

**December 17, 2003**  
**Progress Report**  
**Funding received October 2003**

**PROJECT NAME:** Distribution and Fate of Background and Bioavailable Metals in Oregon Agricultural Soils, Plants and Waters

Principle Investigator: Kim A. Anderson  
 Environmental & Molecular Toxicology Department  
 Tel: 541-737-8501 / Fax: 541-737-0497 E-mail: kim.anderson@orst.edu

**PROJECT RATIONALE**

Background levels of metals in Oregon soils that receive fertilizer treatments are not well understood. The effects of fertilizer use and the long-term effects on biota uptake and on surface and ground waters are also not well understood for Oregon soils. In addition, to understanding background levels, bioaccumulation, bioavailability and partitioning are keys to truly understanding risk. Bioavailability of metals is the accessibility for biological assimilation and possible toxicity. Federal and state regulatory agencies typically rely on analytical methods that entail vigorous extraction of matrices with strong acids. The relevancy of such methods to the toxicity is often not considered, thus decisions are based on data that is often not relevant for prediction of potential exposures and risk. The evidence is compelling that the quantities recovered by vigorous extraction/digestion fail to predict bioavailability of the compounds<sup>1</sup>. Regulatory agencies have recognized the importance of determining bioavailable versus total contaminant concentration; US EPA has allowed certain regions to develop site specific criteria based on bioavailable levels of priority pollutants<sup>2</sup>.

**Health/Risk/Fate- Depends on Chemical form:** For chemical contaminants, aquatic toxicity data, water quality criteria and threshold limit values are based on dissolved concentrations and not total metal levels<sup>3,4</sup>. For example, a study of copper distribution and water effects ratios were recently performed under the auspices of EPA Region 2 for New York/New Jersey<sup>5</sup>. Based on this work (i.e. bioavailable copper) revised criteria were proposed and adopted. The modified criteria saved costly remediation efforts in NY/NJ. Presented below one can see how different conceptual<sup>6</sup> approaches can lead to significantly different estimates of exposure. To efficiently generate quantitative exposure estimates and to accurately characterize risks posed by metals, bioavailability needs to be considered as early as possible in the risk assessment<sup>6</sup>. However, the assessment of hazards posed by contaminated soils has been hampered by the lack of simple

realistic procedures that assess the rates and extent to which metals can be released from soil particles and supplied to biota.

**Background on Bioavailable Metal Methods:**

DGT (diffusive gradients thinfilms) are simple, precision devices that accumulate dissolved substances in a controlled fashion. Conventional analyses back in the laboratory provide the in-situ concentrations at the time of deployment. The device uses a layer of Chelex resin impregnated in a hydrogel to accumulate the metals. The resin-layer is overlain by a diffusive layer of hydrogel and a filter. Ions have to diffuse through the filter and diffusive layer to reach the resin layer.

The concentrations of metal ions in the sediment adjacent to the device are lowered. This can induce supply of metal ions from the soil phase to solution in the layers of sediment near the device. The total metal accumulated during the deployment is measured. DGT measures directly the mean flux of labile species to the device during the deployment. This can be interpreted directly as the mean concentration of labile metal at the interface between the device surface and the sediment, during the deployment. For the situation where

	Compound Release	Analytical Chemistry	Biological Response
↑ Estimated Exposure ⇕		Non-recoverable	Not Environmentally Available
	LOADING	Analytically Recoverable	Not Environmentally Bioavailable
			Not Pharmacologically Bioavailable
			BIOLOGICALLY RECOVERABLE

supply from soil particles to solution is rapid, this interfacial concentration is the same as the concentration of metal in bulk pore-water. For a given device and deployment time, the interfacial concentration can be related directly to the effective concentration of labile metal<sup>9</sup>,  $C_E$ .  $C_E$  represents as a concentration the supply of metal to any sink, be it DGT or an organism, that comes from both diffusion in solution and release from the soil phase.

### ***Relevance to sediment quality regulations***

The effective concentration,  $C_E$ , measured by DGT has been shown to correlate very well with uptake by biota<sup>9,7</sup>. DGT mimics the main mechanism of uptake by lowering the concentration locally and inducing diffusive supply and release from the solid phase. Although this is a dynamic measurement that depends on both the rate of transport and the rate of release, it can be used to provide an effective concentration,  $C_E$ .  $C_E$  is a measure of what the solution concentration would have to be to produce the observed accumulation of metal if there was no supply from the solid phase.  $C_E$  may therefore be related through water quality toxicity tests to a quality standard.  $C_E$  is measured directly and simply. It automatically accounts for all sediment properties, including pH and organic matter content.

### ***Metals in Soils and Plant Uptake***

The first application of DGT in soils showed that in soils where sludge had been applied, Cd and Zn were present in two separate pools with different kinetic availabilities<sup>8</sup>. A follow-up study of plant uptake of Cu, Cd, Co, Zn, Pb and Ni at different moisture contents<sup>7</sup> showed that the change in plant uptake with moisture content was more closely related to the observed change in DGT uptake than to soil solution concentration. It has been shown that measurements of  $C_E$  in a wide range of soils contaminated to various extents with Cu were a very good predictor of Cu uptake by plants.

