than moving off site. The largest rates of increase with treatment were seen at Willamette, a site with one of the highest % O.M., but with the lowest pH. Willamette soils also received the highest fertilizer application rates of all sites. However, this does not necessarily correspond to the increased Cd concentrations found in surface soils. Pendleton soils received the lowest fertilizer application rates, yet had comparable surface soil Cd concentrations to Willamette. Accumulation of Cd in Oregon agricultural soils was further evidenced by significant yearly increases of Cd at all sites. No differences in surface soil Cd concentration were seen between irrigated and dry land sites.

Surface soil Cd from Klamath did not correlate significantly with DGT, soil solution, or plant measured Cd in 2004, nor in 2005. Significant positive correlation was seen with surface soil Cd in 2006 with DGT and soil solution Cd ( $r^2 = 0.59, 0.62$ ;  $P = 0.01, 0.01$  respectively). Surface soil Cd at Hermiston correlated well with Cd measured in wheat berries in 2004 ( $r^2 = 0.64, 0.63$ ;  $P = 0.007, 0.009$  respectively), and with DGT measured Cd at Hermiston in 2005 ( $r^2 = 0.56$ ;  $P = 0.02$ ). At Willamette, surface soil Cd correlated significantly with plant in 2004 and 2005 ( $r^2 = 0.63, 0.60$ ;  $P = 0.009, 0.02$ ), with soil solution in 2004 ( $r^2 = 0.61$ ;  $P = 0.01$ ), and strongly with DGT in 2006 ( $r^2 = 0.83$ ;  $P = 0.001$ ). Surface soil Cd could best be predicted using a linear combination of the variables CEC, % O.M.,  $\text{NO}_3\text{-N}$ , and K ( $r^2 = 0.77 \pm 0.07$ ;  $N=200$ ). After taking into account multiple field variables using MLR, yearly increases in surface soil Cd were seen at all sites and indicate potential accumulation in agricultural soils using Cd rich phosphatic fertilizers. Surface soil Cd was significantly greater in concentration in 2005-06 compared to the baseline Cd

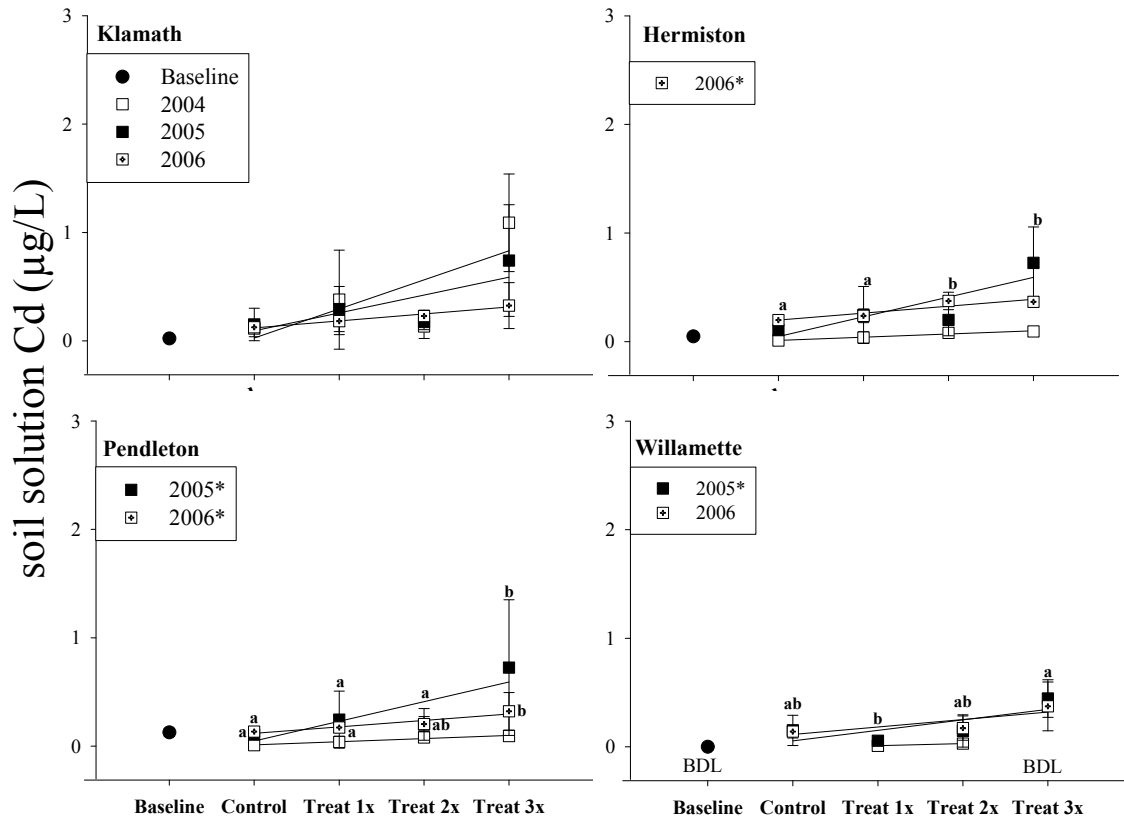
concentration by an average of  $1.25 \pm 1.0 \mu\text{g Cd/kg soil}$  ( $P < 0.001$ ). In 2005 and 06, surface soil Cd was also significantly greater in concentration than in 2004 by  $1.3 \pm 1.0 \mu\text{g/kg}$  ( $P < 0.001$ ). Although the average surface soil Cd in 2006 is larger than in 2005, the results are not statistically significant. In general, there were positive slopes for the study duration of increasing Cd concentrations in surface soil over time.



**FIGURE 11. Cadmium concentrations (µg/kg) in surface soil sampled at harvest from four field sites in Oregon (n=4).**

*Cadmium in soil solution.* The mean baseline Cd concentration in soil solution at all four sites was 0.07 µg/L (Klamath 0.02 ± 0.0008, Hermiston 0.05 ± 0.003, Pendleton 0.13 ± 0.04 µg/L, Willamette BDL). The average method detection limit for Cd in soil solution was 0.04 µg/L soil solution. No significant effect was observed at Klamath in 2004 and 2005, although the significance level was marginal (P = 0.054, 0.053) and trends suggest that treat 3x is greater than treat 2x, 1x and the control (**Figure 12**). No significant cadmium treatment effect was observed in Klamath soil solution 2006. No significant cadmium treatment effects were seen at Hermiston 2004-05, but in 2006 treat 3x and 2x were significantly greater than treat 1x (0.18, 0.17 µg/L, P < 0.001) and the control (0.14, 0.13 µg/L, P < 0.01). Cadmium concentrations at Pendleton in 2004 showed no significant increases with treatment. In 2005 soil solution samples showed that treat 3x had 0.24, 0.36, 0.40 µg/L more Cd than treat 2x, 1x, and the control respectively (P < 0.01), while 2006 treatment 3x soil solution samples had 0.35 µg/L more than the control samples (P = 0.003). Willamette soil solution samples were near detection limits. 2004 samples were BDL, while in 2005 treat 3x was significantly larger than treat 1x by 0.0073 µg/L (P = 0.002). No treatment effect was observed for Cd concentrations in 2006 samples. Soil solution was strong correlated with DGT measured Cd at all sites. Positive, significant correlations were seen at Klamath 2004-2006 ( $r^2 = 0.89, 0.91, 0.86$ ; P = 0.001, 0.0001, 0.0001 respectively). At Hermiston in 2005 and 2006, positive correlations were also observed ( $r^2 = 0.59, 0.95$ ; P = 0.01, 0.0001). At Pendleton, soil solution correlated well with DGT in 2004 and 2006 ( $r^2 = 0.84, 0.95$ ; P = 0.004, 0.0001), and at Willamette 2004-2006

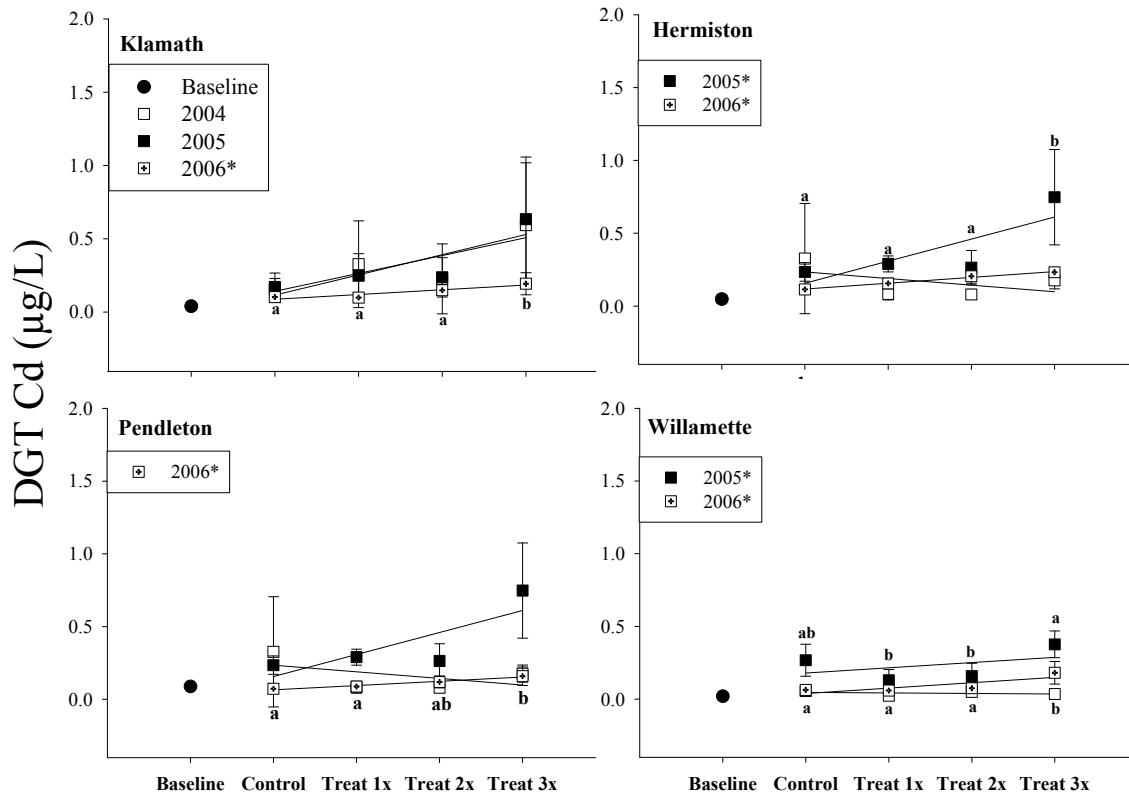
( $r^2 = 0.97, 0.70, 0.65$ ;  $P = 0.05, 0.002, 0.03$  respectively). Soil solution also correlated with plant tissue from Klamath, Hermiston and Pendleton. At Klamath in 2004 and 2005, soil solution correlated marginally well with Cd found in the potatoes and wheat berries ( $r^2 = 0.55, 0.57$ ;  $P = 0.05, 0.02$ ). In 2004, and 2006 Cd concentrations in Hermiston and Pendleton wheat also correlated with soil solution ( $r^2 = 0.65, 0.65$ ;  $P = 0.04, 0.006$  Hermiston) ( $r^2 = 0.67, 0.52$ ;  $P = 0.04, 0.04$  Pendleton). The best predictors of Cd concentrations in soil solution utilized a linear combination of the variables CEC, % O.M., pH, P, and irrigation practice ( $r^2 = 0.62 \pm 0.3$ ;  $N=167$ ). The soil solution concentrations of Cd in 2004-2006 were significantly less than those of the baseline by an average of  $0.07 \mu\text{g/L}$  ( $P < 0.001$ ), although in practical application, the total change in soil solution Cd concentration over the duration of the study is just over 1 part per billion.



