5-4-2009

Prediction of Persistence of Fertilizer-derived Cadmium in Oregon Agricultural Soils using Equilibrium Modeling and Fertilizer Release Kinetics

Fungai Mukome
Portland State University

Recommended Citation
Mukome, Fungai, "Prediction of Persistence of Fertilizer-derived Cadmium in Oregon Agricultural Soils using Equilibrium Modeling and Fertilizer Release Kinetics" (2009). *Dissertations and Theses.* Paper 6152.
https://doi.org/10.15760/etd.8012

PREDICTION OF PERSISITENCE OF FERTILIZER-DERIVED CADMIUM IN OREGON AGRICULTURAL SOILS USING EQUILIBRIUM MODELING AND FERTILIZER RELEASE KINETICS

by

FUNGAI MUKOME

A dissertation submitted in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY
in
ENVIRONMENTAL SCIENCES AND RESOURCES

Portland State University
2009

DISSERTATION APPROVAL

The abstract and dissertation of Fungai Mukome for the Doctor of Philosophy in Environmental Sciences and Resources were presented May 4, 2009, and accepted by the dissertation committee and the doctoral program.

COMMITTEE APPROVALS:

William Fish, Chair

[redacted]

Robert B. Perkins

[redacted]

Trygve Steen

[redacted]

Alan Yeakley

[redacted]

Dean Atkinson
Representative of the Office of Graduate Studies

DOCTORAL PROGRAM APPROVAL: [redacted]

Aslam Khalil, Director
Environmental Sciences and Resources
Ph.D. Program

ABSTRACT

An abstract of the dissertation of Fungai Mukome for the Doctor of Philosophy in Environmental Sciences and Resources presented May 4, 2009

Title: Prediction of persistence of fertilizer-derived cadmium in Oregon agricultural soils using equilibrium modeling and fertilizer release kinetics

Organic farming has become a multimillion dollar industry and while much emphasis is put on subsequent fertilizer inputs onto these fields, very little consideration is given to the prior fertilization activities of these soils. For a farm to be certified organic it means no harmful chemicals, have been applied for at least three years.

The overall hypothesis tested by this research was that equilibrium adsorption models can adequately represent the behavior of fertilizer-derived cadmium in Oregon agricultural soils and that such model results can be easily incorporated into risk assessment models, transport study models and persistence studies for organic or other sustainable farming considerations. Soil chemistry and soil characterization were used to calculate the doubling time and mass flux of cadmium-derived fertilizer in loamy and sandy agricultural soils with a rich farming history. We also investigated the processes controlling the release of fertilizer-derived cadmium in the micro scale zone around the fertilizer to determine if a local equilibrium model was appropriate for explaining cadmium behavior in agricultural soils.

The Kd values and adsorption trend of the soil sites was Pendleton> Klamath> Hyslop> Hermiston. The cadmium Kd values were most correlated to the pH of the soils (R^2=0.94). The buffer capacity of the soils was highly correlated to the clay content ($R^2 = 0.98$). The adsorption coefficients were important for predicting the doubling times of cadmium in the soils (Hermiston, 4.8yrs > Hyslop, 3.7yrs > Klamath, 2.9 yrs> Pendleton 2.3 yrs). Precipitation was not the most important parameter in predicting the mass loss due to leaching after three years (46.2, 19.9, 16.7 and 8.3 mg/ha-yr for Hyslop, Hermiston, Pendleton and Klamath respectively). The period was found to have a negligible effect on the background concentrations of cadmium in agricultural soils.

Scanning electron microscopy, X-ray diffraction and column displacement experiments were used to investigate the fertilizer kinetics of fertilizer-derived cadmium and the processes controlling the release of fertilizer-derived cadmium were found to be a Cd-phosphate phase, possibly cadmium hydroxyapaptite, and iron oxides. The release of Cd from phosphate fertilizer was slow so a local equilibrium model was appropriate for agricultural soils.

"...for only rarely have we stood back and celebrated our soils as something beautiful, and perhaps even mysterious. For what other natural body, worldwide in its distribution, has so many interesting secrets to reveal to the patient observer? "- *Les Molloy, 1988*

Dedication

To mom and dad; my siblings; and my loving wife Nathalie, thank you all for your unwavering support and belief. This is for you.

Acknowledgments

I would like to thank my advisor, Professor William Fish for his support and words of wisdom that kept body and soul together at all stages of this research. His encouragement, insight, even temperament and work ethic have been inspirational and made this research a great learning experience. It has been a pleasure working with you.

To my advisory committee Professors D. Atkinson, R. Perkins, T. Steen and A. Yeakley, thank you for the constructive criticism and ideas that definitely improved the quality of the final product. I acknowledge Drs. Burns, Hugo and Johnson for advice, support and guidance at key stages of this research.

I would also express my appreciation to my lab family: Anjan, Julie, Kiara, Mia, Mike and Shahrzad, for putting up with my thoughts and musings and still becoming my friends. Each one of you has added much to my learning experience and made it all the more worthwhile.

To Keith Bellingham and Stevens Water Monitoring, who helped me with instrumentation for part of my dissertation, thank you for the opportunities and support. I would also like to acknowledge the Oregon Department of Agriculture for the research grant that funded most of my research.

To my family and wife Nathalie, I thank you for putting up with all the difficulties and hardships over the years. I appreciate all the love, encouragement and prayerful support without which I would not have made it this far.

Lastly, I thank God for his amazing favor and blessings on my life. I am able to do all things through Christ who strengthens me.

Table of Contents

List of Tables

List of Figures

Abbreviations

AAS – Atomic Adsorption Spectrophotometer

AITC – Agriculture in the Classroom

Cd – cadmium

CEC – cation exchange capacity

DHHS- Department of Health and Human Services

DTPA - Diethylenetriaminepentaacetic Acid

EC – electrical conductivity

EDS- Energy dispersive spectroscopy

EDX- Energy dispersive X-ray spectroscopy

EDTA – Ethylenediaminetetraacetic Acid

ICP-MS – Inductively Coupled Plasma- Mass Spectrometer

kg – kilograms

L- liters

mg – milligrams

mM – millimoles

MΩ - megaohm

NRCS – Natural Resources Conservation Services

ODA - Oregon Department of Agriculture

OECD - Organization for Economic Co-operation and Development

OM – organic matter

Pb – lead

pH – the negative $\log_{10}$ of the hydrogen ion activity

ppb- parts per billion. Unit of concentration equal to ng/g or ug/kg.

ppm- parts per million. Unit of concentration equal to ug/g or mg/kg.

PUF – Plant uptake factor

PVC – polyvinyl chloride

PWT – perched water table

PZC – point of zero charge
PZNPC – point of zero net proton charge
PZSE – point of zero salt effect
RMSE – Root mean standard error
rpm- revolutions per minute
SEM- Scanning electron microscopy
USEPA – United States Environmental Protection Agency
USGS - United States Department of Geological Survey
WHO – World Health Organization
WRCC – Western Regional Climate Center
WSDA - Washington State Department of Agriculture
XRD – X-ray Diffraction
Zn – Zinc

Chapter One

Background

1.0 Statement of Purpose

The overall hypothesis tested by this research was that equilibrium adsorption models can adequately represent the behavior of fertilizer-derived cadmium in Oregon agricultural soils and that such model results can be easily incorporated into risk assessment models, transport study models and persistence studies for organic or other sustainable farming considerations. The surface chemistry of agricultural soils, adsorptive behavior and fertilizer kinetics of fertilizer-derived cadmium were used to test this hypothesis, as well as a series of sub-hypotheses that are presented in subsequent chapters.

1.1 Introduction

1.1.1 Metal Contamination of Phosphate Fertilizers

In July 1997 the Seattle Times ran a series of articles entitled "Fear in the Fields" that highlighted the use of recycled waste in fertilizer and brought to the fore the need for standards in fertilizer composition (Wilson, 1997). By March 1998 the Fertilizer Regulation Act (Washington State Senate, 1998) was passed into law making Washington the first US state to impose standards for toxic metals in fertilizers. The Act set limits for the levels of nine heavy metals in fertilizers, namely, arsenic (**As**), cadmium (**Cd**), cobalt (**Co**), mercury (**Hg**), molybdenum (**Mo**), nickel (**Ni**), lead (**Pb**), selenium (**Se**), and zinc (**Zn**). Since then, several other states have taken similar strides to impose restrictions of heavy metal levels in fertilizers. Oregon passed a law in 2001 (House Bill 3815) that required all fertilizer sold in the state to have packaging showing the levels of As, Cd, Hg, Ni and Pb. The Oregon Department of Agriculture also began work to set numerical limits for these metals by 2006 based on environmental assessments (ODA White Paper, 2002). The current limits are laid out in 603-059-0100 which stipulates that if a product has a guaranteed analysis of available phosphate (P_2O_5), for each percent of P_2O_5 guaranteed, the maximum allowed level of a metal, expressed in parts per million (ppm), must not exceed: 9 ppm (As), 7.5 ppm (Cd), 43 ppm (Pb), 0.7 ppm (Hg) and 175 ppm (Ni). These limits are reviewed every three years as stipulated by ORS 633.362(11) (ODA).

Regulation of phosphate fertilizers has generated considerable interest due to cadmium, a trace metal and impurity of this fertilizer that can be present in substantial amounts, depending on the parent rock. An accumulation of cadmium in soil can occur due to the long term use of phosphate fertilizers, although this does not always lead to a bio-accumulation of cadmium in plants (Mortvedt et al., 1987; Rogowoski et al., 1998). Williams and David (1976) showed about 80% of the cadmium added as phosphate fertilizer over a 20 year period accumulated in the top 7.5 cm of soil except when the soils were podozols. Continuous fertilization with a high rate of triple superphosphate (1,175 kg P ha^{-1} yr^{-1}) over a period of 36 years resulted in a 14-fold increase in cadmium content of the surface soils (Singh 1994). Jones et al. (2002), however, observed no increase in trace metals in fertilized Montana soils over a similar time period. In 1980, Mulla et al. showed that after a 36 year period, cadmium accumulated in the top 15 cm of the soil and that phosphate was more mobile than the cadmium. A Washington State University study concluded that there was a potential for metals to increase in soil with time, especially cadmium. They also showed that, while extractable cadmium correlated well with lettuce-retained cadmium, it accounted for only 3% of the total cadmium applied to the soil (WSDA, 2001).

Studying the use of phosphate fertilizers in the USA gives ample reason for alarm. Application of phosphate fertilizer in the US rose exponentially from 1960 to 1980 and has since plateaued at about 3.5 million tons per year (Fig.1.1). Approximately 120 million tons of fertilizer have been applied over the last 45 years. Assuming the fertilizer had an average of 50mg Cd per kg of fertilizer (Davister, 1996 calculated the European average to 60mg/kg) then the amount of cadmium introduced into the agricultural fields of the US from diammonium phosphate alone over this time period was about 6000 tons.

Most human exposure to cadmium comes from ingestion and a model proposed by Van Assche (1998) ascribed the following relative sources of cadmium in order of relative importance:

Phosphate Fertilizers	41.3%,
Fossil Fuel Combustion	22.0%,
Iron & Steel Production	16.7%,
Natural Sources	8.0%,
Non-ferrous metals	6.3%, and
Cement Production	2.5%.

The relative importance of phosphate fertilizers as a source of cadmium clearly showed the importance of knowing the fate of fertilizer-derived cadmium.

1.1.2 Phosphate Rock Composition

The term phosphate rock is used to describe naturally occurring mineral formations containing a high concentration of phosphate minerals, about 35-40 percent. About 80 percent of world phosphate rock production is derived from deposits of sedimentary marine origin, while some 17 percent is derived from igneous rocks and their weathering derivatives and the remainder comes from residual sedimentary and guano-type deposits (Zapata and Roy, 2004). The primary occurrence of phosphate rocks is as apaptite minerals with the most common variants being Fluorapaptite $Ca_{10}(PO_4)_6(F,OH)_2$ and Francolite $Ca_{10}(PO_4)_{6-x}(CO_3)_x(F,OH)_{2+x}$ (McClellan and Van Kauwenbergh, 2004). The world's largest sources of sedimentary phosphate rock are in northern Africa, China, the Middle East, and the United States (USGS, 2007).

Igneous deposits of phosphorus are exploited in the Russian Federation, Canada, South Africa, Brazil, Finland and Zimbabwe but also occur in Uganda, Malawi, Sri Lanka and several other locations. These deposits usually contain varieties of fluorapatite that are relatively un-reactive and are the least suitable for direct application. The weathering products of igneous and sedimentary apatites (iron and aluminium phosphate minerals) are generally not useful for direct application in agriculture in their natural state. The higher the phosphate content as apatite, expressed as (P_2O_5), the greater the economic potential of the rock. Important factors in the chemical conversion of phosphate rock to fertilizer are the content of free carbonates, iron (Fe), aluminum (Al), magnesium (Mg) and chloride (Van Kauwenbergh and Hellums, 1995).

The cadmium content varies considerably as can be seen in Table 1-1. Phosphate rock from North Africa and island sources tends to have higher cadmium levels than mainland sources. Igneous phosphate rock typically has much lower concentration of cadmium (< 1mg Cd /kg P) while cadmium sedimentary phosphate rock concentrations range from 38 mg Cd /kg to 380 mg Cd /kg P (UNIDO, 1998). At an OECD workshop held in Stockholm (1995), several papers were presented addressing the issue of reducing cadmium content in phosphate fertilizers (OECD, 1996). Several ideas were proposed including direct extraction of cadmium from the phosphate rock, co-crystallization of cadmium in $CaSO_4$ from phosphoric acid and use of ion-exchange resins selective for cadmium. Most of the methods were deemed financially unviable so better methods are still being sought. The naturally high impurity levels are of concern because research has shown the fertilizer manufacturing process retains about 80% of the cadmium in the parent phospherite rock (Il'in and Kiperman, 2001).

1.1.3 Cadmium Chemistry

Cadmium occurs in the earth's crust at a concentration of 0.1– 0.5 ppm and is commonly associated with zinc, lead, and copper ores (DHHS, 2008). Natural soil background levels of cadmium have been determined to be in the range of 0.01 mg/kg to 0.7 mg/kg (Lindsay, 1979), much lower than the current Oregon clean-up standard for residential sites of 100 mg/kg. Cadmium (Cd) is a soft, silver white metal that has an atomic mass of 112.41g and an element number of 48. It is in Group IIb on the Periodic table, the same group as zinc and mercury. Its melting point and boiling points are 320.9 °C and 765 °C respectively. Cadmium has 8 isotopes namely Cd^{106}, Cd^{108}, Cd^{110}, Cd^{111}, Cd^{112}, Cd^{113}, Cd^{114} and Cd^{116}. Cd^{112} and Cd^{114} are the most abundant occurring at 24.07% and 28.86% respectively. Its electronic configuration is [Kr] $4d^{10}$ $5s^2$ and thus its preferred valence state is Cd^{2+} after the loss of the relatively low energy $5s^2$ electrons. The radius of the Cd^{2+} ion is 0.97 Å while that for Ca^{2+} is 0.99Å. Cd also has an identical electronegativity of 1.7 to zinc (Zn) (Cotton and Wilkinson, 1988).

1.1.4 Cadmium Speciation

In aqueous environments cadmium is typically present as the following species Cd^{2+}, $CdCl^+$, $CdCl_2$, $CdCl_3^-$, $CdOH^+$, $CdHCO_3^+$, CdS, $CdHS^+$, $Cd(HS)_2$, $Cd(HS)_3^-$, $Cd(HS)_4^2$, Cd(s), $CdCO_3(s)$ and $Cd(OH)_2(s)$ with the exact composition depending on pH and redox conditions (Morel, 1983). The chemical speciation of cadmium determines its bioavailability and this in turn is affected by pH, carbonate, organic carbon, calcium, sulfur, zinc and chloride levels (Jackson and Alloway, 1992; McLaughlin et al., 1994a). High pH, high calcium and elevated carbonate or reduced sulfur levels inhibit cadmium uptake whereas high chlorides, low zinc levels and high concentrations of some organic compounds enhance cadmium uptake by plants. The main species in the pH range typical of natural soils is Cd^{2+} with precipitation of cadmium salts only occurring at high pH and in the presence of high concentrations of CO_3^{2-}, S^{2-} and PO_4^{3-} ions. Several methods have been used to determine the species of cadmium in soil solutions. They include dialysis, gel filtration, centrifugation and ultra filtration but there is considerable difficulty in resolving the species (Onyatta, 1997).

1.1.5 Total and Bio-available Cadmium

Extractants of differing strength have been used to differentiate between total cadmium and bio-available cadmium. Total cadmium is a measure of the cadmium present in a soil and typically involves a complete digestion. The bio–available cadmium fraction is the cadmium that can be taken up by the plants and is made up mainly of the free metal ion, Cd^{2+}. Geo-analytical methods using strong acid extractants such as concentrated nitric acid and hydrofluoric acid give the total cadmium content of a soil. However, using much weaker acid mixtures and chelating agents may give a more accurate representation of bio-available cadmium (Zelazny, 1996). EDTA, DTPA, dilute hydrochloric acid, double acid extraction (using 0.05N HCl and 0.25N H_2SO_4) and $CaCl_2$ solutions have been used to estimate bio-available cadmium (Baker and Amacher, 1982).

1.1.6 Cadmium Toxicity and Human Health

Dietary intake is the largest source of cadmium exposure for nonsmoking adults and children in the United States. The estimated daily intakes of cadmium in nonsmoking adult males and females in the United States are 0.35 and 0.30 μg Cd /kg per day, respectively. Vegetables such as lettuce and spinach as well as potatoes and grains contain relatively high values of cadmium and people who regularly consume shellfish and offals (liver and kidney) have increased cadmium exposure. Direct measurement of cadmium levels in body tissues confirms that smoking roughly doubles the cadmium body burden. It has also been found that farm families are the people most at risk due to exposure in the diet and in the field (DHHS, 2008).

Cadmium-induced itai –itai disease in Japan brought the human toxicity of this metal to prominence (Jarup et al., 1998). It was discovered that cadmium can be ingested or inhaled by both animals and humans where it gradually accumulates in the liver and kidneys leading to renal tubular damage, formation of stones in the kidneys, disturbed calcium metabolism, hypercalciuria and bone deterioration. Acute levels of cadmium ingestion can induce lung and prostrate cancer (Jarup et al., 1998) and cadmium is known to replace zinc, a common cofactor in some enzymes, leading to high blood pressure and kidney damage (Jarup et al. 1998). Cadmium has also been shown to destroy testicular tissue and red blood cells (DHHS, 2008). It also stores in the liver forming a metallothionein cadmium complex that can be absorbed by the kidneys in the proximal tubule cells (Onyatta, 1997). The half-life of cadmium in humans is believed to be 10-35 years (WHO, 2003).

1.1.7 Risk Modeling as a tool in rational cadmium regulation

Over the last twenty years setting of regulatory health standards using formal risk based modeling has replaced arbitrarily set “safe levels” of contaminants in fertilizers. These old standards have been found to be inadequate as they often over-estimate the risk associated with the contaminants as they did not consider some loss pathways and also often overestimated the plant uptake factor (PUF) and human exposure. The partition coefficients used were often not agriculturally relevant and variability in soils type, application rates, precipitation and crop type were also not considered. The old standards also tended to look at the total input of contaminants and not consider fate.

The formal risk based models attempt to incorporate all the variables and model risk more accurately. The models also try to reflect the economic and practical aspects of implementing these standards (Weinberg, 2001). Risk is defined as the probability of an adverse health effect (Curtis and Smith, 2002) with the desired level of protection being selected by the modeler. The use of models allows for formulae that can be rearranged to account for variability in other model parameters and this also lends very well to standardized results that can be readily converted to reflect actual changes in a variable by multiplication by a factor (Curtis and Smith, 2002).

To come up with the recommended levels authorities must be able to accurately model the behavior of a contaminant in different media and generate risk based concentrations (RBC). An RBC is the maximum "acceptable" level for a given metal in a fertilizer product at 1% of the nutrient level (P_2O_5, zinc, iron, manganese) (Weinberg, 2001). There are two approaches to determine these levels: the first considers the total mass of contaminant applied to an area or a unit time and the second considers the maximum concentration of a contaminant in a product. The first approach forward calculates potential risks from fertilizers based on concentrations of metals present in fertilizers (DHHS, 2008) and was used by the State of Washington (1998), USEPA (1999) and Canada in determining risk assessment levels. It is called the deterministic approach and uses the high-end estimates for model parameters (Curtis and Smith, 2002). The latter, the probabilistic approach, uses Monte Carlo simulations that take into account the variability in the risk model equation. Repeated simulations give different RBC values and these results form a frequency distribution from which a value is selected that is health protective. This value is typically a value that is greater than 10% of the values simulated and is called the 90% percentile. This was the approach of the California Department of Food and Agriculture (CDFA) study. RBCs are probability based and risk is computed as a percentile possible exposure scenario based on the variability of the inputs with the 90th percentile being commonly chosen (Weinberg, 2001).

Both approaches use similar equations and only differ in the interpretation of their results. Risk assessment is very complex and has a lot of uncertainty associated with it due to the considerable number of variables (USEPA, 1999). The fate and transport component includes modeling for fate in air, soil, surface water and the food chain. The other components are human exposure and toxicity and fertilizer composition and application rates.

Similar work has been done in Europe with the European Union adopting the following phased in EU-wide limit on cadmium concentrations in fertilizers: 60 mg Cd /kg P_2O_5 by 2006; 40 mg Cd/kg P_2O_5 by 2010; and finally 20 mg Cd /kg P_2O_5 by 2015. Some countries like Belgium have even more stringent limits on all fertilizers, 2.5 mg Cd /kg dry weight of fertilizer. The Netherlands has the lowest limit for compost and "very clean" compost, 1.25 mg/kg and 0.7 mg/kg, respectively (Hutton and de Meeus, 2001).

Chapter Two

Persistence of Fertilizer-Derived Heavy Metals in Oregon Soils and its Implications for Sustainable Farming

Abstract

According to the USDA, organic farming is one of the fastest growing segments in US agriculture this past decade. Organic farming has become a multimillion dollar industry and while much emphasis is put on the fertilizer inputs onto these fields, very little consideration is given to the prior fertilization activities of these soils and the associated effect of cadmium accumulation from phosphate fertilizer application. The goal of this study was to determine the importance of soil characterization, soil chemistry, and adsorption coefficients on the prediction of the persistence of cadmium-derived fertilizer in agricultural soils. Persistence of heavy metals soil is important for risk assessment modeling, organic farming and transport studies.

The buffer capacity of the soils was 17.8, 12.8, 9.2 and 7.4 cmol/kg/ pH unit for Hyslop, Pendleton, Klamath, and Hermiston respectively. This was highly correlated to the clay content ($R^2 = 0.98$). The K_d values (in parentheses) and adsorption trend of the soil sites was Pendleton (277.6 L/kg) > Klamath (167.5 L/kg)> Hyslop (195.0 L/kg)> Hermiston (93.8L/kg). The cadmium K_d values were most correlated to the pH of the soils ($R^2= 0.94$). The adsorption coefficients were important for predicting the doubling times of cadmium in the soils (Hermiston, 4.8 yrs > Hyslop, 3.7 yrs > Klamath, 2.9 yrs> Pendleton 2.3 yrs). Soil texture was the most important parameter in predicting the mass loss due to leaching (46.2, 19.9, 16.7

and 8.3 mg/ha-yr for Hyslop, Hermiston, Pendleton and Klamath respectively). Based on the modeling results, the three year waiting period for certification was predicted to have a negligible effect on reducing background concentrations of cadmium in agricultural soils.

2.0 Statement of Purpose

The goal of this study was to determine if laboratory soil characterization and equilbrium modeling could successfully predict the adsorptive behavior of cadmium and lead on agricultural soils. We also tested the hypothesis that, at the probable levels of fertilizer-derived cadmium in soil, adsorption essentially obeys a linear isotherm. A site-specific partition coefficient can be used to assess the expected accumulation and leaching of cadmium in agricultural soils under conditions of linear-equilbrium adsorption.

2.1 Literature Review

2.1.1 Oregon Agriculture

Agriculture is an important part of the Oregon economy with total farming sales topping five billion dollars in 2007. Oregon ranks second only to California in diversity of commodities with 220 on offer and its main two commodities, greenhouse and nursery products and grass seed, are both industries that require considerable fertilization for maximum yield (ODA). Oregon is the nation's leader in production of boysenberries, hazelnuts, loganberries, black raspberries, grass seed, dried herbs, crimson clover and Christmas trees (ODA, 2008). Oregon has over 2000 soil types in nine growing regions of which seven are agricultural (AITC). A wide variety of crops are grown at the four sites studied (Table 2-1).

Despite its productivity, the average rainfall in Oregon ranges from < 20 mm to > 500 mm per year (WRCC). About 78% of the water usage of Oregon goes to irrigation and this heavy reliance on irrigation has implications for leaching of nutrients and contaminants (AITC).

The importance of organic farming in Oregon has seen steady growth, Oregon ranks eighth in the United States in organic certified operations from 1998 to 2004 there was a 130% increase in acreage under organic farming within the state (Portland Business Journal, 2005). By 2008, over 115 500 acres were certified as organic (Kirby and Granatstein, 2008). For a farm to be certified organic it means no harmful chemicals have been applied for at least 3 years; the farmer and processor have annual certification inspections; detailed records of farming practices are kept and ecologically-friendly methods and substances are used to improve the soil and control pests (Tri-county Farm, 2009).

2.1.2 Agricultural Soils and Heavy Metals

Studies have shown heavy metals may accumulate in soils over time (Mulla et al., 1980; Abollino et al., 2002). Continuous use of phosphate fertilizers, addition of waste water bio-solids, atmospheric deposition and the presence of other anthropogenic sources such as smelting plants can lead to accumulation of heavy metals in soils. In Washington State, Rogowski et al. (1998) found fertilizer to increase soil concentrations of heavy metals (cadmium and zinc). Increases in cadmium concentration were found for three out of six fertilizer application sites studied in Alabama. However accumulation is not always observed. The three other sites studied in Alabama and a study in Illinois did not show an appreciable accumulation despite decades of phosphate fertilizer use (Mortvedt, 1987). A study of three soils from Montana, following 20 years of fertilization and cropping, also showed no significant increase in available metals (Jones et al., 2002).

Holmgren et al. (1993) found that background levels of cadmium in 3045 U.S. agricultural soils ranged from < 0.01 to 2 mg/kg with a mean of 0.265 mg/kg. Eighty eight of the soils studied were from the northwestern, south central and southeastern parts of Oregon. In a similar study in Australia, McLaughlin et al. (1996) found a range of 0.05 to 1 mg/kg. Sauve et al. (2000) found the cadmium content from 64 soils ranged from 0.1 to 38 mg/kg. Chen et al. (2008) studied 84 soils in California and the results are shown in Table 2-2. Compared to ODA limits the background levels in the soils are negligible but still at levels of some concern. The effects of fertilization seem to be dependent on soil type, fertilizer source, location and length of agricultural activities (Jones et al., 2002).

2.1.3 Surface charge

Adsorption, desorption, precipitation and formation of inner or outer complexes are all determined by the functional groups at the soil surface. These groups are all affected by the soil pH with protonation and de-protonation changing the charge on them. Soil pH is one of the major factors controlling metal sorption (Christensen, 1984; Sposito, 1984); thus, determining the pH-dependent soil-surface charge and point of zero charge is important for modeling the adsorptive nature of a soil.

2.1.4 Variable vs Permanent Charge

Surface charge develops in three ways: isomorphic substitution among ions of differing valence; protonation and deprotonation reactions; and specific adsorption of cations and anions (Bolan et al., 1999). Permanent charge arises from the first process while variable charge results from the last two.

Isomorphic substitution of tetravalent silicon by trivalent aluminum or trivalent aluminum by divalent magnesium leaves a net negative surface charge. For example:

$$Si_2O_8 \xrightarrow{Al^{3+} substitutes Si^{4+}} [SiAlO_8]^- \qquad (2.1)$$

As permanent negative charges originate in the formation process of the minerals, they are not susceptible to environmental conditions such as pH and electrolyte concentration (Yu and Ji, 1997).

Variable charge arises from the reactions of surface functional groups of humics, aluminum and iron oxides. Humics have functional groups such as carboxyl, amino, phenolic and hydroxyl groups with a range of ionization energies so that their cumulative charge varies over a wide pH range. Typical reactions under acidic and alkali conditions are given in equations 2.2 to 2.4 with R being the hydrocarbon chain of the humics.

$$R - OH + OH^- \rightarrow R - O^- + H_2O \qquad (2.2)$$

$$R - COOH + HPO_4^{2-} \rightarrow R - OHO_4^- + OH^- \qquad (2.3)$$

$$R - NH_2 + H^+ \rightarrow R - NH_3^+ \qquad (2.4)$$

Metal (hydr)oxides undergo similar reactions, hydrating to form surface hydroxyl groups that can hydrogen bond water molecules and also react with hydrogen and hydroxide ions. The resultant amphoteric reactions are:

$$X-OH_2^+ \xleftrightarrow{\pm H^+} X-OH \xleftrightarrow{\pm H^+} X-O^- \qquad (2.5)$$

with X being the metal or silicon atom. Another important source of variable charge is the edge face of layer silicates. Partial bonding of the oxygen atoms to aluminum or silicon atoms and hydrogen atoms occurs and under alkali or acidic conditions the oxygen atoms can accept or lose protons giving rise to variable charge (Yu and Ji, 1997).

Specific adsorption of cations and anions occurs due to ion exchange and coordination bonding to surface ligand sites. The strength of these bonds is greater than those due to electrostatic attraction. Manganese, iron and aluminum oxides present in large quantities in soils tend to adsorb transition metals such as zinc, copper, cobalt and cadmium. These cations can easily form inner sphere complexes with ligands, such as water, making them more stable and this allows them to exist as hydrated ions in solution that can undergo hydrolysis and the formation of hydroxyl cations. The hydroxyl cations are responsible for adsorption onto the oxide surfaces through different mechanisms such as complex formation or coordinate adsorption and preferential absorption of the hydroxyl metal ions by the oxides (Morgan and Stumm, 1964; Forbes et al., 1976, Tiller et al., 1984; Sposito, 1984). Equations 2.6 and 2.7 show the proposed reactions.

$$M^{2+} + H_2O \Leftrightarrow MOH^+ + H^+ \qquad (2.6)$$

$$SOH_m + M_{liq}^{n+} \Leftrightarrow SOM_{ads} + mH^+ \qquad (2.7)$$

where M is the metal ion, S is the oxide surface and SOM_{ads} is the metal adsorbed to the surface. As with all acid-base and coordination processes, the variable charge of the soil is affected by temperature, the nature and concentration of the background electrolyte and pH of the solution.

2.1.5 Surface charge components

According to Sposito (1984) surface charge is comprised of three components: the intrinsic surface charge density, the structural surface charge density, and the proton surface charge density. The intrinsic surface charge density is defined as the number of coulombs per square meter on the surface functional groups either due to isomorphic substitution in soil minerals or proton association and dissociation reactions. It is measured by the Schofield method (Schofield, 1949). The structural surface charge density is the charge borne by surface functional groups charged due to isomorphic substitutions in soil minerals. It can be estimated from chemical composition and X-ray crystallography. This charge is constant, is not affected by soil and solution interaction and is normally due to substitution of Si^{4+} by Al^{3+} in the tetrahedral layers of the soil minerals (Sparks, 2003). The proton surface charge density (σ_H) is proportional to the difference between the amount of H^+ and OH^- adsorbed or complexed by the surface functional groups. It is defined by equation 2.8

$$\sigma_H = \frac{F(q_H - q_{OH})}{S} \qquad (2.8)$$

where q_H and q_{OH} are the moles of complexed hydrogen and hydroxide ions on proton selective surface functional groups(mol/kg); F is Farday's constant and S is the specific surface area. It measures surface functional surface groups whose charge is pH dependent and is commonly determined by potentiometric titrations (Van Raij and Peech, 1972).

2.1.6 Potentiometric Titrations and Points of Zero Charge

The values of $(q_H - q_{OH})$ are calculated from

$$q_H - q_{OH} = \frac{C_A - C_B - [H^+] + [OH^-]}{c_S} \qquad (2.9)$$

where C_A is the molar concentration of added acid; C_B the added base; H^+ and OH^- the molar concentrations the two ions obtained from the pH readings; c_S is the mass of solid per liter of suspension. The key assumptions for this equation is that all the protons added to the soil solution are either free ions or complexed to surface functional groups and there are no other proton-consuming side reactions (Sposito, 1984). These side reactions include dissolution-precipitation reactions, hydrogen ion and hydroxide ion adsorption in the diffuse layer, flocculation and dispersion processes. At high and low pH changes in ionic strength occur due to dissociation and precipitation and these can further affect the accuracy of the results of the titrations (Bolan et al., 1999). Use of appropriate electrolytes and a CO_2-free environment are some of the steps that can be taken to ensure these side reactions are minimized (Sposito, 1984).

A typical chart output of a stepwise titration of an acid soil is shown in Fig. 2.1. The titration is slow with a quasi-equilibrium being attained between each addition of base. Bases such as NaOH, $Ca(OH)_2$ and LiOH are typically used. After each addition the pH initially rises and then falls back close to the original. When the pH has stabilized (changes by < ± 0.03mV/min) the next amount of base is added. The curves are jaggered and curved in the opposite direction to standard acid base titration curves. The initial pH rise is due to neutralization of free acid in the soil solution, hydronium ions (H_3O^+) and the slower drop in pH is attributed to the re-equilibration between hydronium ions in solution and on soil exchange sites. There may also be release of weakly held protons from either inorganic or organic constituents in the soil so the decrease in pH may be due to reestablishment of equilibrium between the three phases. The cation in the added base exchanges with protons and hydronium ions on the exchange sites releasing them into solution where they can be measured. Due to the many differently bonded protons and hydronium ions there is no clear pKa value for the soil.