### ***Kinetic and thermodynamic constants***

The extent of release of metal from the soil depends on the rate constant for transfer from soil to solution and the size of the labile pool of metal in the solid phase. The **distribution coefficient,  $K_d$** , for the labile metal can be related directly to the labile soil phase pool size. By deploying DGT for different times in soils where the concentrations of metals in the pore-waters are separately measured, it is possible to provide direct estimates of  $K_d$  and the re-supply rate constant.

### ***Summary of Project Rationale - Conventional metals concentrations in all matrices and bioavailability***

Conventional metal concentrations are important to collect given the larger body of comparative data. We propose to determine metals by US EPA methods (SW-846) on Oregon soils, plants and surface and ground waters. However, the collection of biologically relevant data is also important, bioavailability, bioaccumulation and partitioning of metals under typical agronomic fertilizer applications rates and on Oregon soils needs to be a part of any risk assessment study. One excellent approach is the use of DGT where research has clearly demonstrated that insight into the supply of metals from soils can be gained by using DGT as physical surrogates for plant/organism uptake.

## **PROJECT GOALS AND OBJECTIVES**

### ***Establishing background metal levels in Oregon soils and waters***

Multiple sites around Oregon, in established agricultural regions are under development as “agricultural-fertilizer-used” sites. The following locations were used: Hyslop (Willamette) Farm (HF), Hermiston Experiment Station (HES), Columbia Basin Agricultural Research & Extension Center (CBAREC), and Klamath Agricultural Research station (KARS). Standard grab samples have been and will be collected at each site. Establishing background/baseline numbers will be accomplished by pulling samples from all sites prior to treatments. Background samples were pulled in August/September of 2003 to establish background/baseline at all research stations. Total recoverable metals (Cd, Pb, Ni, Hg, As) will be determined on soil, runoff (dissolved in water (not available summer 2003) and sediment), surface and

ground waters, see attached tables for specific sampling #s per matrix, per site, per application, per year. Chemical analyses are on-going currently in the laboratory.

### ***Validating risk assessment input***

In the human health risk assessments, the soil-water partition ( $K_d$ ) is an important input parameter. All stations will have controls and three fertilizer treatments levels. With this experimental design we will have setup the opportunity to determine metal levels (ultimately  $K_d$ 's) for several application scenarios for the types of soil in Oregon. This will provide for the eventual validation of  $K_d$ 's, for Oregon soils, an important input parameter of the risk assessment calculations, in a series of Oregon soils. For each soil series used at each site we will also have chemically characterized these soils so additional chemical considerations will be known for interpretation of  $K_d$ 's (e.g. lime effects, pH effects, moisture, organic matter, etc.)

### ***Factors affecting fate and transport***

Paired studies will be setup at all sites. The experiment station sites around the state have been chosen in part because they also have different soil chemistries (pH, organic matter, CEC, etc.). By utilizing the same procedures at multiple sites we will begin to understand the impact of soil chemistries on metal fate and transport due to fertilizer applications.

### ***Fertilizer Treatments (dose study - four randomized field replications)***

Four treatment trials will be conducted. One will be control/benchmark, these plots will have no heavy metal rich fertilizer applied. The control plots will have N/P added to duplicate the 1X treatments. Three treatments of heavy metal rich fertilizer have been setup the treatments are 1X (same N as the control), and 2X and 3X. See the appendix for examples of the treatment levels. These treatments will be duplicated at all sites (crop rotation permitting). By utilizing the same treatments at multiple sites we will begin to understand the impact of soil chemistries on metal fate and transport due to fertilizer applications from yearly high dose conditions. In addition, all study plots will be duplicated, this will allow for a better understanding of the heterogeneity of the field ecosystem within each treatment at each research station. Dose affect, soil levels, and plant uptake levels will be evaluated.

Each treatment (C, 1X, 2X, and 3X) will be replicated four times at each research station, a total of 16 field plots. Composite samples (6-9) will be collected from each of the 16 plots. A total of 96 to 144 samples will be pulled from the field for each sampling event. For each plot the samples will be a composite (6-9). The replicate field plots will be kept separate this will add to the statistical power of the study.