**FIGURE 12. Cadmium concentrations ( $\mu\text{g/L}$ ) in soil solution sampled at harvest from four field sites in Oregon (n=4).**

*Cadmium in DGT.* The time integrated Cd concentrations as measured by DGT ranged from 0.01 – 1.05 µg/L Cd from the soil slurries. The mean baseline cadmium concentration in DGT at all four sites was 0.05 µg/L (Klamath 0.04 ± 0.02, Hermiston 0.05 ± 0.03, Pendleton 0.09 ± 0.01, Willamette 0.02 ± 0.02 µg/L). The average method detection limit for cadmium in DGT was 0.04 µg/L soil solution. No significant treatment effect was seen at DGT measurements of cadmium at Klamath 2004-05 ( $P > 0.07$ ) though trends show increasing DGT measured cadmium with increasing treatment level (**Figure 13**). In 2006, treat 3x was marginally greater than treat 1x and the control ( $P = 0.05$ ). No significant treatment effect was observed at Hermiston for 2004. In 2005, treat 3x was 0.46, 0.39, 0.49 µg/L greater than treat 2x, 1x and the control ( $P < 0.004$ ). In 2006, treat 3x was 0.07 and 0.12 µg/L greater than treat 1x and the control, while treat 2x was also 0.09 µg/L greater than the control ( $P < 0.008$ ). Pendleton DGT samples showed no significant increases in cadmium concentration in 2004 and 2005. In 2006, treat 3x was significantly greater than treat 1x and the control by 0.071 and 0.087 µg/L. Cadmium concentrations in Willamette DGT samples showed no significant treatment effects in 2004, while significant effects were seen in 2005 and 2006. Treat 3x was significantly larger than treat 2x and 1x by 0.22 and 0.25 µg/L in 2005 DGT samples. In 2006, treat 3x was 0.38, 0.46, and 0.44 mg/kg larger than treats 2x, 1x and the control ( $P < 0.006$ ). At Klamath in 2004, DGT was a better predictor of Cd concentration found in potatoes than soil solution measurements of Cd ( $r^2 = 0.68$ ;  $P = 0.003$ ). DGT also significantly correlated with Cd concentration in wheat from Hermiston in 2006, and wheat from Pendleton in 2004 ( $r^2 = 0.71, 0.65$ ;  $P = 0.002$ ,

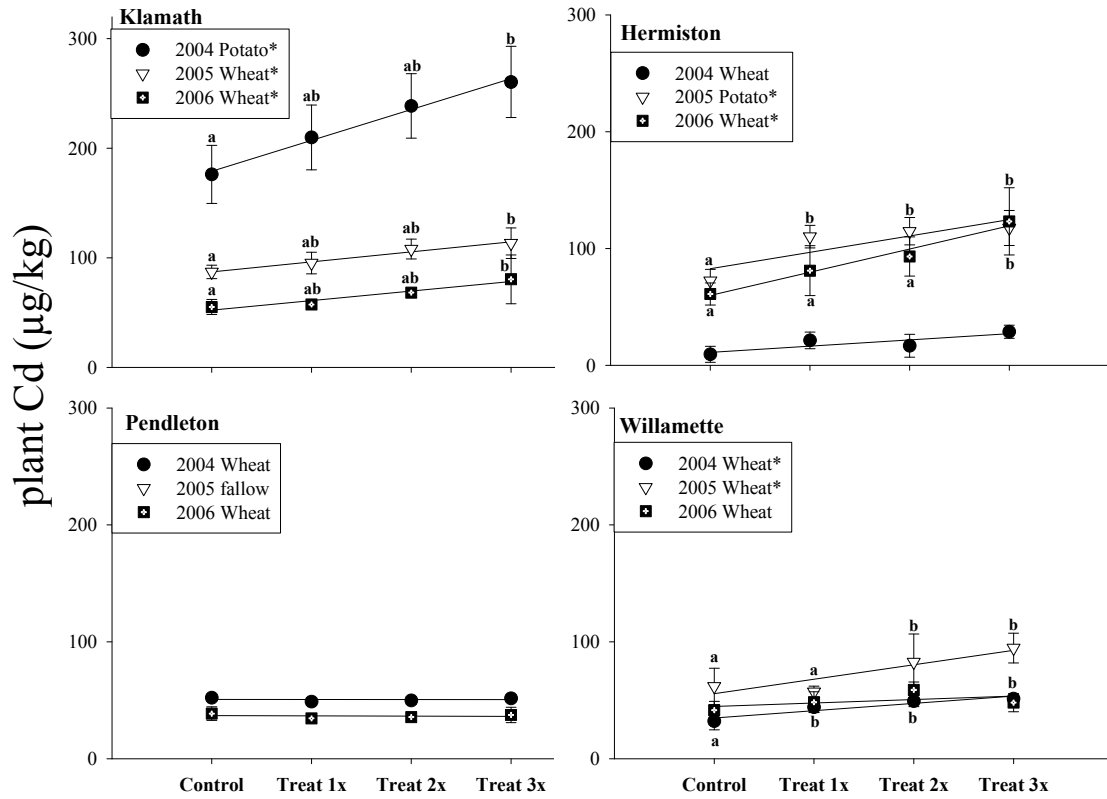
0.02). Using MLR to predict a DGT measured Cd, the following variables were significant: CEC, % O.M., pH, NH<sub>4</sub>-N, NO<sub>3</sub>-N, K, and irrigation practice ( $r^2 = 0.59 \pm 0.2$ ; N=185).



**FIGURE 13. Cadmium concentrations ( $\mu\text{g/L}$ ) measured by DGT soils sampled at harvest from four field sites in Oregon ( $n=4$ ).**

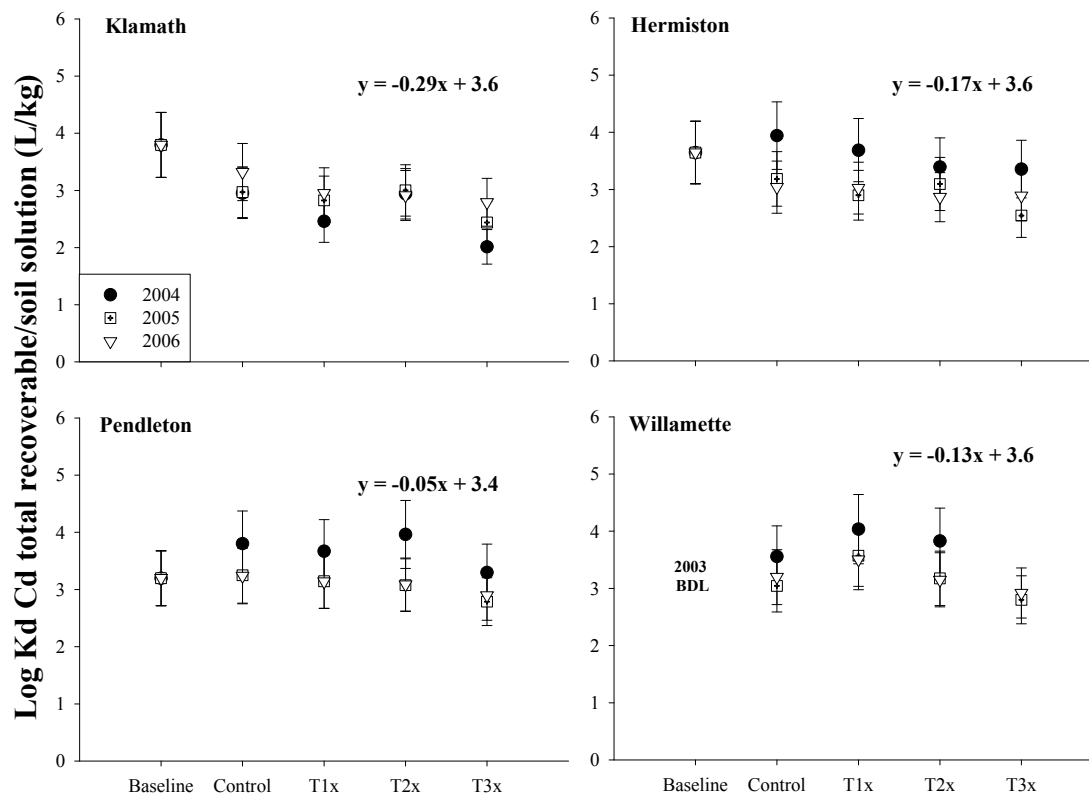
*Cadmium in plant.* Cd is bioavailable to wheat (*Tritium aestivum*) and potato (*Solanum tuberosum*) crops. Only the edible portion of each crop was analyzed (wheat berries, tubers). The total recoverable Cd concentration in wheat berries ranged from 0.022-0.161 mg/kg, and 0.063-0.283 mg/kg in potato. The average method detection limit for cadmium in plant tissue was 0.06 mg/kg. At Klamath, a significant cadmium treatment effect was observed 2004-06 in plant tissue (**Figure 14**). In 2004 (Russet Norkotah potato), 2005 (Hank hard red wheat), and 2006 (Hank hard red), treat 3x was significantly greater than the control by 0.084, 0.027, 0.0015 mg/kg ( $P = 0.002, 0.003, 0.005$ ). The Klamath Basin site, as per typical crop rotation should have followed a potato-wheat-potato rotation schedule. However, due to a nematode infestation at the site in 2006, the potato crop was abandoned and replaced with spring wheat. At the Hermiston sampling site, a wheat-potato-wheat rotation was followed. No significant treatment effect was seen in 2004 Stephens winter wheat berries at Hermiston. In 2005, Ranger Russet potato samples showed a significant treatment effect, where treat 3x was 0.038, 0.042, and 0.045 mg/kg greater than treat 2x, 1x, and the control ( $P < 0.0007$ ). In 2006, Hermiston Stephens winter wheat showed a significant difference between treat 3x and the control, where treat 3x had 0.062 mg/kg more cadmium than the control ( $P = 0.0001$ ). At the Pendleton site, a crop rotation schedule of wheat-fallow-wheat was followed. At Pendleton, there were no significant differences between treatment groups for cadmium in Stephens winter wheat. Willamette Basin followed a wheat-wheat-wheat cropping schedule. Cadmium in Willamette wheat showed significant treatment effect 2004-05. In 2004, Foote winter wheat treatments 3x, 2x, and 1x were significantly larger than the control samples by 0.011, 0.017, and 0.019 mg/kg ( $P < 0.007$ ). In 2005, Foote

wheat treatment 3x was significantly larger than treat 1x and the control by 0.036 and 0.037 mg/kg. A caveat of the 2005 Willamette sampling was the occurrence of a fungus, stripe rust, which affected wheat throughout the Willamette Valley in 2005. Wheat yields were particularly low, as wheat growth was significantly stunted. After consultation with station directors, the Foote wheat variety was exchanged for the Madsen winter wheat variety for the 2006 growing season. In 2006 Madsen wheat showed no treatment effect. In this study, increases in Cd concentration in wheat and potato crops were observed at all sites, except Pendleton. The largest rates of increase by treatment were seen at the irrigated sites. This along with MLR results from soil solution and DGT analysis suggests that the soluble Cd species are either directly or indirectly increased by the addition of phosphatic fertilizer. This was evidenced by increases in soil labile Cd by treatment, measured using DGT and in soil solution Cd at all sites for at least one or more years. Soil application of monoammonium phosphate, with no detectable Cd, resulted in increased Cd uptake into wheat grain suggesting that the fertilizer material had a greater effect on Cd accumulation in wheat, than Cd alone (33). In conclusion, there is sufficient risk for Cd uptake into the edible portion of crops with phosphatic fertilizer alone, a problem that may be exacerbated by repetitive application of Cd rich fertilizer.

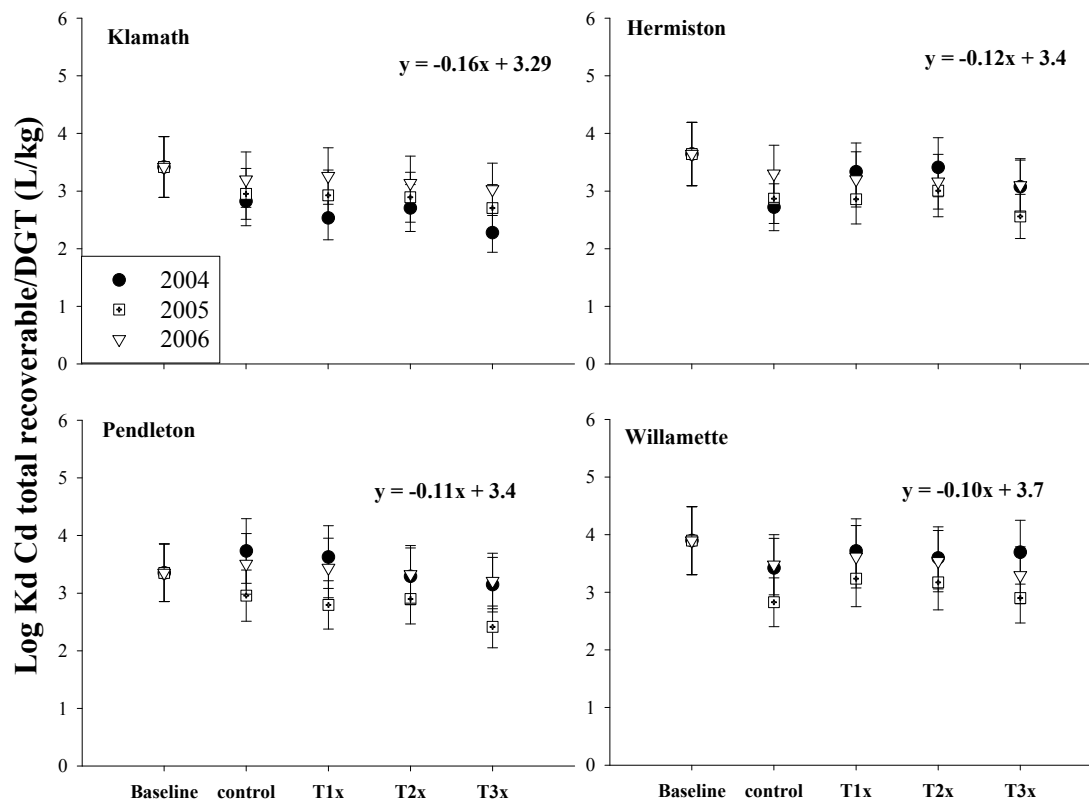


**FIGURE 14. Cadmium concentrations ( $\mu\text{g}/\text{kg}$ ) in plant tissue sampled from four field sites in Oregon ( $n=4$ ).**