The pH at which the net proton surface charge density is zero ($\sigma_H = 0$) is called the point of zero net proton charge (PZNPC) and is dependent on the concentration of background electrolyte as well as the concentration of ionizable functional groups. The points of zero charge are pH values associated with specific conditions on the soil surface and they give information on adsorption characteristics and colloidal stability (Zelazny, 1996). There are several other points of zero charge suggested by Sposito (1984). One such is the point of zero salt effect (PZSE) or pH_0 which can be determined as the point of common intersection of plots of net proton surface charge versus pH measured at different ionic strengths of a background electrolyte. These plots are attained from a series of potentiometric titrations. The PZNPC gradually approaches the PZSE with increasing supporting electrolyte concentration. The PZSE is independent of the permanent charge of a soil (Yu and Ji, 1997). The relationship between the PZSE and PZNPC is

$$PZNPC = pH_0 + \frac{\sigma_P}{0.135C^{1/2}} \qquad (2.10)$$

where σ_P is the permanent surface charge density of the soil and C is the concentration of the background electrolyte. Fig. 2.2 shows the relationship graphically.

The point of zero charge (PZC) commonly quoted in literature is not the same as two above mentioned points of zero charge. The conventional PZC is the pH value when the total net particle charge vanishes and is determined using ion-retention. This point is also called the isoelectric point when measured by an electokinetic experiment. It tends to be lower than the PZSE, so care must be used when defining a point of zero charge. The differences between the PZSE and PZC are due to the permanent negative charge on the solid surfaces, consumption of protons by reactions other than charge balancing and selective adsorption of index ions during measurements in ion-retention experiments (Bolan et al., 1999).

A soil with a native pH greater than its PZC has a net negative charge while a lower pH will give the soil a net positive charge (Appel et al., 2003). Soils with the PZPNC lower than the PZSE will have a permanent negative charge while a higher value signifies a permanent positive surface charge. The difference in magnitude between the PZNPC and PZSE is the quantity of permanent surface charge (Yu, 1997). The separation in the curves above the PZSE shown in Fig. 2.2 is due to a reduction in buffer capacity with decreasing electrolyte concentration. The value of the PZSE of a soil can be affected by pH, concentration of electrolyte, the kind of electrolyte and adsorption of anions.

2.1.7 pH Buffering

Buffer capacity is the ability of a soil to resist a change in pH under variable acidic or alkaline conditions. Buffering is important for understanding any process that affects or is affected by soil pH. Buffer capacity (also called buffer intensity) has been closely correlated to clay content, cation exchange capacity and organic matter (Aitken et al., 1990) and is defined as:

$$\beta = \frac{dC_B}{d_{pH}} = -\frac{dC_A}{d_{pH}} \qquad (2.11)$$

where β is buffer capacity and C_A and C_B are the concentration of acid and base.

2.1.8 Metal Adsorption

In soil, metals are found in one or more of several "pools" of the soil, as described by Shuman (1991):

1) dissolved in the soil solution;
2) occupying cation exchange sites or as inorganic soil constituents;
3) specifically adsorbed on inorganic soil constituents;
4) associated with insoluble soil organic matter;
5) precipitated as pure or mixed solids;
6) present in the structure of secondary minerals;
7) present in the structure of primary minerals.

Anthropogenic metal sources are associated with the first five pools.

Pools two, three and four are all associated with adsorption. Adsorption is the accumulation of a substance or material (adsorbate) at the interface between the solid phase (adsorbent) and the surrounding solution. This process is one of the most important chemical processes occurring in soils as it controls the quantity and transport of metals, pesticides and other organic chemicals retained at the soil surfaces. The adsorption of ions on the surface is dependent on the quantity of surface charge while the strength of the adsorption is determined by the charge density (Yu and Ji, 1997). Adsorption is affected by pH, ionic strength, the presence of competing and complexing ions and the nature of the substrate or adsorbing ion (Srivastava et al., 2005). Soils typically have a higher affinity for lead than cadmium (Forbes et al., 1976; Chaturvedi et al., 2006).

Three adsorption models used to describe the binding of metals onto soil surfaces are the Linear, Langmuir and Freundlich isotherms. The latter two isotherms have been found to more accurately explain heavy metals sorption which is often non-linear due to the many interactions and reactions occurring at the soil surfaces.

The linear equilibrium is the simplest expression of equilibrium adsorption expression

$$S = K_d C \qquad (2.12)$$

where S is mass of solute sorbed per dry unit weight of solid (mg/kg), C is concentration of solution in equilibrium with the mass of solute sorbed onto the solid (mg/L), and K_d is the partition coefficient (L/kg). A plot of S vs. C will result in a straight line with a slope of K_d.

The Langmuir model assumes adsorption only occurs at independent sites with constant sorption energy independent of surface cover and the adsorption capacity is limited by the formation of a surface monolayer (Weber and DiGiano, 1996). The isotherm is linear at low surface coverages, non linear at higher surface adsorbent coverages, and asymptotically approaches the maximum capacity of the surface. The Langmuir isotherm is represented by this equation:

$$\mathrm{S} = \frac{\mathrm{S_m K C_{eq}}}{1 + \mathrm{K C_{eq}}} \qquad (2.13)$$

where S is the mass of solute sorbed per dry unit weight of solid (mmol/kg), S_m is the maximum sorption capacity (mmol/kg), K is the Langmuir sorption constant (L/kg), that is presumed to be proportional to the binding energy of the metals, and C_{eq} is the concentration of solution in equilibrium with the mass of solute sorbed onto the solid (mM). The linearized form is

$$\frac{\mathrm{C_{eq}}}{S} = \frac{\mathrm{C_{eq}}}{\mathrm{S_m}} + \frac{1}{\mathrm{KS_m}} \qquad (2.14)$$

A so called double reciprocal plot of C_{eq}/ S vs C_{eq} yields a straight line with a slope of $1/S_m$ and an intercept of $1/\ KS_m$.

The Freundlich isotherm expresses the relationship between the sorbate and sorbent to be an empirical exponential function of the solution.

$$\mathrm{S} = \mathrm{K_f\ C^{nf}} \qquad (2.15)$$

Where S is the mass of solute sorbed per dry unit weight of solid (mmol/kg), K_f is the Freundlich coefficient (L^n mg^{n-1}/kg), C is the concentration of solution in equilibrium with the mass of solute sorbed onto the solid (mM), and *nf* the Freundlich exponent. Christensen, 1984; Kookana and Naidu, 1998 and Sauve et al., 2000 are some of the studies that have used the Freundlich isotherm to model metal sorption. The Langmuir isotherm is often preferred to the Freundlich form as it allows for calculation of a sorption maximum that can be correlated to intrinsic soil properties.

$CaCl_2$, $NaNO_3$ and $NaClO_4$ are common background electrolytes used to control the ionic strength with the assumption being they only form weak outer-sphere complexes at the soil surface by electrostatic attraction, depending on soil charge. Heavy metals are believed to form inner-sphere complexes, thus the background electrolytes do not compete for binding sites on the soil surface.

2.1.9 Factors affecting adsorption

Knowledge of sorption behavior and buffer capacity of a soil are key to understanding the fate and transport of contaminants in this media (Lee and Doolittle, 2002). Unfortunately, batch isotherms, although representative, provide equilibrium condition results and may not give an accurate depiction of field conditions that are very dynamic. Temperature, soil moisture, vegetation and exposure to the sun all affect the reactivity of the contaminants (Allen et al., 1995). Equilibrium adsorption assumes sorption is relatively fast and an instantaneous sorption expression can be used.

Many cadmium isotherms have been done and some of the values of K_d obtained are: 239.5 L/kg by Lee et al. (1996) for sorption to 15 New Jersey soils; 290 L/kg by Rodriguez-Maroto et al.(2003) for some soil samples from Spain; 1132 (L/kg) for organic soil samples from Canada; and 2869 L/kg for a mineral soil by Sauve et al. (2000). These studies showed the magnitude of K_d is influenced by pH, soil organic matter, competing ions, counter ions, ionic strength and solution metal concentration. Other factors such as pressure, temperature, soil/solution ratio, and the manner in which soils to be studied are sampled and stored before investigation are also important. It is difficult to compare results from different laboratories due to the non standardization of methods (Harter and Naidu, 2001). This study used an ionic strength of 0.01 N, background electrolyte of $NaNO_3$, pH (between 5.5 and 6.0), and temperature $25 \pm 3\ ^{o}C$ to standardize adsorption isotherms to enable easier comparisons.

2.2 Materials and Methods

Ultra-pure water (18 MΩ) was used in the preparation of all reagent samples. All the glassware used was cleaned in (liqui-nox) detergent, placed in a 5% HNO_3 acid bath for at least 24 hrs and then triple rinsed with nanopure water prior to use.

2.2.1 Sampling Sites

The soils used in this study were collected from cultivated soils at four Oregon state agricultural experiment stations: Hyslop Farm, Corvallis Oregon; Columbia Agricultural Research Center, Pendleton; Klamath Basin Experiment Station, Klamath Falls and Hermiston Agricultural Center, Hermiston (Fig. 2.3). These sites were chosen to be representative of the main farming regions in Oregon, which are under very different climatic conditions and have different soil types (Table 2-3).

Samples at each site were taken from a gridded experimental plot approximately 30 m x 12 m in size that was dedicated to this research project. At all stations the sampled plots had been cultivate and cropped for many years and were therefore typical of active agricultural soils in Oregon. A plot design showing the demarcation of the agricultural fields into 16 subplots at each site is shown in Fig. 2.4. Pegging of the study area was done beginning at the North East corner after allowance of a 3 m setback from the field edges. Nine random surface (0-5 cm) and deep (15-20 cm) samples were collected from each plot and composite surface and deep samples made by thoroughly homogenizing the soil samples giving rise to two samples for each plot and a total of 32 samples per site. Trowels were used to collect the surface samples and cleaned PVC pipes (2.54 cm diameter) were used for the deep samples.

In the laboratory, the samples were air dried, crushed and passed through a 2 mm sieve (U.S. Standard Sieve Series No. 10) using a Tyler Combustion Engg. Inc. Portable Sieve Shaker Model RX24 prior to characterization.

2.2.2 Soil Characterization

Soil pH was determined using a 1:2 soil/ solution mixture, with 0.01M $LiClO_4$ as the background electrolyte and an Orion EA920 IonAnalyzer pH meter. An ionic strength of 0.01M is a good simulation of field soil solution conditions (Harter and Naidu, 2001). Particle size analysis was done using the wet sieving method (Bouyoucos, 1962) and the hydrometer method (Day, 1965).

Extraction of the bio-available background Cd levels was done using the double acid extraction method (Perkins, 1970) followed by AAS determination (Perkin Elmer AAnalyst-300 Atomic Absorption Spectrophotometer) or ICP-MS (HP-4500 Inductively Coupled Plasma Mass Spectrometer); the steps and conditions used were those recommended by the manufacturers. The samples were acidified using concentrated nitric acid to a $pH < 1$ prior to analysis. Analysis of available metal content was preferred to total metal concentration due to the former being a better indicator of the plant available and leaching available fractions.

2.2.3 Potentiometric Titrations

Soil (1.0 g) was mixed with 0.01N LiClO4 background electrolyte (100 ml) and allowed to equilibrate, typically for 1hr. The soil solution was acidified with standardized 0.1N HCL to a pH of 4.5. The soil solution was gently stirred continuously and equilibrated overnight in a CO_2 free environment under purified N_2 gas. Fig. 2.5 shows the apparatus schematic. From the pH of 4.5, the soil solutions were titrated in 8 to 10 steps up to 8.5 using CO_2 free, standardized 0.50 M LiOH as the titrant, to a pH of 8.5. After each addition the system was allowed to equilibrate and the pH monitored until the pH drift was < 0.03 mV/min, typically after 30 min. The titration vessel was maintained at a slight over pressure of N_2 throughout the titration to exclude atmospheric CO_2. The point of zero salt effect was determined by changing the background electrolyte concentration of 0.001 M $LiClO_4$ to 0.01 M $LiClO_4$ and 0.1 M $LiClO_4$. The assumptions made in these experiments were that the temperature of the reaction vessel did not significantly vary from an average ambient temperature of 22^0C and that no precipitation of a solid occurred on the soil surfaces.

2.2.4 Batch Metal Isotherm Experiments

Batch equilibrations for determining metal adsorption were performed by placing1.0 g soil samples in 50ml polypropylene screw-cap vials and equilibrating with 0.01 N $LiClO_4$ (30 ml) containing 5.6 ppm (0.05 mM), 28 ppm (0.25 mM) and 56 ppm (0.5 mM) Cd and 10.3 ppm (0.05 mM), 51.8 ppm (0.25 mM) and 103.6 ppm (0.5 mM) Pb (The analytical concentrations were made from 1000 ppm Assurance certified standards). All isotherms were peformed in duplicate with controls with no soil and no Cd also being run.

The soil suspensions were equilibrated for 36 hrs at $25 \pm 2\ ^{O}$C using a table top shaker (IKA Vibrax VXR) at 150 rpm. The pH of the soil solutions was adjusted to the measured native soil pH prior to shaking. Adjustment was done using 0.1 N HCL and 0.1 N NaOH. The pH of the sorption isotherms was not controlled after metal additions in order to better approximate field soil conditions. Following equilibration the samples were centrifuged for 30 mins at 3600 rpm (International Clinical Centrifuge Model CL) and the supernatants were filtered using 0.45 µm Millipore membrane pore filters. The filtrates were analyzed for Cd and Pb by a flame atomic adsorption spectrophotometer (Perkin Elmer AAnalyst-300 Atomic Absorption Spectrophotometer (AAS)) or Inductively Coupled Plasma- Mass Spectrophotometer (HP-4500 Inductively Coupled Plasma Mass Spectrometer) depending on the concentration level. The samples were stored at 4 ^{0}C prior to analysis if not immediately analyzed.

For the AAS analysis, the samples were diluted to get the sample concentrations in the linear range of Cd, 0.2 to 2ppm. The differences between the initial (C_0) and the equilibrium solution concentrations (C_e) were calculated to determine the sorbed concentration (S) per unit mass of soil. The data was fit to linearized Freundlich and Langmuir isotherms to determine the best fit and determine distribution coefficients. The following assumptions were made: the temperature of the batch vessel was constant throughout the experiment; adsorption of Pb and Cd onto the walls of the polypropylene vessel was negligible, verified by controls and no precipitation of cadmium or lead salts occurred (unlikely for the pH and composition of these soils).

2.3 Results

2.3.1 Soil Characteristics

Soil analyses (Table 2-4) show that all the soils are acidic with Hermiston having the most acidic soil at a pH of 4.9 and Pendleton the most basic at pH 5.9. The sandy soils at Hermiston and Klamath had very similar particle size distributions differing in clay content by only 2%. The other two soils were both loams differing only in the sand content. The particle size analysis also showed considerable difference in the silt content of the sites ranging from 7% (Klamath) to 46% (Hyslop). The most clay-rich site, Hyslop, had eight times the clay content of the Hermiston site. There was not a large variation of cation exchange capacity (CEC) values among the sites. The CEC values for Pendleton and Hyslop were identical (18 cmol/kg) and the values for Klamath and Hermiston were 13 cmol/kg and 11 cmol/kg respectively. Organic matter content was more varied. The Pendleton and Hyslop soils had slightly different organic matter content (2.6% and 2.4% respectively) with both having more than twice the OM content of the Hermiston soils and almost three times that of the Klamath soils. The soils appeared to separate into two groups, one with sandy soil and the other with loamy soil.

The background levels of cadmium were low for all the sites with Hermiston soils having the highest concentrations and Hyslop site soils the lowest concentrations (Table 2-5). The strength of the extraction solution used dictates the cadmium concentration observed and explains the difference in concentrations between the studies. The EPA 3050B method is a strong acid digestion method designed to give the environmentally available cadmium content whereas the double acid extraction technique uses dilute acid and is intended to better represent the bio-available cadmium content. The largest variation in the surface soil concentrations was at the Klamath site (Fig. 2.6). The deep soil samples had lower concentrations than the surface samples at all the sites which may be due to Cd accumulation on the surface from prior fertilization or atmospheric deposition. The deep soil concentrations were similar for all four sites.

2.3.2 Soil Acid-Base Chemistry

2.3.2.1 Potentiometric Titrations

The potentiometric titrations (Fig. 2.7) show a gradual increase in pH with increasing addition of base. As is typical for soils, the potentimetric curves for all four sites had no clear points of inflection, unlike the blank titration which had a clear point of inflection, as seen in the inset. The titrations show that for a given volume of added base, the greatest change in soil pH occurred in the Hermiston soils and the least in the Pendleton soils. Expanded plots of the titration data between pH 4.5 and 6.5 (Fig. 2.8) were very linear (R^2 values 0.9958 to 0.9995) and therefore the soil buffer intensity (dn/dpH) could be accurately determined from the reciprocal of the slopes of these regression lines (Stumm and Morgan, 1981). Soil buffer capacity diminished in the order of Hyslop(17.8 cmol/ kgsoil/pH unit) > Pendleton (12.8 cmol/ kgsoil/pH unit) > Klamath Falls (9.2 cmol/kgsoil/pH unit) > Hermiston (7.4 cmol/ kgsoil/pH unit) (Table 2-6). Buffer capacity was correlated (R^2= 0.98) with the clay content and to a lesser extent with %OM (R^2= 0.69). The change in buffer capacity as a function of pH (Fig. 2.9) showed an increasing variability in buffer capacity with increasing pH for three of the soils.

2.3.2.2 Point of zero charge

The change in net surface charge as a function of pH in varying background electrolyte concentration at the four sites was very different among the four soils (Figs. 2.10-2.13). Increasing I (ionic strength) did little to separate the titration curves of the Hermiston, Hyslop and Klamath sites. In contrast the Pendleton soils demonstrated increasing separation in the titration curves above the PZSE. The buffer capacity of the soils increased with increasing background electrolyte concentration either side of the PZSE with the least buffered soil, Hermiston showing the least effect of background electrolyte concentration.

The PZSE varied from 7.1 (Klamath) to 6.08 (Hyslop) and the native soil pH of all the sites was less than the calculated PZSE pH. The Hermiston soil had the shortest range in its PZNPC (Table 2-7) values while the largest difference in the PZNPC values at different electrolyte concentration was evident in the Pendleton soil.

2.3.3 Adsorption Isotherms

2.3.3.1 Cadmium

At an initial concentration of 0.05 mM all the sites had similar adsorption but as the Cd concentration increased there was considerable deviation from linearity (Fig. 2.14). All of the isotherms exhibited L-curves. Sorption followed the general trend of Pendleton > Klamath > Hyslop > Hermiston. The data from the adsorption isotherm experiments were modeled using the Langmuir and Freundlich models (Figs 2.15-2.18) and model parameters determined are summarized in Table 2-8.

The Langmuir monolayer sorption maxima (S_{max}) were quite large with median values of 1074 to 1680 mg/kg. The Langmuir adsorption coefficients (K) which are related to energy of adsorption had values from 0.50 -0.60 L/mg. The Freundlich coefficient (nf) values for all the soils were all < 1 indicating a favorable adsorption process. The median value of the other coefficient (Kf) ranged from 290 to 398 $L^{nf}mg^{nf-1}/kg$ at the sites. The soil with the highest pH, Pendleton had the greatest adsorption maximum for Cd. Hermiston, the most acidic soil, had the least adsorption of cadmium. The intermediate adsorption strength of the Hylsop and Klamath soils correlated directly with pH and the more acidic soil, Klamath, had a higher sorption maximum than the Hyslop soil. At the low concentration the relationship between the sorbed Cd and Cd in solution was approximately linear.

2.3.3.2 Lead

All the soils showed a greater affinity for lead than cadmium. The Langmuir monolayer sorption maxima (S_{max}) were large with median values of 1049 to 7700 mg/kg. The Langmuir adsorption coefficients (K) which are related to energy of adsorption had values from 0.30 -0.80 L/mg. Only the Hermiston data was reasonably modeled by the Freundlich isotherm. The lead isotherms showed very different adsorption behavior at the sites. The Hermiston and Klamath sites had L-curve adsorption isotherms, and Hyslop and Pendleton exhibited H-curve shaped isotherms (Fig. 2.19). Lead had a similar adsorption trend of Pendleton > Klamath > Hyslop > Hermiston. The data from the adsorption isotherm experiments were modeled using the Freundlich model (Figs. 2.20-2.22) and the model parameters are summarized in Table. 2-9.

2.3.3.3 Cd Accumulation and Depuration Times

The doubling times, the time it takes to double the background soil concentration, were calculated to be 4.8 years, 2.5 years, 1.5 years and 4 years for Hermiston, Hyslop, Klamath and Pendleton respectively (Appendix C). Several assumptions were made: the application rate of phosphate fertilizer remained unchanged and at the 2003 levels; the fertilizer was applied twice during the year; the only mass input of cadmium into the soil was from the phosphate fertilizer and the adsorption of cadmium was essentially linear allowing the use of K_d. Making the background concentration and application rates uniform at all the sites showed the order of the doubling time to be Hermiston, 4.8yrs > Hyslop, 3.7yrs > Klamath, 2.9 yrs> Pendleton 2.3 yrs.

Knowledge of the adsorption behavior of the soils also allowed for the determination rate of leaching of cadmium from the sites (Appendix C). The leaching rates were 6.65 mg/ha-yr (Hermiston); 15.4 mg/ha-yr (Hyslop); 2.75 mg/ha-yr (Klamath) and 5.56 mg/ha-yr (Pendleton). The assumptions were: plant uptake, runoff and volatization were negligible loss pathway of cadmium from the soil compared to leaching; annual rainfall was the only source of precipitation; the cadmium concentration was uniform throughout the soils and there was no further input of cadmium into the soils

2.4 Discussion

2.4.1 Soil Characteristics and Acid Base Chemistry

Within at least one pH unit of the native soil pH, the relationship between added base and pH for all the soils was linear. Similar behavior was observed for other soils (Oorts et al., 2004). Over the pH range of 4.5 to 6.5 few side reactions occurs so the soil buffer capacity can be readily determined. The four sites had comparable buffer capacity.

The soils from Pendleton and Hyslop had comparable organic matter and CEC. The difference in the clay content of the two sites accounted for the difference in their buffer capacities. The Pearson's correlation coefficient was 0.99 between buffer capacity and clay content and it was significant at the 95% confidence level. The particle size analysis results were very similar to those expected from the NRCS classifications. NRCS classifications are not site specific and are generally used as a guide for what to expect at a site.

As expected, the highest CEC values were in the soils with the highest clay content and organic matter content, both properties that account for CEC in soils. The CEC, clay and organic matter content of soils are expected to influence the observed chemical properties of soil such as buffer capacity and metal adsorption parameters. The buffer capacity of the four soils studied had a strong correlation to clay content. Aitken et al. (1990) also found buffer capacity to be strongly correlated to clay content indicating a relationship between weak-acid (buffering) surface functional groups and exchangeable sites on clays or organic matter. Other studies have shown strong relationships between buffer capacity and pH, CEC and organic matter (Mowbary and Schlesinger, 1988; Bailey et al., 1989 and Curtin and Rostad, 1997, Weaver et al., 2004).

2.4.2 Surface charge as a function of pH

As protons are added to or removed from the soil solution in a titration, charge develops due to the amphoteric nature of mineral oxides. Organic matter is generally not amphoteric so there is a greater probability for a negative charge than a positive surface charge if organic matter content is significant. For example, pure $Fe(OH)_3$ (s) would show approximately equal positive and negative charge build up but pure humic acid would exhibit almost no positive charge but lots of negative charge. The data in this study agree with this observation (Table 2-10). The change in pH ±1.5 pH units from the PZSE for all the soils in 0.1M background electrolyte was investigated. The curves show that it is easier to build up positive and negative charge at high ionic strength and more negative than positive charge is built. This is due to suppression of the diffuse double layer at the soil surface with increasing ionic strength and a decrease in the Stern layer potential.

All the soils had a PZSE value higher than their native soil pH suggesting all the sites had a positive permanent surface charge under field conditions. Above the PZSE there is a reduction in buffer capacity seen as a large increase in charge density. The increased separation in the titration curves above the PZSE as seen in the Pendleton and Hyslop sites is evidence of this phenomenon (Appel et al., 2003).

The location of the PZSE relative to the native soil pH can be important information for farmers as its shows the pH behavior of the soils and the implications of adjusting pH. For example, liming, an activity commonly done on agricultural soils with a soil pH below 5.5, would raise the pH of the Hermiston and Hyslop soils and looking at Figs. 2.10 and 2.11, move the surface charge of these soils to the neutral or slightly negative zones. This would translate into an increase in adsorption of Cd and Pb at these sites.

The accuracy of the titration curves is affected by side reactions that occur instead of the simple charge balancing. These interferences result in the PZSE being different to the PZC. These include the reaction of the background electrolyte and dissolution and precipitation reactions at high and low pH. The change in ionic strength that occurs during the titration can also affect the reliability of the results.

High organic matter content tends to lower the point of zero charge (van Ranij and Peech, 1972). Klamath, the site with the lowest organic matter had the highest PZSE and this trend was consistent for the other sites except for Pendleton. Despite a high clay content and high organic matter content, the PZSE at this site was high. This may be due to larger quantities of Fe and Al oxides, which have a PZSE greater than 6.5, at this site (Sposito, 1984). This site also had the largest difference in the PZNPC values with increasing electrolyte concentration.

The large differences in the values of the PZNPC at Pendleton, in different electrolyte solution concentration, suggest variable charge may be relatively more important at this site than permanent charge. Buffer capacity is a function of variable charge and soils with a high variable charge are more greatly affected by background electrolyte concentration changes (Yu and Ji, 1997). This site has a high CEC and % OM, both components that greatly contribute to variable charge in a soil.

2.4.3 Adsorption

The L-curve isotherms observed here for Cd on all soil types are commonly seen for Cd on soils (Appel and Ma, 2002 and Hooda and Alloway, 1994) and suggest a high-relative affinity of the metal at low concentration followed by a decreasing adsorption at the surface due to steric factors (Sposito, 1984).

Most soil studies have determined pH to be the master variable, for example Anderson and Christensen, 1988 and Sauvé et al., 2000. The same was true for this study. The reduced adsorption at low soil pH is attributed to a high concentration of hydronium ions at low pH that exceed Cd^{2+} ions, and occupy the surface sites. In this pH range electrostatic repulsion of the Cd^{2+} ions by the positively charged surfaces further reduces adsorption. With increasing pH, Cd^{2+} and $Cd(OH)^{+}$ become more competitive at the sorption sites due to the decreasing proton concentration (Agrawal and Sahu, 2006). Despite the greater organic matter and clay content at the Hyslop site, the Klamath site had a higher adsorption maximum.

For the range of concentration studied, all the Cd isotherms had sorption maxima (S_{max}), obtained from Langmuir modeling, and the order of adsorption was obtained from this term. S_{max} is used as a qualitative measure of adsorption comparison. Use of the binding strength (K) for comparison purposes is questionable (Sparks, 2003). The Freundlich isotherm parameters do not lend themselves to similar interpretation because they are fitting parameters and there is no physical basis for them.

In a concurrent study the log K_d values for Cd of these four sites was found to range from 2.3 to 3.9 L/kg (Perez and Anderson, 2007). The Kd values in this study were also similar to those reported for other topsoils (Christensen, 1989). Pore water concentration levels of cadmium are typically < 0.1mM and at these concentration levels, from the adsorption isotherms, the adsorption of cadmium could be considered to be essentially linear.

Pb adsorbed much more strongly than Cd to all soils and exhibited an H-type isotherm. The H-curve is said to be an extreme version of the L-curve arising either due to highly specific interactions between the soil and the cations or significant Van der Waals interactions in the adsorption process (Sposito, 1984). Only the Hermiston Pb isotherms exhibited an L-curve type isotherm and had a clear sorption maximum over this concentration range.

The dramatic difference in the adsorptive behavior of Cd and Pb seen can be explained in terms of a combination of the smaller hydrated radius of Pb, 0.401nm compared to 0.426 nm for Cd and the higher intrinsic affinity of Pb for most functional groups in organic matter, both of which make Pb more likely to undergo strong inner sphere complexation (Evans, 1989; Appel and Ma, 1994). Organic functional groups such as carboxylate and phenolic are hard Lewis bases and because lead is a borderline hard acid, according to the Pearson's Hard Acid Soft Base Principle, there is a stronger attraction (Appel and Ma, 2002). Lead also forms monodentate inner-sphere complexes compared to bidentate complexes for cadmium (Srivastava, 2005). Similar sorption behavior was seen by Appel and Ma, 1994 and Hooda and Alloway, 1998.

The high correlation of pH, CEC and organic matter with the linear K_d (R^2 = 0.89, 0.87 and 0.80 respectively) suggested, aside from pH, the soil variable charge was an important determinant for adsorption in these soils. Studies by Boekhold and van der Zee (1992) and Gray et al. (1998) also found organic matter to be most correlated to K_d. The higher organic matter and pH of the Pendleton soils explains the greater distribution coefficient (K_d) relative to the Klamath soils. The other factors, clay content and CEC, can account for the difference in the adsorption coefficients between the Hyslop soil and the Hermiston soil.

Statistical modeling of the different basic characteristics (clay content, organic matter content, buffer capacity, pH and CEC) of the soil sites to infer the sorptive behavior of the sites was attempted but because of the small number of degrees of freedom, there was an over-fit of data decreasing the power of the test.

The distribution coefficients from this study were compared to regression models proposed by Christensen (1983) and the USEPA (1999), that predicted K_d as a function of pH and both models underestimated the observed K_d values but were of the right order of magnitude. As discussed by Curtis and Smith (2002) risk assessment models for heavy metals in fertilizer are very sensitive to the distribution coefficients at low risk based assessment values. The two sets of estimates of K_d currently used in most in risk based modeling are derived from literature (Baes and Sharp, 1983; Sauve et al, 2000) and differ by a factor of 100 for Cd and 20 for Pb leading to great uncertainty when modeling. This research showed both estimates were out by a factor of 10 and this knowledge adds to the information necessary for setting accurate regulation levels for Oregon.

2.4.4 Application of Distribution coefficient

The doubling time results showed the fertilizer application rate and the background cadmium concentration were more important than the distribution coefficient and soil texture in the calculation of this term. When the variables in the application rate and background concentrations were removed, the order of the soils in terms of doubling time was opposite to that of the distribution coefficient K_d. This information is important for risk assessment studies that require calculation of the rates of accumulation of contaminants in soils.

Trace metal leaching from agricultural soils is important for accurate trace metal balances (Bengtsson et al., 2006). Despite the many assumptions made in the calculation of the leaching rates the calculations showed the rates due to this loss pathway are very small. Plant uptake at these sites has been shown to be a negligible loss pathway (Perez and Anderson, 2007) Volatilization and radioactive decay are not important loss pathways for cadmium (Curtis and Smith, 2002). The loss rates calculated suggested that after 3 years, the period required for a field to be certified organic, there was a negligible decrease in the soil background cadmium concentration. .The loss of cadmium due to leaching over this time period was 46.2, 19.9, 16.7 and 8.3 mg /ha-yr for Hyslop, Hermiston, Pendleton and Klamath respectively. Soil texture was the most important characteristic in predicting the leaching flux and this was evident even when the background concentration cadmium concentration and precipitation were uniform at all the sites. The sandy soils had higher depuration rates than the loam soils.

Due to the high affinity of lead for the solid phase calculations of doubling time and accumulation flux were not done.

Chapter Three

Fertilizer Kinetics

Abstract

The behavior of fertilizer-derived cadmium has been studied on a macroscale but very little is known about the kinetics and the chemical processes occurring in the zone immediately around the fertilizer granule. The purpose of this study was to determine the processes controlling the release of fertilizer-derived cadmium in this zone. In particular we tested the following hypotheses: 1) the release of cadmium and phosphorus are similar; 2) soil-water electrical conductivity (EC) is a good indicator for the release of cadmium; 3) phosphorus can inhibit the release of cadmium; 4) the size or structure of the fertilizer matrix plays a role in cadmium release; and 5) organic complexing agents such as humic materials increase the release rate of cadmium.

We also tested if pH, commonly the master variable in soil chemistry, had a significant effect on the release of cadmium from the fertilizer granules and if fertilizer-derived cadmium release kinetics are relatively slow compared to uptake of cadmium by agricultural soils. A displacement method using sequential washing of fertilizer overlain Monterey sand was used to mimic field conditions and the short term release profiles (10 pore volumes) of cadmium, phosphorus, EC and pH of the eluants were determined.

Cadmium release did not mimic the release of the phosphorus from fertilizer; an initial high release of Cd quickly dropped off to a very slow rate, even as rapid P release continued. Electrical conductivity was a good indicator of the release profile

of cadmium. The pH of the soil did not have a significant effect on the cadmium release as elution of the fertilizer phosphate apparently creates a buffer solution in the microzone surrounding the fertilizer granule.

The release of cadmium in the fertilizer-water system appeared to be inhibited by a Cd-phosphate solid phase. This was shown by an approximately inverse relationship between the release of P and Cd from crushed fertilizer granules, as well as by the observation that a Cd-complexing agent (EDTA) enhanced the release of fertilizer-derived cadmium. The release-regulating a Cd-phosphate phase is propsed to be a cadmium hydroxyapaptite, but release may also be influenced by fertilizer-derived iron oxides that enhance cadmium adsorption.

3.0 Statement of Purpose

The purpose of this study was to determine the processes controlling the release of cadmium from fertilizer. In particular we tested 1) if the release of cadmium and phosphorus were similar, 2) if electrical conductivity was a good indicator for the release of cadmium, 3) if phosphorus was an important inhibitor of further release of the cadmium, 4) if the fertilizer matrix in played a role in cadmium attenuation, 5) if complexing agents such as humic materials affected the release of cadmium, and 6) if pH, commonly the controlling variable in soils, had a significant effect on the release of cadmium from the fertilizer granules. The possible role of iron oxides in the adsorption of cadmium was also investigated.

3.1 Literature Review

3.1.1 Fate of fertilizer derived cadmium

The largest flux of cadmium entering the soil resides in the soil solution where is it is in steady state with organic phases, solid phase minerals and exchangeable ions (Fig. 3.1). Soil solution is defined as the aqueous liquid phase of soil field moisture and it is the soil's most important pool in the determining the toxicity, availability and fate of heavy metals (Adams, 1974).

Most studies of the behavior of metals in soils have been carried out under equilibrium conditions. Equilibrium data indicate which reactions are likely to occur under prescribed conditions, but do not indicate the time period involved. While equilibrium measurements are useful in providing information on the final state of a system, no information is garnered on the rates of the reactions. The kinetic aspect of oxidation/ reduction, precipitation/ dissolution and adsorption/ desorption reactions involving metals in soil matrix suffers from lack of published data. The kinetic component which in many cases is critical to predict the behavior of metals in soils cannot be assessed easily. Such kinetic information is extremely important in accurately predicting the fate and transport of plant nutrients, metals, radionuclides, pesticides and other organic chemicals in soil with time. Without the kinetic component, the current accepted approach is to assume that local equilibrium occurs in the soil profile (McClean et al., 1992).