### ***Bioavailability of metals in plants and organisms***

DGT are an excellent surrogate for plant and organism uptake. Measurements of Cu as its effective concentration ( $C_E$ ), its soil solution concentration, by EDTA extraction and as free  $Cu^{2+}$  in soil solution were made on 29 different soils covering a large range of copper concentrations<sup>9</sup>. They were compared to Cu concentrations in the plant material of *Lepidium heterophyllum* grown on the same soils. Plant concentrations were linearly related and highly correlated with  $C_E$ , but were more scattered and non-linear with respect to  $Cu^{2+}$ , EDTA extraction or soil solution concentrations. These results demonstrated that the dominant supply processes in these soils were diffusion and labile metal release, which the DGT-soil system mimics. The work showed that insight into the supply of metals from soils can be gained by using DGT as a physical surrogate for plant uptake. DGT are a better method for determining "generic" plant uptake than simply looking at one plant (crop) species, there are always outstanding questions when looking at a single crop for estimating plant uptake. For example, what portion of the plant is to be analyzed, should the plant part be based on typical human consumption or wildlife consumptions? If a test crop is used then there is always the nagging question, "but what would the metal uptake be if another crop were grown?". DGT measures what is bioavailable and therefore gives one confidence, regardless of crop what the likely metal risk presents.

### ***Distribution of metals in soils, waters and plants –CONVENTIONAL METHODS***

Conventional analytical methods (US EPA SW-846 methods) will be used to determine metal content in soils, surface waters, plants<sup>11</sup> and ground waters (when available). Analyses will include Cd, As, Pb, Hg, and Ni. The development of this data base will be critical to understanding the distribution of metals in Oregon soils under various defined agricultural fertilizing<sup>10</sup> conditions. Plant tissue will be analyzed for all heavy metals as well as about 10 other elements. Other elements are included for plant tissue analyses to discern whether synergistic or antagonistic effects occur with other essential and non-essential elements in plants<sup>10</sup>.

### ***Distribution of metals- speciation***

Our hypothesis is that bioavailable contaminant levels are much better suited to study the true ecological impact from fertilizer applications. To test this hypothesis we will investigate the bioavailable concentrations of Cd, Pb, Hg, As(III), and Ni using DGT. Equally important are the chemical characterizations of the ecosystem (study sites), bioavailable fractions, effects of physical/chemical perturbations on the ecosystem and their effects on the bioavailable concentrations. To these ends this project will attempt to make strides towards understanding some of the critical factors effecting mobility of bioavailable metals (As (III), Cd, Ni, Pb and Hg).

### **PROCEDURES AND EXPERIMENTAL DESIGN**

We will conduct field studies to investigate the impact of fertilizer applications on total metals and bioavailable metals at agriculturally relevant sites. The sampling sites are designed to quantitate current persistent, bioaccumulative metals concentrations prior and post fertilizer application. The proposed sites include: HF, HES, CBREC and KARES. Land use history is known for all agricultural sites currently proposed. Field sampling for all locations will be recorded using GPS. See appendix for a field plot arrangements and sampling at each study site. Samples were taken a minimum of 10 m from the edge of a field to minimize road effects, utility poles, etc. A 2-in bucket auger was used to collect soil samples from the surface to 20 cm at each location (excluding organic debris). At each site, 6-9 samples randomly separated will be collected in each plot. Three samples of ca. 500 g were collected, one for metal analyses described here, one for standard soil fertility (chemical characterization) analyses and one for archiving. The archived sample were labeled, frozen, and maintained in a GLP facility freezer. Total recoverable metals (As, Cd, Ni, Pb) will be determined via US EPA method 3050B (digestion) and either US EPA method 6010B (ICPAES) or 6020 (ICPMS) if lower detection limits are needed. Mercury digestions will follow a modified US EPA method 7472/7471A. These methods provide adequate sensitivity and interferences and other analytical challenges have been previously defined<sup>11,12</sup>. Each year, at each site, chemical characterization of the soils will be performed via standard agronomy methods (e.g. pH, NO<sub>3</sub>, NH<sub>4</sub>, K, P, SO<sub>4</sub>, B, organic matter, cation exchange capacity)<sup>13</sup>. Within each site several 1 m deep samples will be collected for metal analyses. Samplers will be used to collect runoff waters and sediments, these will be composited depending on the amount of runoff, dissolved metals in the waters and total recoverable metals in the runoff sediments will be determined, see table for a complete listing of the sampling schedule. Water samples high in arsenic will be analyzed for arsenic (III), the toxic arsenic species, by anodic stripping voltametry, US EPA Method 7063. DGT will be deployed along transects at the same time as soil sampling and each year a time dependence study will be setup to estimate K<sub>d</sub>'s (both conventional and with DGT).

### **Quality Assurance and Quality Control Statement:**

Our facility is a full **GLPS** (good laboratory practices standard) program and has successfully completed five **GLPS** audits within the last 18 months, in compliance with FIFRA, 40 CFR Part 160 and TSCA, CFR part 792. As a GLP facility, we have in place a standard operating procedures (SOP) manual and a quality assurance program plan<sup>14</sup>, both have withstood several external audits. We will adhere to the guidelines of our QA plan. A sampling of *some* of our QC goals as applicable to individual projects include: 10% of our field deployments will be duplicates, 3-5 point calibration and correlation coefficient of >0.98, fortification studies, certified reference materials, continuing analysis of blanks run at 10% of total samples, and formal

method detection limit study according to EPA standard procedures (40 CFR 136). The full QA plan was attached in the original proposal (not included here).