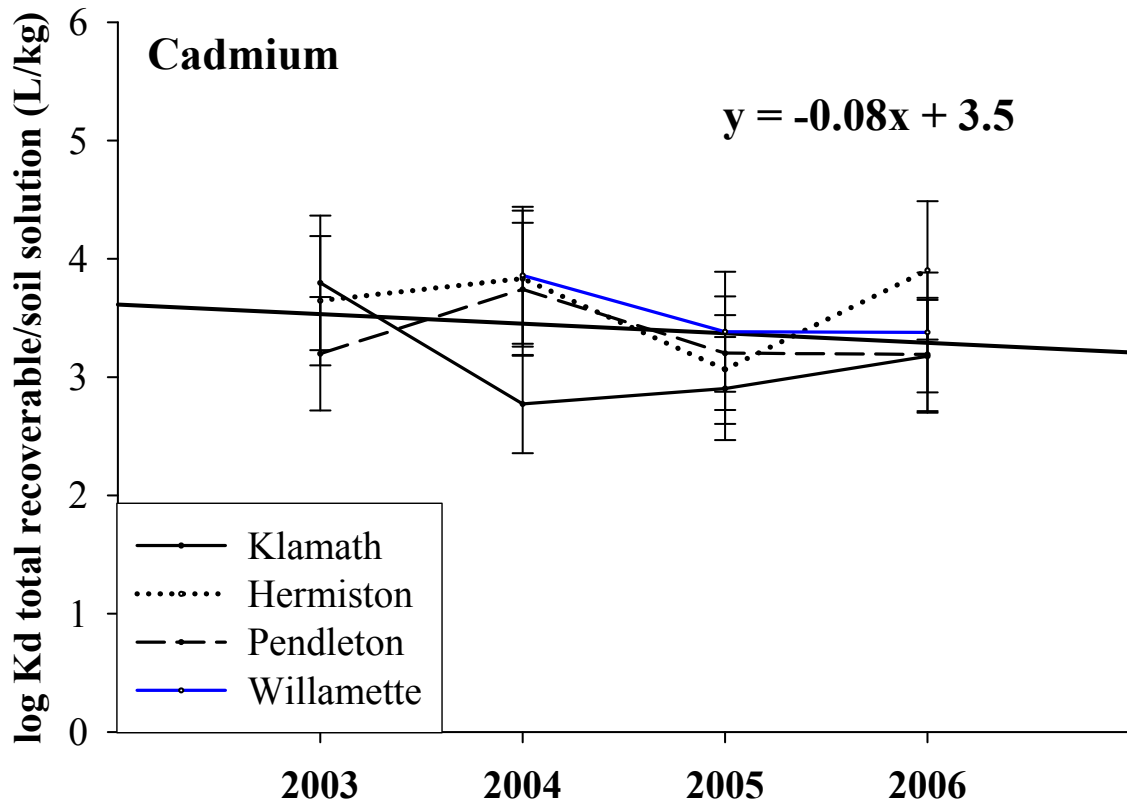
The log Kd values for Cd at all sites ranged from 2.3-3.9 L/kg. Negative trends are seen with increasing treatment level at all four sites. In general, Kd values for 2005-06 were less than those in 2004. The steepest decline in log Kd occurred at Klamath falls with a decrease of 0.29 L/kg per year (**Figure 15**). The bio-distribution coefficients (Kd-dgt) values showed similar decreases over time (**Figure 16**). The overall trends of Kd and Kd-dgt for Cd in Oregon agricultural soils for the control and treatment 1x only is shown in **Figures 17-18**. Both Kd and Kd-dgt show negative slopes, indicating an increase in the soluble and labile fractions of Cd in soil waters. These results suggest that over time Cd is becoming more available for crop uptake, and/or offsite movement at relevant application levels of a commercially available fertilizer.



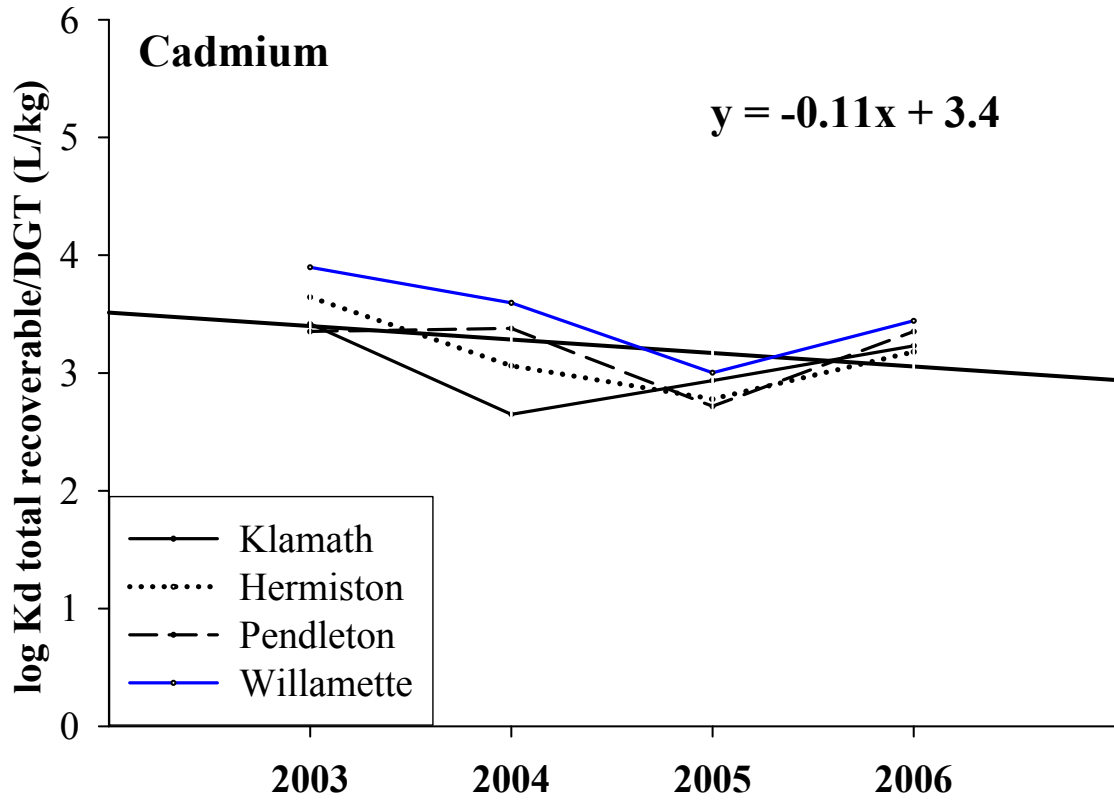
**FIGURE 15. Log Kd Cd (total recoverable/soil solution) (L/kg) grouped by treatment level, measured 2003 (Baseline)-2006, at four Oregon field sites. Regression equations represent a best fit line through all of the data points.**



**FIGURE 16. Log Kd-DGT (total recoverable Cd / DGT measured Cd) (L/kg) grouped by treatment level, measured 2003 (Baseline)-2006, at four Oregon field sites. Regression equations represent a best fit line through all of the data points.**



**FIGURE 17. Log Kd measured at four Oregon field sites. Each year represents a composite of control and treatment 1x samples only. Treatment 2x, and 3x were omitted.**



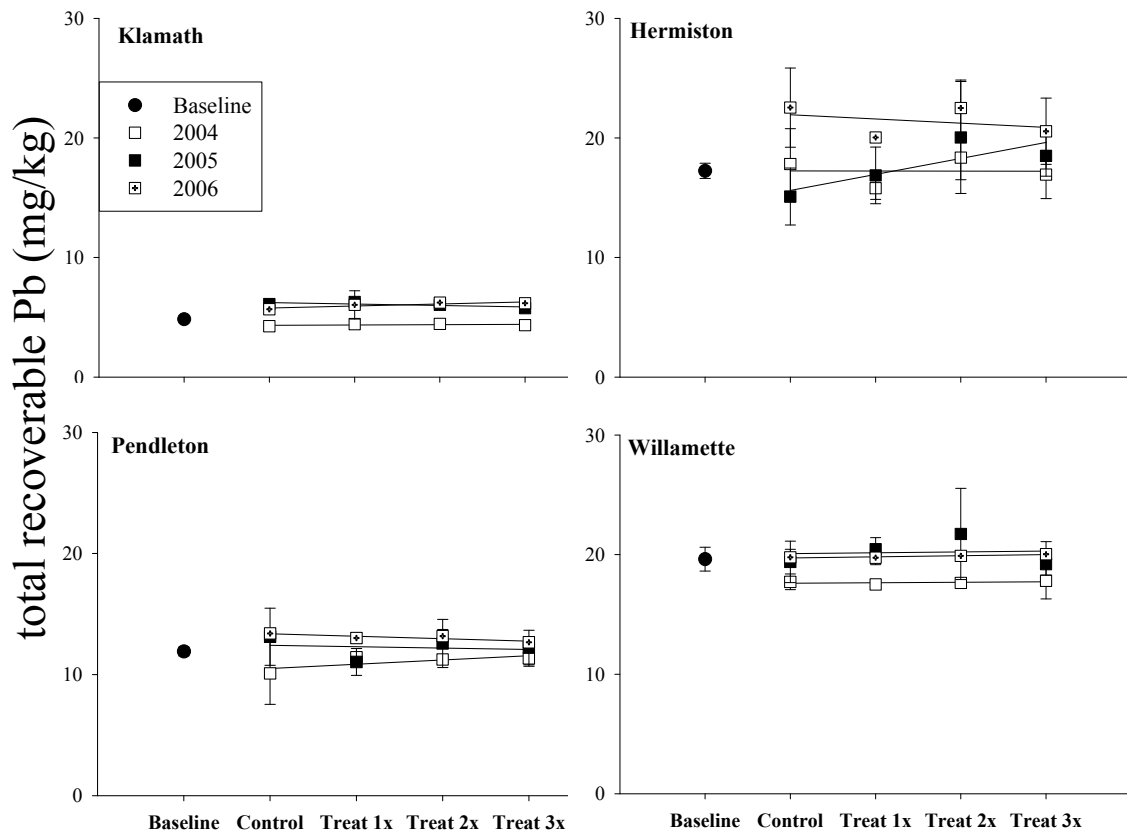
**FIGURE 18. Log Kd-DGT measured at four Oregon field sites. Each year represents a composite of control and treatment 1x samples only. Treatment 2x, and 3x were omitted.**

## **Lead**

*Lead in surface soil.* The mean baseline Pb concentration in surface soil at all four sites was 13.4 mg/kg (Klamath  $4.84 \pm 0.01$ , Hermiston  $17.24 \pm 0.64$ , Pendleton  $11.91 \pm 0.36$ , Willamette  $19.62 \pm 1.0$  mg/kg). The average method detection limit for Pb in surface soil was 1.3 mg/kg. Surface soil measurements of surface soils showed no significant Pb treatment effect 2004-06 at all sites ( $P > 0.05$ ) (**Figure 19**). The concentration of Pb in the control fertilizer in 2004 was 5 times greater than the Pb concentration in the treatment fertilizer. Furthermore, the background concentration of Pb in the soil is over 10 times greater than the highest concentration in the fertilizer per unit mass, without taking into account the dilution to the fertilizer in the soil. This makes creating a relevant, yet effective Pb treatment scheme very difficult. This may explain why lead in surface soil negatively correlated with Pb measured in soil solution at Pendleton in 2004 ( $r^2 = -0.92$ ;  $P < 0.0001$ ). The negative slope in the soil solution concentration of Pb could be an artifact of the higher Pb concentrations in the control fertilizer, rather than the treatment fertilizer. While there is no significant treatment effect in surface soil lead, the addition of Pb in surface soil may be masked by the original background Pb levels.