3.1.2 Soil solution measurement techniques

Measurement of soil solution in-situ is difficult and its chemical composition differs depending on the soil moisture especially in weakly buffered soils (Wolt, 1994). It is challenging to experimentally collect the true soil solution so the definition of soil solution is dependent on the extraction method use to attain it. Many extraction methods have been proposed to get an accurate representation of this phase, with the methods falling into three techniques: centrifugation, saturation extracts and displacement.

The centrifugation method uses an immiscible liquid to remove the soil solution from the moist soil; common extractants are carbon tetrachloride (CCl_4) and ethyl benzoacetate (Sparks, 2003). During centrifugation the immiscible liquid passes through the soil causing displacement of the soil solution upwards. The supernatant is then decanted, filtered and analyzed. For the saturation extract technique a saturated soil paste is made using distilled water and allowed to stand for 4-16 hrs. The paste is then suction dried using a Buchner vacuum funnel and the filtrate collected (Sparks, 2003). Displacement techniques such as column displacement involve displacing the soil solution by elution followed by collection of the soil solution at the bottom of a soil column and analyzing for ions (Sparks, 2003). All these techniques recover less than 50 % of the soil water at field capacity so it is difficult to equate the displaced soil solution composition with the in situ soil solution composition (Wolt, 1994).

The intention of this research study was to replicate field conditions to obtain results that would be relevant to farmers and other agricultural professionals. The time scale, high tension and disturbance to the soil in centrifugation technique made it unsuitable for this study. Saturation extracts were also not relevant as agricultural soils are often unsaturated. The displacement technique most fit conditions expected by farmers. The displaced soil solution is affected by the soil moisture content, sample pre-treatment and duration of displacement so experimental conditions had to be adjusted to incorporate these effects.

Field displacement methods for obtaining soil water involve an in situ technique called lysimetry. It measures the water that has moved by diffusion and / or conduction through the soil column as well as water that has moved via preferential flow. One general type of lysimetry is zero-tension lysimetry and so named because it is open to the ambient atmosphere. The displaced water in the column moves in through percolation. Percolation requires formation of a near-saturated zone near the bottom of the soil profile before the water can drain due to the surface tension between the soil – air boundary at the lysimeter bottom (Wolt, 1994). This zone can modify the soil – water conditions especially for shallow profiles and makes it difficult for modeling solute transport (Wolt, 1994). The soil solution collected by lysimeters has been found to closely estimate soil solution and would have been ideal for modelling however, as lysimeters have a long equilibration time (months to a year) and could not be used in the laboratory a method that gave similar results had to be found (MacDonald et al., 2004).

A displacement method using sequential washing of soil leading to the loss of excess soluble material at the soil surface was selected. The concentrations of elements in the percolating solution were a result of exchange reactions with the soil exchange complex. This method was found to give similar results to zero tension field lysimeters for pH, dissolved organic matter and electrical conductivity (MacDonald et al. 2004).

3.1.3 Fertilizer Dissolution

Fertilizer dissolution has been studied with a view to determining nutrient release and resultant environmental problems (Liang et al., 2007, He et al. 2005, Shavit et al., 1997). Slow-release fertilizers are a result of this research and although they can address the issue of nutrient release, they do not address the issue of ultimate environmental fate, particularly of non-nutrient components such as Cd. There is a dearth of information on the fate and transport of the nutrients and trace metals such as cadmium that leach into soils as a result of fertilization.

There is very little information on the short term release kinetics (0-24 h) of phosphate fertilizers which can be of issue in waterlogged, heavily irrigated and areas with frequent heavy rains. The dissolution of one of the major minerals in phosphate fertilizer, mono-calcium phosphate monohydrate has been shown to involve the incongruent dissolution to brushite and monetite accompanied by a drop in pH (Lehr et al., 1959; Lindsay and Stephenson, 1959).

$$\mathrm{Ca\,(H_2PO_4)_2.H_2O + H_2O \Leftrightarrow CaHPO_4.2H_2O + H_3PO_4} \quad (3.1)$$

Ammonium ions in ammonium phosphate fertilizer also contribute to the drop in pH according to the following reaction

$$NH_4^{\ +} + 2O_2 \rightarrow NO_3^{\ -} + 2H^+ + H_2O \quad (3.2)$$

The drop in pH mobilizes heavy metals such as cadmium which is very mobile for pH < 5 conditions. However, the localized drop in pH can be corrected by the buffer capacity of the soil and precipitation of phosphate salts.

Cadmium and phosphorus soil level concentrations are typically well correlated. Substantial evidence has also shown that phosphate rock, the chief constituent of phosphate fertilizers, is capable of immobilizing heavy metals in contaminated soils (Ruby et al., 1994; Ma et al., 1995). Co-adsorbents such as oxalate, sulphate and phosphate are known to affect the adsorption of cadmium onto soils (Collins et al., 1999; Lee and Doolittle, 2002) with phosphate being known to enhance cadmium adsorption on goethite (Wang and Xing, 2002). Naidu et al. (1994a) found that Cd^{2+} sorption was increased in the presence of PO_4^{3-} in oxisols and xeralfs with solids like $Cd_3(PO_4)_2$ precipitating. Krishnamurti et al. (1999) showed the opposite was true due to the formation of phosphate complexes in solution. The source of phosphate, mono-potassium phosphate versus di-potassium phosphate, also affects adsorption with the former decreasing adsorption and the latter enhancing adsorption (Lee and Doolittle 2002). In a study of potassium phosphate fertilizer, the release profile of potassium was found to be very similar to that of phosphate (Notario del Pino et al., 1995). These researchers also found the phosphorus release follow first-order kinetics with an initial slow step.

Knowledge of the mechanisms involved in the retention and mobility of Cd is necessary to ascertain allowable load capacity for a given soil and its distribution in the soil profile (Naidu et al., 1997). By understanding the release kinetics the environmental fate and transport of both P and Cd can be better understood. To determine the chemistry behind the release of cadmium from the fertilizer the following research questions were addressed: what are the release profiles of cadmium, phosphate, pH and conductivity from the fertilizer; what effect do chelating agents have on cadmium release; can pH affect the release; what effect does the fertilizer matrix have on the release profiles and what is the fate of the cadmium in agricultural soils.

3.2 Materials and Methods

3.2.1 Fertilizer Sample

The phosphate fertilizer, Lot No. 08080301C, (NPK: 16-20-0) used in this study was supplied by the Oregon Department of Agriculture (ODA) and assumed to be representative of commercially available fertilizer.

3.2.2 Fertilizer Analysis

Extraction of the background Cd levels was done using the double acid extraction or Mehlich #1 method (Mehlich, 1953) and determination was done using the ICP-MS (HP-4500 Inductively Coupled Plasma Mass Spectrometer); the steps and conditions used were those recommended by the manufacturers.

3.2.3 Scanning Electron Microscope (SEM) imaging

Fertilizer granules were characterized by scanning electron microscopy (SEM) using energy dispersive spectroscopy (EDS) analysis. The instrument used was a JEOL 35C Scanning Electron Microscope equipped with a Kevex X-ray detector. Before analysis the granules were embedded inside an epoxy resin and then coated with 120 Å of Carbon for 20 minutes. Images and EDS analysis were recorded at an acceleration voltage of 15 kV. EDS spectra directly revealed the presence of the atomic elements in the sample. Their study led to the relative proportion of the atoms present in the fertilizer. The elements analyzed were Ca, K, V, Fe, S, Na, Mg, Cl, P, Mn, Si and Cd. Similar micrographs were taken at different magnifications using a FEI Sirion FESEM, 30 kV microscope equipped with Oxford Inca Energy 250 EDX system.

3.2.4 Iron Determination

The total iron content of the fertilizer granules used in the SEM analysis was determined using Method FM-822 (Huang, 2002). The fertilizer granules were weighed in 100 ml volumetric flasks and then 10ml of concentrated hydrochloric acid was added. The flasks were placed on a hotplate, located in the fume hood, and allowed to slowly boil for 30 minutes. A 1:1 hydrochloric acid to water (v/v) solution was used as needed to ensure the flasks did not run dry. The flasks were allowed to cool, pH adjusted to between pH 3-5 using a 50% NaOH solution and then diluted to the mark. An aliquot (5 ml) of this solution was used for the colorimetric determination of iron (Hach 8008). Addition of Ferrover pillows to the samples gave an orange color from the reaction of ferrous ions with 1, 10-phenanthroline indicator. Ferrous sulphate heptahydrate was used to make standards for the calibration curves and absorbance was measured at 510 nm. The linear range of this method is 0-3 mg/L.

3.2.5 X-ray Diffraction

X-ray diffraction (XRD) measurements, which allowed identification of the mineralogical phases constituting the fertilizer, were performed on a PHILIPS X-pert XRD MPD using the Cu$K\alpha$ radiation (1.5418 Å). The data collection was carried out in the 2θ range 5^{O}–$70^{O}$with a step of 0.02^{O} and an acquisition time of 10 s. Peak matching was used to determine the phases present.

3.2.6 Column Experiments

Acid-washed Monterey sand (Uniformity coefficient =1.5, Effective size = 0.45 - 0.55 cm) was repeatedly washed with de-ionized water and then allowed to air dry for 2 days prior to use. The sand (200 g) was placed in a polyethylene column (internal diameter, 15 cm; length, 10 cm). The column was flushed with ultrapure water to moisten it and determine the background Cd and phosphate concentrations, which were determined to be negligible. Fertilizer (1 g, 30 grains) was then embedded in the sand and solutions of differing composition were flushed through as discrete washes of 50 ml/hr. The pH and conductivity of the 45 ml of eluate collected were measured and aliquots were taken and analyzed for orthophosphate content (10 ml) using the Hach ammonium paramolybdate test and cadmium content (5 ml) using flame atomic adsorption spectroscopy (FAAS -Perkin Elmer AAnalyst-300 Atomic Absorption Spectrophotometer) and ICP-MS (HP-4500 Inductively Coupled Plasma Mass Spectrometer). The aliquot for cadmium analysis was acidified with nitric acid to a pH < 1 prior to analysis. Fig. 3.2 shows an apparatus schematic.

To address several research questions, different experimental conditions were used: an eluent of 18 MΩ ultrapure water; an eluent of 10^{-4} M disodium EDTA dihydrate at a final pH of 7.5, the pH was initially adjusted to 8 to get the salt into solution; an eluent of 0.01M acetate buffer solution at pH 5.5; ground fertilizer instead of granulated; and field agricultural soils instead of sand.

3.3 Results

3.3.1 Elution with Ultra-pure Water.

Elution of the fertilizer by ultrapure water resulted in a striking and reproducible pattern in which Cd concentrations spike relatively quickly but then drop to low levels (Fig. 3.3) as seen by Notario del Pino et al. (1995) for K^+ from solid potassium phosphate and zeolite fertilizers. The Cd release is mirrored in the elution by a very similar time course for electrical conductivity (EC) (Fig. 3.4), which is an index of total salts released from the fertilizer. The pH (Fig. 3.5) dipped only slightly (< 0.2 units) during the spike of Cd and EC and not to the extent that might be expect from the dissolution reaction noted above. P release rose rapidly, as expected, and unlike the Cd, remained high throughout the elution (Fig. 3.6). As the Cd release rose and dropped so quickly compared to P release, the fate of Cd and P in the system was next examined to identify the total amount of each that was released from the original fertilizer levels.

Cd and P were measured in the water phase, the amount clinging to the sand after a brief rinse, and in the remaining identifiable pieces of fertilizer granules. As shown in Fig. 3.7, only about 10% of the Cd in the fertilizer was released in the first 24 hr of elution, whereas over 95% of the total P was released in the same period. This important finding showed that Cd release cannot be assumed to mimic the release of the parent P minerals in the fertilizer and that some chemical process inhibits the solubility of Cd in the fertilizer-water system. This was tested by the addition of a chelator to the eluent.

3.3.2 Elution with EDTA Chelator

If a Cd-P solid phase inhibits the release of Cd, then the addition of a chelating agent that binds up soluble Cd and thereby reduces the activity of Cd^{2+} in solution should enhance the release of Cd. A dilute (1×10^{-4}M) Na_2EDTA solution was used to investigate this. The reaction for an unspecified "Cd-P" solid is:

$$\text{“Cd-P”} + \text{EDTA} \leftrightarrow \text{Cd-EDTA} + \text{P} \qquad (3)$$

where the soluble Cd-EDTA complex appears in solution as released Cd.

When the column was eluted with 10^{-4}M EDTA at pH 7.5, there was indeed a marked increase in the amount of Cd released in the initial spike. The peak concentration was about 80% higher and the total Cd released in the first 7 h was 3.5 times greater (Figs. 3.3 & 3.8). The EDTA had negligible effect on the P release (Fig. 3.6). The initial EC spike was enhanced by the EDTA, in approximate proportion to the enhancement of Cd release, suggesting that EC is a fairly consistent marker of the release of Cd from the fertilizer.

3.3.3 Elution with a Buffered Solution to Fix pH.

To test the effect of only pH on Cd release, a dilute acetate buffer was used to fix the pH of the eluent at the lowest pH (approximately 5.5) observed in the EDTA elution. This elution thus mimicked the lowest pH created by EDTA but with no chelating agent (acetate is an extremely weak ligand for Cd). Eluting the column at pH 5.5 resulted in an initial peak of Cd that was similar to that of the water-only elution and which was about 50% less than the peak Cd observed in the EDTA elution (Figs. 3.3 & 3.8).

3.3.4 Effect of Pellet Size: Grinding Fertilizer.

To determine whether the size of the fertilizer pellet significantly affected the release of Cd, fertilizer pellets were ground in a mortar and pestle to a coarse powder and then the water elution experiment replicated using the same mass of fertilizer. The peak Cd in the initial spike was virtually identical in the crushed fertilizer compared to the original uncrushed result and the EC and pH patterns were likewise almost identical for crushed and uncrushed (Figs. 3.3, 3.4 & 3.5). However, the cumulative release of Cd over time was actually less for the crushed pellets for the uncrushed (Fig. 3.8).

3.3.5 Elution of Fertilizer in Oregon Agricultural Soils.

The sand-column elution experiments were repeated using columns packed with homogenized soil samples from the four Oregon sampling sites (Hyslop, Columbia Basin, Klamath, and Hermiston). The soils were eluted under the same condition as the sand experiments using ultrapure water with a dilute neutral electrolyte (0.01 M $LiClO_4$) to simulate rainfall or irrigation. In all cases, no measurable Cd (< 1ppb) was eluted from the columns, even after over 100 pore volumes were passed through the columns. The detection limit for Cd with the ICP-MS was less than 1 ppb. These results were consistent with adsorption isotherm data that showed that Cd was strongly bound to all soils at the low total Cd concentrations produced by the elution of fertilizer ($Cd_{sorbed}/Cd_{soluble} > 10^{2.5\text{-}3.5}$.

3.3.6 Energy Dispersive X-ray Analysis and SEM Imaging.

Energy Dispersive X-ray spectroscopy (EDX or EDS) was used to determine the chemical composition of the granule surface. The results show the main cation is Ca while Cd is only about 1% by weight (Fig. 3.9). The palladium (Pd) detected was from the coating put on prior to analysis on the SEM. EDS analysis of the fertilizer granules after sequential washes also showed the change in composition of the fertilizer surface (Fig. 3.10). The percentage by weight of iron on the fertilizer surface appeared to increase with decreasing granule size except after the initial wetting of the fertilizer surface.

SEM images of the fertilizer surfaces were taken to determine if there were any evident irregularities in the fertilizer surfaces that might contribute or inhibit the release of Cd and P. Prior to elution (Fig. 3.11a), surfaces generally were more amorphous and less microporous than the surfaces after 4-h of elution (Fig. 3.11b) where exposed crystals were more evident on the fertilizer surface and there was possibly greater microporous structure as a result of the dissolution of readily soluble amorphous phases.

3.3.7 X-Ray Diffraction

An XRD spectrum of the fertilizer (Fig.3.12) showed the main components of the fertilizer to be Mascagnite $(NH_4)_2SO_4$ and Biphosphammite ($NH_4H_2PO_4$).

3.4 Discussion

These experiments showed the importance of dissolution kinetics in understanding the release of Cd from fertilizer in unsaturated soils. Under typical field conditions it is expected that only about 10- 20% of Cd will be released quickly in soluble form and that most of the Cd will remain associated with very slowly dissolving solids. The experiments with EDTA, acetate buffer, and particle grinding were all consistent with a Cd-phosphate phase regulating the slow release of Cd.

It is likely that, at the microscale of the zone immediately surrounding a fertilizer pellet, the pH drop is greater, but the results show that even in a poorly buffered (pure water) eluent, the pH at a porous-medium scale of just a few centimeters is relatively constant and is probably buffered by the combination of phosphate salts eluting from the fertilizer.

EC is a measure of the total concentration of dissolved ions. As expected the largest drop in EC is seen in the experiments with the crushed fertilizer (Fig. 3.4) and the other solutions show an initial increase in EC followed by a sharp decline. The EC curves closely tracked the Cd curves. The EC values for all the solutions returned to background levels after 350 ml of solution except for the acetate buffered curve. The high EC values noted with solution could be due to the dissolved ions in the eluting solution itself.

Eluting with EDTA appears to promote the dissolution of the phase that otherwise limits the release of Cd. However, the pH of the solution can also affect release rates. The pH varies more in the EDTA experiments than in the water-only elution (Fig. 3.5). The initial pH with EDTA is 6.8 (compared to 6.1 for water only) because of the mildly basic effect of the sodium EDTA salt, but the pH quickly drops to about 5.5 as Cd ions displace protons from the EDTA. The pH then gradually rises back to 6.1 after 6 h of elution, presumably because of the buffering effect of the dissolved phosphates. The drop in pH potentially complicates the interpretation of the EDTA experiment because a lower pH could also enhance solubility of a Cd-P solid phase. The EDTA experiment results also suggest that chelating agents have the greatest influence on fertilizer Cd release and although EDTA is a stronger Cd chelator than humic or fulvic acids, similar results are to be expected in soils where natural humic substances are believed to be the main ligands for Cd (Fish et al., 1986).

A consistently lower pH (near 5.5) does enhance Cd release but that the effect of EDTA is substantially greater than the effect of pH alone, especially given that the pH in the EDTA experiments was higher than 5.5 for most of the elution. It was concluded that the Cd-chelating effect of the EDTA explains most of the enhanced dissolution that the EDTA induced. Note that both the EDTA and the acetate buffer results are consistent with the release of Cd being regulated by a relatively insoluble phase after the initial flush of rapid dissolution.

The reduction in cumulative release of Cd from smaller pellet sizes is counterintuitive until one examines the cumulative release of P which is expectedly larger for the crushed pellets. This result was interpreted to indicate that Cd solubility after the initial peak flush was indeed controlled by a relatively insoluble Cd-phosphate phase. The higher P concentration in the pore fluids would facilitate greater precipitation of the Cd-P solid phase, thereby suppressing the total release of Cd. The finding of limited rapid release followed by slow release of most Cd was significant because the rate of uptake of Cd by soil surfaces typically will be more rapid than the release of most Cd. That is, Cd released by the fertilizer will be sorbed by the soil faster than it can leach away. This finding is confirmed by the experiments in which Oregon agricultural soils were used instead of the washed sand. The uptake of Cd by the soil surfaces prevented detectable Cd from eluting from the columns, even after 100 pore volumes or more. A local equilibrium model is thus appropriate for these Oregon agricultural soils because the release of Cd fertilizer is slow enough to allow sorption equilibrium to be assumed.

The solution chemical reactions and mechanisms of the $CdPO_4$ system is not well documented but the existence of low solubility Cd- phosphate phases such as $Cd_5H_2(PO_4)_4 \cdot 4H_2O$ and cadmium hydoxyapaptite or Cd-Hap (Seaman et al., 2001 and Ayati and Lundager Madsen, 2001) have been suggested and characterization of some of these solids has been attempted by Matusik et al., 2007. Another explanation for the behavior observed was offered by Valsami-Jones et al. (1998) who suggested at low Cd concentrations sorption of Cd forms a mixed cadmium-calcium phosphate complex with a lower solubility than that of hydroxyapaptite and formation of these complexes is pH dependent with near neutral pH conditions being most conducive. Calculation of the apparent ion activity products of the different possible CaCd-Hap solids suggested possible precipitation of some of these solids.

$$Ca_{10}(PO_4)_6(OH)_2 + xCd^{2+} \rightarrow Cd_xCa_{10-x}(PO_4)_6(OH)_2 + xCa^{2+} \quad (3.4)$$

Wang and Xing (2002) also postulated P accelerated adsorption of Cd on goethite surfaces, goethite is a constituent of some soils, by increasing the negative surface charge through occupying and blocking the surface meso and micro-pores. Bolan et al. (2003) showed that phosphate immobilized cadmium in soils through phosphate-induced Cd^{2+} adsorption and precipitation as $Cd(OH)_2$ and $Cd_3(PO_4)_2$. However, calculation of the ion activity products for all the soil solutions indicated no evidence of $Cd_3(PO_4)_2$ forming and the pH was too low for formation of substantial amounts of $Cd(OH)_2$.

Iron oxides appeared to have a role in the sequestration of cadmium released by the fertilizer and the change in the relative contribution of iron to the surface chemistry seems to suggest this (Table. 3-1). The increase in iron content as a percentage of the fertilizer just after wetting of the fertilizer could be due to the loss of other constituents of the fertilizer matrix, leaving the iron as the most prominent phase at the fertilizer surface. Iron appeared to become the major constituent of the fertilizer granules remaining with subsequent washes. The drop in pH seen after the first wash was significant because low pH and the presence of phosphate have previously been shown to enhance cadmium adsorption onto iron oxides (Wang and Xing 2002). The paper suggested the formation of Cd-phosphate complexes ($CdH_2PO_4^+$, $CdHPO_4^0$), that can readily adsorb onto the iron oxides, was more likely to occur in a system where there was a simultaneous release of the two species and that aptly describes the process of fertilizer dissolution.

A plot of the release of Cd (Fig. 3.13) shows two stages of release, a very steep slope for the initial release in the first five hours followed by a much slower release. The release profile appears to follow first order kinetics. A similar plot for P (Fig. 3.14) showed three stages of phosphorus release, initially fast followed by a much slower release and then a fast release again. Similar results were observed by Notario del Pino et al. (1995) when investigating the release of phosphorus and potassium from phosphate fertilizer. The release profiles are very different for the two components of interest.

The relative disappearance of amorphous material in the early stages of particle dissolution seen in the SEM images was consistent with the initial spike in both Cd and EC. The residual, more crystalline, phases can be expected to have lower solubility.

Soil and solute pH, major variables for many soil processes (Sposito, 1984) were not seen to greatly affect the fertilizer dissolution. The large phosphate concentration from the fertilizer dissolution and the associated buffering properties may be responsible. Phosphate fertilization can lead to gradual acidification of soil, a corresponding decrease in the CEC (Nicholson and Jones, 1994; Fest et al., 2005) and an increase in susceptibility to leaching that can be rectified through liming.

These data show that Cd is most likely to accumulate in rather than leach from Oregon agricultural soils. Any losses of Cd from the soil column are expected to be at extremely low (part per billion) levels and are expected to occur over long spans of time (time scale of years).

Chapter Four

Conclusions

4.1.1 The Surface Chemistry of Oregon Soils

The acid-base chemistry of the sites revealed the pH buffering ability of soils and that buffer capacity correlated well with soil CEC. The development of surface charge as a function of pH also varied widely among the soils, but was well correlated with CEC and slightly less well with %OM. Although PZSE could be predicted by organic matter content, the quantities and effects of aluminum and iron oxides need to be considered. The data also showed the adsorption of cadmium and lead on sandy and loamy agricultural soils was independent of texture and was well predicted from the pH and CEC, with the latter being predicted from the organic matter content and clay content of the soil. At the cadmium concentrations levels of phosphate fertilizer the adsorption behavior of cadmium was found to be linear allowing for the use of K_d in accumulation and leaching calculations.

This study showed the importance of doing region specific research as the values of K_d determined were an order of magnitude different to commonly used in risk assessment models for Cd. The value of K_d was also found to be important in determining the doubling time of cadmium in agricultural soils. Knowledge of basic soil characterization such as texture, was important in order to make proper comparisons of leaching loss between soils sites, a issue of great importance for organic farming systems. The three year time period designated for a field to be certified organic was found to be an insufficient time period for an impactful decrease in background cadmium concentration.

4.1.2 Fertilizer Chemistry

Cadmium release was found to not mimic the release of the phosphorus from fertilizer and this was evident from the location of cadmium and phosphorus after 24 hrs. Electrical conductivity was found to be a good indicator of the release profile of cadmium however measuring this parameter in the field can present some experimental challenges. The solubility of cadmium in the fertilizer water system appeared to be inhibited by a Cd-phosphate phase. This was evident from the cumulative release of P and Cd from crushed fertilizer granules.

Complexing agents appeared to have a substantial influence on the release of fertilizer-derived cadmium and natural humic substances are believed to have a similar effect in the field. The pH of the soil of the soil did not appear to have an effect on the cadmium release as elution of the phosphate fertilizer created a buffer solution in the fertilizer water system that effectively reduced the mobility of Cd^{2+} in the microscale zone immediately surrounding the fertilizer granule.

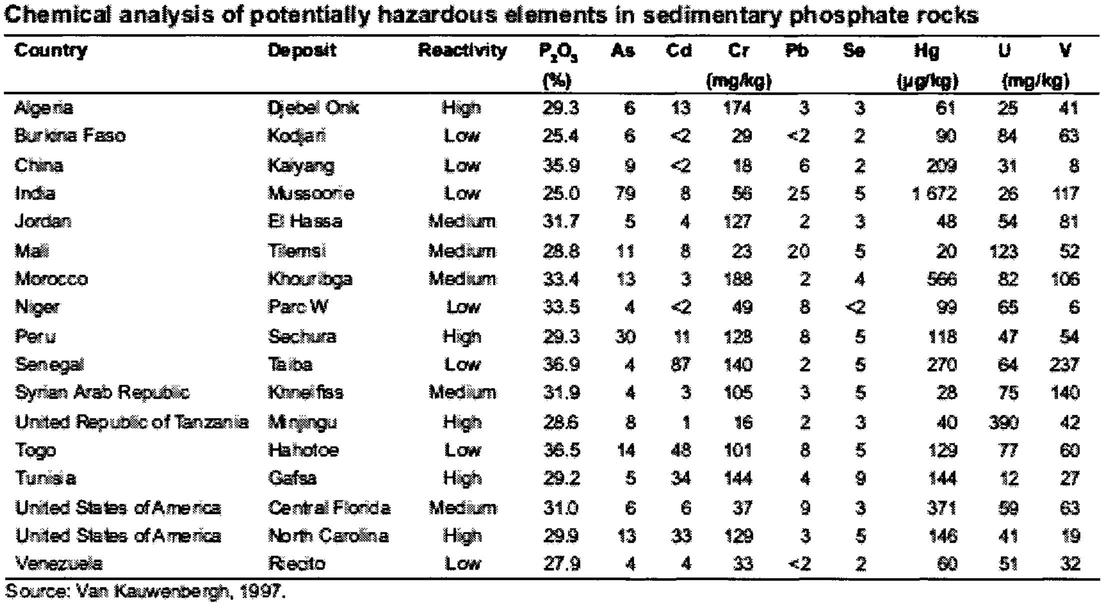
The processes controlling the release of fertilizer-derived cadmium were found to be a Cd-phosphate phase, possibly cadmium hydroxyapaptite and iron oxides which have been to have enhanced cadmium adsorption in the presence of phosphates.

4.1.3 Overall Conclusion

For these Oregon agricultural sites, the partition coefficients (K_d) of Cd can be used in the soil modeling part of risk assessment models to calculate risk based concentration as fertilizer-derived cadmium is released slowly and accumulates in the soil. The order for potential of accumulation of cadmium in the surface soil of the sites from fertilizer is Pendleton > Klamath > Hyslop > Hermiston. The susceptibility of the Pendleton soils to Cd accumulation was confirmed by the Perez and Anderson (2007) who noticed treatment effects over a three year period at this site comparable to the other sites despite having lower fertilizer application rates. The predicted persistence data suggest the historic use of phosphate fertilizers should have greater importance in considering a field for organic farming certification and that the three year standard may not be appropriate for all soil types.

Tables

Table1-1: Heavy Metal Concentration of Phosphate rock deposits



Chemical analysis of potentially hazardous elements in sedimentary phosphate rocks

Country	Deposit	Reactivity	P_2O_5	As	Cd	Cr	Pb	Se	Hg	U	V
			(%)			(mg/kg)			(µg/kg)	(mg/kg)	
Algeria	Djebel Onk	High	29.3	6	13	174	3	3	61	25	41
Burkina Faso	Kodjari	Low	25.4	6	<2	29	<2	2	90	84	63
China	Kaiyang	Low	35.9	9	<2	18	6	2	209	31	8
India	Mussoorie	Low	25.0	79	8	56	25	5	1 672	26	117
Jordan	El Hassa	Medium	31.7	5	4	127	2	3	48	54	81
Mali	Tilemsi	Medium	28.8	11	8	23	20	5	20	123	52
Morocco	Khouribga	Medium	33.4	13	3	188	2	4	566	82	106
Niger	Parc W	Low	33.5	4	<2	49	8	<2	99	65	6
Peru	Sechura	High	29.3	30	11	128	8	5	118	47	54
Senegal	Taiba	Low	36.9	4	87	140	2	5	270	64	237
Syrian Arab Republic	Khneifiss	Medium	31.9	4	3	105	3	5	28	75	140
United Republic of Tanzania	Minjingu	High	28.6	8	1	16	2	3	40	390	42
Togo	Hahotoe	Low	36.5	14	48	101	8	5	129	77	60
Tunisia	Gafsa	High	29.2	5	34	144	4	9	144	12	27
United States of America	Central Florida	Medium	31.0	6	6	37	9	3	371	59	63
United States of America	North Carolina	High	29.9	13	33	129	3	5	146	41	19
Venezuela	Riecito	Low	27.9	4	4	33	<2	2	60	51	32

Source: Van Kauwenbergh, 1997.

Table 2-1: Major crops farmed at the four Oregon sites

Site	Climate Region	Major Crops
Hermiston	6	potatoes, wheat, alfalfa and green peas
Hyslop	2	tree fruits, nuts, berries, mint, grains, and hay
Klamath	7	potatoes, alfalfa and other hay crops, mint, wheat, oats, barley, and onions
Pendleton	6	wheat, potatoes, alfalfa and green peas

Table 2-2: Some background concentrations of heavy metals in agricultural soils. (All units ppm)

	ODA Limit	Holmgren et al.,1993	Boerngen and Shackette, 1981	Chen et al., 2006
Arsenic	180	N/A	6.4 (4.3-10.3)	8.80
Cadmium	150	0.294	N/A	0.18
Lead	860	8.6	16(10-20)	12.0
Mercury	14	N/A	0.11(0.04-0.26)	N/A

Holmgren et al: samples from northwestern, south central and southeastern Oregon.
Boerngen and Shackette: samples from Benton, Columbia, Marion, Lincoln, Multnomah and Tillamook counties
Chen et al: samples from California

Table 2-3: Physical conditions for the four Oregon sites sampled in this study

Site	Soil Type†	Farming Type	Rainfall (mm)	Altitude Range (m)
Hermiston	Adkins fine sandy loam	Irrigated	177-254	76-701
Hyslop	Woodburn silt loam	Dry	1016-1270	45-121
Klamath	Fordney Loamy fine sand	Irrigated	250-356	1234-1707
Pendleton	Palouse silt loam	Dry	457-659	487-1370

† NRCS classification

Table 2-4: Selected soil characteristics for the four Oregon sites sampled.

Site	Particle Size$_a$	Classification	pH	CEC$_b$[†] (cmol/kg)	% OM$_c$[†]
Hermiston	88-10-2	Sand	4.9	11	1.1
Hyslop	38-46-16	Loam	5.5(5.7)[‡]	18	2.4
Klamath	89-7-4	Sand	5.7	13	0.9
Pendleton	62-27-11	Sandy loam	5.9	18	2.6

[†] Perez and Anderson, 2007 OSU ODA Final Report
a %Sand –%Silt -%Clay
b CEC = Cation Exchange capacity
c OM = Organic Matter
[‡] Lin, 1957

Table 2-5: Background Cd concentrations at the study sites (mg/kg).

Site	This Study[1]	Perez and Anderson[2]
	Cd(n=16)	Cd
Hermiston	0.07±0.016	0.21±0.02
Hyslop	0.03±0.003	0.19±0.008
Klamath	0.04±0.023	0.11±0.004
Pendleton	0.05±0.015	0.20±0.009

1 Double acid extraction method for bio-available metal concentration
2 EPA 3050B method (complete soil digest) for total metal concentration

Table 2-6: Soil buffer capacities for the study soils. “Slope” refers to the gradient of the plot of pH vs added base from pH 4.5 to 6.5. β is buffer capacity and is the reciprocal of the slope

Site	Slope	β (cmol/kgsoil) pHunits^{-1}
Hermiston	0.135	7.4
Hyslop	0.056	17.8
Klamath	0.109	9.2
Pendleton	0.078	12.8

Table 2-7: Soil titration constants for the study soils. (PZSE = the point of zero salt effect; PZNPC= point of zero net proton charge)

	Native pH	PZSE	PZNPC	
			0.1M†	0.01M†
Hermiston	4.9	6.95	6.93	6.9
Hyslop	5.5(5.7)	6.08	6.23	6.35
Klamath	5.7	7.2	7.05	6.8
Pendleton	5.9	7.1	6.55	5.85

† Background electrolyte concentration $LiClO_4$

Table 2-8: Langmuir and Freundlich modeling parameters for Cd at the study soils.