### **IMPLEMENTATION PLAN**

Sites at Hyslop (Willamette), Columbia Basin (Pendleton), Hermiston and Klamath were established summer/fall of 2003. Analytical methods are already established in our laboratory<sup>14</sup>. Sampling began in summer of 2003. Chemical analyses began shortly thereafter. Baseline data gathering is currently underway for 2003. All chemical and data analyses for the 2003 season will be completed by spring 2004. Post fertilizer samples will be pulled at each station, at Hyslop (Willamette), Pendleton (Columbia Basin) and Hermiston this will occur in the winter, at Klamath this will occur each spring. Replication will occur in from 2004- 2006, see attached spreadsheets. Annual reports for sampling, chemical analysis, and data analysis will be completed by summer of each subsequent year. A final report for the study will be completed by July 2007. Over 600 composite samples will be collected *each* year for elemental analyses (As, Cd, Pb, Ni & Hg) and As (III) as needed.

Each soil sample listed in the table represents a composite of 6-9 field samples. Sample collection will occur post-fertilizer application, and at harvest. As feasible, samples will be pulled at the same interval (days post application) at all sites so comparison will be relevant. Rain/weather data will be collected via www. Plant tissue will be collect at time of harvest at each research station, at HF, CBRES, and HES.

The crop schedule for Klamath will be potato, wheat, potato. The crop rotation at Pendleton will be wheat, fallow, wheat. The crop rotation at Hermiston will be wheat, potato, wheat. Wheat will be grown all three years at Hyslop. We will analyze wheat kernels on a dry weight bases. The human edible portion (tuber, wheat kernel) will be analyzed each year. Total samples listed in the tables are *approximate since in some years, at some sites, surface waters and ground waters may not be available*. TBD = to be determined. Soils will be pulled (one from each paired field) each yr for extended soil chemical characterization

The proposed project described here will ultimately:

1. provide data and analysis that will develop a better understanding of background levels of Cd, Pb, Hg, Ni, As, & As(III) in agriculturally relevant Oregon soils following fertilizer applications
2. provide data that will be more relevant to toxicity (bioavailability)
3. develop a better understanding of the rate of change of metals in soils under defined agricultural practices
4. allow environmental risk associated with fertilizer applications to be more accurately evaluated
5. provide both the seasonal and magnitude of contributions of bioavailable metals to surface waters
6. further establish the use of DGT probes for use in fieldwork to relate bioavailable metals &  $K_d$ 's
7. provide insight into water quality variability from fertilizer applications

The research proposed here will provide significant data from conventional analytical techniques at defined paired Oregon agricultural sites, typical agronomic practices and known fertilizer application rates. The data will provide the bases for answering questions of what are the impacts and risk from metals from fertilizer applications on Oregon soils. In addition, the research proposed here will provide significant insight into the bioavailability of metals at these paired sites and provide the bases for answering the questions of what are the biological and ecological risks of fertilizer applications on Oregon soils. This research proposed here provides a unique approach to establish links with conventional approaches combined with powerful insight into biologically relevant techniques.

### **SUMMER BACKGROUND sampling**

Field plots were setup at all stations August of 2003. Background samples were pulled after setting up the field plots. A total of 16 soil samples were pulled from each station, each sample was a composite of 6-9 auger samples. Auger samples were pulled randomly from within the each field plot. Four deep core sample

was taken at each station, except at Hyslop where a total of 16 deep core samples were taken. A total of 576 surface auger core samples were collected. These were composited to generate a total of 64 composite surface soil samples taken summer of 2003, (16 at each research station). A total of 28 deep core samples were taken. There was no surface water or irrigation water at any of the stations during sample collection summer of 2003. We are in the process of analyzed the surface soil and deep core samples.

#### **Applications:**

Fertilizer was applied at Hyslop and Hermiston in October of 2003; and at Pendleton in November of 2003. We anticipate that fertilizer will be applied at the Klamath station in May 2004. See below for general applications rates for each treatment and at each research station.

#### **Lime study at Willamette/Hyslop:**

The pH at the study site on the Hyslop farm was 7.2; therefore, normal agronomy practices would not add additional lime to such a soil. Because it is important that normal (typical) agronomy practices are used throughout the study, a paired lime study was not included for 2003. Should the soil pH fall at some point during the study we will re-evaluate the lime-paired study options original proposed. But liming a field that already has such a pH would be very non-typical.

#### **Project Coordination with other Researchers**

Dr. Gwen Johnson, Portland State University, and her research group will be accompanied our group during the site setup and baseline/background data collection August 2003. Sites were established and samples collected by both research groups. Subsequent sampling will most likely occur together, either during post application or harvest each year, although Dr. Johnson may pull samples occasionally at other times during the study. We will assist her staff as needed during field retrievals.