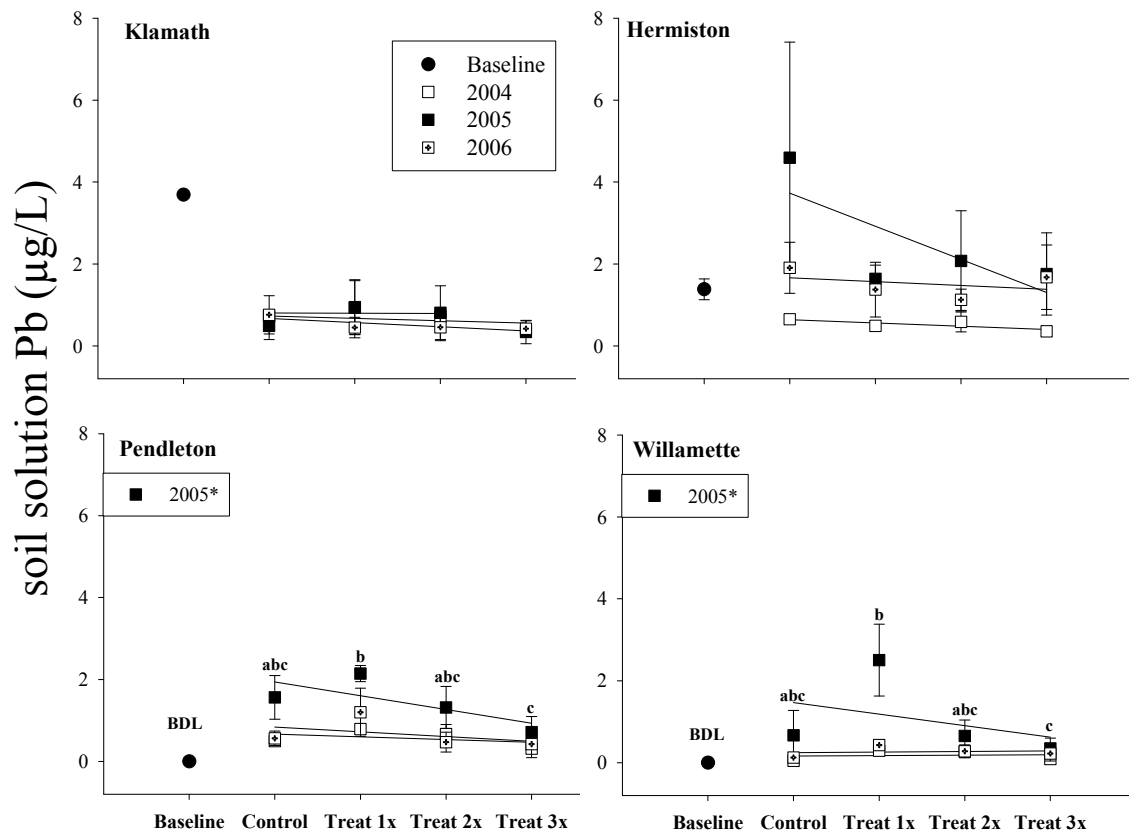
Using backward stepwise regression, the following variables were determined to be the most predictive of the surface soil Pb concentration: CEC, % O.M., pH,  $\text{NH}_4\text{-N}$ ,  $\text{NO}_3\text{-N}$ , P, and irrigation practice ( $P < 0.04$  all factors). To determine whether Pb concentration increased in surface soil each year, all sites and treatments were held constant in the MLR model. The adjusted  $r^2$  for the model was 0.78 with a standard error of estimate 0.11. In 2004-2006, surface soil Pb was significantly greater than the baseline Pb concentration by an average of 2.5 mg Pb/kg soil ( $P < 0.001$ ,  $n=200$ ). In 2004 and 2006 surface soil Pb concentrations were significantly less than those of 2005

by an average of 1.32 mg/kg ( $P < 0.001$ ,  $n=200$ ). The Hermiston field site had the largest average Pb concentrations in soils and the greatest variability. This may be due to the possible addition of small amounts of Pb to the field from irrigation, as the waters contained an average of 4  $\mu\text{g}$  Pb/L water, 12 times more than what was detected in Klamath irrigation waters.



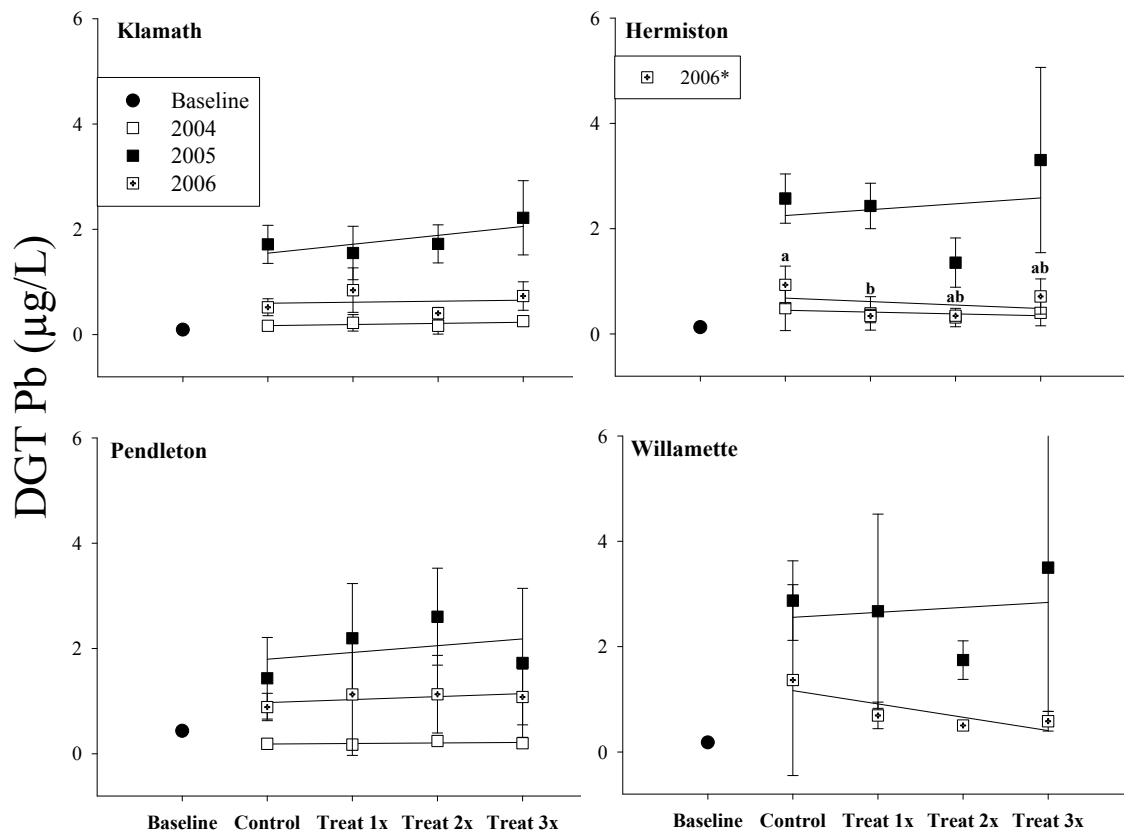
**FIGURE 19. Lead concentrations (mg/kg) in surface soil sampled at harvest from four field sites in Oregon (n=4).**

*Lead in soil solution.* The mean baseline Pb concentration in soil solution at all four sites was 2.54 µg/L (Klamath 3.69 n=1, Hermiston 1.38 ± 0.25, Pendleton BDL, Willamette BDL). The method detection limit for Pb in soil solution was 0.23 µg/L soil solution. **(Figure 20).** No significant Pb treatment effect was observed in soil solution at all four sites 2004-2006. Although the treatment fertilizers did contain higher concentrations of Pb than the control fertilizers in 2005 and 2006, the ratios of control to treatment were very small and the highest Pb treatment level for all years was 2.3 mg Pb/kg fertilizer not taking into account the dilution to fertilizer. Pb in soil solution was significantly correlated with Pb measured using DGT at Hermiston and Pendleton in 2005 ( $r^2 = 0.77$ , 0.65;  $P = 0.0004$ , 0.006). This may be due to the significantly increased Pb concentrations in 2005 compared with 2004 by  $2 \pm 1.1$  µg Pb/L soil solution ( $P < 0.001$ ,  $N = 159$ ) using MLR. At Klamath and Hermiston, the baseline Pb concentrations were significantly greater than those in 2004-2006 by an average of  $6 \pm 1.4$  µg/L. Over all sites, Pb in 2005 soil solution was not significantly different from 2006. Taking in to account all of the variables put in to the MLR model, the best predictors of Pb concentrations in soil solution were pH, NH<sub>4</sub>-N, NO<sub>3</sub>-N, K, P, and irrigation practice ( $P < 0.04$ ).



**FIGURE 20. Lead concentrations ( $\mu\text{g/L}$ ) in soil solution sampled at harvest from four field sites in Oregon (n=4).**

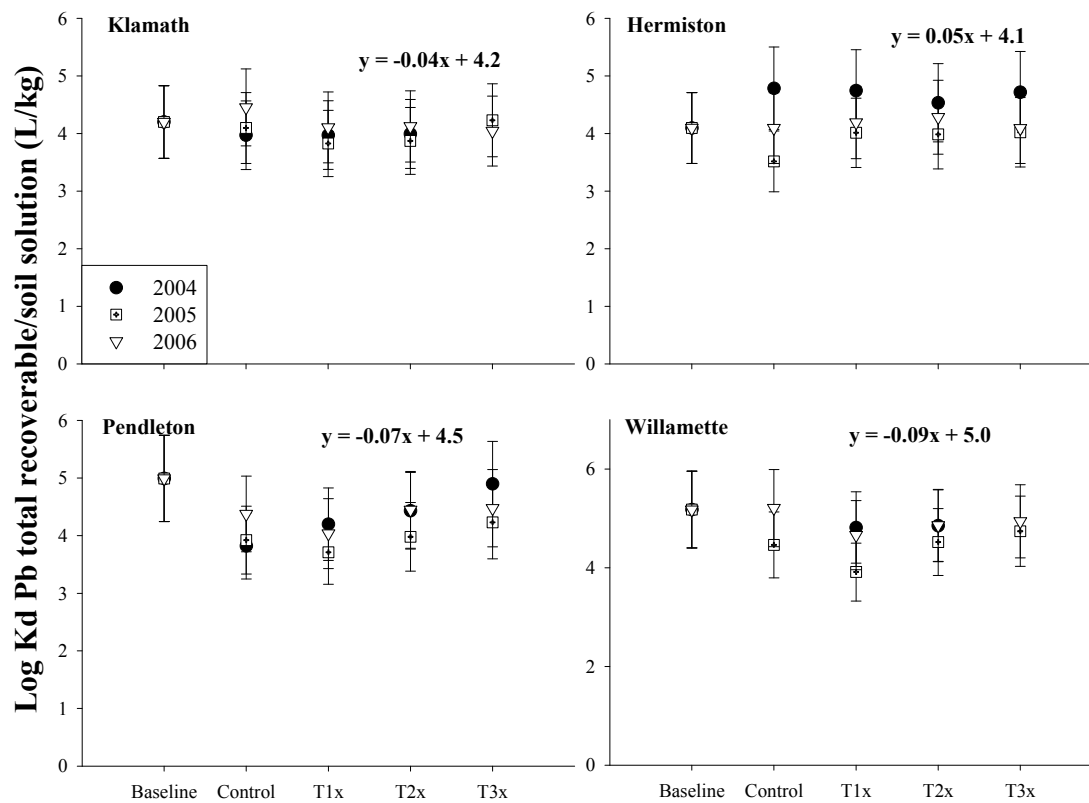
*Lead in DGT.* The mean baseline Pb concentration measured by DGT is 0.21 µg/L (Klamath 0.09 n=1, Hermiston 0.13 ± 0.02, Pendleton 0.44 n=1, Willamette 0.18 n=1 µg/L). The average method detection limits for Pb measurement using DGT was 0.23 µg/L soil solution (**Figure 21**). No significant treatment effect was observed in DGT measured Pb concentrations at all four sites 2004-2006. Most sites were near or below detection limits in 2004. At Hermiston in 2006, a slight decrease was observed from the control to treatment level 1x, albeit minor. DGT measured Pb did not correlate with Pb measured in plant, as plant Pb was BDL for all sites, all years. The concentration of DGT measured Pb could best be predicted by using a linear combination of the variables CEC, pH, NH<sub>4</sub>-N, and P ( $r^2 = 0.64$ , standard error 0.39, N=179). The highest concentration of Pb in a fertilizer application occurred in 2005, and DGT effectively captured this increase. In 2005 and 2006, DGT measured Pb concentrations were significantly greater than those measured in 2004 and at baseline by an average of 1 µg/L ± 0.09 standard error). In 2005, DGT Pb concentrations were also greater than those measured in 2006 by 0.5 ± 0.8 µg/L. In spite of the exceedingly low dosing levels of lead, yearly increases of both surface soil and DGT measured Pb were observed. Although the 2005 yearly increase for Pb was statistically significant, it's overall 'real world' significance was questionable, considering the increases that were seen were less than 2 parts Pb per billion parts of soil.