		Hermiston	Hyslop	Klamath[†]	Pendleton
Langmuir Parameters	S_{max} (mg/kg)	1044-1163 (1074)	972-1207 (1127)	1238-1522 (1473)	1446-2170 (1680)
	K (L/kg)	0.30-0.58 (0.50)	0.36-1.0 (0.63)	0.20-0.60 (0.40)	0.22-0.86 (0.71)
Freundlich Parameters	K_f (L^{nf} mg^{1-nf}/ kg)	258-364 (290)	229-408 (327)	209-362 (346)	257-497 (398)
	nf	0.32-0.46 (0.38)	0.34-0.50 (0.44)	0.56-0.64 (0.60)	0.45-0.64 (0.50)

[†] Sinha, 2006

Average values in parentheses

Table 2-9: Langmuir and Freundlich modeling parameters for Pb at the study soils

		Hermiston	Hyslop	Klamath	Pendleton
Langmuir Parameters	Cmax (mg/kg)	1049-1412	2370-5340	1310-4925	5380-7700
	K (L/kg)	0.7-0.8	0.3-0.5	0.4-0.7	0.6-0.7
Freundlich Parameters	Kf ($L^{nf}$$mg^{1-nf}$/kg)	377-488	-	-	-
	nf	0.43-0.57	-	-	-

Table 2-10: Change in surface charge 1.5 pH units above and below the PZSE for I=0.1M

	Δ(-)chg	Δ(+)chg	%OM	CEC	Δ(-)chg/Δ(+)chg
Hermiston	18	12.5	1.1	11	0.69
Klamath	21	15	0.9	13	0.71
Pendleton	41	30	2.6	18	0.73
Hyslop	46	30	2.4	18	0.65

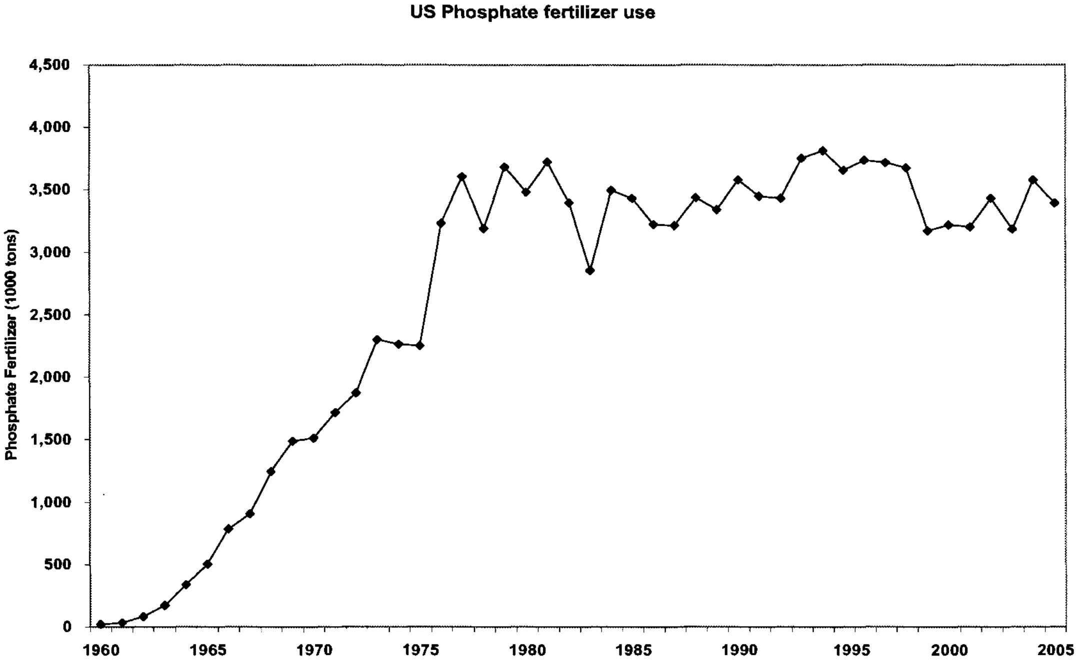
Table 3-1: Iron composition of fertilizer granules from Energy Dispersive X-ray Spectroscopy and fertilizer analysis.

Fertilizer State	% wt†	wt (mg/g) ‡
Dry	5.31	30.16
After Wetting	45.48	202.7
After 1 wash	30.55	172.7
After 5 washes	65.98	77.03

† Energy Dispersive X-ray Analysis for surface composition

‡ Total iron determination using FM 822 and Hach Method 8008

Figures



www.ers.usda.gov/Data/FertilizerUse/Tables/Table5.xls

Fig.1.1. US Di-ammonium phosphate fertilizer use over the last 45 years

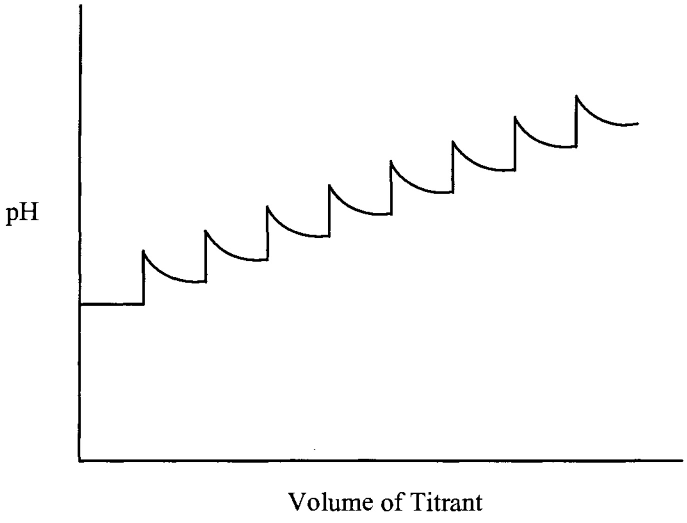


Fig. 2.1. Typical Stepwise Titration Plot for an acidic soil adapted from Conklin, 2005.

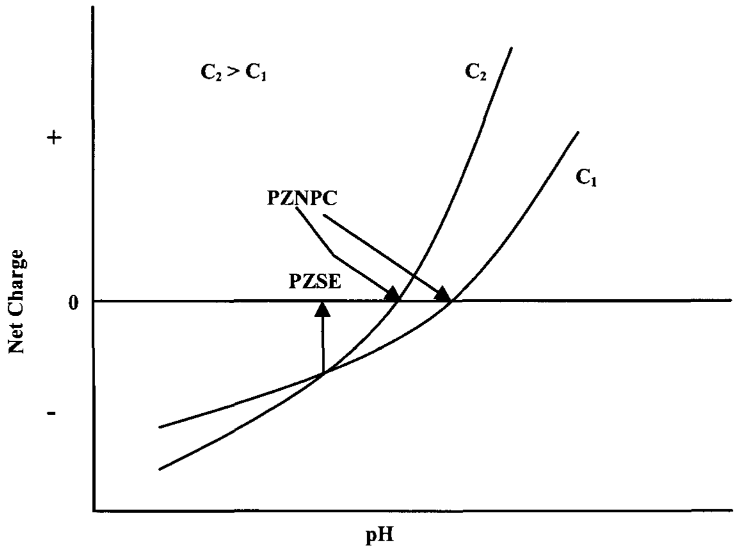


Fig. 2.2. PZSE, PZNPC at different electrolyte concentrations (C). Adapted from Yu and Ji, 1997.

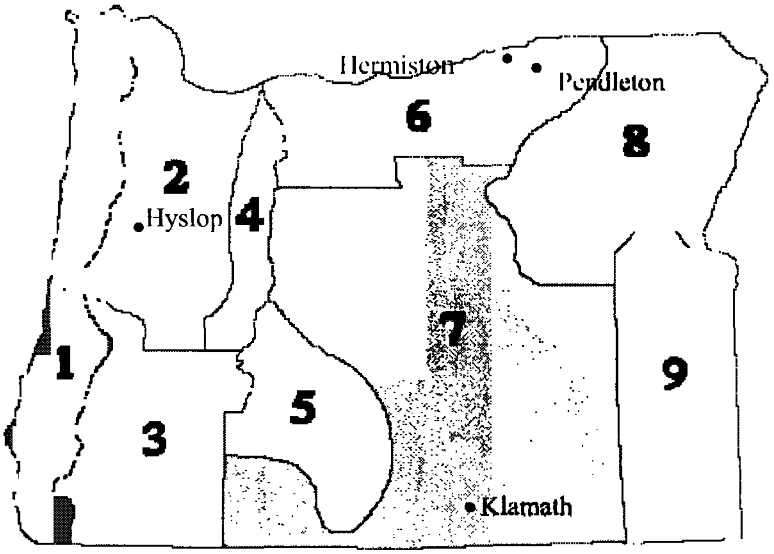


Fig.2.3. Map of Oregon showing the locations of the four study sites and their climatic regions.

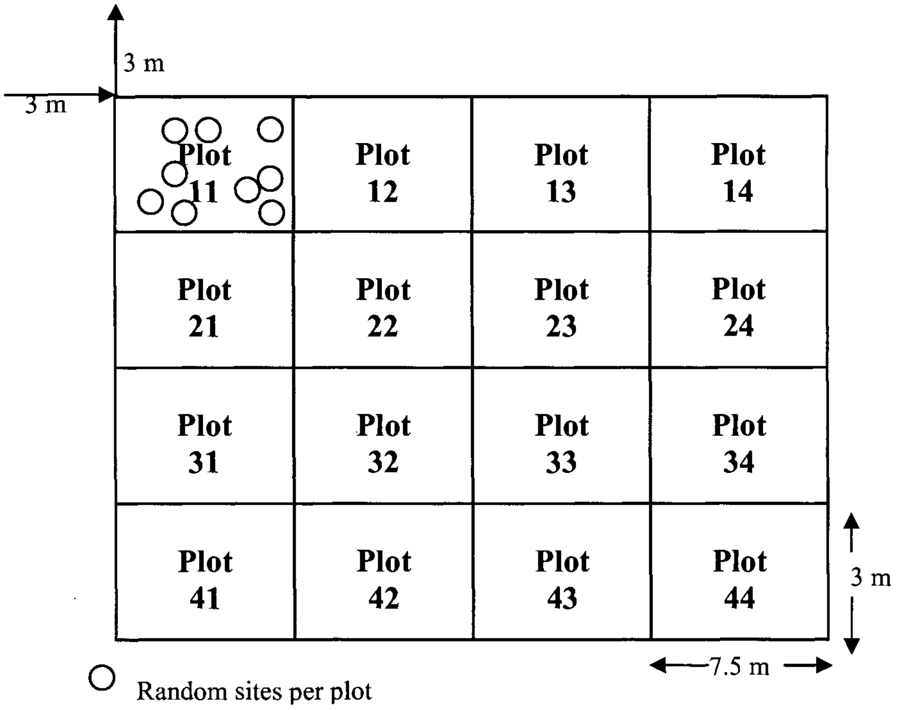


Fig. 2.4. General plot and sampling layout for each of the four Oregon agricultural experiment station sites. The plot size differed slightly at each site

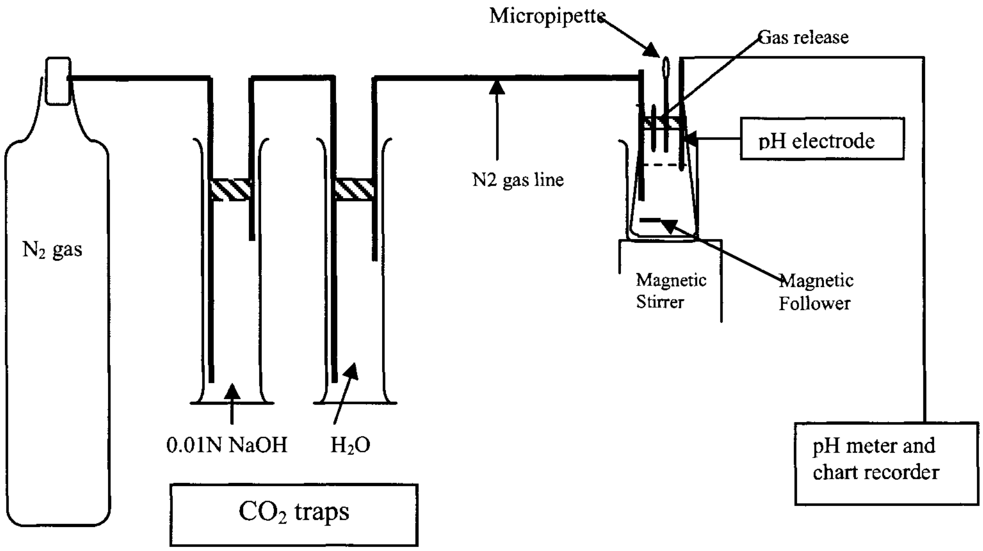


Fig. 2.5. Potentiometric titration setup for titrating and recording changes using pH in a CO_2 free environment

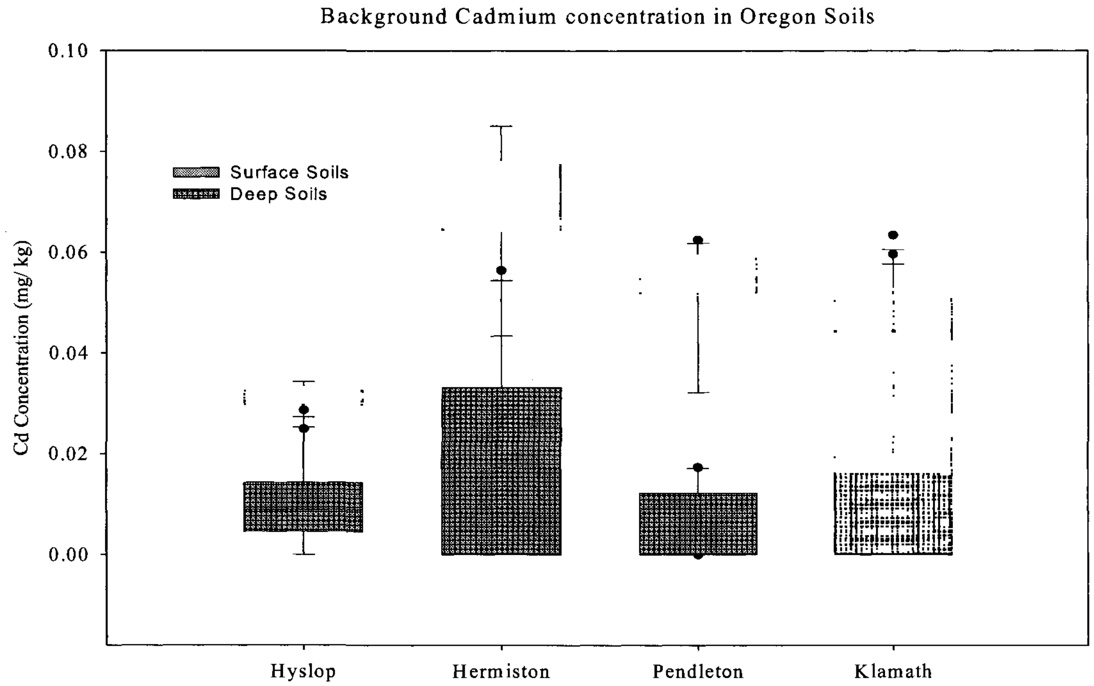


Fig.2.6. Background cadmium concentration levels at the four Oregon sites.

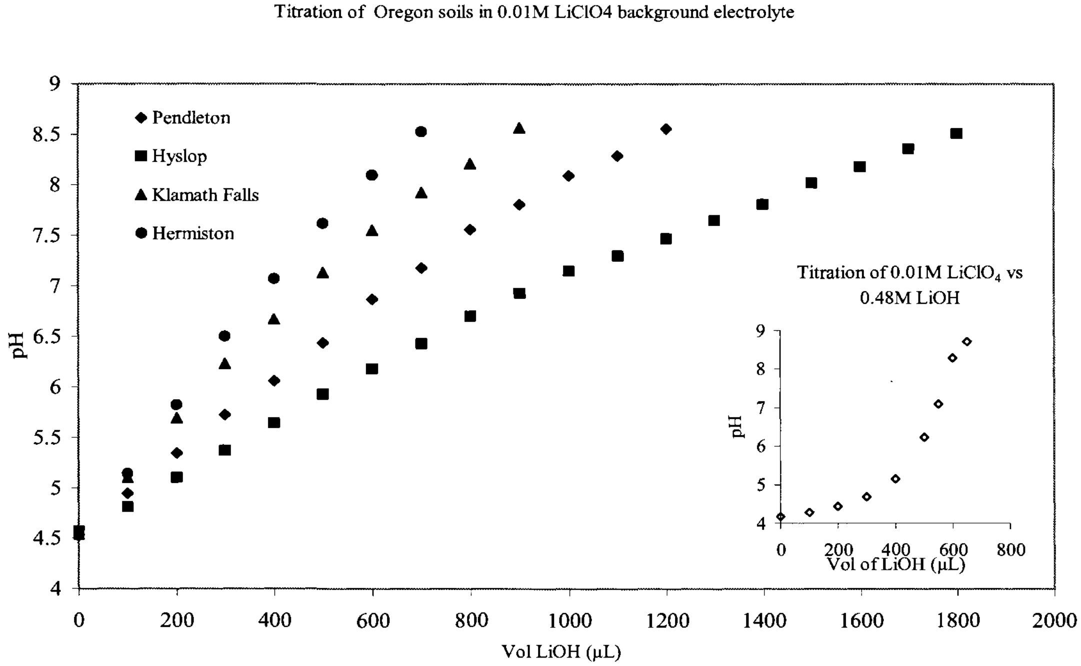


Fig. 2.7. Potentiometric titration curves for soil samples from Hyslop, Hermiston, Klamath and Pendleton. The titrations were done using 10g of soil in 100 ml of 0.01M LiClO4 as background electrolyte vs 0.48M LiOH.
Inset: Titration curve of background electrolyte

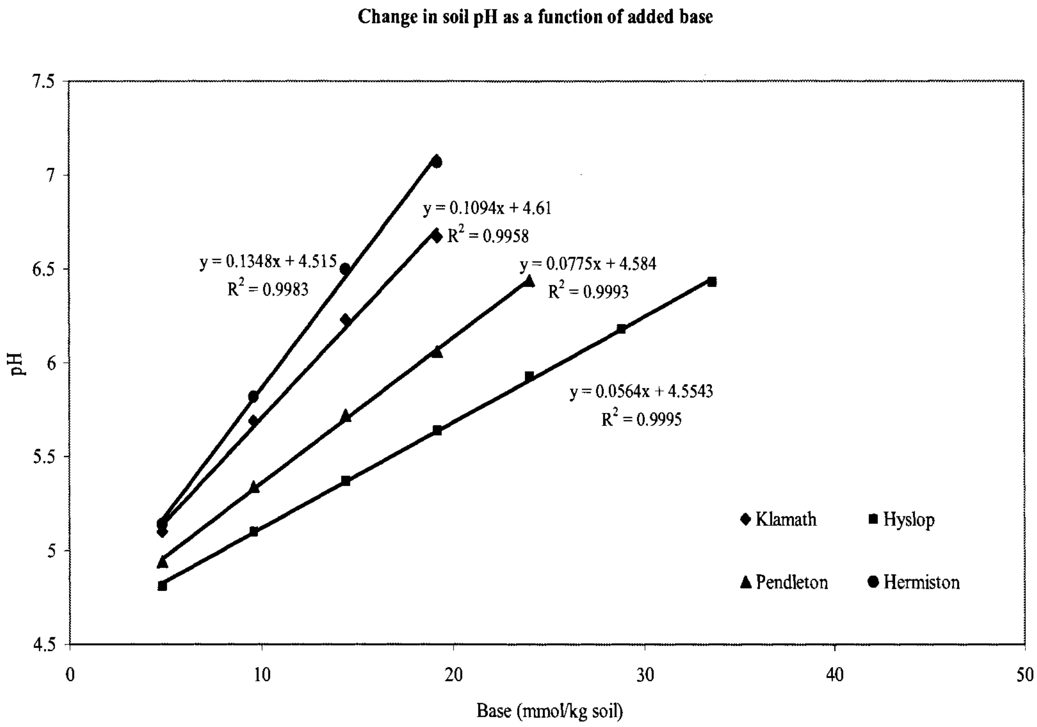


Fig. 2.8. Plots for the determination of buffer capacities (β) of the soil samples from Hyslop, Hermiston, Klamath and Pendleton.

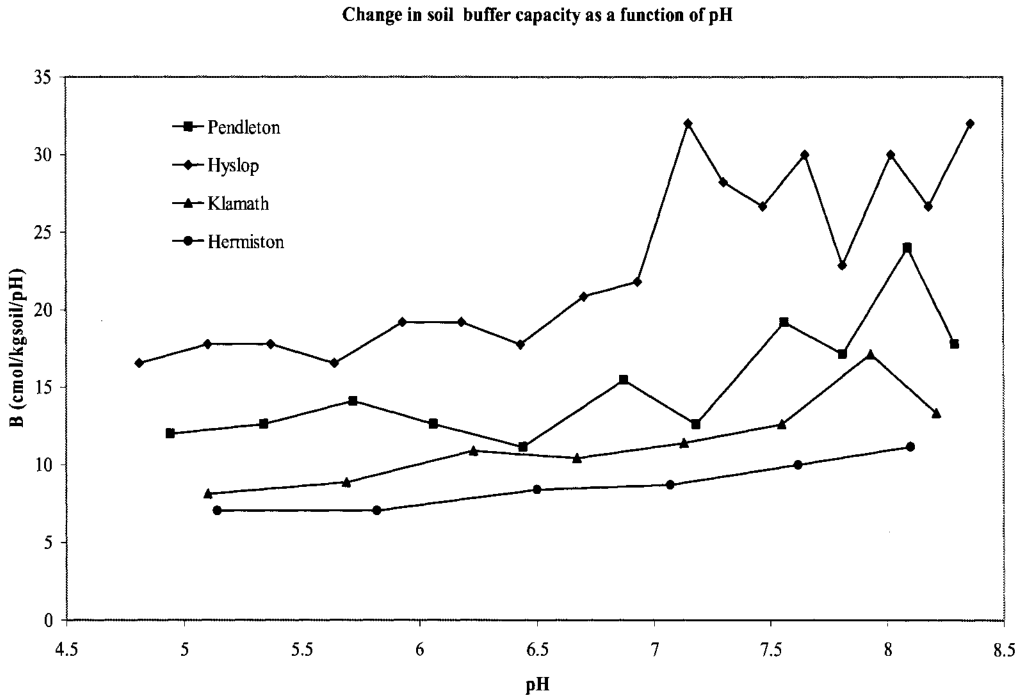


Fig. 2.9. Plot to show the change in buffer capacity as a function of pH.

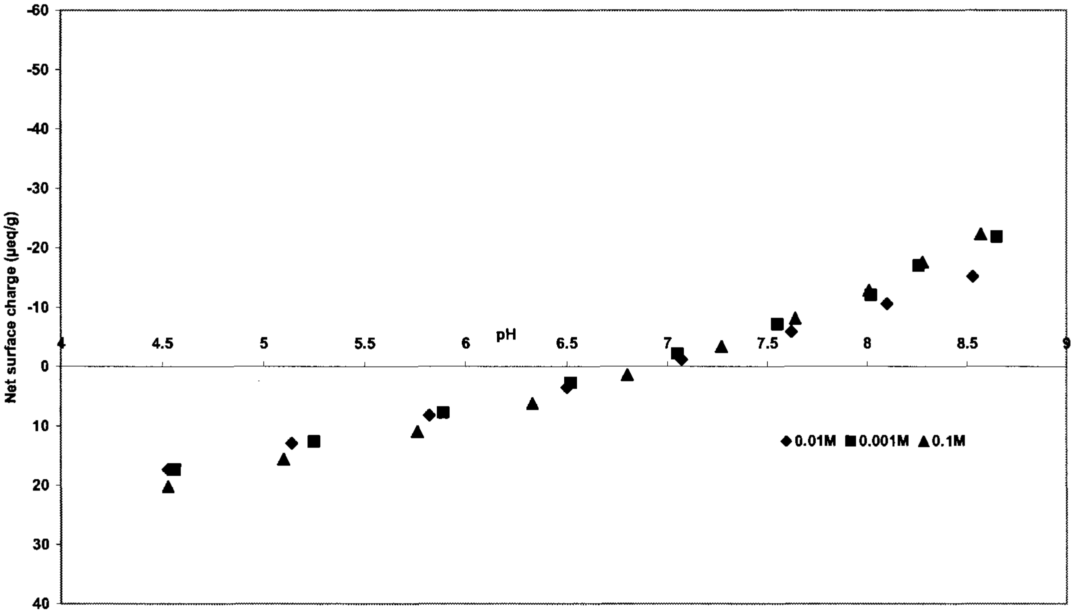


Fig. 2.10. Net surface charge as a function of pH Hermiston soil site at concentrations of $LiClO_4$: 0.001M, 0.01M and 0.1M. The titrations were performed using 10 g of soil in 100 ml of solution and additions of 0.5M LiOH.

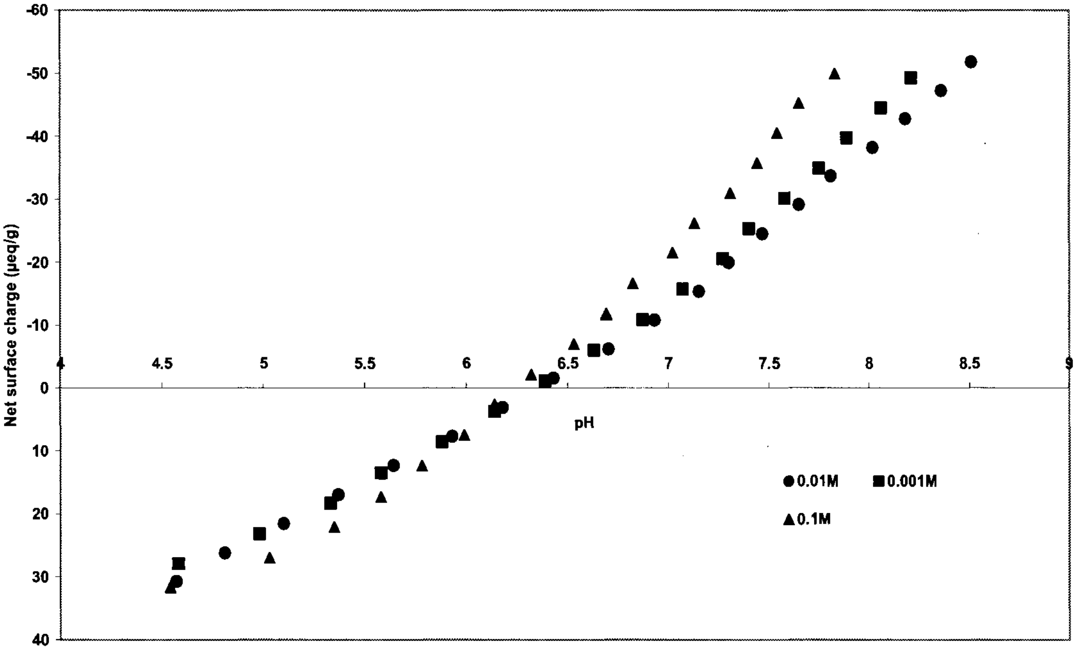


Fig. 2.11. Net surface charge as a function of pH Hyslop soil site at concentrations of $LiClO_4$: 0.001M, 0.01M and 0.1M. The titrations were performed using 10 g of soil in 100 ml of solution and additions of 0.5M LiOH.

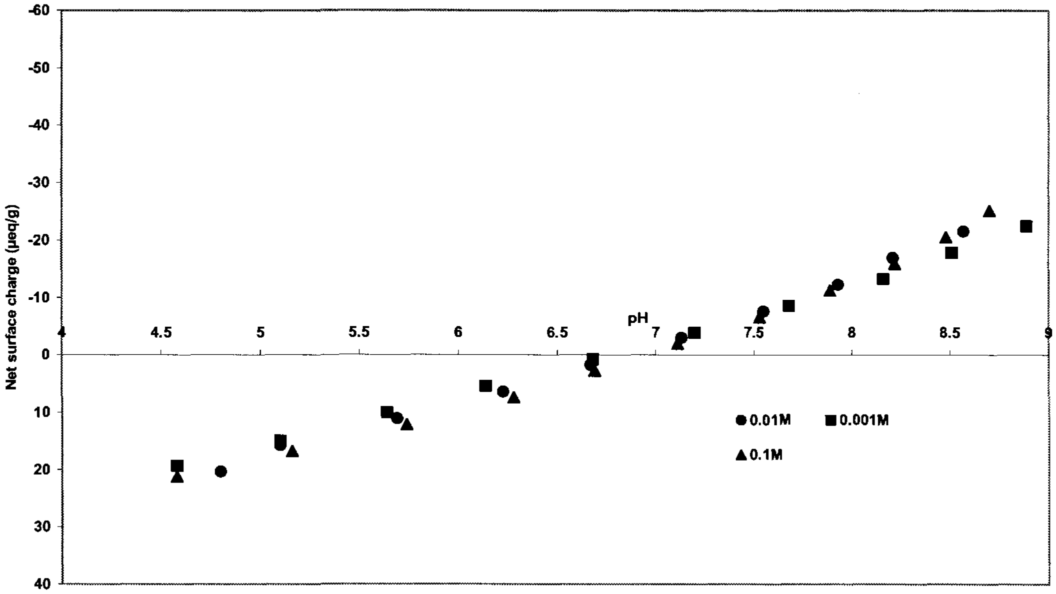


Fig. 2.12. Net surface charge as a function of pH Klamath soil site at concentrations of $LiClO_4$: 0.001M, 0.01M and 0.1M. The titrations were performed using 10 g of soil in 100 ml of solution and additions of 0.5M LiOH.

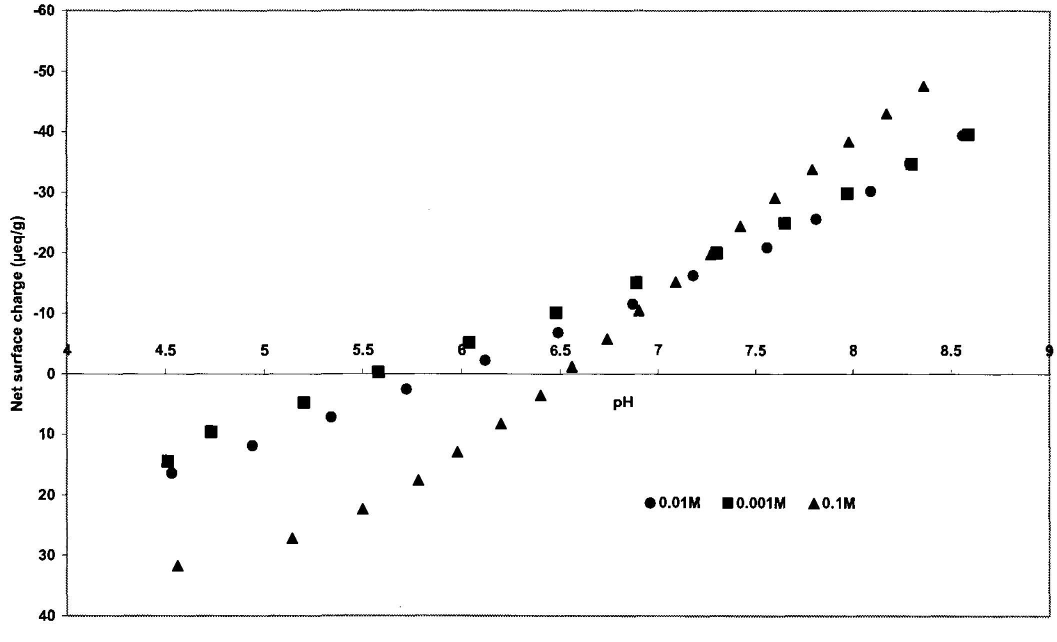


Fig. 2.13. Net surface charge as a function of pH Pendleton soil site at concentrations of $LiClO_4$: 0.001M, 0.01M and 0.1M. The titrations were performed using 10 g of soil in 100 ml of solution and additions of 0.5M LiOH.

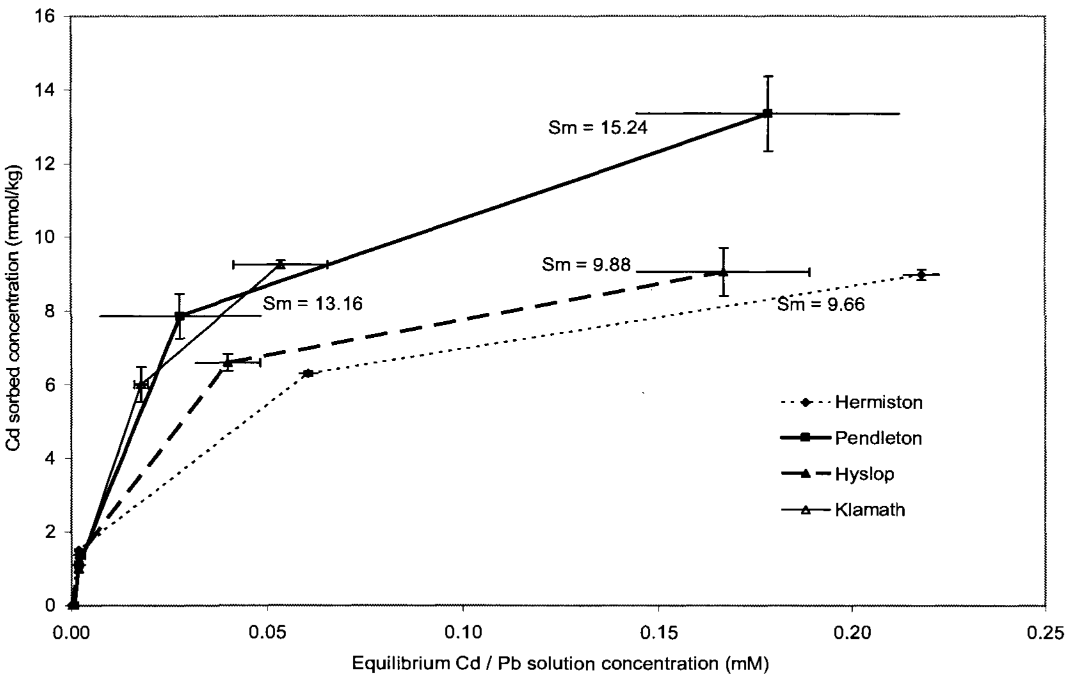


Fig. 2.14. Cd adsorption isotherms (I =0.01 M $LiClO_4$) for the soils from Hermiston, Hyslop, Klamath and Pendleton.