#### **Field Contacts at each Research Station:**

Hyslop Farm: Darly Ehrensing  
Columbia Basin: Steve Petrie & Karl Rhinehardt  
Klamath: Ken Rykbost & Brian Charlton  
Hermiston: Don Horneck & Tim Wienke

#### **CHANGES from original proposal and rational;**

Below is a listing of the changes that were made from the original proposal and justification:

- 1) A Site change was due to logistic requirements at the Malheur station. Malheur could not support the project. Hermiston was added; this was actually a good change since several stake holders mentioned the unique attributes of Hermiston (irrigation, soil type, etc.).
- 2) Another treatment level was added. Instead of a control and 1X and 2X, three treatments were setup. The extra treatment adds to the work and really gives us the chance to look at dose response with the extra dose point we will have. The extra treatment levels will provide a good deal of important data long term for the project.
- 3) Adding replicates of each treatment trial, randomized in a 4 X 4 grid. By reducing duplicates and increasing replicate at the field level this will provide the project with stronger statistics when the final numbers are under review. Although, it took more to get the replicates setup it will be worth the extra work when the data has even stronger statistical merit. We reduced some of the composite duplicates so in the end the sample numbers are nearly the same but we have 4 replicates in the field, overall a good change to the project.
- 4) The lime paired fields were dropped at least for 2003, the pH at Hyslop was quite high (good soil). So as long as the pH is good we will not run a lime paired study. The data would not have meant much since no one would lime a pH 7 field in the valley. Should the pH drop we will revisit this issue.
- 5) Modest changes in plot size, this is to accommodate station farm equipment. Makes no impact on the

study, it only affected the number of lbs of fertilizer that had to be prepared and delivered.

Columbia Basin Fertilizer Treatment Rates:

The fertilizer was delivered to the station fall of 2003. Two fertilizers were delivered one for the treatment fields, it is a 16-20-0 commercial fertilizer that is known to be rich in heavy metals. The heavy metal rich fertilizer will be marked for “**treatments plots**”. The control fertilizer is a homogeneous lot of 21-0-0-24(S). This control fertilizer will be marked for “**control plots**”. We want to use the same control fertilizer for better consistency at all locations. The control plots will approx. the same pounds as the treatment 1X plots. The treatment rates are listed in the table below. Extra fertilizer will be delivered to allow for calibration of application equipment. The control will be the same rate as treatment 1X.

The fertilizer was applied in October (2003) as well the wheat was planted. The wheat is several inches and looks good as of December 2003.

<b>Columbia Basin / Dry Winter</b>	<b>Plot Width</b>	<b>Plot Length</b>	<b>Total Plot Square Feet - 4 Reps</b>	<b>Pounds of N needed per acre</b>	<b>Pounds of N applied per plot</b>	<b>Pounds of 16-20- 0 Needed per plot</b>
Control - Rep 1						
Treat 1X - Rep 1	10	24	240	65	0.36	2.24
Treat 2X - Rep 1	10	24	240	130	0.72	4.48
Treat 3X - Rep 1	10	24	240	195	1.07	6.71
Control - Rep 2						
Treat 1X - Rep 2	10	24	240	65	0.36	2.24
Treat 2X - Rep 2	10	24	240	130	0.72	4.48
Treat 3X - Rep 2	10	24	240	195	1.07	6.71
Control - Rep 3						
Treat 1X - Rep 3	10	24	240	65	0.36	2.24
Treat 2X - Rep 3	10	24	240	130	0.72	4.48
Treat 3X - Rep 3	10	24	240	195	1.07	6.71
Control - Rep 4						
Treat 1X - Rep 4	10	24	240	65	0.36	2.24
Treat 2X - Rep 4	10	24	240	130	0.72	4.48
Treat 3X - Rep 4	10	24	240	195	1.07	6.71
						<b>53.72</b>

Fertilizer Treatment Rates Hermiston:

The fertilizer was delivered to the station fall of 2003. Two fertilizers were delivered one for the treatment fields, it is a 16-20-0 commercial fertilizer that is known to be rich in heavy metals. The heavy metal rich fertilizer will be marked for “**treatments plots**”. The control fertilizer is a homogeneous lot of 21-0-0-24(S). This control fertilizer will be marked for “**control plots**”. We want to use the same control fertilizer for better consistency at all locations. The control plots will approx. the same pounds as the treatment 1X plots. The treatment rates are listed in the table below. Extra fertilizer will be delivered to allow for calibration of application equipment. The control rate will be the same as the treatment 1X.

The fertilizer was applied November of 2003, wheat was planted. The crop looks as of December 2003.