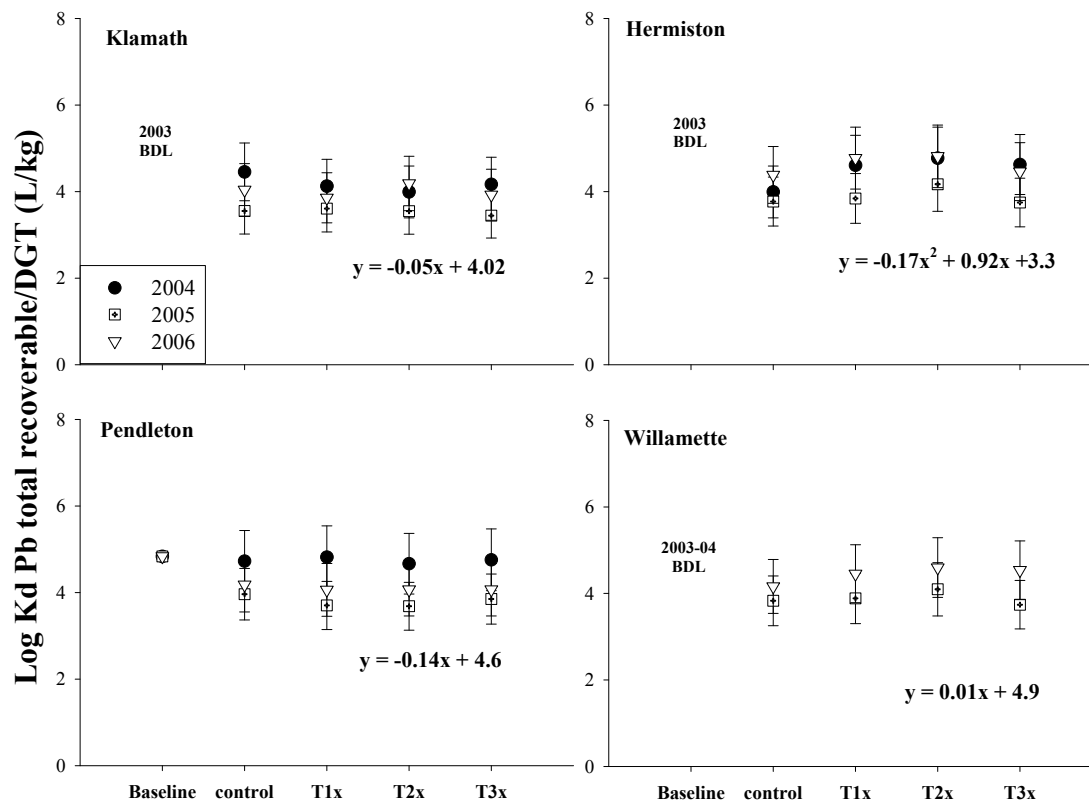
**FIGURE 21. Lead concentrations ( $\mu\text{g/L}$ ) measured by DGT soils sampled at harvest from four field sites in Oregon ( $n=4$ ).**

*Lead in plant.* The average method detection limits for Pb in plant samples was 0.38 mg/kg. Lead concentrations in wheat and potato crops were below detection limits at all sites, for all years. In conclusion, Pb is relatively unavailable for crop uptake at these particular application rates, and under these specific field conditions.

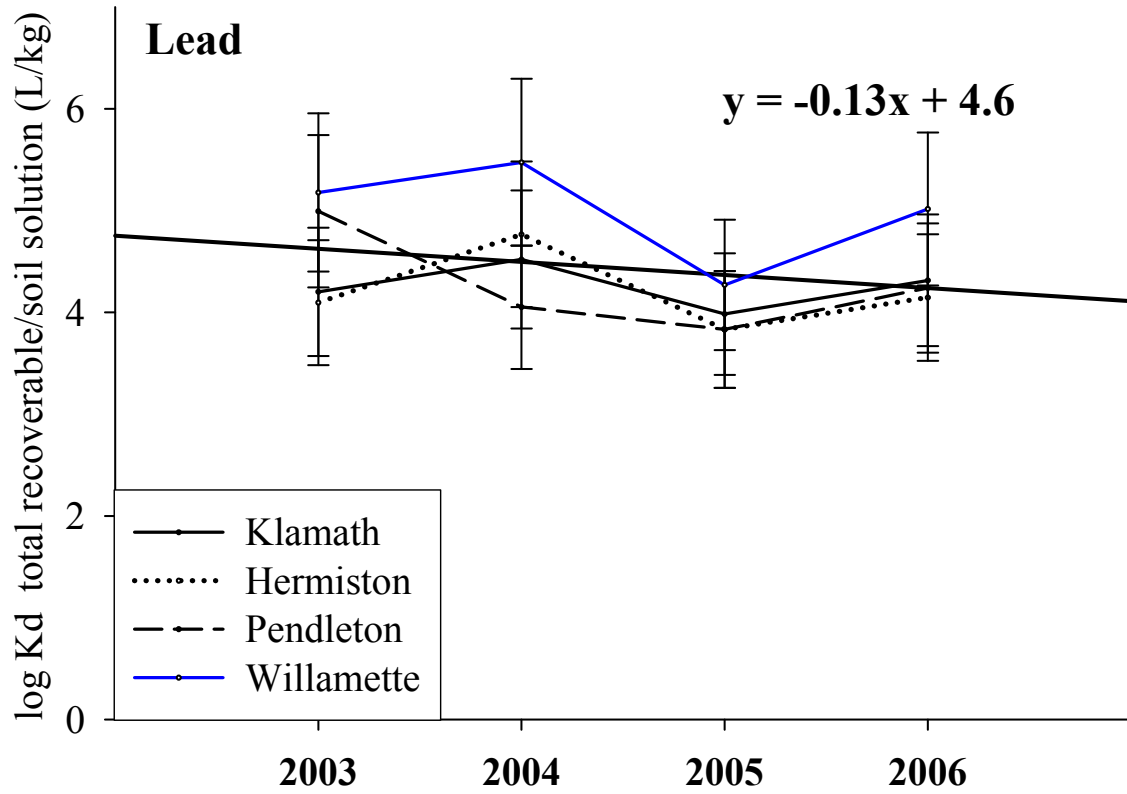
The log Kd values for Pb at all sites ranged from 3.4-6.6 L/kg. Negative trends are seen with increasing treatment level at all sites except Willamette (**Figure 22**). Negative trends are also seen in the Kd-dgt results (**Figure 23**). Although negative slopes are seen at nearly all sites, the rates of Kd and Kd-dgt decrease are relatively small. This result was anticipated as Pb binds strongly to organic matter (36), commonly found in agricultural soils, and rates of release of Pb<sup>2+</sup> into soil solution at circumneutral pH are kinetically very slow (37). Previous work also suggests that Pb can move offsite by erosion of dissolved soil particulates (38). Our results corroborate historical evidence of increased Pb mobility particularly with changes in CEC, pH, and % O.M. Based on real systems data, we report decreasing Kd, and Kd-dgt over time using only the control and treatment level 1x (**Figures 24-25**). Based on the increases in Pb concentration over time, particularly the increase of labile Pb by year, warrants further study over longer periods of time to better estimate risk.



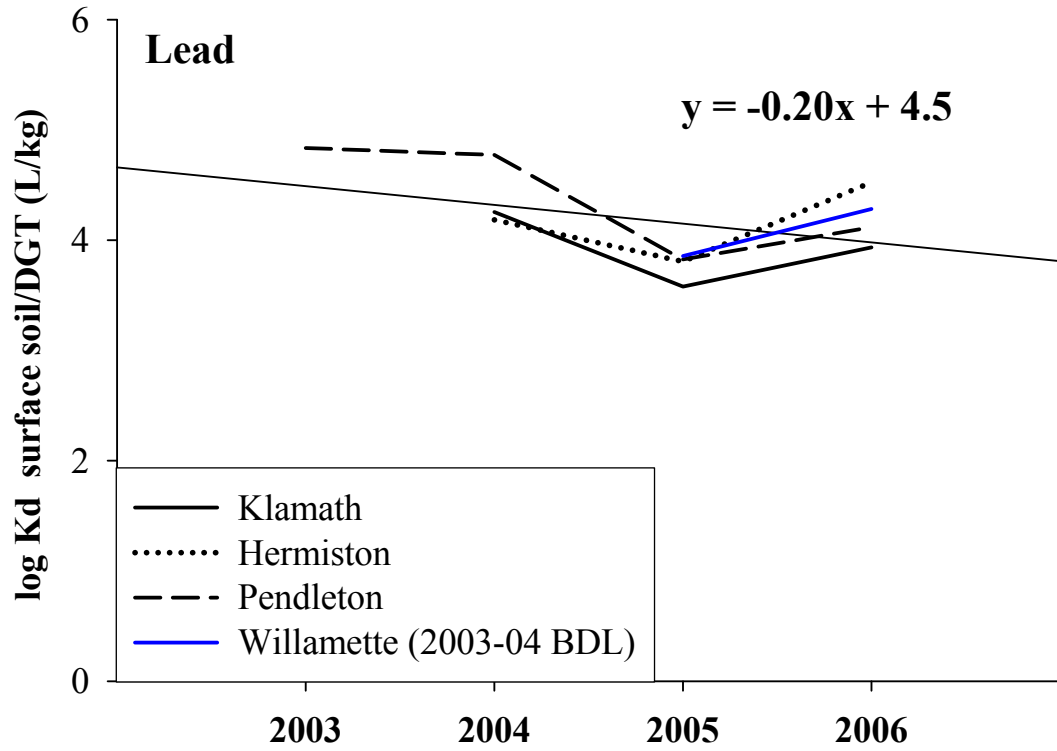
**FIGURE 22. Log Kd (total recoverable Pb / soil solution Pb) (L/kg) grouped by treatment level, measured 2003 (Baseline)-2006, at four Oregon field sites. Regression equations represent a best fit line through all of the data points.**



**FIGURE 23. Log Kd-DGT (total recoverable Pb / DGT measured Pb) (L/kg) grouped by treatment level, measured 2003 (Baseline)-2006, at four Oregon field sites. Regression equations represent a best fit line through all of the data points.**



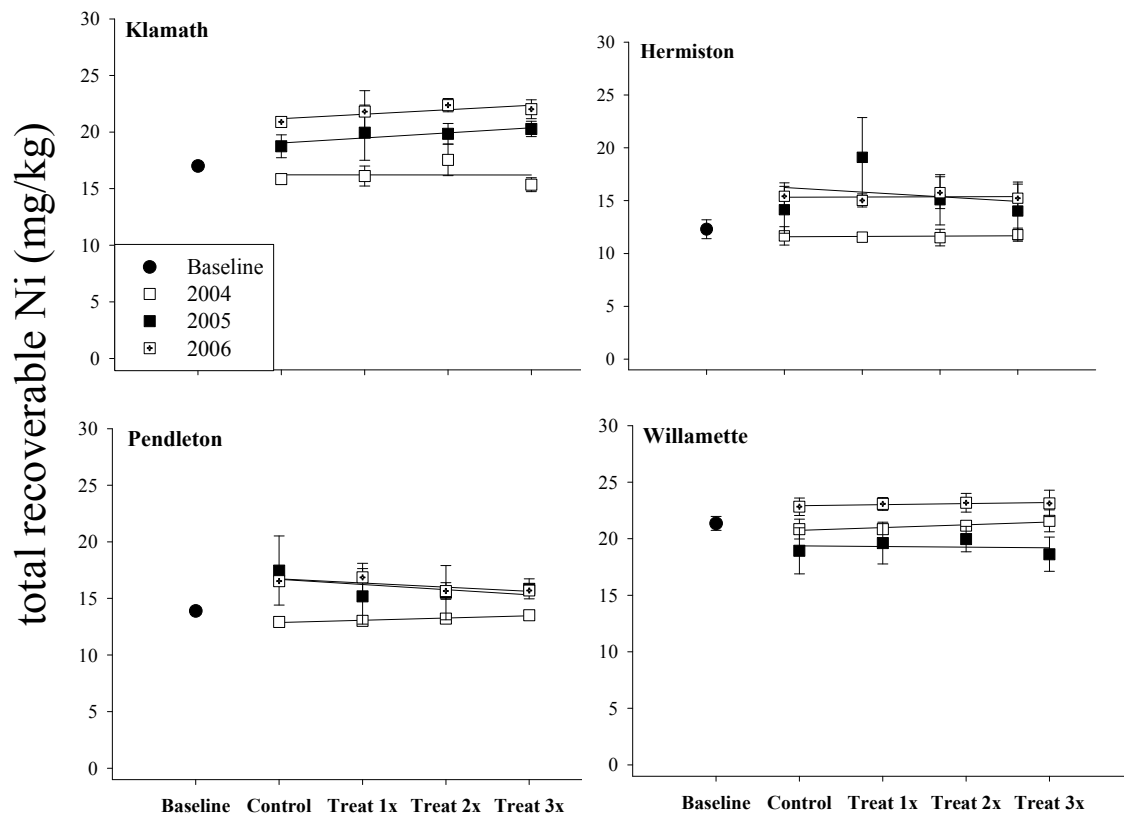
**FIGURE 24. Log Kd measured at four Oregon field sites. Each year represents a composite of control and treatment 1x samples only. Treatment 2x, and 3x were omitted.**



**FIGURE 25. Log Kd-DGT measured at four Oregon field sites. Each year represents a composite of control and treatment 1x samples only. Treatment 2x, and 3x were omitted.**