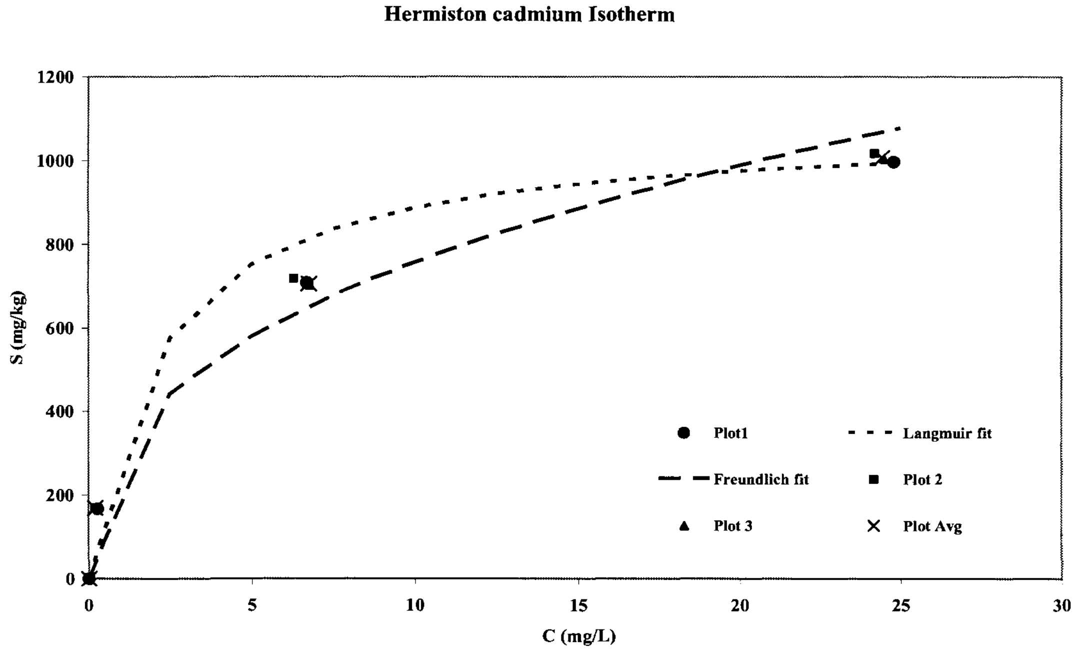


Fig. 2.15. Freundlich and Langmuir model fitting for Cd adsorption at Hermiston

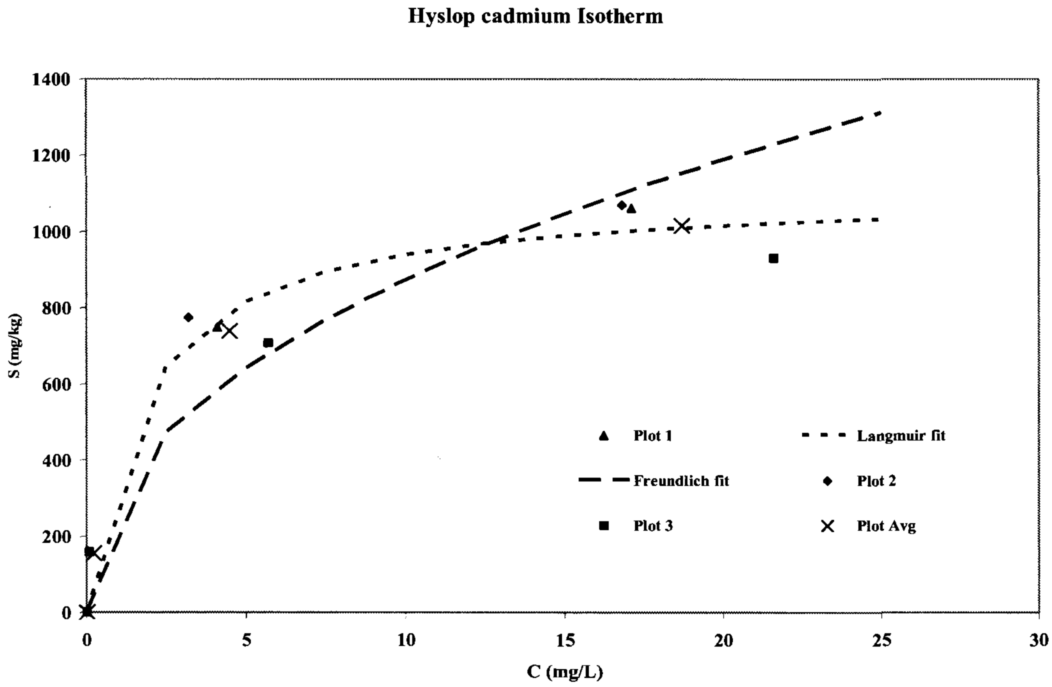


Fig. 2.16. Freundlich and Langmuir model fitting for Cd adsorption at Hyslop

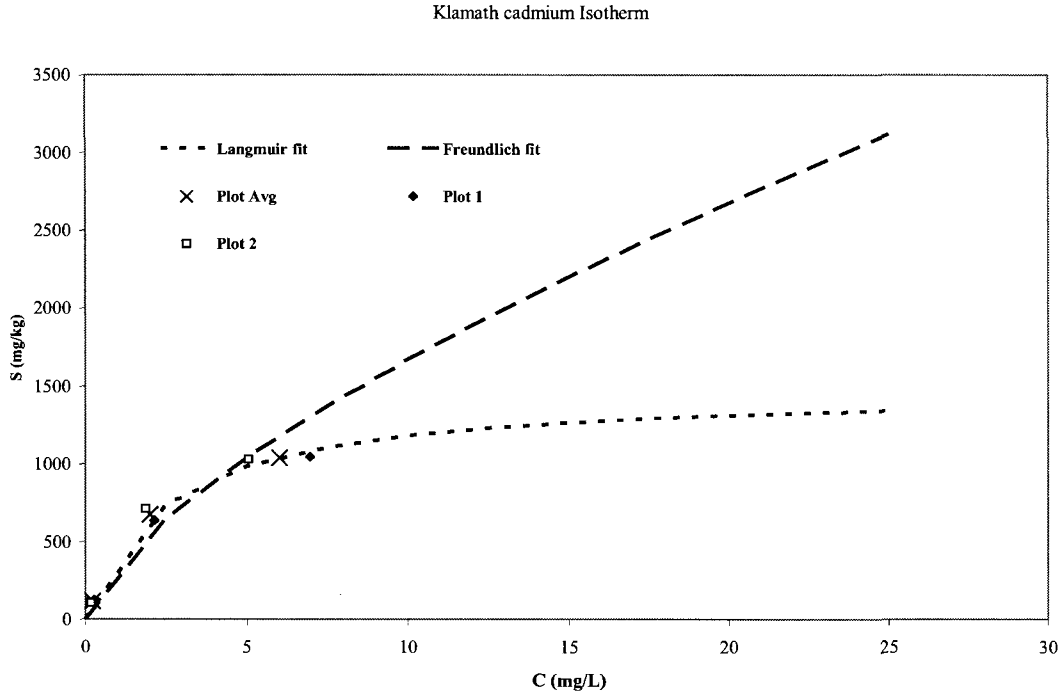


Fig. 2.17. Freundlich and Langmuir model fitting for Cd adsorption at Klamath

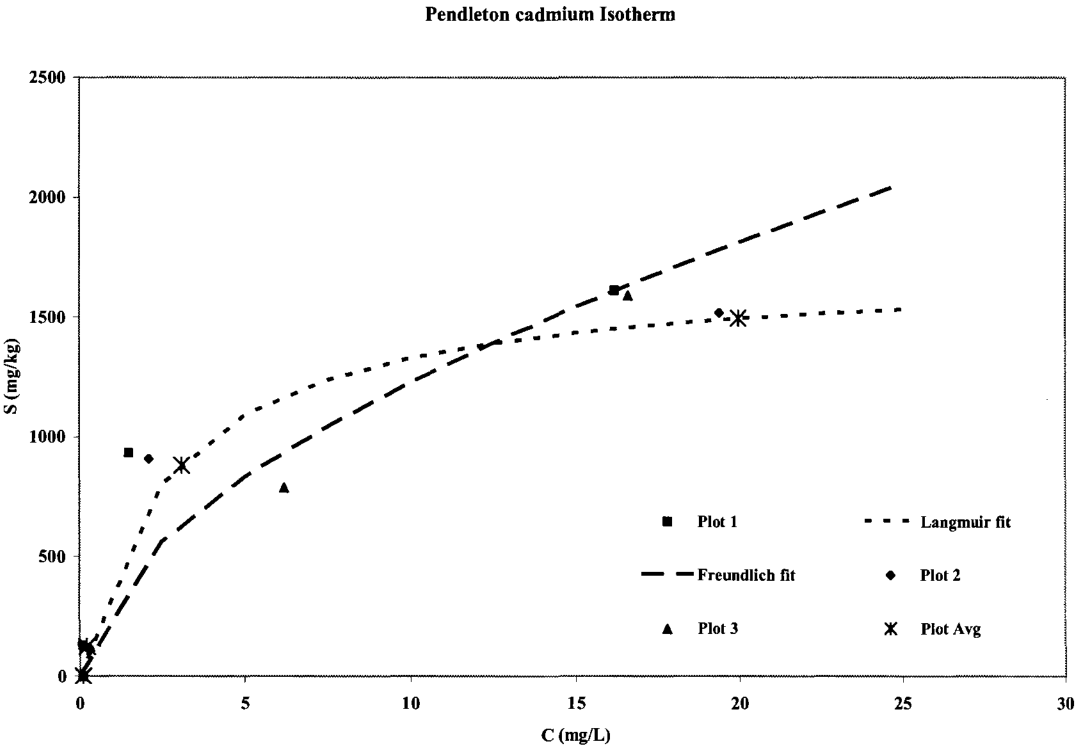

Pendleton cadmium Isotherm

Fig. 2.18. Freundlich and Langmuir model fitting for Cd adsorption at Pendleton

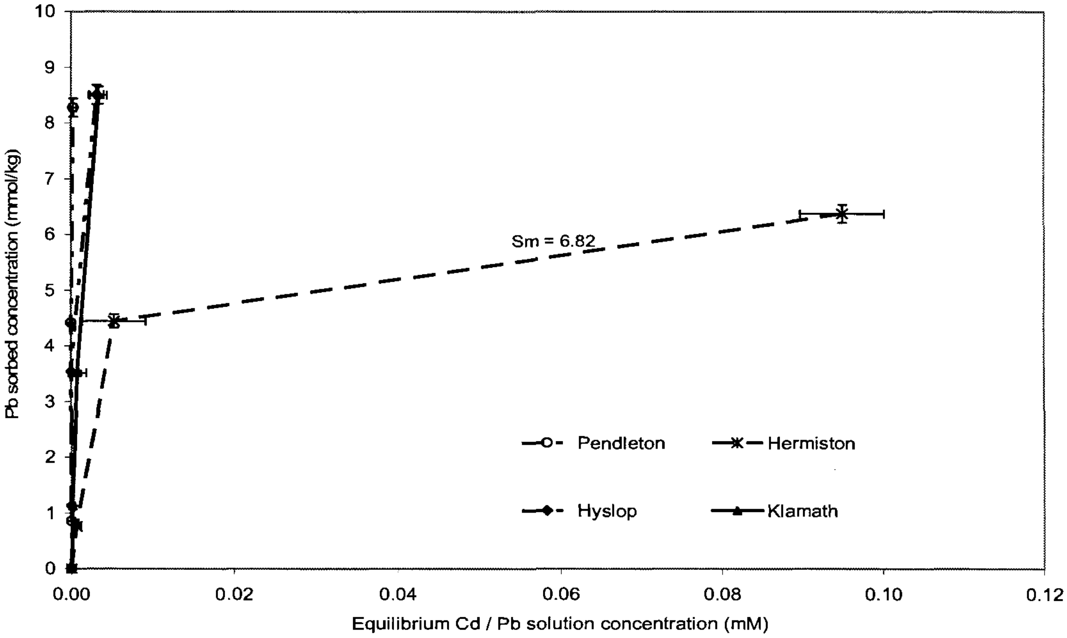


Fig. 2.19. Pb adsorption isotherms (I =0.01M $LiClO_4$) for the soils from Hermiston, Hyslop, Klamath and Pendleton

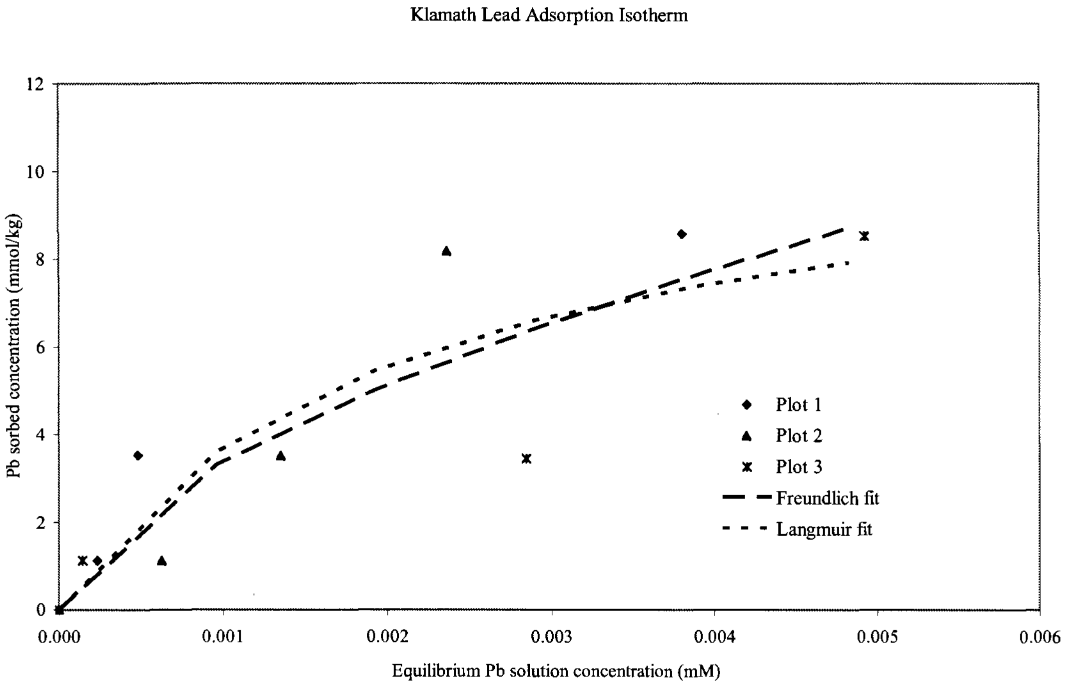


Fig. 2.20. Freundlich and Langmuir model fitting for Pb adsorption at Klamath

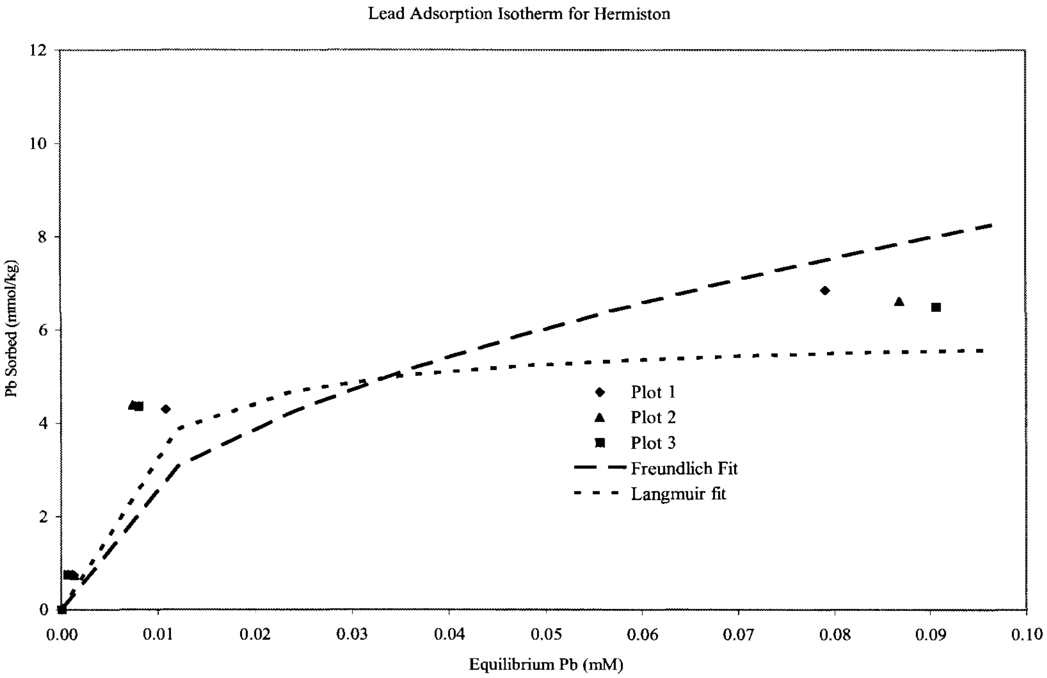


Fig. 2.21. Freundlich and Langmuir model fitting for Pb adsorption at Hermiston

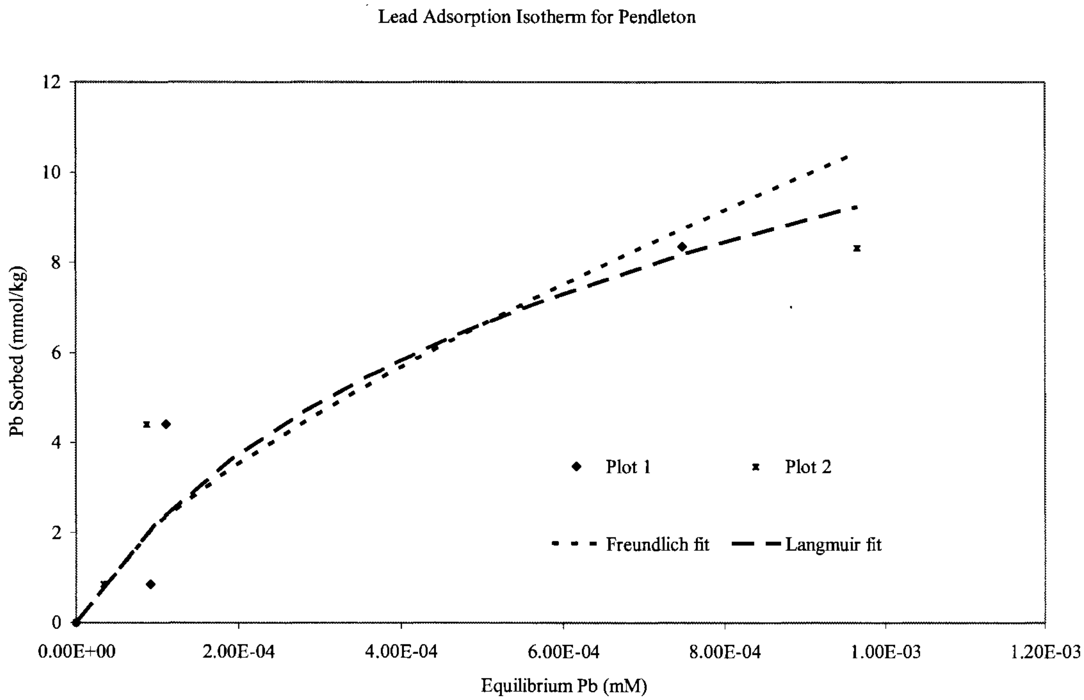


Fig. 2.22. Freundlich and Langmuir model fitting for Pb adsorption at Pendleton

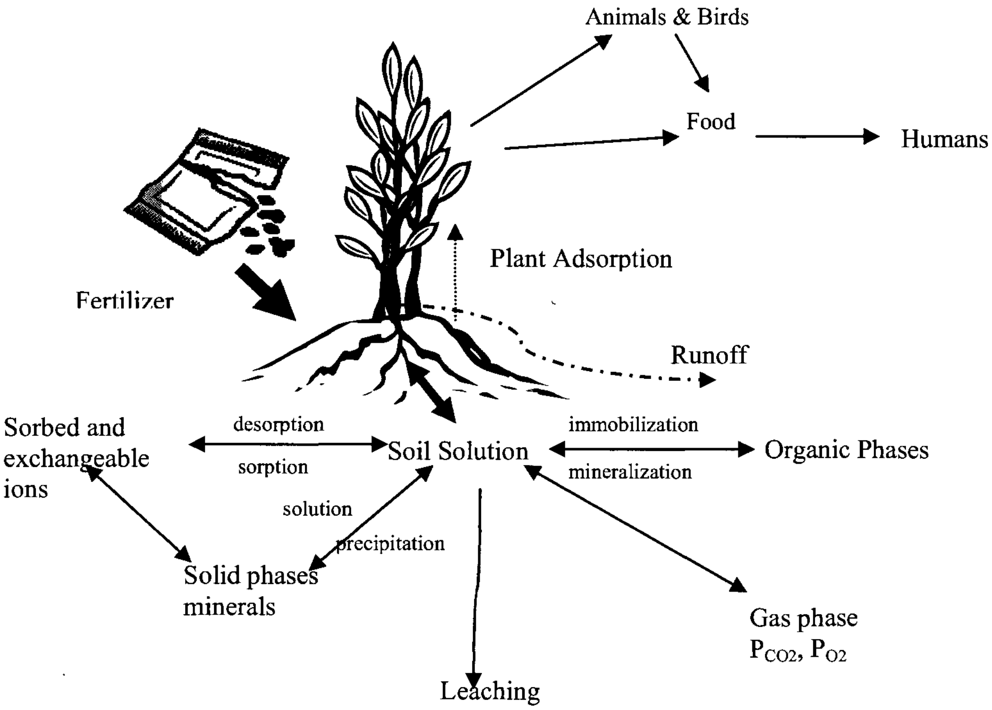


Fig. 3.1. Fate of fertilizer constituents. Adapted from Naidu et al., 1997

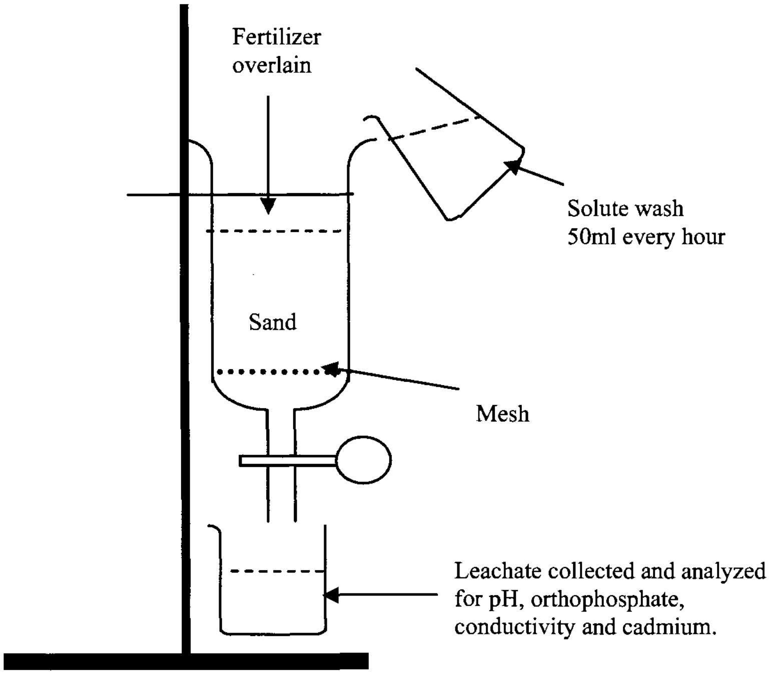


Fig 3.2. Column leaching study setup.

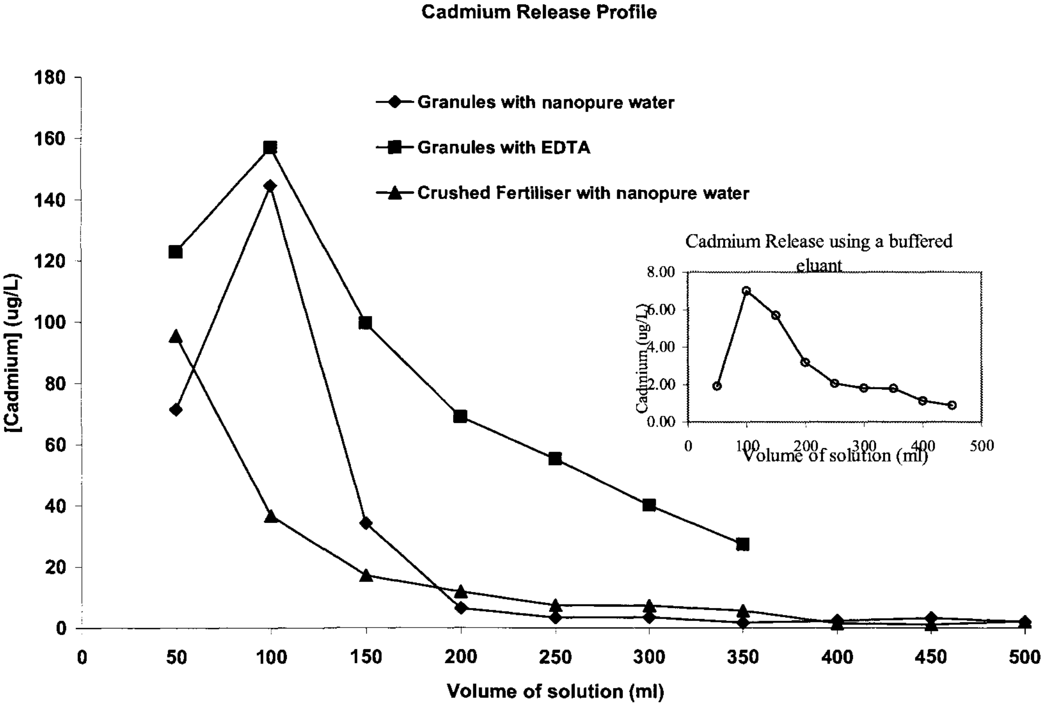


Fig. 3.3. Comparison of eluant Cd concentrations showing relative effects of ultrapure water, EDTA chelation and pellet crushing.

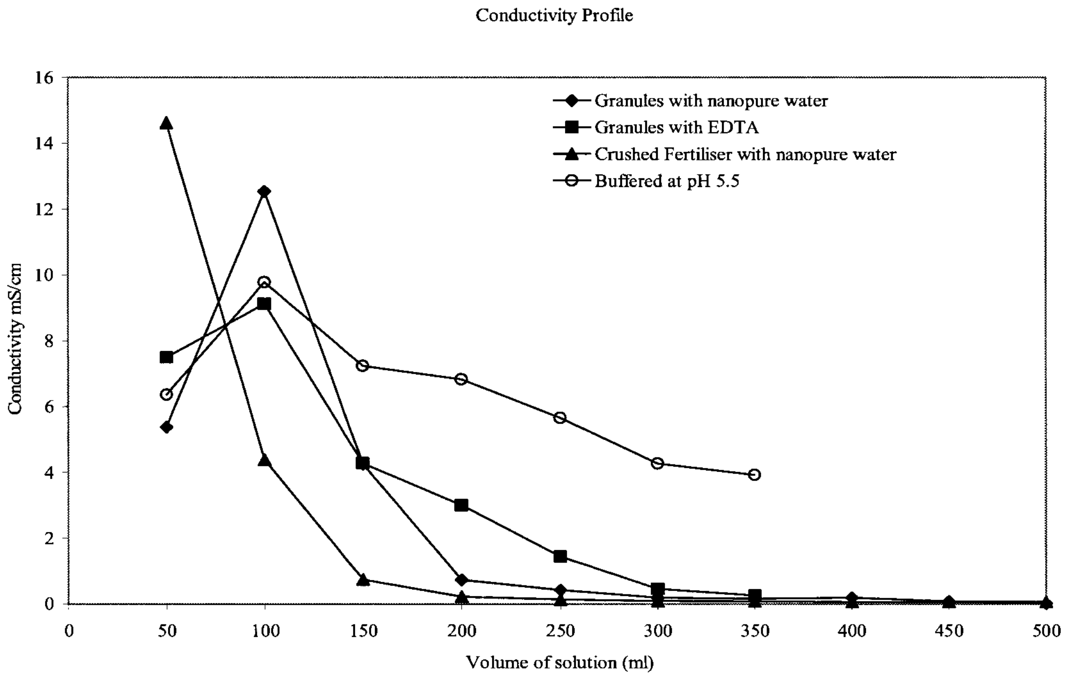


Fig. 3.4. Comparison of eluant electronic conductivity concentrations showing relative effects of ultrapure water, EDTA chelation, acetate buffer and pellet crushing.

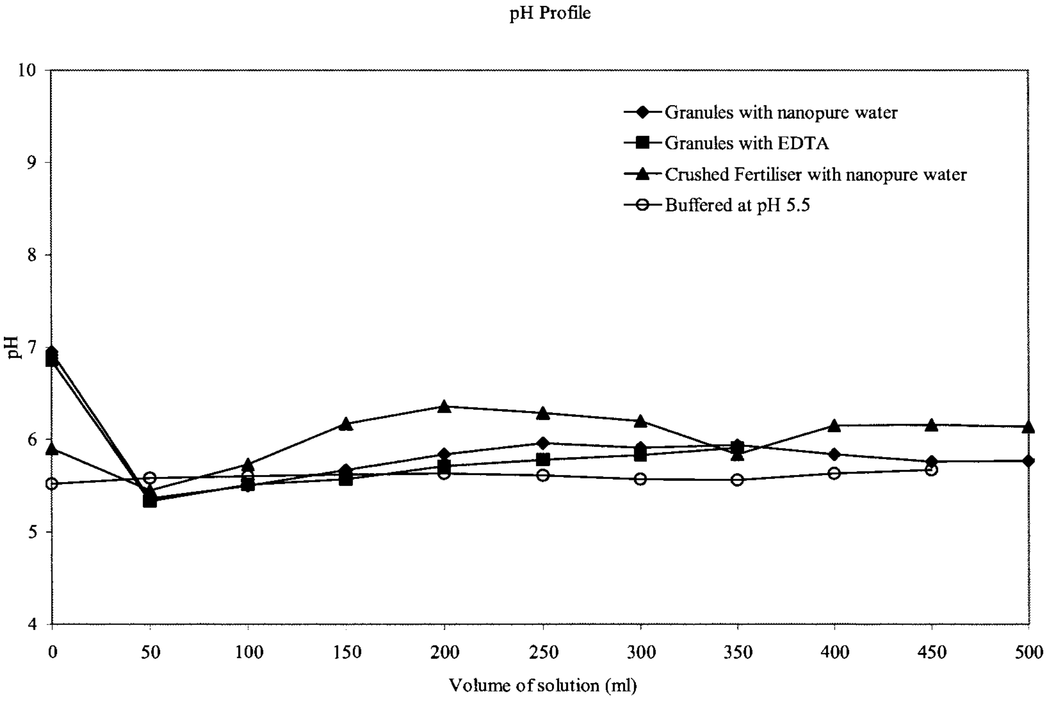


Fig. 3.5. Comparison of eluant pH showing relative effects of ultrapure water, EDTA chelation, acetate buffer and pellet crushing.

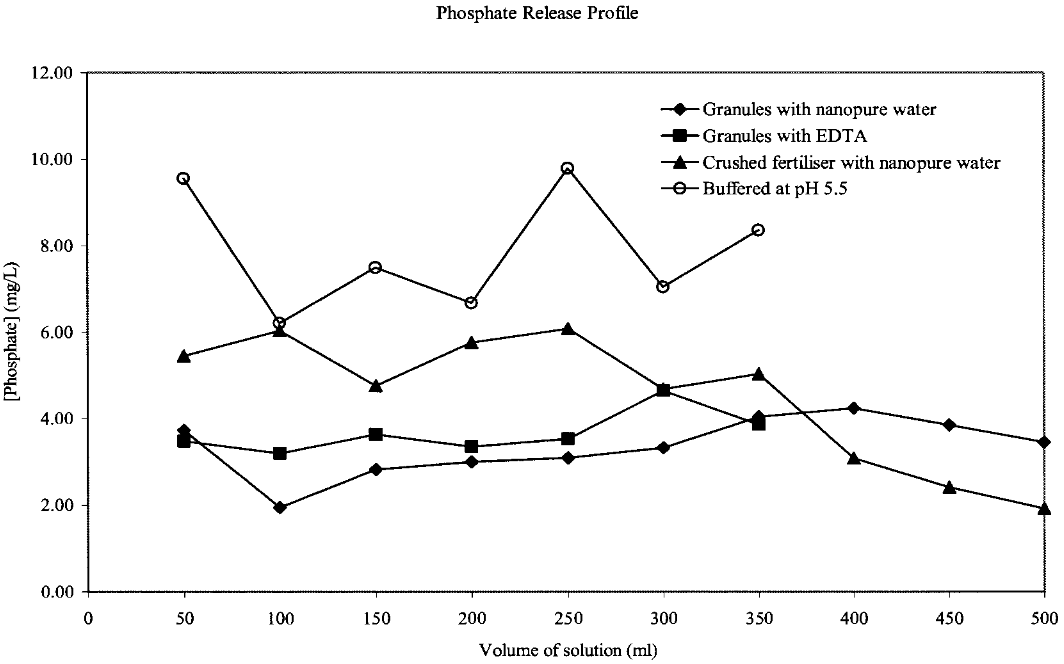


Fig. 3.6. Comparison of eluant P concentrations showing relative effects of ultrapure water, EDTA chelation, acetate buffer and pellet crushing.