<b>Hermiston/ Irrigated Winter</b>	<b>Plot Width</b>	<b>Plot Length</b>	<b>Total Plot Square Feet - 4 Reps</b>	<b>Pounds of N needed per acre</b>	<b>Pounds of N applied per plot</b>	<b>Pounds of 16-20- 0 Needed per plot</b>
Control - Rep 1						
Treat 1X - Rep 1	10	25	250	120	0.69	<b>4.30</b>
Treat 2X - Rep 1	10	25	250	240	1.38	<b>8.61</b>
Treat 3X - Rep 1	10	25	250	360	2.07	<b>12.91</b>
Control - Rep 2						
Treat 1X - Rep 2	10	25	250	120	0.69	<b>4.30</b>
Treat 2X - Rep 2	10	25	250	240	1.38	<b>8.61</b>
Treat 3X - Rep 2	10	25	250	360	2.07	<b>12.91</b>
Control - Rep 3						
Treat 1X - Rep 3	10	25	250	120	0.69	<b>4.30</b>
Treat 2X - Rep 3	10	25	250	240	1.38	<b>8.61</b>
Treat 3X - Rep 3	10	25	250	360	2.07	<b>12.91</b>
Control - Rep 4						
Treat 1X - Rep 4	10	25	250	120	0.69	<b>4.30</b>
Treat 2X - Rep 4	10	25	250	240	1.38	<b>8.61</b>
Treat 3X - Rep 4	10	25	250	360	2.07	<b>12.91</b>
Benchmark						<b>103.31</b>

Hyslop (Willametter) Fertilizer Treatment Rates:

The fertilizer was delivered to the station fall 2003. Two fertilizers were delivered one for the treatment fields, it is a 16-20-0 commercial fertilizer that is known to be rich in heavy metals. The heavy metal rich fertilizer will be marked for “**treatments plots**”. The control fertilizer is a homogeneous lot of 21-0-0-24(S). This control fertilizer will be marked for “**control plots**”. We want to use the same control fertilizer for better consistency at all locations. The control plots will approx. the same pounds as the treatment 1X plots. The treatment rates are listed in the table below. Extra fertilizer will be delivered to allow for calibration of application equipment.

Fertilizer was applied October 2003, wheat was planted. The crop as of December 2003 looks good.

	<b>Plot Width</b>	<b>Plot Length</b>	<b>Total Plot Square Feet - 4 Reps</b>	<b>Pounds of N needed per acre</b>	<b>Pounds of N applied per plot</b>	<b>Pounds of 16-20-0 Needed per plot</b>
<b>Hyslop - Dry Winter</b>						
Control - Rep 1						
Treat 1X - Rep 1	20	35	700	160	2.57	<b>16.07</b>
Treat 2X - Rep 1	20	35	700	320	5.14	<b>32.14</b>
Treat 3X - Rep 1	20	35	700	480	7.71	<b>48.21</b>
Control - Rep 2						
Treat 1X - Rep 2	20	35	700	160	2.57	<b>16.07</b>
Treat 2X - Rep 2	20	35	700	320	5.14	<b>32.14</b>
Treat 3X - Rep 2	20	35	700	480	7.71	<b>48.21</b>
Control - Rep 3						
Treat 1X - Rep 3	20	35	700	160	2.57	<b>16.07</b>
Treat 2X - Rep 3	20	35	700	320	5.14	<b>32.14</b>
Treat 3X - Rep 3	20	35	700	480	7.71	<b>48.21</b>
Control - Rep 4						
Treat 1X - Rep 4	20	35	700	160	2.57	<b>16.07</b>
Treat 2X - Rep 4	20	35	700	320	5.14	<b>32.14</b>
Treat 3X - Rep 4	20	35	700	480	7.71	<b>48.21</b>
						<b>385.67</b>

Klamath Fertilizer Treatment Rates:

The fertilizer will be delivered to the station prior to treatment each year, spring 2004 (probably application will be May depending on weather). Two fertilizers will be delivered one for the treatment fields, it is a 16-20-0 commercial fertilizer that is known to be rich in heavy metals. The heavy metal rich fertilizer will be marked for “**treatments plots**”. The control fertilizer is a homogeneous lot of 21-0-0-24(S). This control fertilizer will be marked for “**control plots**”. We want to use the same control fertilizer for better consistency at all locations. The control plots will approx. the same pounds as the treatment 1X plots. The treatment rates are listed in the table below. Extra fertilizer will be delivered to allow for calibration of application equipment.