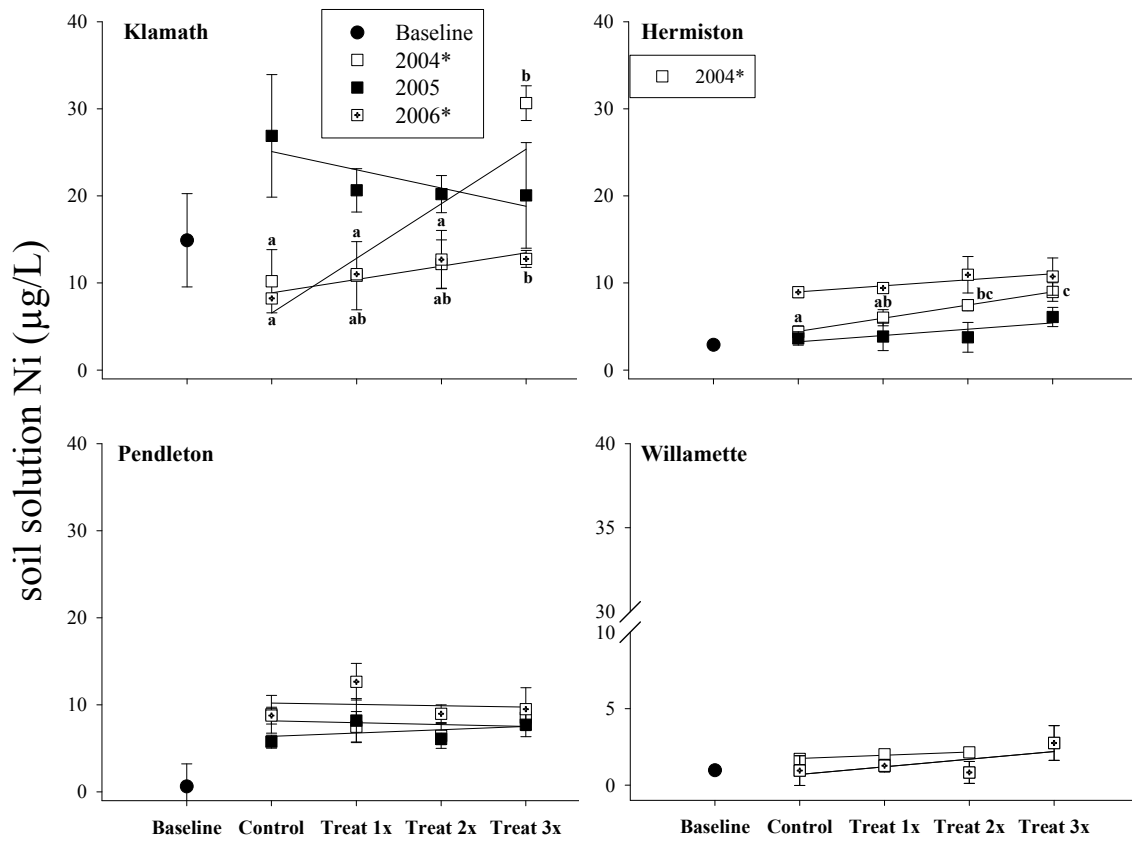
## Nickel

*Nickel in surface soil.* The mean baseline Ni concentration in surface soil at all four sites was 16.14 mg/kg (Klamath  $17.01 \pm 0.01$ , Hermiston  $12.30 \pm 0.90$ , Pendleton  $13.89 \pm 0.31$ , Willamette  $21.35 \pm 0.61$  mg/kg). The average method detection limit for Ni in surface soil was 6.1 mg/kg. No significant treatment effect was observed at any of the four sites 2004-2006 ( $P > 0.05$ ) (**Figure 26**). Surface soil Ni was negatively correlated with soil solution Ni in 2004 ( $r^2 = -0.90$ ;  $P = 0.01$ ), although solution Ni was near detection limits in 2004 and treatment 3x was BDL. Surface soil Ni can best be predicted using a linear combination of the variables % O.M., P, K, and irrigation practice ( $r^2 = 0.69 \pm 0.062$ ;  $N=184$ ). Using MLR, it was shown that 2005 and 2006 had significantly greater surface soil Ni concentrations than the baseline by an average of  $7.6 \pm 0.02$  mg Ni/kg soil ( $P < 0.002$ ) and than in 2004 by  $1.2 \pm 0.01$  mg/kg ( $P < 0.001$ ). Surface soil Ni concentrations were not significantly different from baseline to 2004 and from 2005 to 2006.



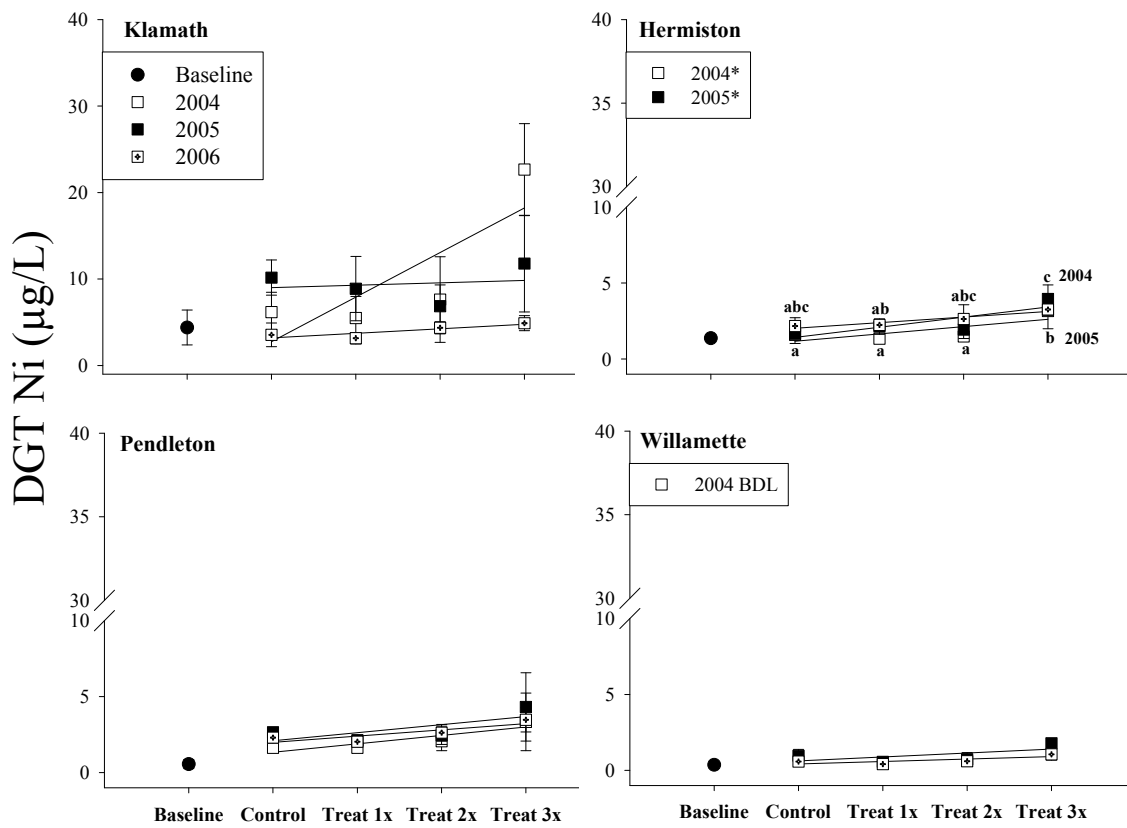
**FIGURE 26. Nickel concentration (mg/kg) in surface soil sampled at harvest from four field sites in Oregon (n=4).**

*Nickel in soil solution.* The mean baseline Ni concentration in soil solution at all four sites was 8.6 µg/L (Klamath 14.91 ± 5.34, Hermiston 2.91 ± 0.006, Pendleton 8.0 ± 2.59, Willamette BDL). The average method detection limit for Ni in soil solution was 2.2 µg/L soil solution. A treatment effect was observed at Klamath in 2004 and 2006 (**Figure 27**). In 2004, treat 3x was significantly larger than treats 2x, 1x and the control by 2.56, 2.92, 3.12 µg/L respectively (P < 0.001). In 2006, treat 3x was on average 1.56 µg/L greater than the control (P = 0.02). Hermiston 2004 showed a significant treatment effect, where treat 3x was significantly greater than treat 1x and the control by 1.5, and 2.1 µg/L. Treat 2x was also significantly greater than the control by 1.7 µg/L (P < 0.006). No significant treatment effect was observed at the Pendleton site, nor at the Willamette site 2004-06 for Ni measurement in soil solution. Concentrations of Ni in solution at Willamette were very near detection limit. Soil solution Ni correlated well with DGT measured Ni at Hermiston 2004-2006 ( $r^2 = 0.66, 0.60, 0.72$ ; P < 0.05), and at Willamette 2005-2006 ( $r^2 = 0.79, 0.61$ ; P = 0.001, 0.01). Soil solution also was significantly correlated to DGT Ni at Klamath in 2004 ( $r^2 = 0.84$ ; P = 0.0001). Soil solution Ni was best predicted using a linear combination of the variables pH, NH<sub>4</sub>-N, NO<sub>3</sub>-N, P, K, and irrigation practice. In 2004, soil solution Ni concentrations were not significantly different from the baseline Ni solution concentrations. In 2005 and 2006, solution Ni was significantly less than the baseline by 1.9 ± 1.3 µg/L (P < 0.03; N = 161). Soil solution measured in 2005 was also significantly less than that measured in 2004 by 1.4 ± 1.0 µg/L.



**FIGURE 27. Nickel concentration (µg/L) in soil solution sampled at harvest from four field sites in Oregon (n=4).**

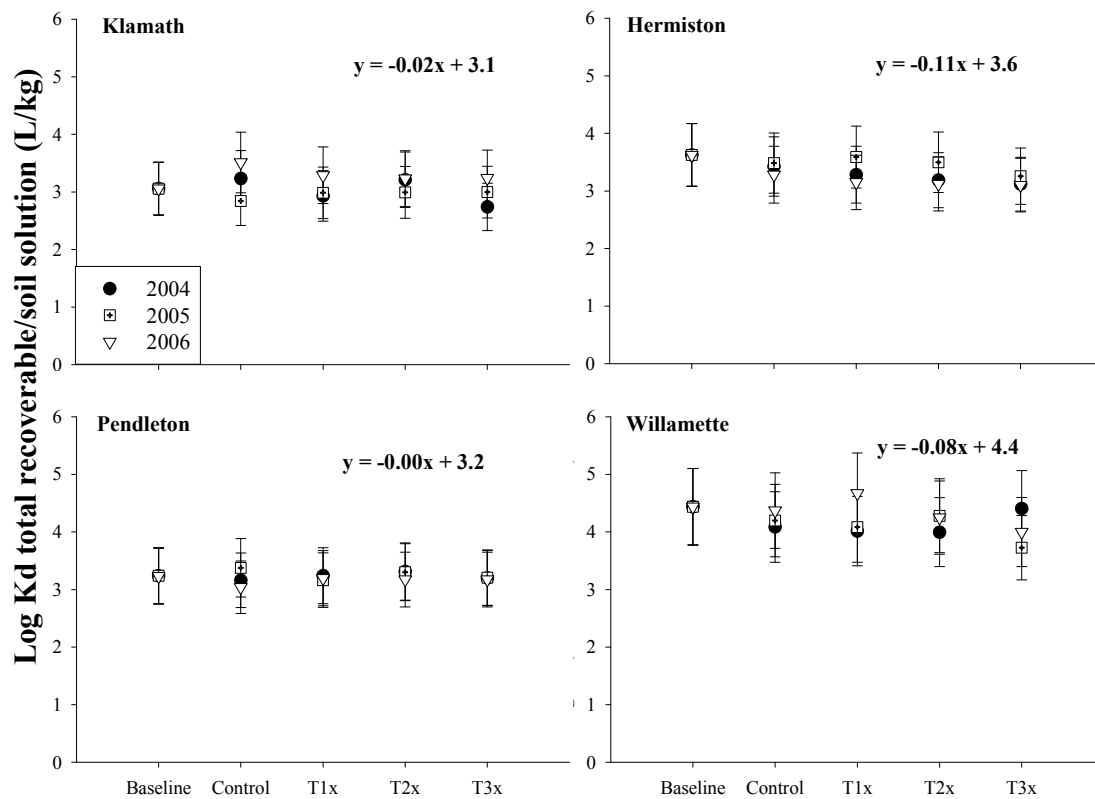
*Nickel in DGT.* The mean baseline Ni concentration in DGT at all four sites was 2.6 µg/L (Klamath  $4.39 \pm 2.02$ , Hermiston 1.37 n=1, Pendleton  $2.0 \pm 0.3$ , and Willamette BDL). The method detection limit of Ni measurement by DGT was 2.2 µg/L soil solution. At Klamath 2004-2006, no significant Ni treatment effect was observed (**Figure 28**). At Hermiston 2004 treat 3x was significantly greater than treat 1x by 2.26 µg/L ( $P < 0.001$ ), while in 2005, treat 3x was significantly greater than treat 2x, 1x and the control by 1.85, 2.08, 2.38 µg/L respectively ( $P < 0.01$ ). There were no significant treatment effects observed for Ni measurement by DGT at Pendleton or Willamette sites 2004-06. Concentrations of Ni at both sites were near the detection limit. Nickel concentrations in DGT were best predicted by a linear combination of the variables pH, NH<sub>4</sub>-N, NO<sub>3</sub>-N, and irrigation practice. In 2004, Ni measured using DGT showed no difference from the baseline Ni measurement. Significant differences were seen between the baseline and 2005-2006, which had significantly less DGT measured Ni by an average  $1.7 \pm 1.0$  µg Ni/L soil solution ( $r^2 = 0.76 \pm 0.23$ ; N = 169).