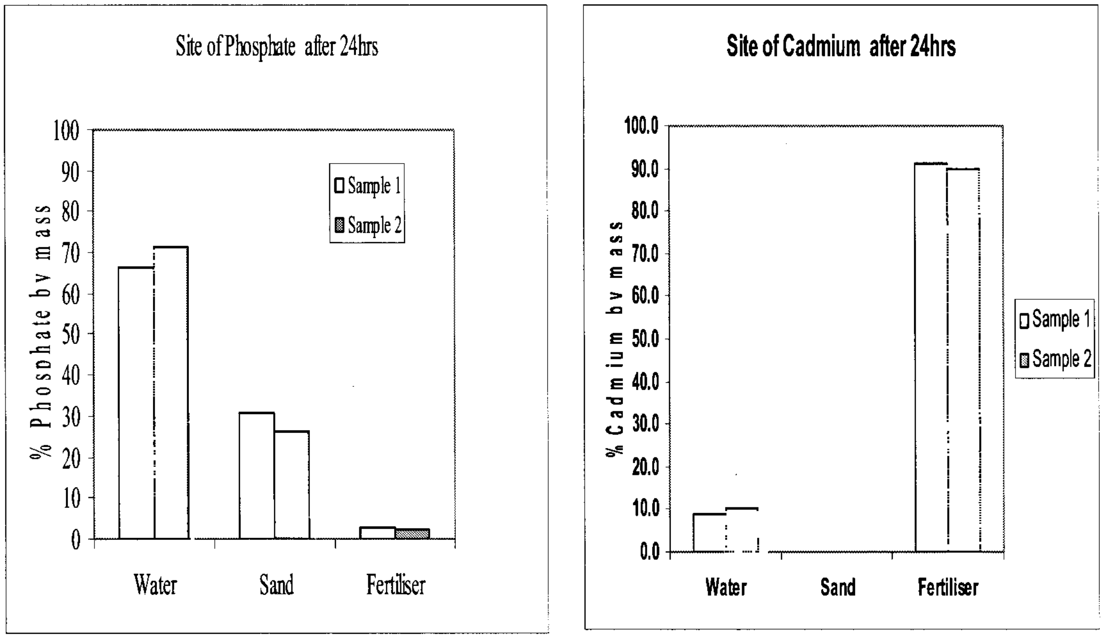


Fig. 3.7 Distribution Cd and P after 24 h: Amounts found in water, sand or remaining fertilizer

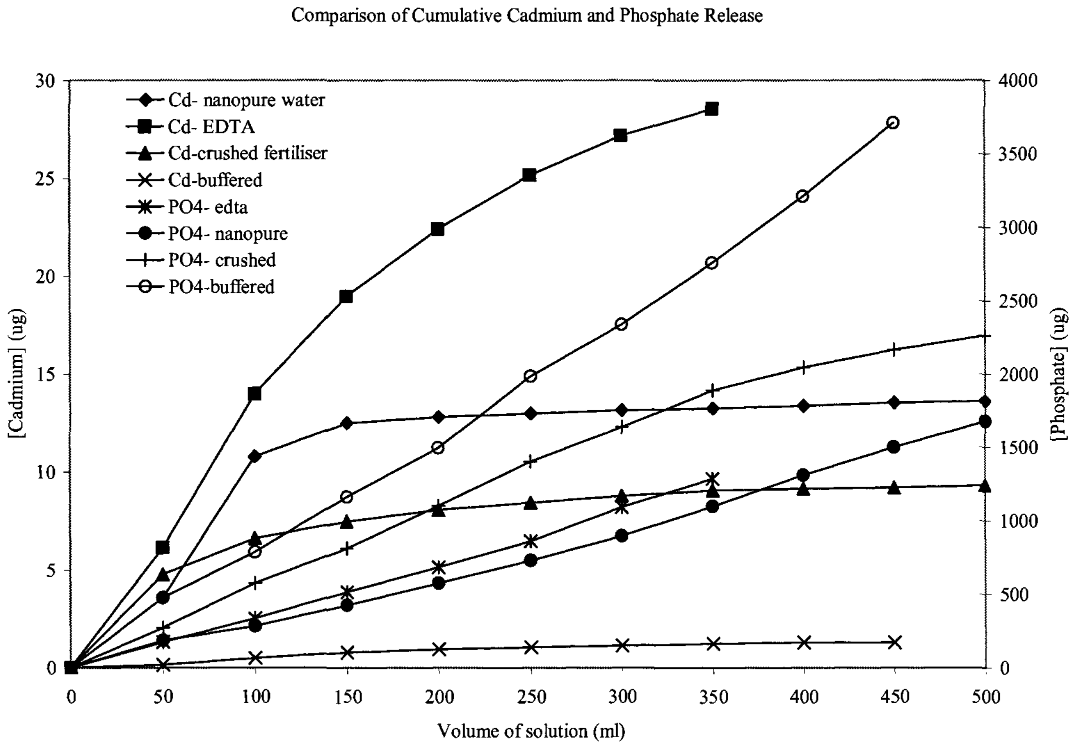


Fig. 3.8. Comparison of the effects of EDTA and pellet crushing on the cumulative elution of Cd and P

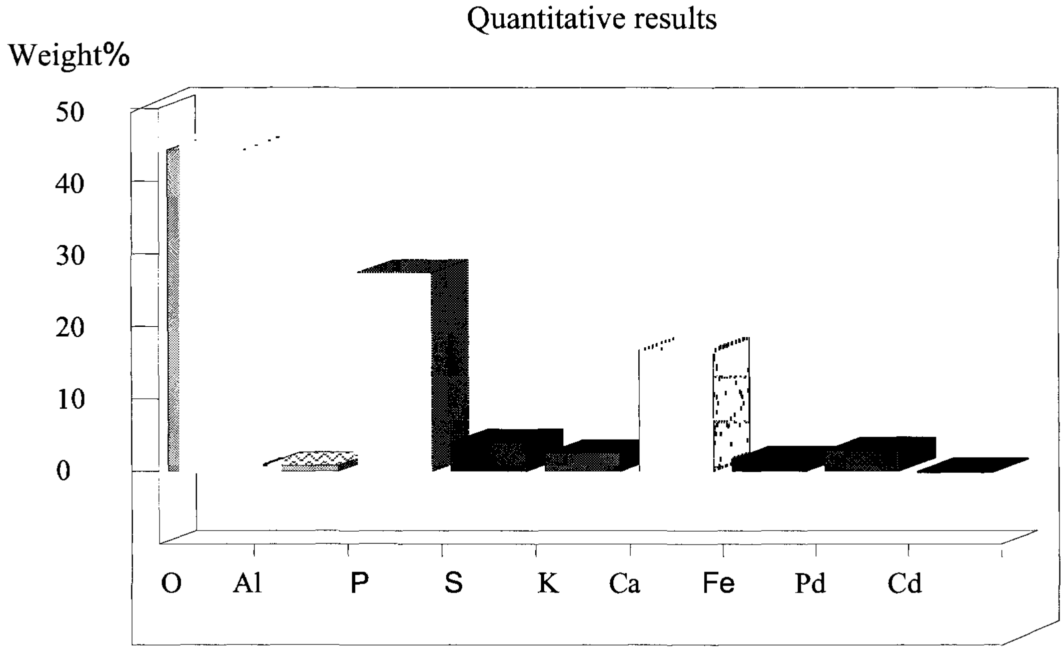


Fig.3.9. Energy Dispersive X-ray (EDX) of fertilizer, showing preponderance of Ca and phosphate at the pellet surface with only a small signal for Cd.

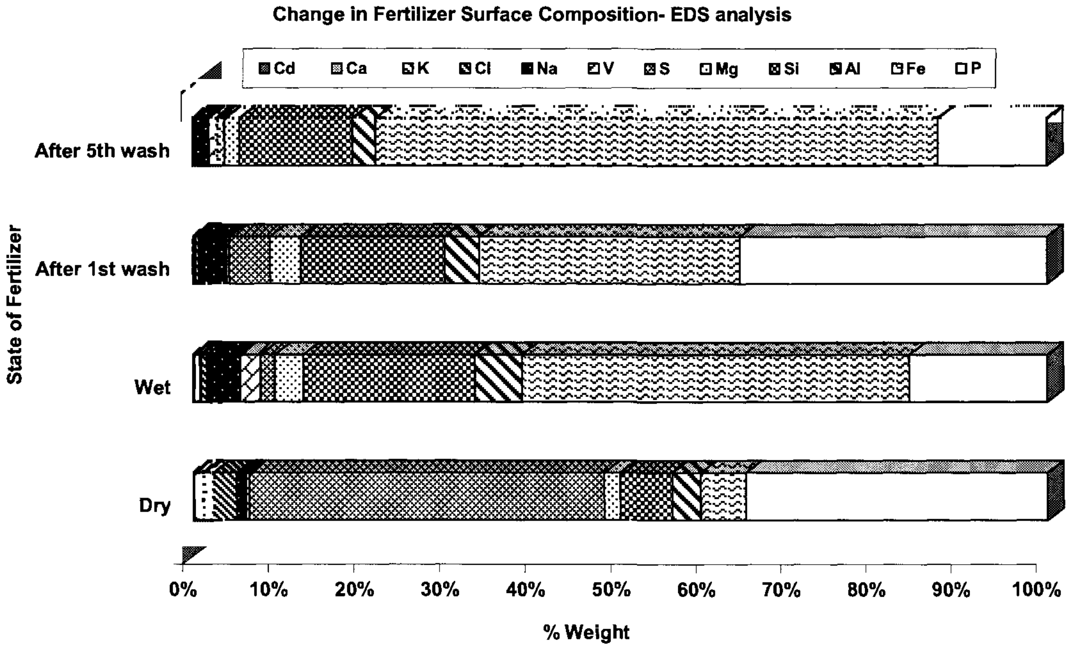


Fig. 3.10. Change in fertilizer surface composition from elemental analysis using Energy Dispersive Spectroscopy.

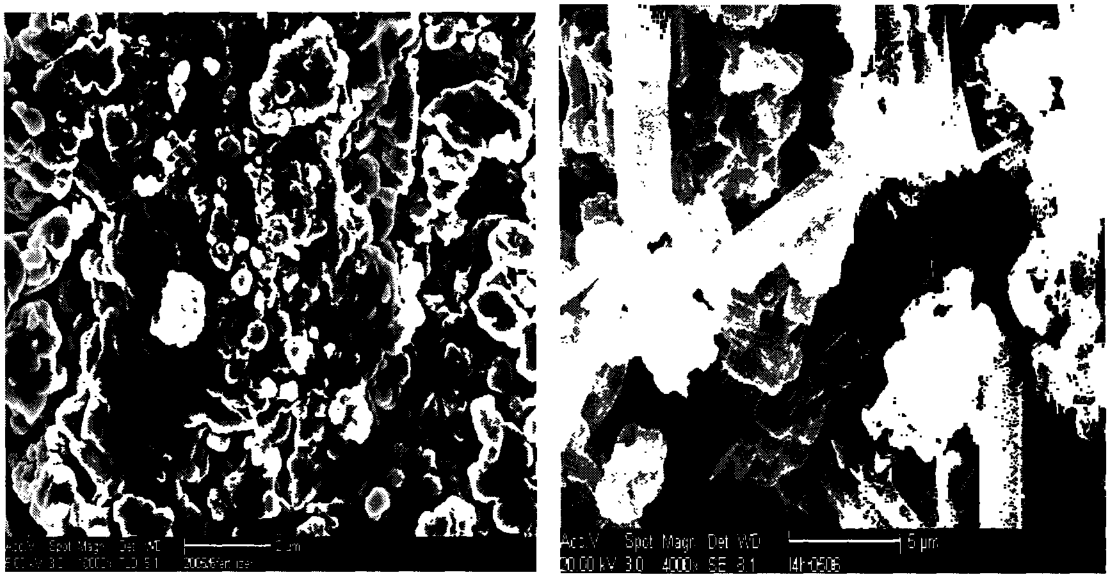


Fig. 3.11. SEM images of the fertilizer a) before elution (left), and b) after 4 hrs of water elution (right).

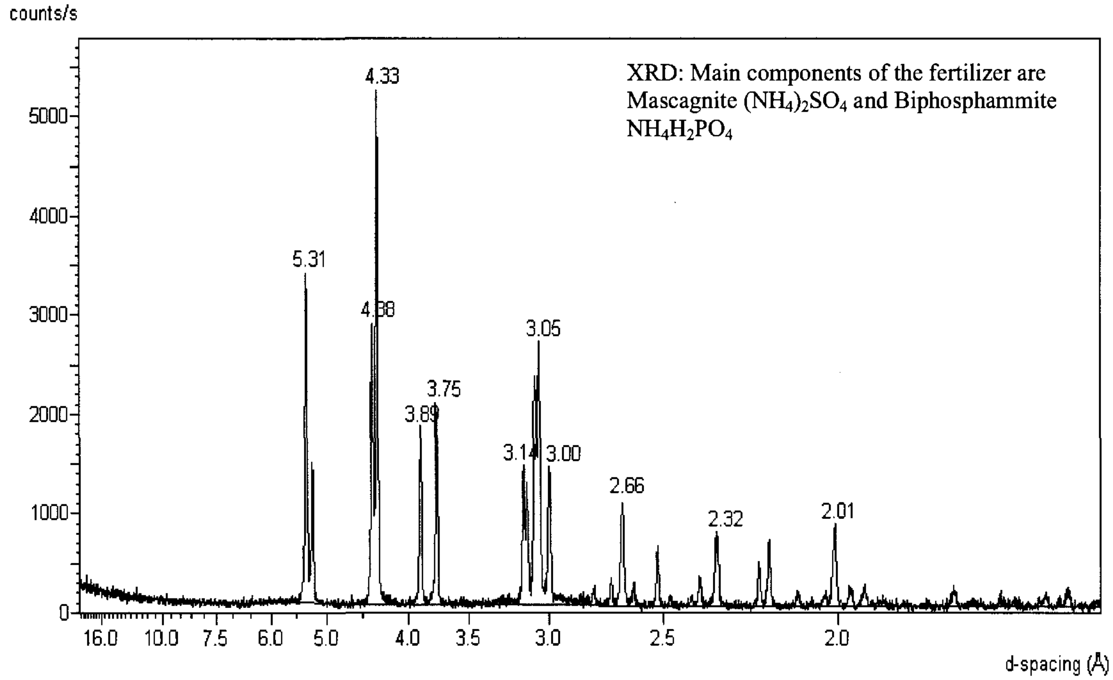


Fig. 3.12. X-ray Diffraction spectra of the phosphate fertilizer

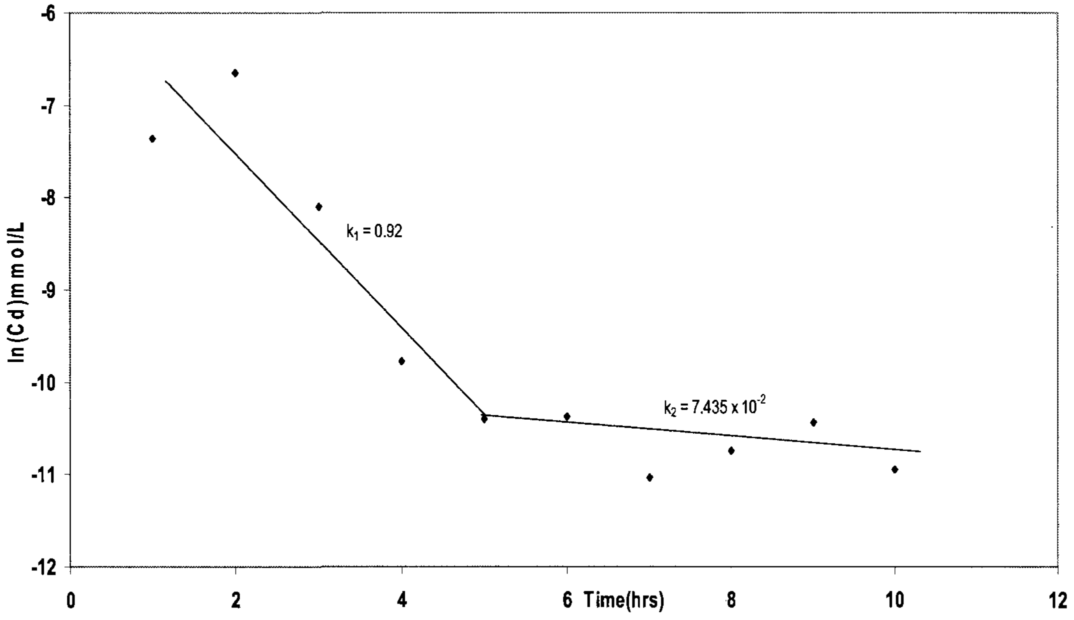


Fig. 3.13. Modeled kinetics of cadmium release from phosphate fertilizer with nanopure water.

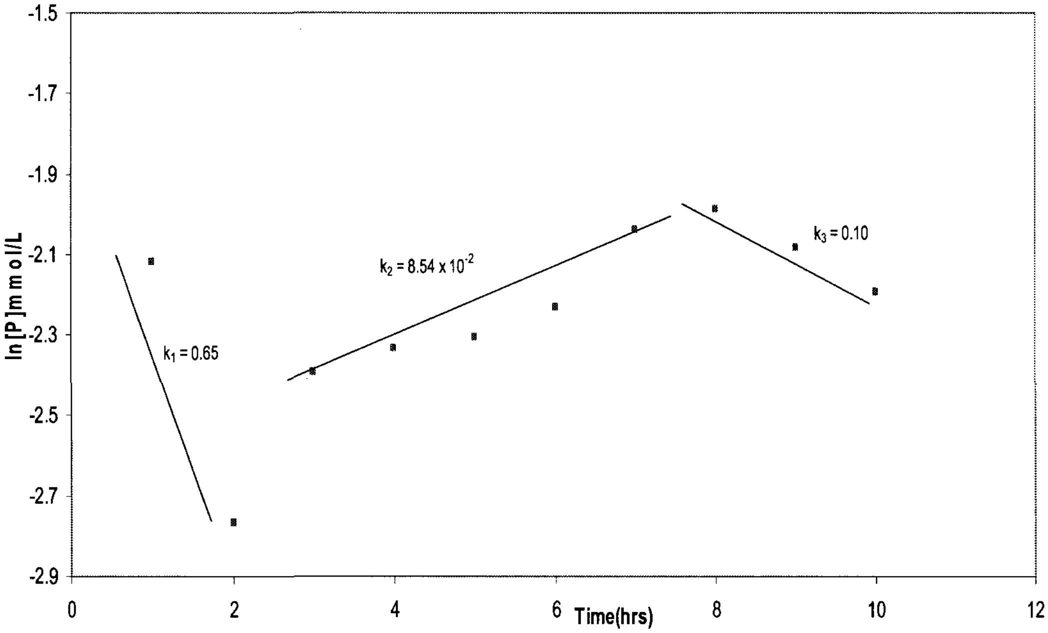


Fig. 3.14. Modeled kinetics of phosphorus release from phosphate fertilizer with nanopure water.

References

Abollino O., Aceto M., Malandrino M., Mentasti E., Sarzanini C. and Petrella F. (2002) Heavy metals in agricultural soils from Piedmont, Italy. Distribution, speciation and chemometric data treatment. Chemosphere. 49, 545-557.

Adams, F. (1974) Soil solution. In The Plant Root and Environment. E.W. Carson (Ed). University Press of Virginia, Charlottesville. p 441-481

AITC A look at Oregon Agriculture. www.agclassroom.org/kids/stats/oregon.pdf (viewed 1/10/09)

Aitken, R.L., Woody, P.W.and Dickson, T. (1990) Lime requirement of acidic Queensland soils. I. Relationships between soil properties and pH buffer capacity. Aus.J. Soil Res. 28, 695-701.

Allen, H.E., Huang, C.P., Bailey, G.W. and Bowers, A.R. (1995) Metal speciation and contamination of soil. Lewis Publishers, Boca Raton, Florida, USA

Amacher, M. C. (1996) Nickel, Cadmium, and Lead: Methods of Soil Analysis Part III Chemical Methods Ed. Sparks, D.L. et al. Chpt. 28

Andjelkovic, T., Perovic, J., Purenovic, M., Blagojevic,S., Nikolic,R., Andjelkovic, D. and Bojic, A. (2006) A direct potentiometric titration study of dissociation of humic acid with selectively blocked functional groups. Ecl.Quim. Sao Paulo 31(3), 39-46

Appel, C., Ma, L.Q., Rhue, R.D. and Kennelley, E. (2003) Point of zero charge determination in soils and minerals via traditional methods and detection of electroacoustic mobility. Geoderma 113, 77-93.

Appel,C. and Ma, L. (2002) Concentration, pH and surface charge effects on Cadmium and Lead Sorption in Three Tropical Soils. J. Environ Qual. 31, 581-589.

Ayati, M. and Lundager Madsen, H.E. (2001) Solubility product of the cadmium phosphate $Cd_5H_2(PO_4)_4$. 4H2O at 37 ^{0}C J. Chem. Eng. Data 46, 113-116

Bailey, J., Stevens, R. and Kilpatrick, D. (1989) A rapid method for predicting the lime requirement of acidic temperate soils with widely varying organic matter contents. I Testing the liming requirement model. Soil Sci. 40, 821-829

Baker, D.E. and Amacher, M.C. (1982) p323-326 In Methods of Soil Analysis: Part II – Chemical and microbiological properties. (Ed. Page, A.L., Miller, R.H. and Keeney, D.R.) 2nd Ed. SSSA Book Ser. SSSA, Madison, WI.

Bengtsson, H., Alvena, G., Nilsson, S.I., Hultman B., and O¨ born, I. (2006) Cadmium, copper and zinc leaching and surface run-off losses at the O¨ jebyn farm in Northern Sweden—Temporal and spatial variation. Agriculture, Ecosystems and Environment. 113, 120–138

Boekhold, A.E., Van der Zee, S.E.A.T.M. (1992) A scaled sorption model validated at the column scale to predict cadmium contents in a spatially variable field soil. Soil Sci. 154, 105-112

Boerngen, J. and Shackette, J. (1981) Chemical analyses of soils and other surficial materials of the conterminous United States. United States Geological Survey Report 81-197

Bohn, H.L., McNeal, B.L. and O'Connor, G. A. (2002) Soil chemistry. John Wiley and Sons, New York.

Bolan, N. S., Naidu, R., Syers, J. K. and Tillman R. W. (1999) Surface charge and solute interactions in soils. Adv. Agron. 67, 87-140.

Bolan, N.S., Adriano, D.C., Duraisamy, P., Mani, A. and Arulmozhiselvan, K. (2003) Immobilization and phytoavailability of cadmium in variable charge soils. Plant and Soil 250, 83-94

Bouyoucos G.J. (1962): Hydrometer method improved for making particle size analyses of soils, Agronomy Journal, 54, 464-465.

Chaturvedi, P.K., Seth, C.S. and Misra, V. (2006). Sorption kinetics and leachability of heavy metal from the contaminated soil amended with immobilizing agent (humus soil and hydroxyapatite). Chemosphere 64 (7): 1109-1114

Chen W., Krage, N., Wu, L., Page, A.L. and Chang A.C. Fertilizer Applications and Trace Elements in Vegetable Production Soils of California. Water,Air and Soil Poll. 190, 1-4.

Christensen, T.H. (1984) Cadmium soil sorption at low concentrations: effect of time, cadmium load, pH and calcium. Water, Air, Soil Poll. 21, 115-125.

Christensen, T.H. (1989) Cadmium soil sorption at low concentrations, VIII. Correlation with soil parameters. Water, Air, Soil Pollut. 44, 71–82.

Collins, C.R., Ragnarsdottir, K.V., Sherman, D.M. (1999). Effect of inorganic and organic ligands on the mechanism of cadmium sorption to goethite. Geochimica et Cosmochimica Acta 63, 2989–3002.

Corwin, D.L., and Lesch, S.M. (2003) Application of soil electrical conductivity to precision agriculture: Theory and principles and guidelines. Agron. J. 95, 455-471.

Cotton, F.A. and Wilkinson, G. (1988) Advanced Inorganic Chemistry. (5th ed.), Wiley

Curtis, L.R. and Smith, B.W. (2002) Heavy Metal in Fertilizers: Considerations for setting regulations in Oregon. Report for Oregon Department of Agriculture.

Dane, J.H. and Topp, G.C. Editors (2002) p1253-1536 Methods of Soil Analysis: Part IV – Physical Methods. SSSA Book Ser. SSSA, Madison, WI.

Davister, A. (1996) Studies and Research on processes for the elimination of cadmium from phosphoric acid. OECD Fertilizer Workshop Proceedings: Fertilizers as a source of cadmium. 21-30

Day, P. (1965): Particle fractionation and particle size analysis, in Methods of Soil Analysis, C. A. Black, éd., American Society of Agronomy. Madison, Wisc. 545-567.

Dowdy, R.H., Latterall, J.J. Hinesly, T.D., Grossman, R.B. and Sullivan, D.L. (1991) Trace metal movement in an aeric ochraqualf following 14 years of annual sludge applications. J. Environ. Qual. 20, 119-123.

Evans, L.J. (1989) Chemistry of metal retention by soils. Environ. Sci. Technol. 23 1046-1056

FAO staff available at http://www.fao.org/docrep/007/y5053e/y5053e07.htm (Viewed 10/3/06)

Fest, E.P.M., Temminghoff, E.J.M., Griffioen, J. and van Riemsdijk, W.H. (2005) Proton buffering and metal leaching in sandy soils. Environ. Sci Technol. 39, 7901-7908

Fish, W., D.A. Dzombak and F.M.M. Morel. (1986) Humate-metal interactions. II. Application and comparison of models. *Environ. Sci. Technol.*, 20, 676-683

Forbes, E.A., Posner, A.M. and Quirk, J.P. (1976) The specific adsorption of divalent Cd, Co, Cu, Pb and Zn on goethite. J. Soil Sci. 27, 154-166.

Fu, G., Allen, H.E. and Cao, Y. (1992) The importance of humic acids to proton and cadmium binding in sediments. Environ. Toxicol. Chem. 11, 1363-1372.

Gray, C.W., McLaren, R.G. and Roberts, H.C. (2003) Cadmium leaching from New Zealand pasture soils. Eur. Soil Sci. 54, 159-166.

Gray, C.W., McLaren, R.G., Roberts, H.C. and Condron, L.M. (1999) Solubility, sorption and desorptionof native and added cadmium in relation to properties of soils in New Zealand. Eur. Soil Sci. 50, 127-137

Harter, R.D. and Naidu, R., (2001) An assessment of environmental and solution parameter impact on trace-metal sorption by soils. Soil Science Society of America Journal 65, 597–612.

He, Z.L., Yao, H., Calvert, D.V., Stofella, P.J., Xang, X.E., Chen, G. and Lloyd, G.M. (2005) Dissolution characteristics of central Florida phosphate rock in a sandy soil. Plant and Soil 273, 157-166

Holmgren, G., Meyer.M., Chaney, R. and Daniels, R. (1993) Cadmium, lead, zinc, copper and nckel in agricultural soils of United States of America. J. Environ. Qual. 22, 335-348.

Hooda, P.S. and Alloway, B.J. (1994) Sorption of Cd and Pb by selected temperate and semi-arid soils: Effects of sludge application and ageing of sludged soils. Water, Air, and Soil Pollution. 74, 235-250.

Huang, G.H.(2002) Fertilizer Methods: Secondary/ Micronutrient Analysis. Method FM-822

Hutton, M. and C. de Meeus, (2001) Environmental Resources Management, Analysis and Conclusions from Member States' Assessment of the Risk to Health and the Environment from Cadmium in Fertilisers.
IFA Technical Conference, Chennai, India, 31 pp

Il'in, A.V. and Kiperman, Y. A. (2001). Geochemistry of Cadmium in Mesozoic Phosphorites of the East European Platform. Lithology and Mineral Resources. 36 (6) 576 – 581.

Jackson, A.P. and Alloway, B.J. (1992) The transfer of cadmium from agricultural soils to the human food chain. Biogeochemistry of Trace Metals. (Ed. D.C. Adriano) 109-158 Lewis Publishers London

Jarup, L., Berglund, M., Elinder, C.G., Nordberg, G. and Vhater, M. (1998) Health effects of cadmium exposure- a review of the literature and a risk estimate. Scand. J. Work. Environ. Health 24 supl.

Jones, C.A., Jacobsen, J. and Lorbeer, S. (2002) Metal concentrations in three Montana soils following 20 years of fertilization and cropping. Commun. Soil Sci. Plant Anal.33 (9&10) 1401-1414

Jury, W.A., Spencer, W.F. and Farmer, W.J. (1983) Behavior assessment model for trace organics in soil: I. Model description. J. Environ. Qual. 12(4):558-564.

Jury, W.A., Spencer, W.F. and Farmer, W.J. (1984) Behavior assessment model for trace organics in soil: II. Chemical classification and parameter sensitivity. J. Environ. Qual. 13(4):567-572.

Jury, W.A., Russo, D. Streile, G. and Abd, H.E (1990) Evaluation of volatilization by organic chemicals residing below the soil surface. Water Res. Research 26(1):13-20.

Kirby, E. and Granatstein, D. (2009) Oregon Organic Crop Acres and Farm Numbers – 2008 http://organic.tfrec.wsu.edu/OrganicStats/OR_Crop_Acres_2008.pdf

Kookama, R.S. and Naidu, R., (1998) Effect of soil solution composition on cadmium transport through variable charge soils. Geoderma 84, 235–248.

Krishnamurti, G.S.R., Huang, P.M., Kozak, L.M. (1999) Sorption and desorption of cadmium from soils: influence of phosphate. Soil Science, 164, 888-898

Lee, J. H. and Doolittle, J. J. (2002) Phosphate application impacts on cadmium sorption in acidic and calcaerous soils. Soil Science. 167(6), 390-400

Lee, S.Z, Allen, H., Huang, C.P., Sparks, D.L., Sanders, P.F. and Peijnenburg, W.J.G.M. (1996) Predicting soil water partition coefficients for cadmium. Environ. Sci. Technol. 30, 3418-3424.

Lehr, J.R., Brown, W.E and Brown, E.H (1959). Chemical behaviour of monocalcium phosphate monohydrate in soils. Soil Sci. Soc. Am. Proc.23, 3-12

Liang, R., Mingzhu, L. and Wu, L. (2007) Controlled release NPK compound fertilizer with the function of water retention. React. Funct. Polym.

Lin, C.J. (1957) The relationship between cation exchange capacity, total bases and exchange acidity in certain Oregon soils. Masters Thesis

Lindsay, W.L. (1979) Chemical Equilibrium in soils. p197-205 John Wiley and Sons Ltd. New York

Lindsay, W.L. and Stephenson, H.F. (1959). The nature of the reactions of monocalcium phosphate monohydrate in soils. The solution that reacts with the soils. Soil Sci. Soc. Am. Proc.23 12- 18

Lutzenkirchen, J., Boily, J., Lovgren, L. and Sjoberg, S. (2002) Limitations of the potentiometric titration technique in determining the proton active site density of goethite surfaces. Geochim. Cosmochim.Acta. 66, 3389-3396.

Ma, Q.Y., Logan, T.J., Traina, S.J. (1995). Lead immobilization from aqueous solutions and contaminated soils using phosphate rocks. Environ. Sci. Technol. 29, 1118–1126.

MacDonald, J.D., Belanger, N. and Hendershot, W.H. (2004) Column Leaching Using Dry soil to estimate Solid-Solution partitioning observed in Zero-Tension Lysimeters.1. Method Development. Soil and Sediment Contam. 13, 361-374.

Martin, H.W. and Kaplin, D.I. (1998) Temporal changes in cadmium, thallium and vanadium mobility in soil and phytoavailability under field conditions. Water, Air and Soil Pollution. 101, 399-410.

Matusik, J., Bajda, T. and Manecki, M. (2007) Immobilization of aqueous cadmium by addition of phosphates. J. Hazard. Mater. doi: 1016/j.hazmat.2007.08.010

McBride, M. (1994) Environmental Chemistry of Soils. Oxford University Press Inc. New York

McLaughlin, M.J., Tiller, K.G., Beech, T.A. and Smart, M.K. (1994a) Soil salinity causes elevated cadmium concentrations in field grown potato tubers. J. Environ. Qual. 34 1013-1018

McLaughlin, M.J., Tiller, K.G., Beech, T.A. and Smart, M.K. (1994a) Soil salinity causes elevated cadmium concentrations in field grown potato tubers. J. Environ. Qual. 34, 1013-1018.

Mclean, J.E. and Bledsoe, B.E. (1992) Behavior of Metals in soils Ground Water Issue EPA/540/S-92/018

Morel, F.M.M. (1983) Principles of Aquatic Chemistry. John Wiley and Sons, New York. 446pp

Mortvedt, J.J. (1987) Cadmium levels in soils and plants from some long term soil fertility experiments in the United States of America. J. Environ. Qual. 16(2), 137-142

Mowbary, T. and Schlesinger, W. (1988) The buffer capacity of organic soils of the Bluff Mountain fen, North Carolina. Soil Sci. 146, 73-79

Mulla, D.J., Page, A.L. and Ganje, T.J. (1980) Cadmium accumulations and bioavailability in soils from long term phosphorous fertilization. J. Environ. Qual. 9, 408-412.

Naidu, R., Bolan, N.S., Kookana, R.S. and Tiller, K.G. (1994a) Ionic strength and pH effects on sorption of cadmium and charge in soils. J. Soil Sci. 45, 419-429.

Naidu, R., Kookana, R.S., Sumner, M.E., Harter, R.D. and Tiller, K.G. (1997) Cadmium sorption and Transport in Variable Charge Soils: A Review. J. Environ. Qual. 26, 602-617.

Naidu, R., Sumner, M.E. and Harter, R.D. (1998) Sorption of heavy metals in strongly weathered soils: An Overview. Env. Geochem. and Health 20, 5-9

Nicholson, F.A. and Jones, K.C. (1994) effect of phosphate fertilizers and atmospheric deposition on long term changes in cadmium content of soils and crops. Environ. Sci. Technol. 28 2170-2175

Notario del Pino, J.S., Arteaga Padron, I.J., Gonzalez Martin, M.M. and Garcia-Hernandez, J.E. (1995) Phosphorous and potassium release from phillipsite-based slow release fertilizers. Journal of Controlled Release. 34 25-29

Notario del Pino, J.S., pardon, A.,Gonzalez Martin and Hernandez, J.E.Z (1995) Phosphorous and potassium release from phillipsite-based slow release fertilizer. J. of Controlled Release. 34 (1) 25-29

ODA Armchair tour of Oregon agriculture. http://oregon.gov/ODA/about_ag.shtml (Viewed 1/10/09)

ODA House Bill 3815 (2001) Oregon Revised Statutes (ORS) Chapter 633

ODA Oregon Agriculture: Facts and Figures (2008)

ODA White Paper (2002) Administrative rule development to declare limits of certain metals in fertilizer, agricultural amendment, agricultural mineral and lime products distributed in Oregon.