<b>Klamath / Irrigated Spring</b>	<b>Plot Width</b>	<b>Plot Length</b>	<b>Total Plot Square Feet - 4 Reps</b>	<b>Pounds of N needed per acre</b>	<b>Pounds of N applied per plot</b>	<b>Pounds of 16-20-0 Needed per plot</b>
Control - Rep 1						
Treat 1X - Rep 1	10.7	25	267.5	120	0.74	<b>4.61</b>
Treat 2X - Rep 1	10.7	25	267.5	240	1.47	<b>9.21</b>
Treat 3X - Rep 1	10.7	25	267.5	360	2.21	<b>13.82</b>
Control - Rep 2						
Treat 1X - Rep 2	10.7	25	267.5	120	0.74	<b>4.61</b>
Treat 2X - Rep 2	10.7	25	267.5	240	1.47	<b>9.21</b>
Treat 3X - Rep 2	10.7	25	267.5	360	2.21	<b>13.82</b>
Control - Rep 3						
Treat 1X - Rep 3	10.7	25	267.5	120	0.74	<b>4.61</b>
Treat 2X - Rep 3	10.7	25	267.5	240	1.47	<b>9.21</b>
Treat 3X - Rep 3	10.7	25	267.5	360	2.21	<b>13.82</b>
Control - Rep 4						
Treat 1X - Rep 4	10.7	25	267.5	120	0.74	<b>4.61</b>
Treat 2X - Rep 4	10.7	25	267.5	240	1.47	<b>9.21</b>
Treat 3X - Rep 4	10.7	25	267.5	360	2.21	<b>13.82</b>
Benchmark						
						<b>110.54</b>

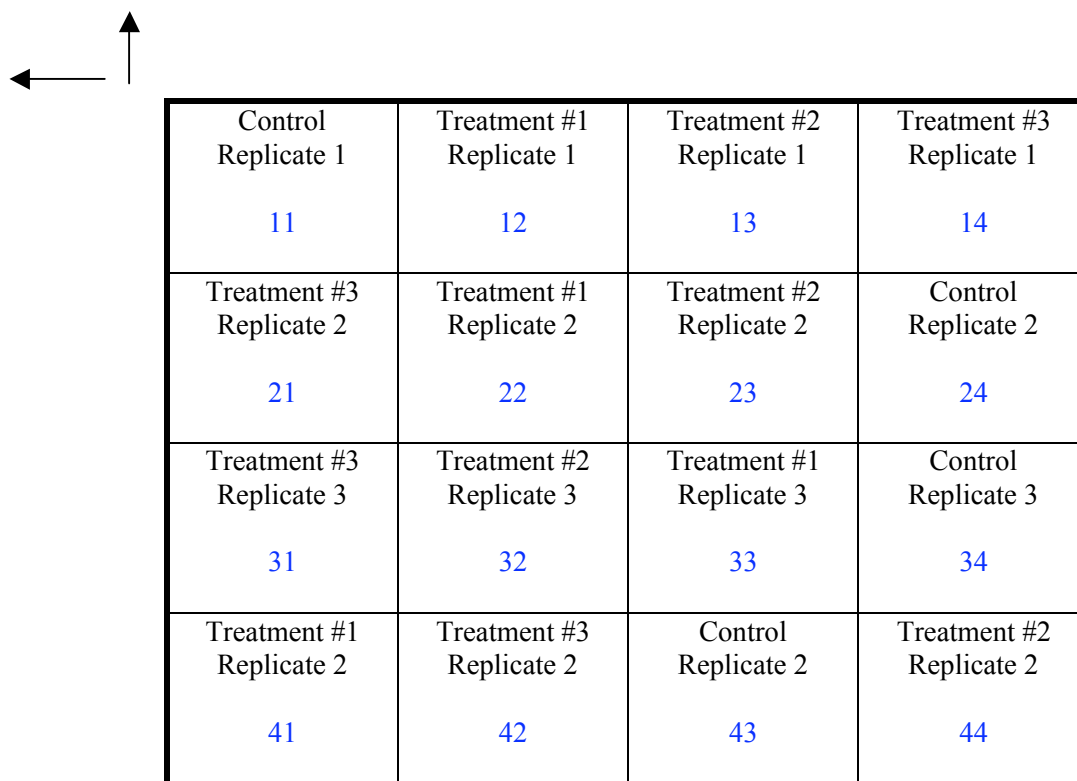
### Plot Design

PLOTS: are approximately 10 feet wide by 24 ft long, slight modifications were made depending on the research station equipment needs. All areas have been adjusted to reflect any change this might have had on fertilizer application rates. There are 16 plots, setup as shown in the figure below, approximately 0.1 ac.