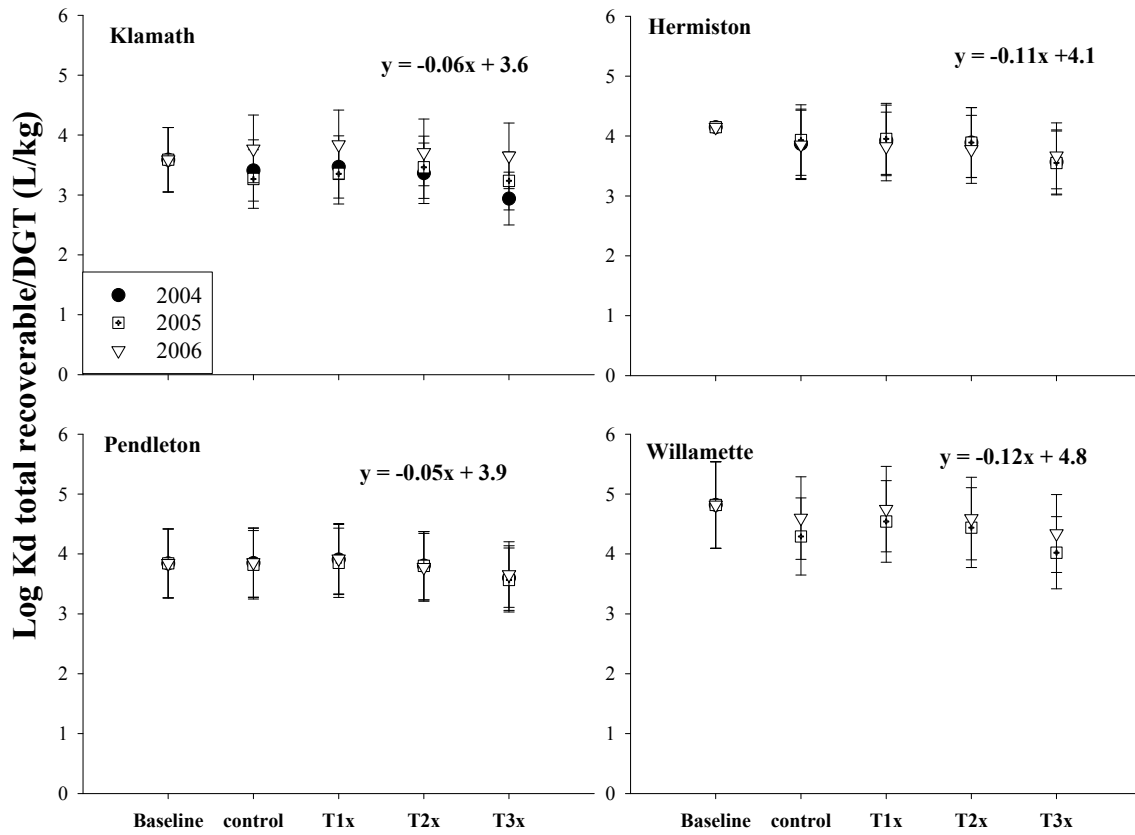
**FIGURE 28. Nickel concentration (µg/L) measured by DGT in soils from four field sites in Oregon (n=4).**

*Nickel in plant.* The average method detection limit for Ni measurement in plant material was 2.6 mg/kg. Hermiston, Pendleton, and Willamette plant samples were all BDL for nickel 2004-2006. At Klamath in 2004, Ni concentrations were detectable and a dose response was seen in potato with fertilizer treatment ( $r^2 = 0.73$ ;  $P = 0.0003$ ). Treat 3x was significantly greater than the control and treat 1x ( $P < 0.01$ ), and treat 2x was significantly greater than the control ( $P = 0.01$ ). Nickel is involved in enzymatic processes in both bacteria and plant and it is widely accepted that Ni is essential for plants (39). Plant urease is a Ni containing enzyme that hydrolyzes the conversion of urea into ammonia and carbonic acid (40). Since much of the urease activity occurs in the leafy portion of vegetation, it is not atypical to find very little Ni concentrations in the edible portion of wheat and potato crops. Rotation with a leafy crop commodity may result in increased Ni concentration found in the edible portion and warrants further study.

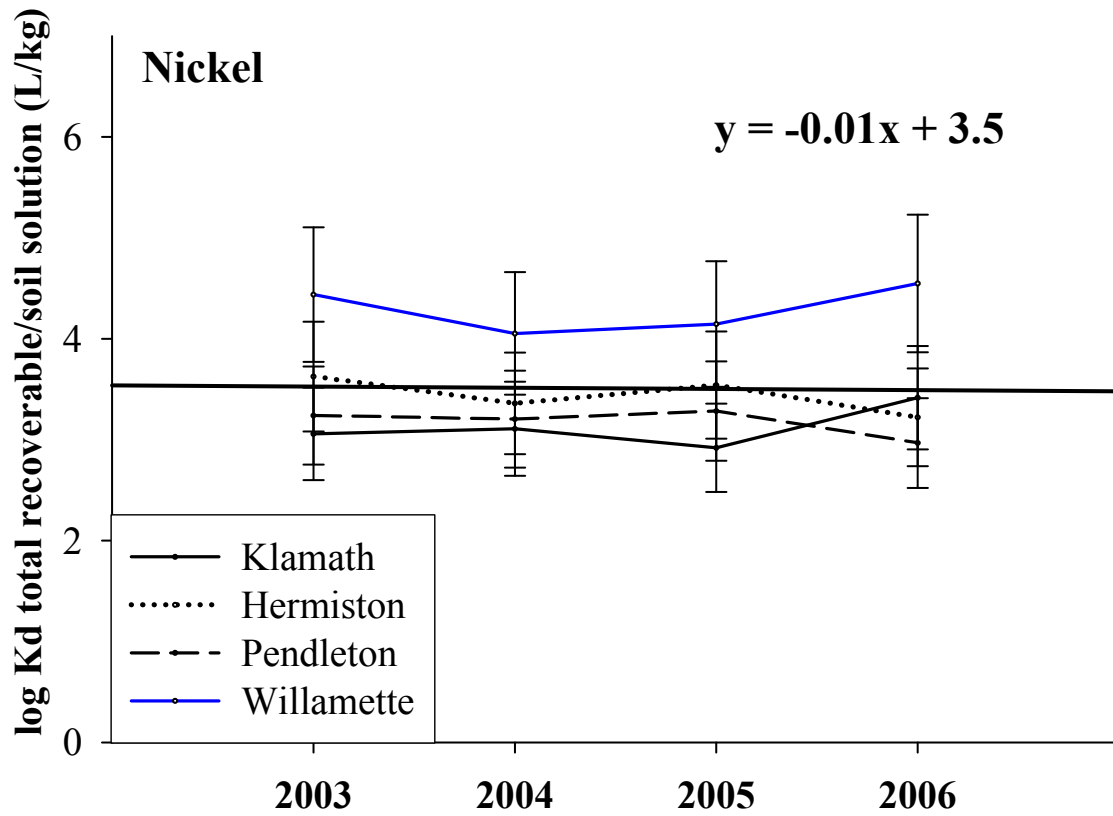
The log Kd values for Ni at all sites ranged from 2.9-4.8 L/kg. Negative trends are seen with increasing treatment level at all sites (**Figure 29**). The Pendleton site shows relatively little decrease with treatment. The log Kd-dgt values for Ni also showed negative slopes at all sites (**Figure 30**). This effect seemed to be directly related to the increasing treatment levels. After removing treatment levels 2x and 3x and plotting the sites by year, negative slopes were still seen. However the values were exceedingly low and the Kd and Kd-dgt do not appear to have any consequential decrease based on our data from 2003-2006 (**Figure 31-32**).



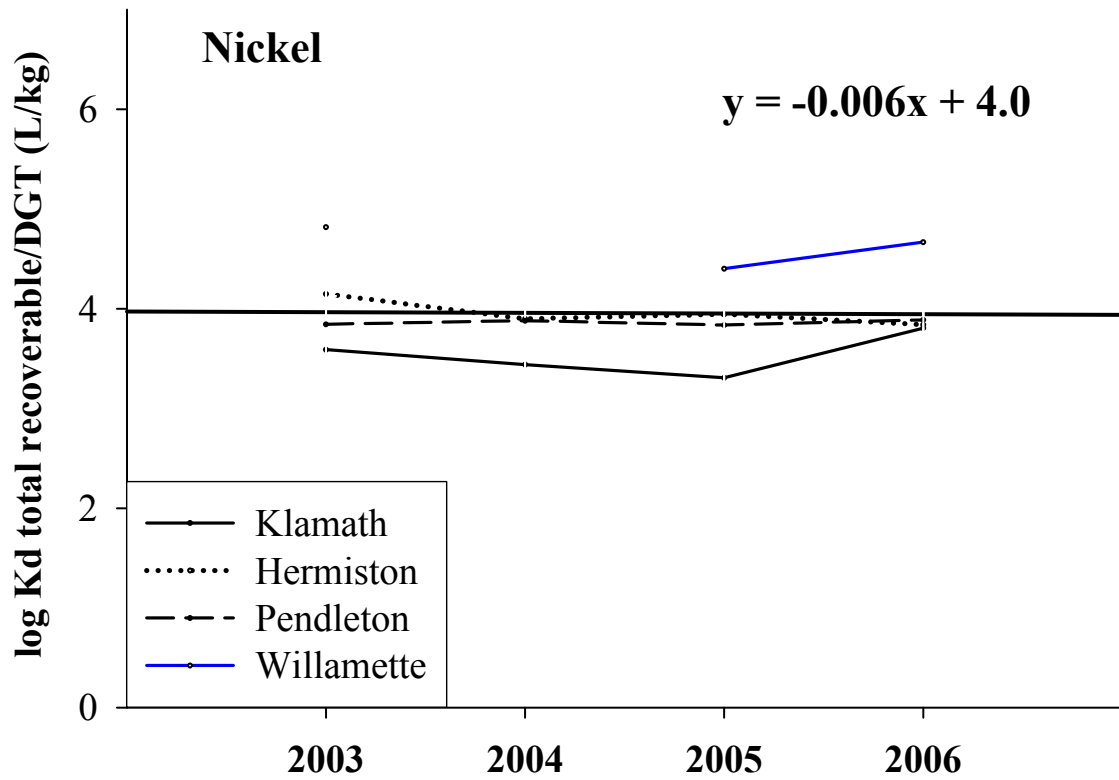
**FIGURE 29. Log Kd (total recoverable Ni / soil solution Ni) (L/kg) grouped by treatment level, measured 2003 (Baseline)-2006, at four Oregon field sites. Regression equations represent a best fit line through all of the data points.**



**FIGURE 30. Log Kd-DGT values for Ni at four Oregon agricultural field sites based on ratios between total recoverable Ni in surface soil and DGT measured Ni (n=4).**



**FIGURE 31. Log Kd measured at four Oregon field sites. Each year represents a composite of control and treatment 1x samples only. Treatment 2x, and 3x were omitted.**



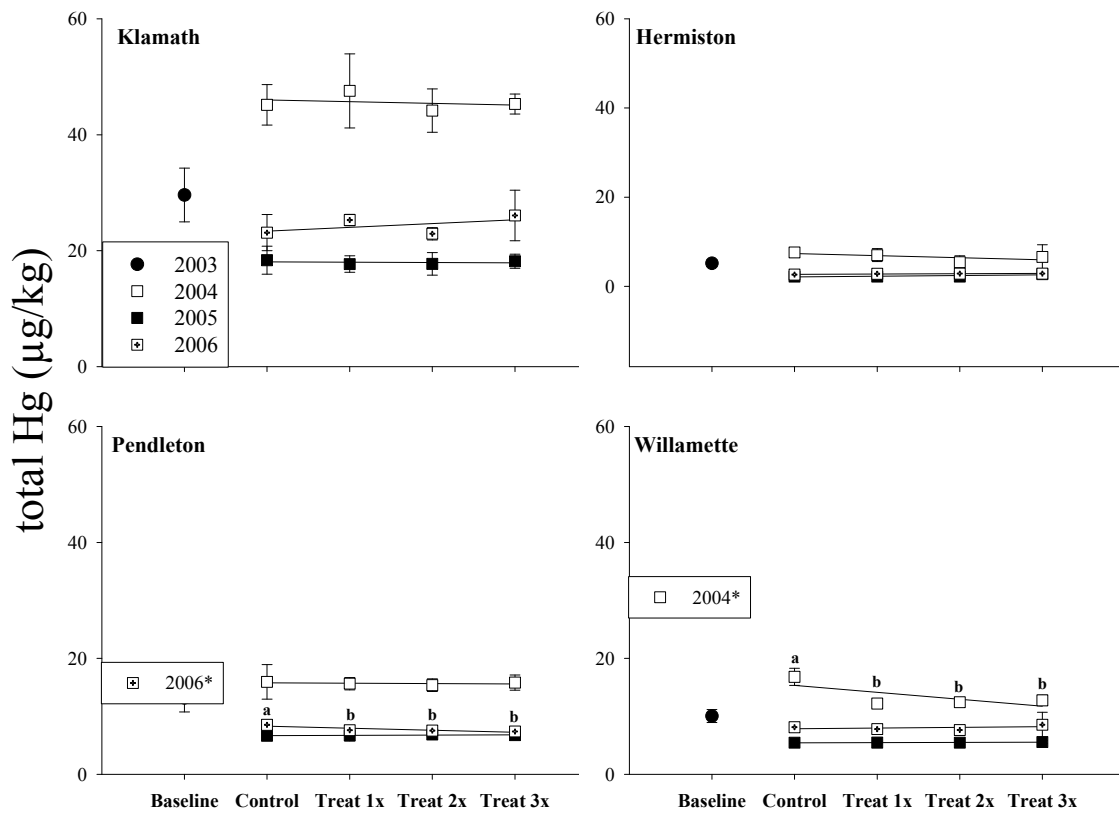
**FIGURE 32. Log Kd-DGT measured at four Oregon field sites. Each year represents a composite of control and treatment 1x samples only. Treatment 2x, and 3x were omitted.**