OECD Stockholm Workshop Proceedings (1996) Sources of Cadmium in the Environment. Inter- Organization Programme for the Sound Management of Chemicals

Onyatta, J.O. (1997) Kinetics and equilibria of cadmium in selected Kenyan soils. Ph.D. thesis, University of Saskatchewan, Saskatoon, SK

Oorts,K. Vanlauwe, B., Pleysier, J. and Merckx, R. (2004) A method for the simultaneous measurement of pH-Dependent cation exchange capacity and pH buffering capacity. Soil Sci.Soc.Am.J. 68, 1578-1585.

Page, A.L., Miller, R.H. and Kenney, D.R. eds., (1982) Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties, Soil Science Society of America, Madison WI, USA p 334

Perez, A.L. and Anderson, K.A. (2007) Distribution and Fate of Background and Bioavailable metals in Oregon agricultural soil and plants. Oregon Department of Agriculture Final report

Perkins, H.F. (1970) A rapid method of evaluating the zinc status of Coastal Plain soils. Commun. Soil. Sci. Plant Anal. 1, 35-42

Petersen, L.W., Moldrup, P., Jacobsen, O.H. and Rolston, D.E. (1996) Relations between specific surface area and soil physical and chemical properties. Soil Sci. 161 (1), 9-20

Portland Business Journal (2005) Organic farming on increase in Oregon April 13, 2005

Richter, J. (1987) The Soil as a Reactor. 14-20, 61-80

Rodriguez-Maroto, R. A., Garcia-Delgado, A., Gomez-Lahoz, C., Vereda-Alonso, C., Garcia-Herruzo, F. and Perez Munoz, M.P. (2003) Competitive retention of lead and cadmium on an agricultural soil. Environ. Monitoring and Assessment. 89, 165-177

Rogowski, D., Golding, S., Bowhay, D. and Singleton, S. (1998) Metals in soils. Screening survey for metals and dioxins in fertilizers, soil amendments and soils in Washington State, Ecol. Publ. No. 98-331. Washington State Dept. of Ecology: Olympia, WA. p 21-34

Rogowski, D., Golding, S., Bowhay, D. and Singleton, S. (1998) Metals in soils. Screening survey for metals and dioxins in fertilizers, soil amendments and soils in Washington State, Ecol. Publ. No. 98-331. Washington State Dept. of Ecology: Olympia, WA. 21-34

Ruby, M.V., Davis, A., Nicholson, A. (1994). In situ formation of lead phosphates in soils as a method to immobilize lead. Environ. Sci. Technol. 28, 646–654.

Sauve, S., Hendershot, W. and Allen, H.E. (2000) Speciation and complexation of cadmium in extracted soil solution. Environ. Sci. Technol. 34, 291-296.

Schofield, R.K. (1949) Effect of pH on electric charges carried by clay particles. J. Soil. Sci. 1, 1-8.

Seaman, J.C., Arey, J.S. and Bertsch, P.M. (2001) Immobilization of Nickel and other metals in contaminated sediments by hydroxyapatite addition J. Environ. Qual. 30, 460-469

Shavit, U., Shaviv, A., Shalit, G. and Zaslavsky, D. (1997) Release characteristics of a new controlled release fertilizer. J. Control. Release. 43, 131-138

Shuman, L.M. (1991) Chemical forms of micronutrients in soils. Micronutrients in agriculture. (Ed. J.J. Mortvedt et al.). 2nd Ed. SSSA Book Ser. 4. SSSA, Madison, WI. p. 113–144.

Shute, T. and Macfie, S. M. (2006) Science of the Total Environment. 371, 63–73.

Singh, D.B., Rupainwar D. C., Prasad, G. and Jayaprakas, K.C. (1998) Studies on the Cd(II) removal from water by adsorption. Journal of Hazardous Materials 60: 29-40

Soil and Plant lab Manual, ICARDA (2001) p 25-30, 38-39

Soil Survey of Multnomah County, Natural Resources Conservation Service. 1983. Viewed November 28, 2006 ftp://ftp-fc.sc.egov.usda.gov/MO1/text_pdf/oregon/or051_text.pdf

Sparks, D.L. (2001) Elucidating the fundamental chemistry of soils: past and recent achievements and future frontiers. Geoderma. 100, 303-319.

Sparks, D.L. (2003) Environmental Soil Chemistry. 2nd Edition Academic Press California

Sposito, G. (1984) The surface Chemistry of soils. Oxford Univ. Press (Claredon), Oxford.

Sposito, G. (1989). The Chemistry of soils. Oxford University Press New York

Sposito, G. (1994) Chemical Equilibria and Kinetics in soils. Oxford University Press New York

Srivastava, P., Singh, B. and Angrove, M. (2005) Competitive adsorption behaviour of heavy metals in kaolinite. J. Colloid. Interface Sci. 290 28-38

Stone, A.D. and O'Shaughnessy, J.C. (2005) Sorption, Desorption and Leaching transport of heavy metals in soils common to New England. Editors: Calabrese, E.J., Kostecki, P.T. and Dragun, J. Contaminated Soils, Sediments and Water: Science in the Real World Vol. 9 Springer Science, NY

Stumm, W. and Morgan, J.J. (1980) Aquatic chemistry. Wiley, New York.

Takamatsu, T. and Yoshida, T. (1978) Determination of stability constants of metal-humic acid complexes by potentiometric titration and ion-selective electrodes. Soil Sci. 125 (6) 377-386.

Tiller, K.G., Gerth, J. and Brummer, G. (1984) Geoderma 34, 17-35.

Tri-county Farm (2009) http://www.tricountyfarm.org/oregon_organic.asp viewed 4/10/09

UNIDO and IFDC (1998) Fertilizer Manual. UN Industrial Development Organization (Ed.), Int'l Fertilizer Development Center (Ed.), 3rd ed. Kluwer Academic Publishers

USDA Department of Agriculture http://www.**ers**.usda.gov/Data/FertilizerUse/Tables/Table5.xls (Viewed 1/24/07)

USDA Staff available at http://www.**ers**.usda.gov/Data/FertilizerUse/Tables/Table5.xls (Viewed 1/24/07)

USEPA Environmental Protection Agency (1996) Method 3050B: Acid Digestion of Sediments, Sludges and Soils in Test Methods for evaluating solid waste. 3rd Ed. USEPA, Washington, DC.

USEPA Environmental Protection Agency (1999) EPA 68-W-98-0085 Estimating Risk from the Use of Agricultural Fertilizers Draft Report

USEPA Environmental Protection Agency (1999) EPA747-R-98-003 Background Report on Fertilizer Use, Contaminants and Regulations

USGS (2007) http://minerals.usgs.gov/minerals/pubs/commodity/phosphate_rock/phospmcs07.pdf (viewed 1/15/09)

Valsami-Jones, E., Ragnarsdottir, K.V., Putnis, A., Bosbach, D., Kemp, A.J. and Cressey, G. (1998) The dissolution of apatite in the presence of aqueous metal cations at pH 2-7. Chemical Geology 151, 215-233

Van Assche, F. J. (1998) "A Stepwise Model to Quantify the Relative Contribution of Different Environmental Sources to Human Cadmium Exposure," *NiCad '98,* Prague, Czech Republic, September 21-22, 1998.

Van Kauwenbergh, S. J. (2002) Cadmium content of phosphate rock and fertilizer. IFA Technical Conference, Chennai, India, September 2002.

Van Kauwenbergh, S.J. & Hellums, D.T. (1995). Direct application phosphate rock: a contemporary snapshot. Phos. Pot., 200: 27–37.

Van Raij, B. and Peech, M. (1972) Electrochemical properties of some oxisols and alfisols of the tropics. Soil Sci. Soc. Am. Proc. 36, 587-593.

Wang, K. and Xing, B. (2002) Adsorption and desorption of cadmium by goethite pretreated with phosphate. Chemosphere 48, 665-670

Wang, K. and Xing, B. (2004) Mutual effects of cadmium and phosphate on their adsorption and desorption by goethite. Env. Poll. 127 13-20

Washington State Senate Bill 6474 (1998) Fertilizer Regulation Chapt. 36

Weaver, A.R., Kissel, D.E., Chen, F., West, L.T., Adkins, W. Rickman, D. and Luvall, J.C. (2004) Mapping soil pH buffering capacity of selected fields in the Coastal Plain. Soil. Sci. Soc. Am.J. 68, 662-668.

Weber, W.J. and DiGiano, F.A. (1996). Process dynamics in Environmental Systems. Environ Sci. Technol. Series John Wiley, New York p943

Weinberg Group Inc (2001) Scientific basis for risk-based acceptable concentrations of metals in fertilizers and their applicability as standards. Washington, DC.

Williams, C.H. and David, D.J. (1976) The accumulation in soil of cadmium residues from phosphate fertilizers and their effect on the cadmium content of plants. Soil Sci. 121: 86-93

Wilson, D. (1997) Fear in the fields. How hazardous wastes become fertilizer. Seattle Times

Wolt, J. (1994) Soil Solution Chemistry: Applications to Environmental Science and Agriculture. John Wiley and Sons, New York

WRCC http://www.wrcc.dri.edu/narratives/OREGON.htm (viewed 12/5/08)

WSDA (2001) A report on the plant uptake of metals from fertilizers. WSDA Publications

Yasukawa, A., Higashijima, M., Kandori, K. and Ishikawa, T. (2005) Preparation and characterization of cadmium-calcium hydroxyapaptite solid solution particles. Colloids and Surfaces A: Physiochem. Eng. Aspects 268, 111-117

Yu, T.R., Ji G.L. (1997) Chemistry of Variable Charge Soils. Editor Yu, T.R. Oxford Press p 3-51

Zapata, F. and Roy, R.N. FAO Fertilizer and Plant Nutrition Bulletin. Use of phosphate rocks for sustainable agriculture. (2004) 13 30-40

Zelazny, L.W., Liming, H. and Vanwormhoudt, A. (1996) Charge Analysis of soils and anion exchange. p1231-1253. Methods of Soil Analysis. Part 3 Chemical Methods, Soil Science Society of America, Madison WI, USA

Appendix A:

Vadose Zone Monitoring using Hydra Probes in a Typic Fragixeralf in Portland, Oregon

ABSTRACT

The high cost of land management inputs has increased demand on precision technology to accurately determine field conditions at all times. Full characterization of the vadose zone, through simultaneous and continuous monitoring of soil moisture, temperature and electric conductivity provides information necessary for environmental assessment, remediation and successful land management. Hydra Probes® were installed in loess overlying basalt bedrock classified as a Typic Fragixeralf on a 25% forested slope in urban Portland, Oregon, USA and used to show the presence of a perched water tables, its behavior and implications for construction and the environment.

Durability and consistency of the probes was also investigated. Five horizons namely the A1, A2, Btx1, Bt2, Btx3 and Bgx were sampled to a depth of 110cm in situ and monitored. Particle size analysis, porosity, bulk density, field capacity and wilting point were also determined for each horizon. Clay content increased and pH decreased with depth. The field analyses showed increased redoxymorphic features and clay films at the depth of the seasonal perched water table. The probes were also able to show a seasonal perched table in the hill slope, the length of its presence and it's dry down behavior. Soil moisture data allowed the movement of the wetting front to be followed and rates of infiltration and percolation to be determined. The probes also showed annual, monthly and diurnal variations in temperature for all the soil horizons as well as lags and damping due to surface vegetation insulation. There was an increase in conductivity with depth although it never exceeded 0.1mS/cm for any of

the horizons. The low root mean square error of all the probes, independent of depth of installation, showed durability and consistency of the probes.

INTRODUCTION

The purpose of this paper was to use Stevens Hydra Probes II to present evidence for the presence of perched water tables in the hill slopes of Portland, Oregon, their behavior and the implications for construction and environmental mitigation. The West Hills of Portland, Oregon are composed of loess overlying basalt bedrock. Similar geology is evident in the regions of Northern Idaho and eastern Washington (McDaniel et al., 2001). Several pedological studies of loessial soils in xeric moisture regimes have shown susceptibility to formation of perched water tables (PWTs) (McDaniel and Falen, 1994; McDaniel et al., 2001; Reuter et al., 1998; Boersma et al., 1972). PWTs form over brittle subsurface horizons that have a high bulk density and are restrictive to water and root movement, namely fragipans (Soil Survey Staff, 1999).

There is still much debate over the formation of fragipans and two good reviews have been written by Smalley and Davin (1982) and Smeck and Ciolkosz, (1989). The Bryant Hypothesis of hydroconsolidation has received much attention particularly with reference to Palouse loess of eastern Washington. A study by Franzmeier et al. (1989) gave three conditions, among others, for the formation of fragipans: a) a parent material consisting of loess, with the underlying material including paleosol horizons that have less than 30% clay; b) a topography with slopes that range from 0-20% and c) a moist climate with precipitation greater than evapotranspiration in the winter surplus and vice versa in the summer. All these conditions are met by the soils in the West Hills of Portland.

The Stevens® Hydra Probes II (Hydra Probes) are used to measure soil moisture, electrical conductivity, and temperature and the data are logged hourly with a Stevens DOT Logger. Besides irrigation management and water shed characterizations, this information is important when characterizing for soil construction or ecological restoration projects. Collecting these parameters in the field and through laboratory analysis is very costly and time consuming. The Hydra Probe with a data logger can collect thousands of data points inexpensively with the majority of costs occurring at installation. The Hydra Probe uses soil's dielectric properties to measure soil water content. It measures both the real (ε_r) and imaginary (ε_i) components of the soil's complex dielectric permittivity (K in Equation 1) at 50 MHz.

$$K = \varepsilon_r + j\varepsilon_i \qquad (1)$$

Where j is $-1^{1/2}$.The Hydra Probe is a terminated coaxial probe using the soil as the dielectric and is based on the work of Campbell (1990) and Kraft (1987). Both components of the complex dielectric permittivity can be characterized from the characteristic impedance of the coaxial (Z_c) by

$$\frac{Z_p}{Z_c} = \frac{1+\Gamma}{1-\Gamma} \qquad (2)$$

where Γ is the complex ratio of the reflected voltage to the incident voltage. With the impedance of the probe, Z_p, one can solve for K with the expression,

$$Z_p = \frac{Z_0}{\sqrt{K}} \cot anh\left(\frac{\omega\sqrt{K}L}{c} j\right) \qquad (3)$$

Where ω is the angular frequency, *c* is the speed of light and *L* is the electrical length of the probe.

Empirical calibrations are then applied to calculate the soil moisture content from the real dielectric permittivity. As the dielectric constant for water (80.3 at 20^0C) is much higher than the dielectric constant for solid soil (~1- 2), the *K* measured in the soil is mostly a function of θ and can thus measure the water content of the soil. Soil moisture is related to ε_r, and the second term, jεi is related to electrical conductivity. The probe measures the loss of energy (which is frequency dependent) that results from soil ions.

The electrical conductivity, σ, can be calculated from the imaginary component of the dielectric permittivity by (Campbell 1990)

$$\varepsilon_i = \varepsilon_i' + \frac{\sigma_{dc}}{2\pi f \varepsilon_0} \quad (4)$$

where ε'_i is the molecular relaxation component of the complex dielectric permittivity (Logsdon 2005a), ε_0 is the dielectric constant of a vacuum and *f* is the frequency in MHz.

In most soils, the molecular relaxation of the orientation polarization of water is assumed to be negligible. At 50 MHz, the Hydra Probe uses the real component of the complex dielectric component to measure the soil moisture and the imaginative component to measure the dc electrical conductivity.

Calibration

Electromagnetic techniques have been used to measure the dielectric properties of soil for the estimation of volumetric water content (θ) since the 1980s (Topp et al., 1980). One such relationship between the dielectric properties of soil and θ ($m^3\ m^{-3}$) (Roth et al., 1990) can be written:

$$\sqrt{\varepsilon_r} = \theta\sqrt{\varepsilon_{r,w}} + \theta_s\sqrt{\varepsilon_{r,s}} + \theta_g\sqrt{\varepsilon_{r,g}} \quad (5)$$

By definition the real dielectric constant of a gas, $\varepsilon_{r,g}$ is equal to 1, and the water vapor in the unsaturated soil pore space is negligible. The relative real dielectric permittivity of soil, $\varepsilon_{r,s}$, is generally less than 5, and the real dielectric constant of pure water, $\varepsilon_{r,w}$, is about 80.

The general empirical calibration equation used in this study may be written:

$$\theta = A\sqrt{\varepsilon_r} + B \quad (6)$$

where the coefficients A and B were chosen to be 0.109 and -0.179 respectively based on the work of Seyfried et al., 2005.

Temperature effects

Both the real and imaginative components of the complex dielectric permittivity are influenced by temperature (Logsdon and Laird, 2004). The real dielectric constant of water will decrease slightly with temperature because molecular vibration will impede molecular orientation polarization. This temperature relationship can be described by (Weast, 1986; Jones, 2005):

$$\varepsilon_{r,w}(T) = 78.54[1-4.579X10^{-3}(T-298)+ 1.19 X10^{-5}(T-298)^2-2.8X10^{-8}(T-298)^3] \quad (7)$$

While $\varepsilon_{r,w}(T)$ will decrease with temperature, the chemistry of clay films tend to cause $\varepsilon_{r,s}(T)$ to increase with temperature. It is hypothesized that an increase in $\varepsilon_{r,s}(T)$ with temperature is the result of the increased ionic bond length of the cations present in clays at warmer temperatures. The ease with which the cations can participate in the polarization at 50 MHz will increase with ionic bond length and thus temperature.

Due to $\varepsilon_{r,w}(T)$ and $\varepsilon_{r,s}(T)$ behaving in an opposite manner, ε_r in calibration equation (6) was not corrected for temperature.

The relationship between ε_i and temperature closely resembles the relationship between σ_{dc} and temperature (Seyfried and Grant, 2007) because the molecular relaxation component of the imaginative dielectric permittivity, ε_i', is negligibly small. The electrical conductivities in this study are temperature corrected to 20 degrees C. Several factors affect soil temperature: incident solar radiation, seasonal changes in overlying air temperature, precipitation, type of soil, vegetation cover and depth in the earth. The soil temperature was monitored and logged at the same interval as θ, and σ.

This project analyzed data collected by a Hydra Probe over a one year period at a soil study site and characterized the same soil using traditional field and lab methods. The two results were compared to determine whether the Hydra Probe II provided consistent results for the three parameters relative to site soil characteristics determined in the field and laboratory.

SITE DESCRIPTION AND BACKGROUND

The study site was at Mt. Calvary Catholic Cemetery in Multnomah County (45.52 (45°31') N | -122.73 (-122°44') W within the city limits of Portland, Oregon, USA (Figure 1). The cemetery covered over 120 acres in the West Hills of Portland. Soil samples were taken, and the probes were installed approximately 130 meters behind the cemetery's mausoleum building in a forested area on a 25 percent slope. Elevation at the site is approximately 150 meters in a temperate climate. Summers are generally warm (average 18°C) and dry, and winters are moist and cool. Temperatures at the site reached freezing, although the average winter temperature was approximately 4°C. Average annual precipitation is 940 to 1016 mm and vegetation in the area includes numerous Douglas fir trees, the non-native invasive species such as Himalayan blackberry and to a lesser extent other deciduous trees and shrubs.

MATERIALS AND METHODS

Field Methods

During Fall of 2006 six Stevens Hydra Probes were installed in a soil pit as shown in Figure 2. The Hydra probes were connected to a data logger (Stevens Data logger DX75) that recorded the probes hourly measurements of soil moisture (m^3/m^3), electrical conductivity in (S/m), and temperature (^{0}F). Daily weather observations for the time of study were collected at a station located 2 kilometers south west of the site.

Laboratory Work

Soil samples for each horizon were collected, air dried, crushed and sieved through a 2 mm sieve (U.S. Standard Sieve Series No. 10) using a Tyler Combustion Engg. Inc. Portable Sieve Shaker Model RX24 prior to characterization. Soil particle size distribution was determined using the hydrometer method (Ryan et al., 2001). Soil pH was measured (pH meter Orion Expandable ion-Analyzer EA920) in a background electrolyte of 0.01N $CaCl_2$ (1:2 solid to solution).

Soil moisture was determined using the procedure used by Hesse, 1971. The clod method was used to determine bulk density of each horizon. Porosity, field capacity and permanent wilting point were calculated using equations from literature. (Dingman, 2002)

RESULTS AND DISCUSSION

The field study of the soil profile suggested the presence of several fragipans, the Btx1, Btx3 and the Bgx. The Btx1 and Bt2 horizons were considered the same horizon in the field analysis, due to similar color and texture, and only after determination of the bulk densities was a distinction made. The site has mostly very fine sand and silt with as much as 50% sand in the A1 horizon and this decreased with depth. Consistent with a loess deposit, the clay content increases with depth and most of the redoxymorphic features and clay films were in the Btx3 horizon. The soil classification is a mesic Typic Fragixeralf, due to a well defined argillic (Bt) horizon with abundant clay films and fragipans. The well developed Bt horizons indicate an approximate age of 12,000 C-14 years. The absence of an E horizon seen in similar soils McDaniel et al., (2001) and Weisenborn (2001) confirmed the young age of the soil.

The change in pH is consistent with surface deposition of cations and subsequent leaching. Nutrient bases such as Ca^{2+} and K^{+} are displaced by hydrogen ions and as the concentration of the hydrogen ions increases, more bases are released into the soil solution, resulting in a reduction in soil pH and a drop in soil fertility due to leaching. The pH is less than 5.5 and decreases with depth suggesting a lowering of base saturation.

All the horizons have relatively high bulk densities which are associated with large, structureless soils that are hydraulically restrictive and slow the downward percolation of water. Bulk density decreases with increasing clay content, and water retention increases with decreasing bulk density due to the permanent negative charge on the clay surfaces that attracts the polar water molecules (Petersen et al., 1996). The residual water content measured by the Hydra Probes showed this (Table 2); both the A2 and Bt2, horizons of lower bulk density have larger residual water contents at the end of summer than the very dense Btx1. The values of the bulk densities were used to calculate the porosities, and the values obtained were consistently lower than effective porosities measured by the Hydra Probe II in the field. The difference could be due to inaccuracies in the determination of the horizon bulk densities.

Soil Moisture and Perched Water Table

Soil moisture data collected are presented in Figure 3 and show the sensitivity of the Hydra Probe II in responding to small changes in moisture content. Missing data occurred due to data drops, experimenters' errors and instrument adjustments. Despite these challenges, the Hydra Probes at each depth clearly detected the arrival of the wetting front, and associated lags after precipitation events during winter and the dry down of the horizons during the summer. The large drops in soil moisture observed in the A1 horizon are due to temporary freezing of the water in the horizon which affected its dielectric property and subsequently the soil moisture output. After both occasions the probe rebounded to its previous reading after thawing of the horizon.

The presence of a perched water table (PWT) was suggested by the behavior of the soil moisture in the Bt2 horizon. This horizon exhibited very high moisture levels after precipitation events, had a very slow dry down rate in the summers and had the highest residual moisture content as of October 2006. The PWT was evident from November to May as seen in similar soils in Idaho (McDaniel et al., 2001; Rockerfeller et al., 2004). The shallow PWT's have implications for housing developments (installation of septic tanks and construction of basements) and the environment (recharge of stream and drainage of the hill slope).

The saturation level of the profile was high for much of the year, and it showed quick response to surface precipitation events. In October of 2006 it took 4 days for all the horizons to be at or near their saturation. Using the wetting front from the initial rain event of October 2006, the movement of the wetting front was used to determine the rate of percolation of the soil horizons (Figure 4). The A horizon easily allowed infiltration of water (3.1 x10^{-4} cm/s), but on reaching the Bt1x horizon, the rate of percolation decreased to 5.4 x 10^{-6} and 1x 10^{-6} cm/s. This difference is again due to the bulkier Bt horizons causing the greatest attenuation of the percolating water.

Temperature

The probes were able to show the soil profile exhibiting annual, monthly and diurnal temperature fluctuations (Fig.5) with insulation from vegetation and the upper horizons causing a lag and damping in the temperature variations with depth. The temperature changes through the profile were substantially different with the A1 horizon changing by as much as 20^0C in 5 days, while the temperature in the Bgx changed by only 1.3^0C over the same time period. The fragipan (Bgx) had a higher temperature than four of the shallower horizons from September to January.

A plot of the daily soil profile temperatures with changing seasons (Fig 6) showed the largest temperature gradient was in the summer (7^0C) whilst the Fall showed only a 1^0C difference. For three of the four seasons the surface temperature was less than the temperature in the deepest horizon.

Electrical Conductivity

Conductivity was never greater than 0.1 S/m for any of the horizons (Fig. 7). Baseline conductivity increased with depth, and this is consistent with gradual leaching of ions from the surface horizons to lower horizons. There was a slight increase with the arrival of the wetting front in the lower three horizons. This can be attributed to an increase in pore water containing leached ions from the A1 and A2 horizons or pathway effects from the increased pore water (Corwin and Lesch, 2003). The lower horizons had greater conductivity values as they remained moist longer, and as the soil dried out in June, the conductivity decreases. The low conductivity of the profile was consistent with a soil with a low base saturation, leaching and low fertility.

The root mean standard error (RMSE) in the conductivity data was used to estimate the background noise for the probes (Table 3). Data over 3 days in the month of October of 2006 and 2007 and June 2008 were used. The results show the noise in the data was very low and was negligible over the study period despite the high saturation conditions and highly variable conditions. Other probes have been reported to fail under similar conditions.

Correlation matrices of the data from the probes were done to see if temperature affected moisture content as previously reported for other capacitance soil sensors by Seyfried and Grant (2007) and Verhoef et al. (2006). The results suggest correlation increases (28- 61%) with depth, however the Bgx only showed a correlation of 46% between temperature and soil moisture.

Conclusions

With the data from the Hydra Probes, the seasonal perched water table was characterized from observations of recharge, length of presence, and seasonal depletion. Soil moisture data allowed the movement of the wetting front to be followed and rates of infiltration and percolation to be determined. The probes also clearly showed annual, monthly and diurnal variations in temperature for all the soil horizons as well as lags and damping due to surface vegetation insulation. The low root mean square error of all the probes, independent of depth of installation, showed durability and consistency of the probes.

Characterizations of perched water tables with soil sensors and data loggers are insightful and cost effective. Information about perched water tables can be correlated to estimation of landslide potential and help address harmful runoff on irrigated lands.

REFERENCES

Boersma, L., Simonson, G. H., and Watts, D. G. 1972. Soil morphology and water table relations: I. Annual water table fluctuations. Soil Sci. Soc. of Am. J. 36, 644-648.

Calmon, M.A., Day, R.L., E.J.Ciolkosz, and G.W.Petersen. 1998. Soil morphology as an indicator of soil hydrology on a hillslope underlain by a fragipan. Soil Sci. Soc. Am. J.

Campbell, J.E. 1990. Dielectric properties and influence of conductivity in soils at one to fifty Megahertz. Soil Sci. Soc. Am. J. 54:332–341

Corwin, D.L., and Lesch, S.M. (2003) Application of soil electrical conductivity to precision agriculture: Theory and principles and guidelines America, Soil. Agron. J. 95 455-471

Dingman, S.L. 2002. Physical Hydrology. Chpt. 6. p. 210-255. Prentice-Hall, New Jersey.

Franzmeier, D.P., L.D.Norton, and G.C.Steinhardt. 1989. Fragipan formation in loess of the Midwestern United States. p. 69-97. *In* N.E.Smeck, and E.J.Ciolkosz (ed.) Fragipans: Their occurrence, classification and genesis. Soil Science Society of Science Society of America.

Hesse, P.R. 1971. A textbook of soil chemical analysis. John Murray, London, England.

Jones, S. B. 2005. Standardizing Characterization of Electromagnetic Water Content Sensors: Part 1 Methodology. Vadose Zone Journal 4:1048-1058.

Kraft, C. 1987. Constitutive parameter measurements of fields and soils between 500 kHz and 5 MHz using a transmission line technique. J Geophy. Res. 92:10650-10656.

Logsdon, S and D. Laird. 2004. Cation and Water Effects on Dipole Rotation Activation Energy of Smectites, Soil Sci. Soc. Am. J. 68:1586-1591

Logsdon, S.D. 2005a. Soil dielectric spectra from vector network analyzer data. Soil Sci. Soc. Am. J. 69:983–989.

McDaniel, P.A., and A.L.Falen. 1994. Temporal and spatial patterns of episaturation in a Fragixeralf landscape. Soil Sci. Soc. Am. J. 58:1451-1456.

McDaniel, P.A., R.W.Gabehart, A.L.Falen, J.E.Hammel, and R.J.Reuter. 2001. Perched water tables on Argixeroll and Fragixeralf Hillslopes. Soil Sci. Soc. Am. J. 65:805-810.

Palkovics, W.E., G.W.Petersen, and R.P.Matelski. 1975. Perched water table fluctuation compared to streamflow. Soil Sci. Soc. Am. J. 39:343-348.

Petersen, L.W., P.Moldrup, O.H.Jacobsen, and D.E.Rolston. 1996. Relations between specific surface area and soil physical and chemical properties. Soil Sci. 161:9-20.

Portland maps. Available at http://www.portlandmaps.com/ (Viewed Oct. 2006) City of Portland, OR.

Reuter, R.J., P.A.McDaniel, J.E.Hammel, and A.L.Falen. 1998. Solute transport in seasonal perched water tables in loess-derived soilscapes. Soil Sci. Soc. Am. J. 63:977-983.

Rockerfeller, S.L., P.A.McDaniel, and A.L.Falen. 2004. Perched water table responses to forest clearing in Northern Idaho. Soil Sci. Soc. Am. J. 68:168-174.

Roth, K., R. Schulin, H. Fluhler, and W. Attinger. 1990. Calibration of time domain reflectometry for water content measurement using a composite dielectric approach. Water Resour. Res. 26:2267–2273.

Ryan J, G Estefan, and A Rashid. 2001. Soil and Plant Analysis Laboratory Manual. 2nd ed. ICARDA and NARC, Aleppo, Syria. p. 25-30.

Seyfried, M.S., and L.E.Grant. 2007. Temperature Effects on soil dielectric properties measured at 50MHz. Vadose Zone J. 6:759-765.

Seyfried, M.S., L.E.Grant, E.Du, and K.Humes. 2005. Dielectric loss and Calibration of the Hydra Probe Soil Water Sensor. Vadose Zone J. 4:1070-1079.

Smalley, I.J., and J.E.Davin. 1982. Fragipan horizons in soils:A bibliographic study and review of some of the hard layers in loess and other materials. p. 122. New Zealand Bureau Bibliography, New Zealand Bureau Bibliography.

Smeck, N.E., and E.J.Ciolkosz. 1989. Fragipans: Their occurrence, classification and genesis. p. 151-153. *In* N.E.Smeck, and E.J.Ciolkosz (ed.) Soil Science Society of America, Soil Science Society of America.

Soil Survey Staff. 1999. Soil taxonomy: A basic system of soil classification for making and interpreting soil surveys. 2nd ed. USDA Agric. Handb. 436. U.S. Gov. Print. Office, Washington, DC.

Topp, G.C., J.L. Davis, and A.P. Annan. 1980. Electromagnetic determination of soil water content: Measurement in coaxial transmission lines. Water Resour. Res. 16:574–582.

Verhoef, A., J.Fernández-Gálvez, A.Diaz- Espejo, B.E.Main, and M.El- Bishti. 2006. The diurnal course of soil moisture as measured by various dielectric sensors: Effects of soil temperature and the implications for evaporation estimates. Journal of Hydrology 321:147-162.

Weast, R.C. 1986. CRC handbook of Chemistry and Physics. CRC Press, Boca Raton, FL. USA

Weisenborn, B.N. 2001. A model for fragipan evolution in Michigan soils. M.S. thesis, Michigan State University.

ACKNOWLEDGEMENTS

Special thanks to: Ms. Margaret Russell, Portland State University for field and lab assistance and Mr. Jim Randall, Portland State University for field assistance.

FIGURES

Figure 1. The dot on the maps indicates the location of the field site at Mt. Calvary Catholic Cemetery where the Hydra Probe was installed.

Figure 2. Soil pit at Mt. Calvary Catholic Cemetery showing the location of the six installed sensors.

Figure3. Soil moisture as a fraction of volume

Figure 4. Percolation rates from movement of the wetting front.

Figure 5. Temperature readings for each horizon.

Figure 6. Seasonal Temperature Profile

Figure 7. Electrical conductivity profile.

Table 1: Laboratory Characterization Soil Horizons							
Horizon	**Depth**	**Bulk Density**	**Color(dry)**	**Structure**	**Clay**	**Texture**	**Features**
	cm	g/cc			%		
A1	0-13	1.62	10YR 5/3	1 f sbk	10	Loam	
A2	13-30	1.56	10YR 4/3	2 m sbk	16	Loam	
Btx1	30-54	1.83	10YR 4/6	2 m sbk	20	Loam	1 cf
Bt2‡	54-74	1.65	10YR 4/6	-	-	-	1 cf
Btx3	74-100	1.71	10YR 5/6	3 m sbk	22	Loam	2 cf redox
Bgx	100-104+	1.53	10YR 6/8	3 c pr	28	Clay loam	3 cf redox

†1 = weak; 2 = moderate; 3 = strong; f = fine; m = medium; c = coarse; sbk = subangular blocky; pr = prismatic; cf = clay films; redox = redoxymorphic features. ‡Bt2 initially considered part of Btx1

Table 2: Soil Horizon Hydrological Parameters

Horizon	Probe Depth (cm)	pH	Porosity (Lab)	Porosity (Probe)	Field Capacity	Residual θ (Probe)
A1	6	5	0.39	0.48	0.27	0.19
A2	22	5.1	0.41	0.45	0.29	0.21
Btx1	43	4.7	0.38	0.43	0.21	0.17
Bt2	54	4.7	0.31	0.52	0.18	0.31
Btx3	81	4.3	0.35	0.5	0.26	0.25
Bgx	104	4.4	0.42	0.46	0.29	0.3

Table 3: Background noise in data

	Probe(Horizon)					
Date	1(A1)	2(A2)	3(Btx1)	4(Bt2)	5(Btx3)	6(Bgx)
Year 1	5.95E-07	3.06E-07	1.91E-08	2.67E-07	8.26E-08	1.63E-08
Year 2	1.69E-07	1.19E-07	1.78E-07	1.20E-07	8.06E-08	9.11E-08
Year 3	2.32E-07	1.64E-07	2.19E-07	6.01E-07	1.97E-07	3.50E-07

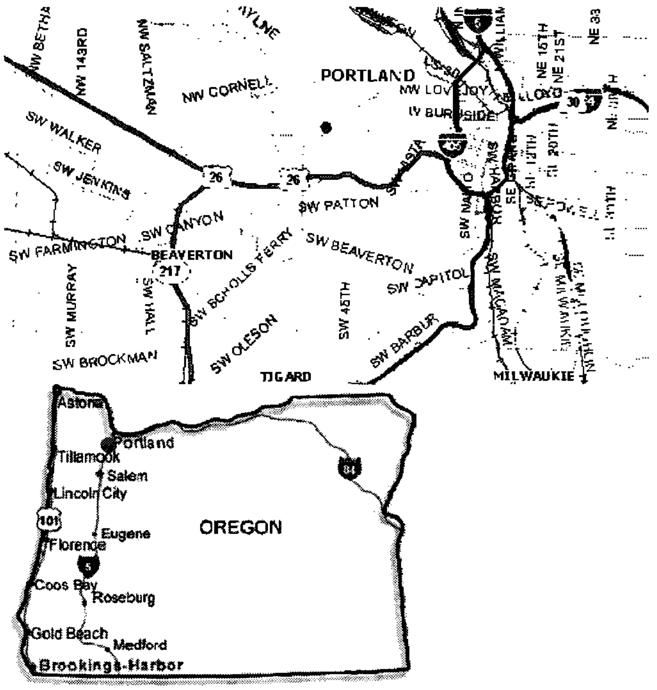


Figure 1. The dot on the maps indicates the location of the field site at Mt. Calvary Catholic Cemetery where the Hydra Probe was installed.