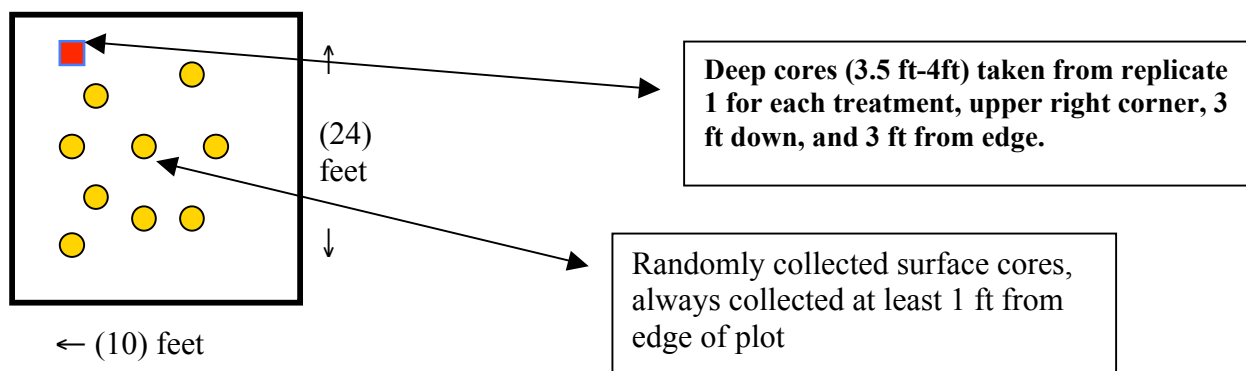
One composite surface sample will be pulled from each plot, EACH surface soil sample will be a composite of 6-9 randomly collected (0-20cm ) cores. Appropriate borders to the fields are required (*10 and 10 ft setup used*). A deep sample (3.5ft-4 ft) will be pulled from one replicate for each treatment. Deep cores collected from each plot, pulled from the upper right corner 3 feet down three feet from edge.

Setbacks are 10 and 10ft,

Direction ↑



Field uniformly seeded, fertilizer broadcast, rates determined by ODA, fertilizer provided and delivered to research station by ODA, fertilizer application and agronomy provided by station.



- 
- <sup>1</sup> Alexander, M. "Aging, Bioavailability, and Overestimation of Risk from Environmental Pollutants" (2000) *Environ. Sci. Tech.* 34, 20, 4259-4265.
- <sup>2</sup> US EPA, Office of Water, National Recommended Water Quality Criteria-Correction (1999) EPA 822-Z-99-001, National Center for Environmental Publ and Information, Kenwood Rd, Cincinnati, OH 45242
- <sup>3</sup> Nowell, & Resek, "National Standards and Guidelines for Pesticides-Water Sediment and Aquatic Organisms: Application to Water-Quality Assessments" (1994) *Rev. Env. Contam & Toxicol* 140, 1-164.
- <sup>4</sup> Campbell, P.G.C. "Interactions between trace metals and organisms: critique of the free-ion activity mode. In: A. Tessier & D.R. Turner (Eds) *Metal Speciation and Bioavailability in Aquatic Systems*. Wiley & Sons, NY, NY 1995, p 45-102.
- <sup>5</sup> Locicero, F., Jackson, W.F., Pergola, P.M., Brosnan, T.M., Hansen, D.J., Thrusby, G.B., Allen, H.E., & Lewis, D.A. "Development of Site-Specific Copper Criteria for a NY/NJ Harbor" (1998) in H.E. Allen, A. W. Garrison, & G.W. Luther, III (EDs), *Metals in Surface Waters*, S. Bear Press, Chelsea, MI, (5), 92-105.
- <sup>6</sup> Adapted from: Clark, J.R., Bland, J.A., Harrass, M.C., Brown, S.S., Pittinger, C.A., Stahl, R.G., "Use of Bioavailability Factors in Ecological Risk Assessment" Poster presented at 1999 Annual SETAC mtg.
- <sup>7</sup> Davison, W., Hooda, P. Zhang, H. and Edwards, A. C. (2000) DGT measured fluxes as surrogates for uptake of metals by plants. *Advances in Environ. Res.*, Vol. 3 (4), 550-555
- <sup>8</sup> Zhang, H., Davison, W., Knight, B. and McGrath, S. (1998). In situ measurement of solution concentrations and fluxes of trace metals in soils using DGT. *Env. Sci. Technol.* 32, 704-71
- <sup>9</sup> Zhang, H., Zhao, F. J., Sun. B., Davison, B. and McGrath, S. P. (2001) A new method to measure effective soil solution concentration predicts Cu availability to plants. *Env. Sci. Technol.*, 35, 2602-2607.
- <sup>10</sup> Gaskin, J.W. Brobst, R.B. Miller, W. Tollner, E., "Long-term biosolids applications effects on metal concentration in soil and bermudagrass forage" (2003) *J. Envir. Qual.* 32, 146-152
- <sup>11</sup> Anderson, Kim A. Analytical Techniques for Inorganic Contaminants, AOAC INTERNATIONAL, Gaithersburg, MD, 1999 (193 pages) ISBN 0-935584-65-X.
- <sup>12</sup> Anderson, K.A, Isaacs, B, Tracy, M, and Moller, G; "Cold Vapor Generation for ICPAES Analysis Part 3: Mercury" *J. Assoc. Off. Analytical Chemists* 1994, 77, 2, 473-480
- <sup>13</sup> Rhoades, J.D. 1982, . Page (ed.), *Methods of Soil Analysis, Part 2, Agronomy* 9:173-174.
- <sup>14</sup> Food Safety & Environmental Stewardship Quality Assurance Program Plan, Standard Operation Procedures Manual and Standard Analytical Methods Manual, 1999, Oregon State University, Corvallis, Oregon