## Mercury

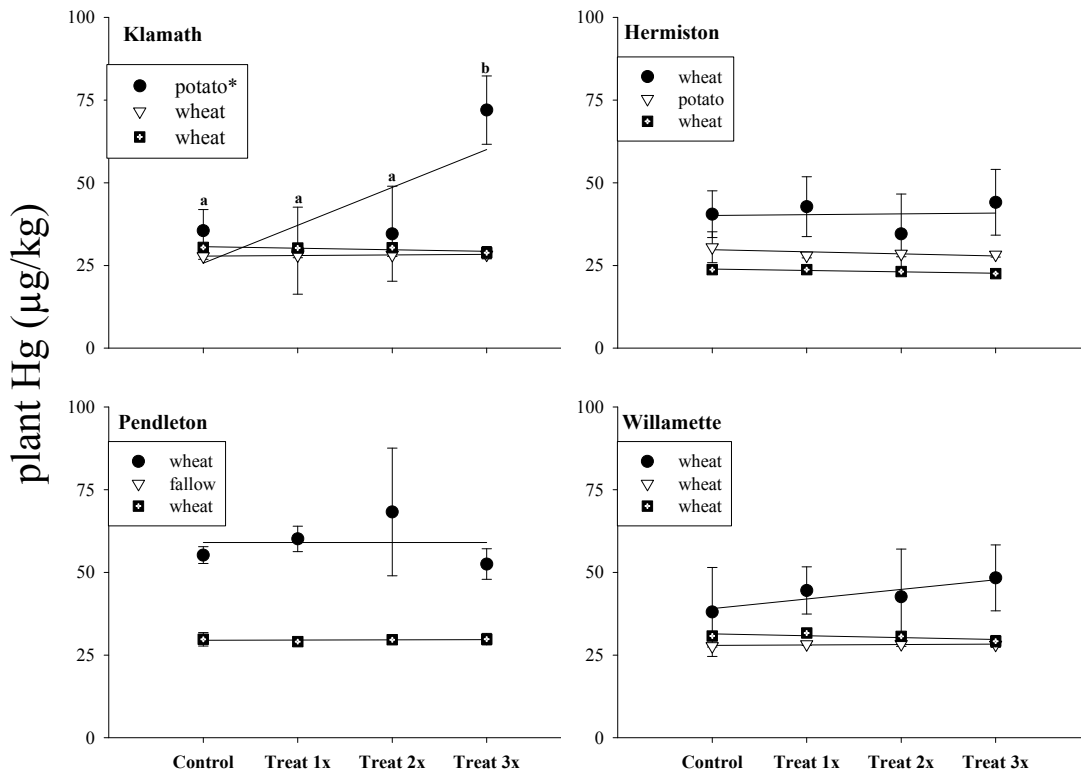
*Mercury in surface soil.* The mean baseline Hg concentration in surface soil at all four sites was 14.1 µg/kg (Klamath 29.6 ± 4.6, Hermiston 5.1 ± 0.80, Pendleton 12.3 ± 3.5, Willamette 10.1 ± 1.1 µg/kg). The average method detection limit for Hg in surface soil was 0.81 µg/kg. No treatment effects were observed in surface soil Hg with the exception of Pendleton and Willamette, which showed the control as having significantly higher Hg concentration than the treatment levels. No significant treatment effect was observed at Klamath or Hermiston 2004-2006 ( $P > 0.05$ ). Significant differences were seen between the control and all treatment levels at Pendleton 2006, and Willamette 2004 ( $P = 0.019, 0.022$  respectively) as seen in **Figure 33**. This could be due to the higher Hg levels in the control fertilizer in 2004 and 2006. Mercury in surface soil and plant samples could not be evaluated based on treatment by the fertilizer due to the lack of mercury concentration in the treatment fertilizer. The control fertilizer contained 28 and 8 times more Hg than the treatment fertilizer in 2004 and 2006. While the 2005 treatment fertilizer did contain more Hg than the control, the difference was less than 2x that of the control. One way to consider this dilemma would be to designate the control as a treatment level and the treatments as pseudo-control samples. Although two of the sites show significantly higher Hg concentration in the control samples, the general trends over all sites, suggest no change in Hg concentration with increasing fertilizer loads.

*Mercury in Plant.* The concentrations of Hg in plant material are equal to or higher than the concentrations in surface soil. This suggests that most of the Hg in soil is bioavailable. Mercury concentrations in plant samples showed no change with fertilizer

loads, with the exception of Klamath wheat, where treat 3x was significantly greater than treats 2x, 1x, and the control by 43, 37, and 36  $\mu\text{g}/\text{kg}$  respectively ( $P < 0.001$ ) (**Figure 34**).



**FIGURE 33. Mercury concentrations (µg/kg) in surface soil sampled at harvest from four field sites in Oregon (n=4).**

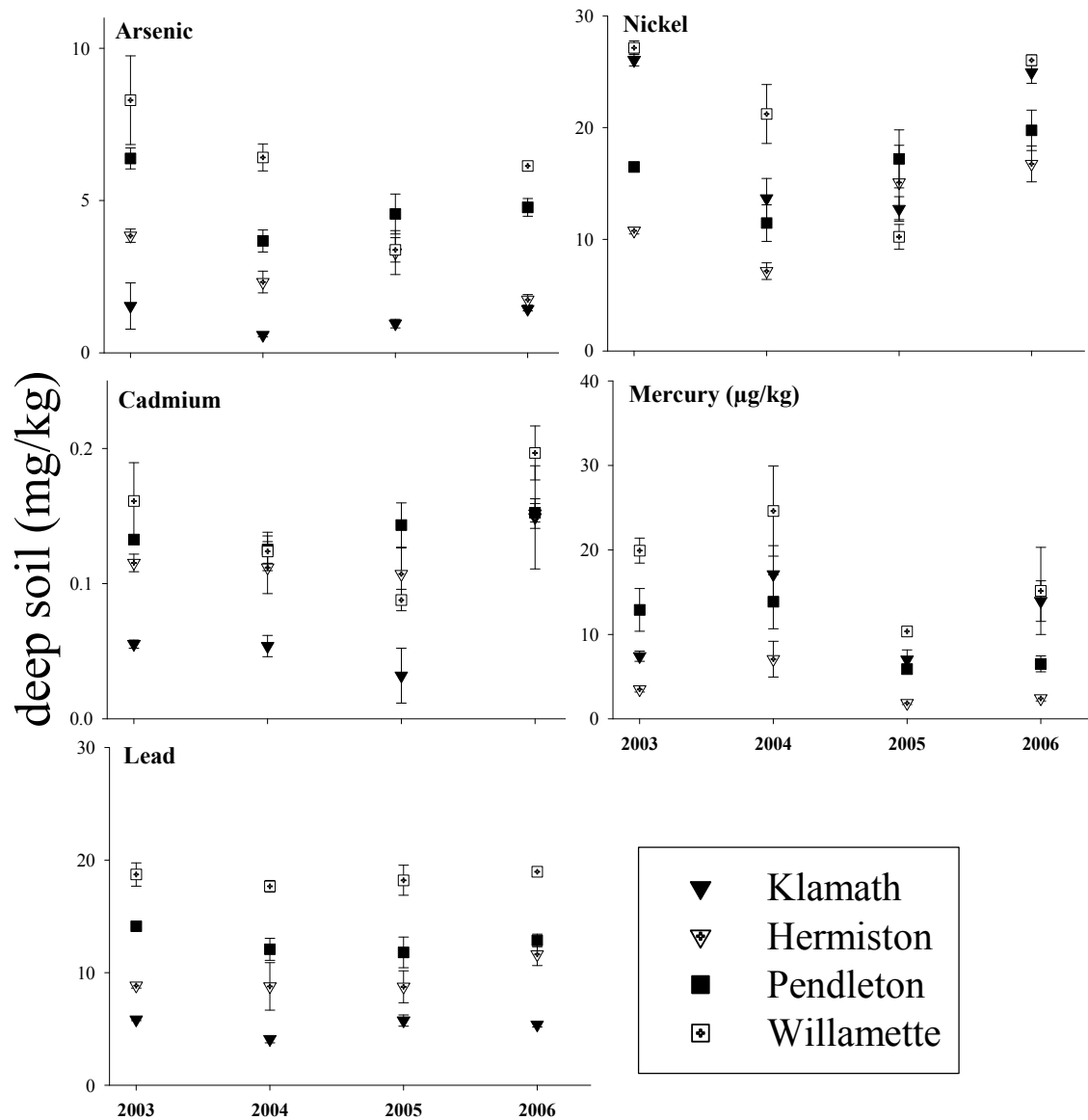


**FIGURE 34. Mercury concentrations ( $\mu\text{g}/\text{kg}$ ) in plant tissue sampled from four field sites in Oregon ( $n=4$ ).**

## Deep soil

No observable differences were seen between treatment levels of deep soil samples 2003-2006 (**Figure 35**). Due to the low sample size of deep soil ( $n=1$  per treatment level), treatments were composited to achieve a sample size of 4 per site. Each site was statistically different from one another based on a two way anova, all pairwise multiple comparison procedures (Holm-Sidak method) ( $P < 0.05$ , 86 d.f.). Site differences ranged from 1.2-4.9 mg As/kg soil. Significant yearly effects were also observed for deep soil As, however the difference of means is relatively small over all sites (0.48-1.9 mg/kg;  $P < 0.05$ ). The biggest change within year for As was seen at Willamette with a difference of means ranging from 1.9-4.9 mg/kg ( $P < 0.03$ ). Deep soil Cd trends resulted in a 'V' shaped curve, where increasing trends are seen from 2004-2006, however, the 2006 concentration is only marginally larger than the baseline deep soil measurement. Significant yearly effects were seen with deep soil Cd ( $P < 0.05$ ; 84 d.f.) ranging from 0.02-0.07 mg/kg, as well as site differences ( $P < 0.03$ ) ranging between 0.02-0.07 mg Cd/kg soil. The largest change within year for Cd was seen at Klamath with a range of differences in means of 0.02-0.12 mg/kg. Deep soil Pb showed no environmentally significant change over the four year study. Averaged yearly effects over all sites were marginal for deep soil Pb ranging from 1.2-1.6 mg Pb/kg soil ( $P < 0.05$ ; 86 d.f.), while differences between sites were strongly significant ranging from 3.2-13.1 mg/kg ( $P < 0.05$ ). The largest change within year for Pb was seen at Hermiston with a range of 2.8-2.9 ( $P < 0.01$ ). Yearly effects for Ni in deep soil were significant ranging from 1.8-8.1 mg Ni/kg soil ( $P < 0.05$ ). The difference of Ni concentrations between sites was also strongly significant ranging from 1.8-8.7 mg/kg. The largest yearly effect was

seen at Willamette ranging from 5.9-15.8 mg/kg. However, this range did not succeed in a linear fashion, but rather was staggered. Significant yearly changes in deep soil Hg concentrations over all sites ranged from 3.2-9.4  $\mu\text{g}/\text{kg}$  ( $P < 0.05$ ). At all sites, deep soil Hg concentrations were significantly different and differences ranged from 1.6-13.8  $\mu\text{g}/\text{kg}$ . The site with the largest significant yearly difference in deep soil Hg was Willamette, which ranged from 4.7-14.2  $\mu\text{g}/\text{kg}$  ( $P < 0.05$ ).



**FIGURE 35. Metal and metalloid concentrations in deep soil (mg/kg) measured 2003-2006 at four field sites in Oregon (n=4).**

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## **APPENDIX I**

Examples of sampling tracking documents, including field and analytical bench sheets

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Soils Digestion for Metal Analysis SAM

Soil and Plant Sample analysis by LECO Mercury Analyzer SAM

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