Figure 2. Soil pit at Mt. Calvary Catholic Cemetery showing the location of the six installed sensors.

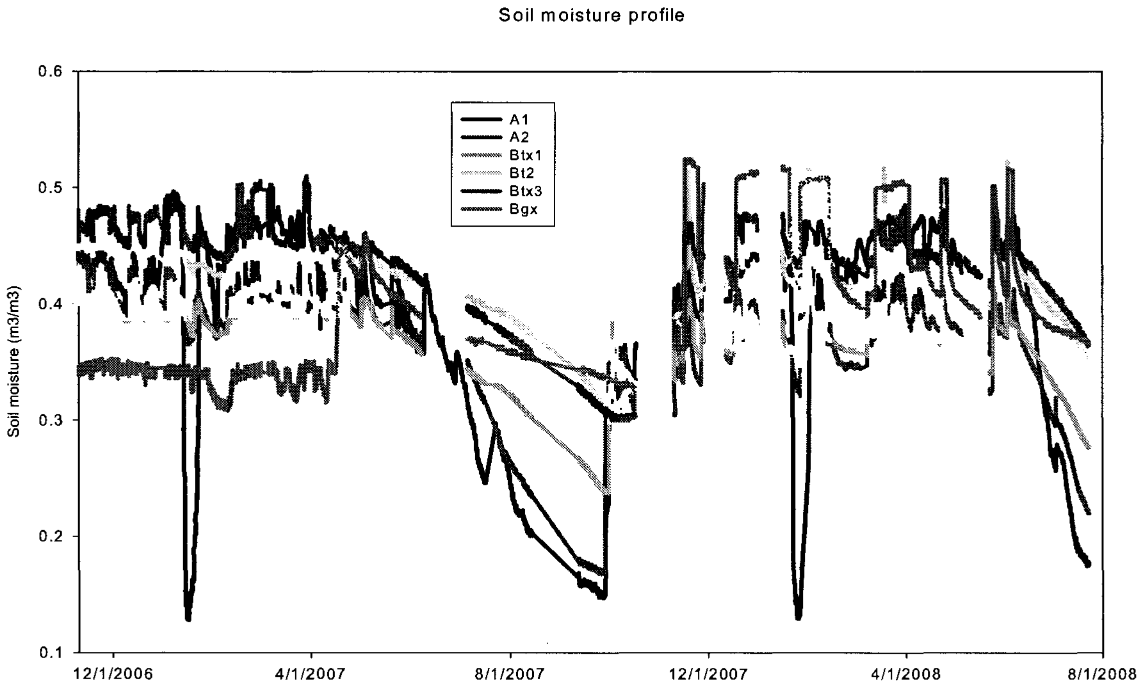


Figure 3. Soil moisture as a fraction of volume

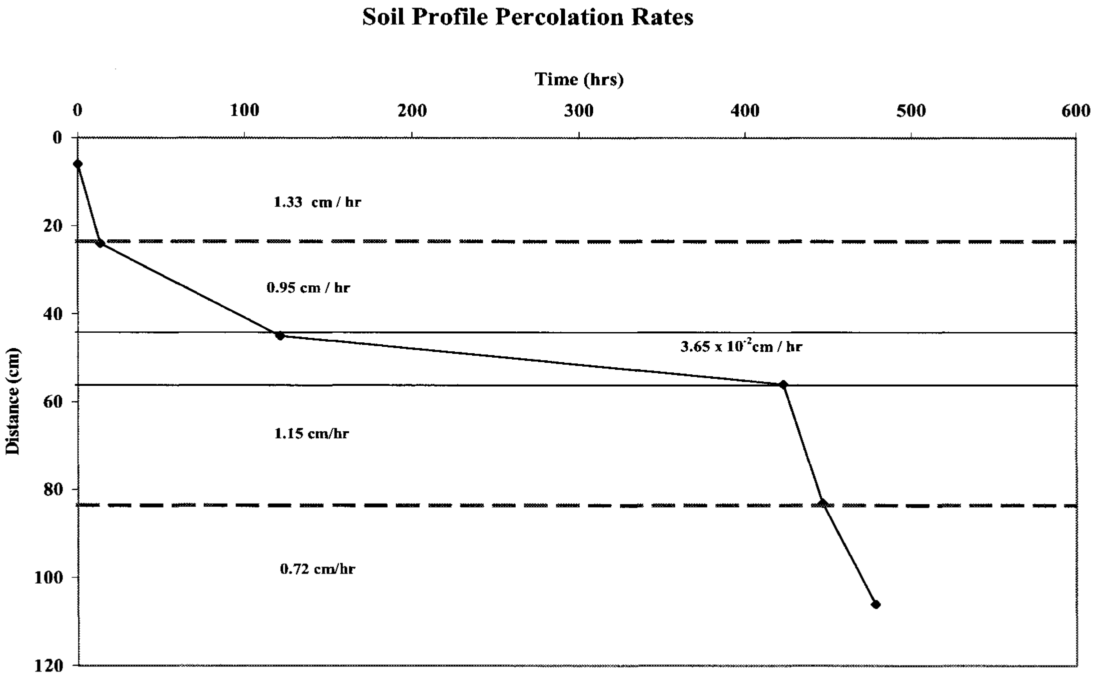


Figure 4. Percolation rates from movement of the wetting front.

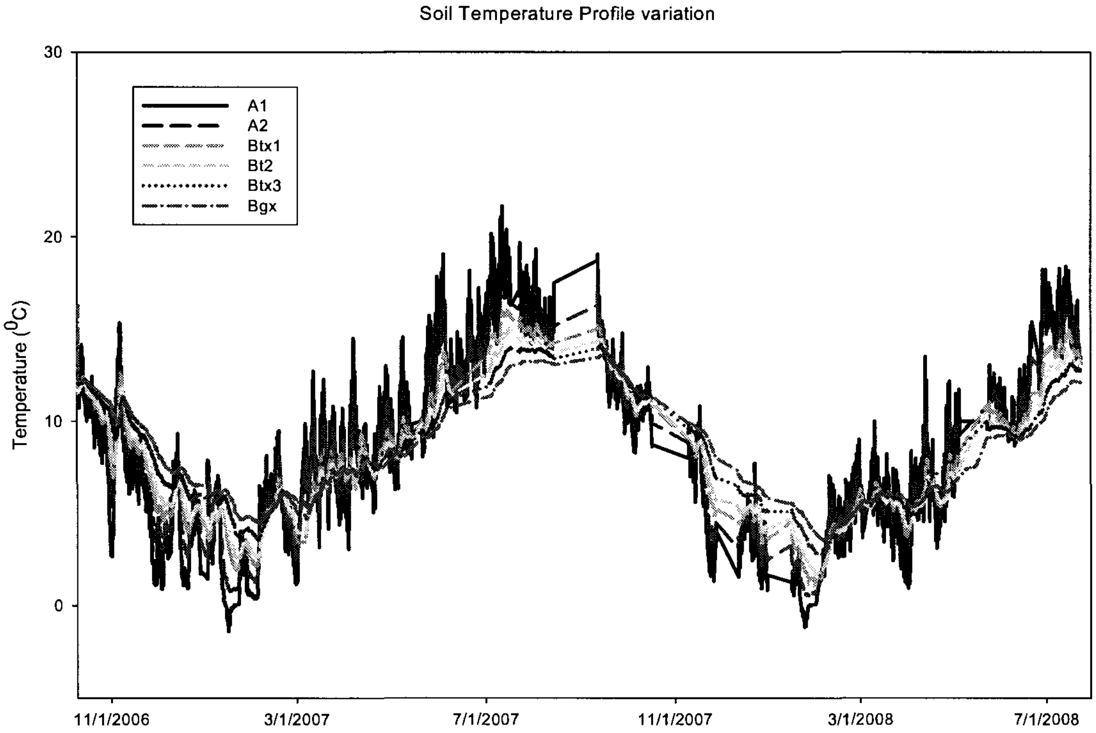


Figure 5. Temperature readings for each horizon.

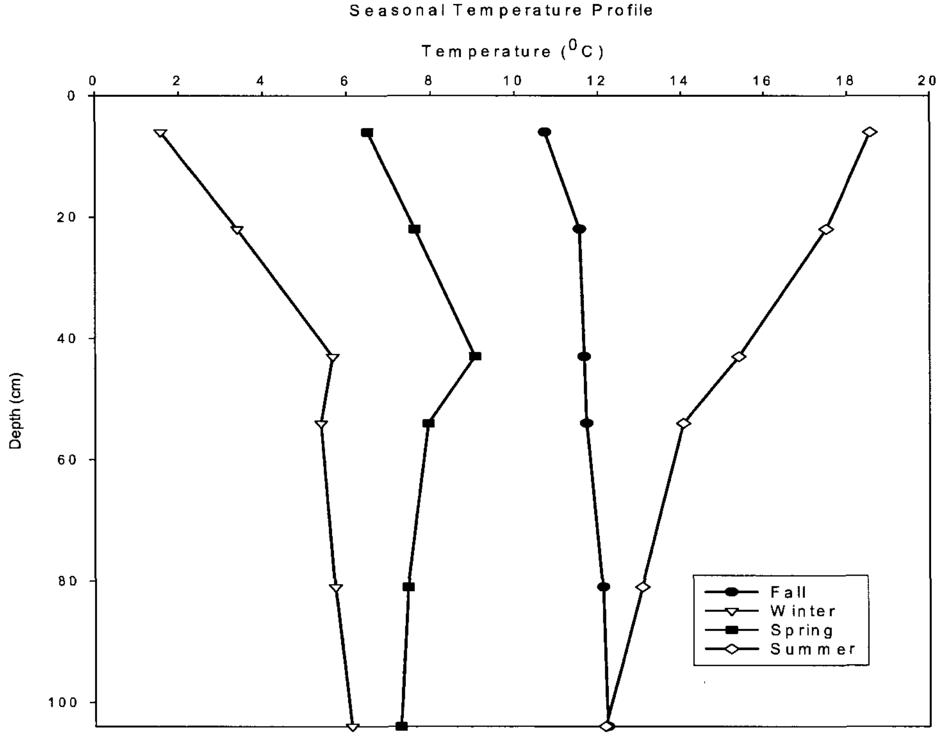


Figure 6. Seasonal Temperature Profile

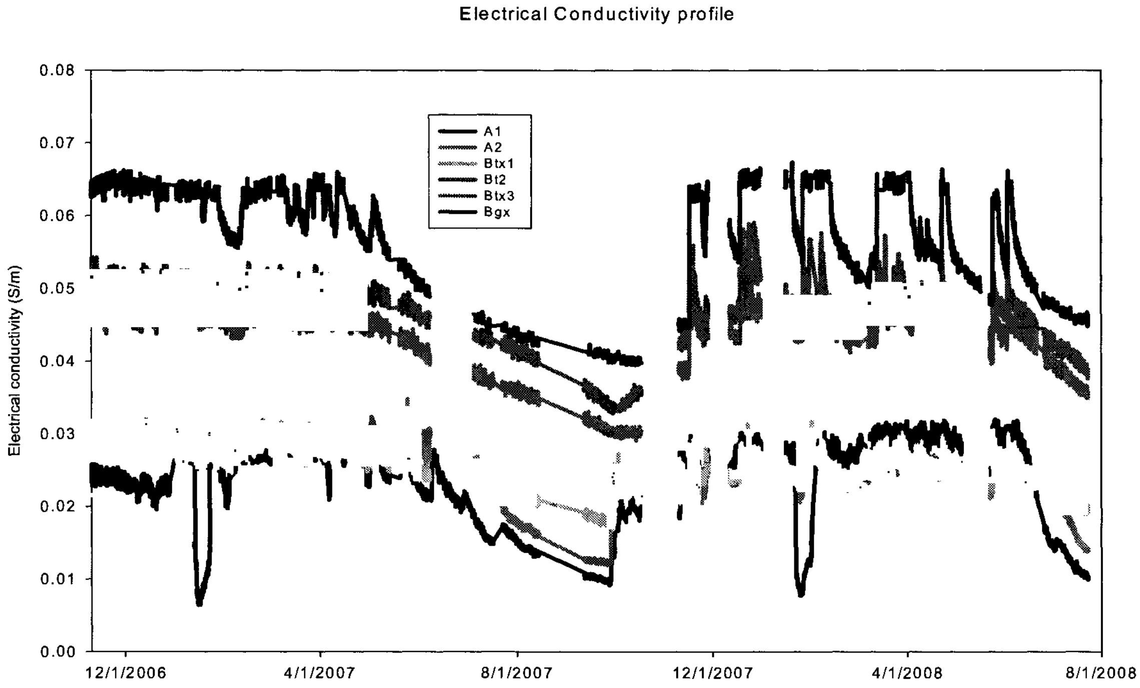


Figure 7. Electrical conductivity profile.

Appendix A-1

Field Report: St Calvary Cemetery Soil Description

Classification: mesic Typic Fragixeralf

Location: St. Calvary Catholic Cemetery, Portland, Multnomah County, Oregon, USA, North side of W Burnside Road, 300 feet North of maintenance building.

Physiographic position: Upper third of slope on an ancient landslide. T. 1 S., R. 1.E.

Topography: 25% slope

Drainage: well-drained soils

Vegetation: Douglas fir (P*seudotsuga menziesii)*, bigleaf maple (*Acer macrophyllum*), and Himalayan blackberry (*Rubus discolor)* other deciduous shrubs and trees.

Parent Material: Basalt bedrock soils, loess deposits

Sampled by: Scott Burns, Keith Bellingham, Fungai Mukome, Jim Randall, Margaret Russell

Remarks: Weather conditions the day of sampling were sunny 21°C. Sampled starting 10 October, 2006.

Typical Pedon: Goble clay loam series

Soil No.: Not applicable

Colors are for dry soil unless otherwise noted*..

O1	5 – 0 cm (2 – 0 in) thin layer of leaves and fur needles; mostly dead deciduous leaves and fern leaves.
A1	0 – 13 cm (0 – 5 in) reddish brown soil, (10 YR 5/3 dry); silt loam; subangular blocky; slightly hard-dry; not sticky, transitional boundary not abrupt but straight; (lab pH 5).
A2	13 – 30 cm (5 – 12 in) reddish brown soil, dark organic matter in small patches (10 YR 4/3 dry); silt loam, slightly hard; very friable, subangular blocky; transitional boundary not abrupt but straight; (lab pH 5.1).
Bt1	30 -60 cm (12 – 24 in) brownish red , (10 YR 4/6 dry), silt loam; more structure, common clay films, visible distinct contrast, ped faces, slightly hard, friable, slightly sticky subangular blocky; transitional boundary not abrupt but straight;(lab pH 4.7).
Bt2	60 – 100 cm (24 – 39 in) brownish red (10 YR 5/6 dry) silty clay loam, many clay films, distinct contrast, ped faces, Mg Oxides dark spots, more structure, subangular blocky, transitional boundary not abrupt but straight, (lab pH 4.3).
Bgx	100 cm – (39 in –) brown deeper red (10 YR 6/8 dry) silty clay loam, abundant clay films, Mg Oxides dark spots, structure slightly platy, hard, friable, mottling (lab pH 4.4).

*Moist colors not recorded.

Appendix B

Raw Soil Titration Data

Hermiston											
HBT 3303-SS Titration Curve (0.001M)				**HBT 3303-SS Titration Curve (0.01M)**				**HBT 3303-SS Titration Curve (0.1M)**			
Vol	**pH**	**ΔpH**		**Vol**	**pH**	**ΔpH**		**Vol**	**pH**	**ΔpH**	
0	4.56			0	4.53			0	4.53		
100	5.25	0.69		100	5.14	0.61		100	5.1	0.57	
200	5.89	0.64		200	5.82	0.68		200	5.76	0.66	
300	6.52	0.63		300	6.5	0.68		300	6.33	0.57	
400	7.05	0.53		400	7.07	0.57		400	6.8	0.47	
500	7.55	0.5		500	7.62	0.55		500	7.27	0.47	
600	8.02	0.47		600	8.1	0.48		600	7.64	0.37	
700	8.26	0.24		700	8.53	0.43		700	8.01	0.37	
800	8.65	0.39						800	8.28	0.27	
								900	8.57	0.29	

Klamath											
KBT 3303-SS Titration Curve (0.001M)				**KBT 3303-SS Titration Curve (0.01M)**				**KBT 3303-SS Titration Curve (0.1M)**			
Vol	**pH**	**ΔpH**		**Vol**	**pH**	**ΔpH**		**Vol**	**pH**	**ΔpH**	
0	4.58			0	4.8			0	4.58		
100	5.1	0.52		100	5.1	0.3		100	5.16	0.58	
200	5.64	0.54		200	5.69	0.59		200	5.74	0.58	
300	6.14	0.5		300	6.23	0.54		300	6.28	0.54	
400	6.68	0.54		400	6.67	0.44		400	6.69	0.41	
500	7.2	0.52		500	7.13	0.46		500	7.11	0.42	
600	7.68	0.48		600	7.55	0.42		600	7.53	10:04	
700	8.16	0.48		700	7.93	0.38		700	7.89	0.36	
800	8.51	0.35		800	8.21	0.28		800	8.22	0.33	
900	8.89	0.38		900	8.57	0.36		900	8.48	0.26	
								1000	8.7	0.22	

Hyslop											
WBT 3303-SS Titration Curve (0.001M)				**WBT 3303-SS Titration Curve (0.01M)**				**WBT 3303-SS Titration Curve (0.1M)**			
Vol	**pH**	**ΔpH**		**Vol**	**pH**	**ΔpH**		**Vol**	**pH**	**ΔpH**	
0	4.58			0	4.57			0	4.54		
100	4.98	0.4		100	4.81	0.24		100	5.03	0.49	
200	5.33	0.35		200	5.1	0.29		200	5.35	0.32	
300	5.58	0.25		300	5.37	0.27		300	5.58	0.23	
400	5.88	0.3		400	5.64	0.27		400	5.78	0.2	
500	6.14	0.26		500	5.93	0.29		500	5.99	0.21	
600	6.39	0.25		600	6.18	0.25		600	6.14	0.15	
700	6.63	0.24		700	6.43	0.25		700	6.32	0.18	
800	6.87	0.24		800	6.7	0.27		800	6.53	0.21	
900	7.07	0.2		900	6.93	0.23		900	6.69	0.16	
1000	7.27	0.2		1000	7.15	0.22		1000	6.82	0.13	
1100	7.4	0.13		1100	7.3	0.15		1100	7.02	0.2	
1200	7.58	0.18		1200	7.47	0.17		1200	7.13	0.11	
1300	7.75	0.17		1300	7.65	0.18		1300	7.31	0.18	
1400	7.89	0.14		1400	7.81	0.16		1400	7.44	0.13	
1500	8.06	0.17		1500	8.02	0.21		1500	7.54	0.1	
1600	8.21	0.15		1600	8.18	0.16		1600	7.65	0.11	
				1700	8.36	0.18		1700	7.83	0.18	
				1800	8.51	0.15					

Pendleton											
CBT 3303-SS Titration Curve (0.001M)				**CBT 3303-SS Titration Curve (0.01M)**				**CBT 3303-SS Titration Curve (0.1M)**			
Vol	**pH**	**ΔpH**		**Vol**	**pH**	**ΔpH**		**Vol**	**pH**	**ΔpH**	
0	4.51			0	4.53			0	4.56		
100	4.73	0.22		100	4.94	0.41		100	5.14	0.58	
200	5.2	0.47		200	5.34	0.4		200	5.5	0.36	
300	5.58	0.38		300	5.72	0.38		300	5.78	0.28	
400	6.04	0.46		400	6.12	0.4		400	5.98	0.2	
500	6.48	0.44		500	6.49	0.37		500	6.2	0.22	
600	6.89	0.41		600	6.87	0.38		600	6.4	0.2	
700	7.3	0.41		700	7.18	0.31		700	6.56	0.16	
800	7.65	0.35		800	7.56	0.38		800	6.74	0.18	
900	7.97	0.32		900	7.81	0.25		900	6.9	0.16	
1000	8.3	0.33		1000	8.09	0.28		1000	7.09	0.19	
1100	8.59	0.29		1100	8.29	0.2		1100	7.27	0.18	
				1200	8.56	0.27		1200	7.42	0.15	
								1300	7.6	0.18	
								1400	7.79	0.19	
								1500	7.98	0.19	
								1600	8.17	0.19	
								1700	8.36	0.19	

Appendix C

Soil Modeling

Modeling Equations

The basic equation used for the calculation of metal addition to soil (mg/kg) was:

$$\frac{mgX}{kgsoil} = \frac{mgX}{kgproduct} x \frac{1 kgproduct}{(\% Y / 100) kga.i.} xAR \frac{kga.i.}{ha} x \frac{ha}{xkgsoil} \quad (1)$$

where: X = metal contaminant

Y = fertilizer nutrient (e.g., zinc, nitrogen, P_2O_5, K_2O)

AR = application rate (kg/ha)

Fertilizer application rate is the amount of a nutrient required by a soil not the total amount of fertilizer added. It is determined by doing a soil test for the nutrient of interest and ascertaining the deficiency of the soil. Different crops have different application rates for different nutrients.

a.i. = active fertilizer ingredient (e.g. nitrogen, N)

The conversion of hectares to kgsoil was arrived at using

$$\frac{100\,\mathrm{m} \times 100\,\mathrm{m} \times 0.15\,\mathrm{m}}{ha} x \frac{\rho\,(\mathrm{g/cm}^3)}{0.01\,(\mathrm{m/cm})^3} \times \frac{\mathrm{kg}}{1000\mathrm{g}} = \frac{kgsoil}{ha} \quad (2)$$

where the tilling depth was assumed to be 15 cm and ρ is the soil density. The till depth was selected after observing the accumulation depth of the background cadmium in the agricultural soils. These calculations gave the total concentration of a contaminant being added to a soil per year.

The total concentration of the contaminant in the soil can be expressed as the sum of the masses of the contaminant adsorbed on the soil, dissolved in the aqueous phase, and volatilized in the pore spaces, divided by the total mass of contaminated soil as follows:

$$C_T = C_s + \theta_W C_W / \rho_b + \theta_a C_a / \rho_b \quad (3)$$

where

C_T = total contaminant concentration (mg/kg)

C_s = concentration of contaminant adsorbed on soil (mg/kg)

θ_w = water-filled soil porosity (m^3 water/m^3 soil)

C_w = concentration of contaminant dissolved in the water ($\mu g/cm^3$)

ρ_b = soil dry bulk density (g/cm^3)

θ_a = air-filled soil porosity (m^3 air/m^3 soil)

C_a = concentration of contaminant in air ($\mu g/cm^3$).

The adsorbed contaminant concentration can be determined by assuming it to be linearly related to the aqueous phase concentration so K_d is an appropriate parameter to use.

$$C_s = K_d C_w \quad (4)$$

where

K_d = soil-water partition coefficient (cm^3/g)

Combining Equations (3), (4), and (5) gives

$$C_T = C_s [1 + \theta_w/(K_d \rho_b) + \theta_a H'/(K_d \rho_b)] \quad (6)$$

Equation (6) can be rearranged to calculate the adsorbed soil contaminant concentration given the total contaminant concentration as follows:

$$C_s = C_T K_d \rho_b/(K_d \rho_b + \theta_w + \theta_a H') \quad (7)$$

The ideal soil moisture condition for crops is field capacity. At field capacity is the soil moisture at which there is water movement downwards due to gravity. Field capacity is dependent on soil type and can be calculated as follows:

$\theta_{fc} = \Phi(\psi_{ae}/340)^{1/b}$ (8)

where

θ_{fc} = water content at field capacity

Φ = porosity

ψ_{ae} = air entry tension

b = constant (dependent on soil texture)

For cadmium volatilization is negligible loss pathway so equation (7) can be further simplified to

$C_s = C_T\, K_d\, \rho_b/(K_d\, \rho_b + \theta_{fc})$ (9)

Knowledge of background concentration of cadmium and Cs allowed for the calculation of the **doubling time** of cadmium at each site.

The Jury equations (Jury et al., 1983, 1984, 1990) are used in soil modeling to estimate soil contaminant concentrations losses through volatilization, runoff and leaching.

The mass flux loss of a contaminant due to leaching is estimated by assuming the leachate is in equilibrium with the soil so:

$J_{\mathrm{leach,t}} = C_T\, \rho_b\, (0.01V_L)/(\rho_b\, K_d + \theta_W + \theta_a\, H')$ (10)

where

$V_L = (P + I - R - E)/\ (365 \times 24 \times 3{,}600]$ = leachate rate (cm/s) (11)

P = annual average precipitation rate (cm/yr)

I = annual average irrigation rate (cm/yr)

R = annual average runoff rate (cm/yr).

For simplicity, annual precipitation was considered the only source of water at each site and runoff and evapotranspiration were considered negligible compared to leaching therefore Equation (10) simplified to

$$J_{\text{leach,t}} = C_T \rho_b (0.01V_L)/(\rho_b K_d + \theta_W)$$

From this mass flux, the loss of cadmium per year at each site could be approximated. The number of years to get to a zero level of cadmium in the soils was calculated and the amount of cadmium lost over the three year period necessary in organic farm certification was also determined.

Assumptions

The Jury et al. modeling incorporates several basic simplifying assumptions. Some of the more significant assumptions and limitations are as follows:

- The adsorbed contaminant concentration is assumed to be linearly related to the aqueous-phase concentration.
- The only mass additions to the system occur during fertilizer applications.
- The contaminant concentrations are assumed to be uniform over the tilling depth.
- There is a thin layer of untilled contaminated soil (the depth equal to the depth of fertilizer added during the annual application) just below the tilling depth. As this layer is buried, it is lost from the system and not expected to contribute

significantly to the exposure pathways.

Doubling Time

Modeling Characteristics				
	Site			
	Hermiston	Hyslop	Klamath Falls	Pendleton
Using nutrient requirements for 2003				
ρ_b	1.15-1.3	1.25-1.45	1.3-1.4	1.1-1.3
avg ρ_b	1.225	1.35	1.35	1.2
θ_{fc}	0.25	0.31	0.17	0.17
total porosity	0.53	0.49	0.49	0.54
θ_A	0.28	0.18	0.32	0.37
K_d L/kg	93.85	195	167.5	277.66
K_d L/g	0.09385	0.195	0.1675	0.27766
mgCd/kg	50	50	50	50
%N /100 kg a.i	16	16	16	16
highest AR N lbs/a	360	480	360	195
highest AR N kg/a	164	218	164	89
highest AR N kg/ha	404.18182	538.90909	404.1818182	218.93182
kgsoil/ha	1837500	2025000	2025000	1800000
C_T Cd mg/ kg soil(one application)	0.07	0.08	0.06	0.04
C_T (two application)	**0.14**	**0.17**	**0.12**	**0.08**
Cs	0.04	0.08	0.07	0.05
Background levels	0.21	0.19	0.11	0.2
Doubling Time years	**4.8**	**2.5**	**1.5**	**4.0**

Doubling Time with same background concentration and similar application rates

	Site			
	Hermiston	Hyslop	Klamath Falls	Pendleton
Using nutrient requirements for 2003				
ρ_b	1.15-1.3	1.25-1.45	1.3-1.4	1.1-1.3
avg ρ_b	1.225	1.35	1.35	1.2
θ_{fc}	0.25	0.31	0.17	0.17
total porosity	0.53	0.49	0.49	0.54
θ_A	0.28	0.18	0.32	0.37
K_d L/kg	93.85	195	167.5	277.66
K_d L/g	0.09385	0.195	0.1675	0.27766
mgCd/kg	50	50	50	50
%N /100 kg a.i	16	16	16	16
highest AR N lbs/a	360	360	360	360
highest AR N kg/a	164	164	164	164
highest AR N kg/ha	404.18182	404.18182	404.1818182	404.18182
kgsoil/ha	1837500	2025000	2025000	1800000
C_T Cd mg/ kg soil(one application)	0.07	0.06	0.06	0.07
C_T (two application)	**0.14**	**0.12**	**0.12**	**0.14**
Cs	0.04	0.06	0.07	0.09
Background levels	**0.21**	**0.21**	**0.21**	**0.21**
Doubling Time years	**4.8**	**3.7**	**2.9**	**2.3**

Deturbation

Modeling Characteristics					
		Hermiston	Hyslop	Klamath	Pendleton
	Using nutrient requirements for 2003				
	ρb	1.15-1.3	1.25-1.45	1.3-1.4	1.1-1.3
	avg pb	1.225	1.35	1.35	1.2
	θfc	0.25	0.31	0.17	0.17
	total porosity	0.53	0.49	0.49	0.54
	Kd L/kg	93.85	195	167.5	277.66
	Kd L/g	0.09385	0.195	0.1675	0.27766
	kgsoil/ha	1837500	2025000	2025000	1800000
Cdmg/kgsoil	Backgd levels	0.21	0.19	0.11	0.2
Cdmg/ha		385875.00	384750.00	222750.00	360000.00
Cd g/ha		385.88	384.75	222.75	360.00
Cd g/m2		3.86E-02	3.85E-02	2.23E-02	3.60E-02
cm/yr	Precip	21.5	114.3	30.3	55.8
cm/s	V_L	9.E-07	5.E-06	1.E-06	2.E-06
m/s	V_L	9.E-10	5.E-09	1.E-09	2.E-09
g/m2-s	Jleach	2.10767E-14	4.88E-14	8.73E-15	1.764E-14
	Time (s)	1.83E+12	7.88E+11	2.55E+12	2.04E+12
	g/ha/s	2.10767E-10	4.88E-10	8.73E-11	1.764E-10
	mg/ha-yr	6.65	15.40	2.75	5.56
Years to NO Cadmium		4837.89	2081.68	6742.38	5393.40
3 year Organic Standard					
	mg/ha-yr	19.9	46.2	8.3	16.7
Amt Left	**Cd g/ha**	**385.86**	**384.70**	**222.74**	**359.98**

Assume Similar ppt					
		Site			
		Hermiston	Hyslop	Klamath	Pendleton
	Using nutrient requirements for 2003				
	ρb	1.15-1.3	1.25-1.45	1.3-1.4	1.1-1.3
	avg pb	1.225	1.35	1.35	1.2
	θfc	0.25	0.31	0.17	0.17
	total porosity	0.53	0.49	0.49	0.54
	Kd L/kg	93.85	195	167.5	277.66
	Kd L/g	0.09385	0.195	0.1675	0.27766
	kgsoil/ha	1837500	2025000	2025000	1800000
Cdmg/kgsoil	Background levels	0.21	0.19	0.11	0.2
Cdmg/ha		385875.00	384750.00	222750.00	360000.00
Cd g/ha		385.88	384.75	222.75	360.00
Cd g/m2		3.86E-02	3.85E-02	2.23E-02	3.60E-02
cm/yr	Precip	**114.3**	**114.3**	**114.3**	**114.3**
cm/s	VL	5.E-06	5.E-06	5.E-06	5.E-06
m/s	VL	5.E-09	5.E-09	5.E-09	5.E-09
g/m2-s	Jleach	1.1205E-13	4.88E-14	3.293E-14	3.613E-14
	Time(s)	3.44E+11	7.88E+11	6.76E+11	9.96E+11
	g/ha/s	1.1205E-09	4.88E-10	3.293E-10	3.613E-10
Leach flux	**mg/ha-yr**	**35.3**	**15.4**	**10.4**	**11.4**
Years to NO cadmium		910.01	2081.68	1787.35	2633.00
		Greatest loss in sandy soils, Kd not as important			

Similar ppt and similar background concentration					
		Site			
		Hermiston	Hyslop	Klamath	Pendleton
	Using nutrient requirements for 2003				
	ρb	1.15-1.3	1.25-1.45	1.3-1.4	1.1-1.3
	avg pb	1.225	1.35	1.35	1.2
	θfc	0.25	0.31	0.17	0.17
	total porosity	0.53	0.49	0.49	0.54
	θA	0.28	0.18	0.32	0.37
	Kd L/kg	93.85	195	167.5	277.66
	Kd L/g	0.09385	0.195	0.1675	0.27766
	kgsoil/ha	1837500	2025000	2025000	1800000
		0.21	**0.21**	**0.21**	**0.21**
Background levels		385875.00	425250.00	425250.00	378000.00
		385.88	425.25	425.25	378.00
		3.86E-02	4.25E-02	4.25E-02	3.78E-02
At highest	Precipitation	**114.3**	**114.3**	**114.3**	**114.3**
	VL	5.E-06	5.E-06	5.E-06	5.E-06
	VL	5.E-09	5.E-09	5.E-09	5.E-09
	Jleach	1.1205E-13	5.4E-14	6.287E-14	3.794E-14
	Time (s)	3.44E+11	7.88E+11	6.76E+11	9.96E+11
	yrs	910.01	2081.68	1787.35	2633.00
	g/ha/s	1.1205E-09	5.4E-10	6.287E-10	3.794E-10
Leach flux	**mg/ha-yr**	**35.3**	**17.0**	**19.8**	**12.0**