Final Report

Screening Survey for Metals and Dioxins in Fertilizer Products and Soils in Washington State

April 1999

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Final Report

Screening Survey for Metals and Dioxins in Fertilizer Products and Soils in Washington State

by
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Atomic Symbols for Metals

Arsenic	As
Barium	Ba
Cadmium	Cd
Chromium	Cr
Copper	Cu
Lead	Pb
Mercury	Hg
Nickel	Ni
Selenium	Se
Silver	Ag
Zinc	Zn

Glossary

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

Biosolids* – municipal sewage sludge that is primarily an organic, semi-solid product resulting from the wastewater treatment process that can be beneficially recycled.

Bulk fertilizer* – fertilizer available in unpackaged form for agricultural application.

By-product – a substance that is not one of the primary products of a production process.

Congener – a series of compounds with the same base structure but varying degrees of substituted functional groups.

Contaminant* – any substance that does not occur naturally or occurs at concentrations greater than natural background levels.

Dangerous waste* – solid wastes designated in WAC 173-303-070 through WAC 173-303-100 as dangerous, extremely hazardous, or mixed waste. In this report, "dangerous waste" refers to those wastes regulated by the Washington State WAC 173-303. These wastes may also be federally regulated by 40 CFR Part 261. In general, these wastes pose a threat to human health or the environment. See also "hazardous waste."

Dioxins – in this report, refers to polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans with chlorine atoms in the 2,3,7,8, positions of the molecule.

Fertilizer* – any substance containing one or more recognized plant nutrients and which is used for its plant nutrient content and/or which is designated for use or claimed to have value in promoting plant growth, and includes commercially valuable concentrations of nitrogen, phosphoric acid, available phosphorus, potash, calcium, magnesium, or sulfur, limes, gypsum, manipulated animal and vegetable manures.

Fertilizer products – in this report, refers to all fertilizers and related products sampled. These products include bulk agricultural fertilizers, home-use fertilizers, micronutrients, and soil amendments.

Hazardous waste* – solid wastes designated by 40 CFR Part 261, and regulated as hazardous and/or mixed waste by the U.S. EPA. In this report, "hazardous waste" refers to those wastes regulated by EPA and not necessarily by Washington State (e.g., wastes designated hazardous outside of Washington). In general, these wastes pose a threat to human health or the environment

Micronutrient* – a trace plant nutrient or minor element (other than a primary nutrient) such as boron, chlorine, cobalt, copper, iron, manganese, molybdenum, sodium, or zinc.

Natural background* – the concentration of a substance consistently present in the environment which has not been influenced by localized human activities.

Nutrient – an element required for normal growth and development of plants or animals.

Persistent, bioaccumulative and toxic chemicals of concern (PBTs) **–** highly toxic, long-lasting substances that can build up in the food chain to levels that are harmful to human and ecosystem health. Certain chemicals and chemical byproducts that persist in the environment for a long time build up in the tissues of humans, fish, and animals, and can have toxic effects such as cancer or reproductive failure on living organisms (Ecology, 1999).

Relative percent difference (RPD) – a measure of precision, it is the ratio of the difference and the mean of the results expressed as a percentage. A low RPD (i.e., less than 25%) indicates good precision.

Soil amendment – any of various organic or inorganic materials added to soil to affect its physical properties.

Solid waste* – all liquid, solid, and semi-solid materials that are not the primary products of public, private, industrial, commercial, mining and agricultural operations.

Tag-along – an unintended or unnecessary element or substance found in a product.

Toxic* – an element or substance that is or has potential to be harmful to human health or the environment.

Toxic equivalent (TEQ) – the sum of congener concentrations times the corresponding TEF.

Toxic equivalent factors (TEFs) – the relative toxicity value of different types of dioxins. TEFs are established relative to the toxicity of 2,3,7,8-TCDD.

Waste-derived – a waste or by-product from any industrial process that is recycled into fertilizer or soil amendments.

* Terms codified in the Washington Administrative Code.

Acronyms and Abbreviations

CEC –	cation exchange capacit
CKD –	cement kiln dust
CFR –	Code of Federal Regulations
d –	day
DL –	detection limit
DTPA –	diethylene triamine pentaacetic acid
dw –	dry weight
Ecology	Washington State Department of Ecology
EDL –	estimated detection limit
EPA –	U.S. Environmental Protection Agenc
GC/MS –	gas chromatograph/mass spectrometer
IARC –	International Agency for Research on Cancer
ICP –	inductively coupled plasma
kg –	kilogram
K061 –	RCRA waste code for emission control dust/sludge from the primar production of steel in electric furnaces (i.e., steel mill flue dust)
mg –	milligram
meq –	milliequivalents
MGD –	millions gallons per da
MTCA –	Model Toxics Control Act
ND –	non-detects
NSSS –	national sewage sludge survey
ng/kg –	nanogram/kilogram
NT –	not tested
PBT –	persistent, bioaccumulative and toxic chemicals
PCA –	principal component analysis
PCB –	polychlorinated biphenyl
PCDD/F –	polychlorinated dibenzo-*p*-dioxin and dibenzofuran
PCP –	pentachlorophenol
ppb –	parts per billion
ppm –	parts per million
pptr –	parts per trillion
QA/QC –	Quality Assurance/Quality Control
RCRA –	Resource Conservation and Recovery Act
RCW –	Revised Code of Washington

RPD – relative percent difference
SWFAP – Solid Waste and Financial Assistance Program
TCDD – 2,3,7,8-tetrachlorodibenzo-*p*-dioxin
TCDF – 2,3,7,8-tetrachlorodibenzofuran
TCLP – toxicity characteristic leaching procedure
TEF – toxicity equivalent factor
TEQ – toxic equivalent
TOC – total organic carbon
USDA – U.S. Department of Agriculture
USEPA - U.S. Environmental Protection Agenc
USGS – U.S. Geological Surve
WAC – Washington Administrative Code
WWTP – wastewater treatment plant

Changes from the Preliminary Report

The following summarizes substantive changes made since the *Preliminary Survey for Metals and Dioxins in Fertilizers, Soil Amendments, and Soils in Washington State* was published in November 1998 (Rogowski et al., 1998).

- Results from fertilizer product Frit F-420G have been removed, as this product has not been sold or registered in Washington State
- Introduction has new, clarifying text describing TEFs and TEQs
- Expanded background text on metals and metals toxicolog
- Text on TCLP has been updated and clarified
- New text on waste-derived products and the review process
- Table 1-2, listing TCLP test results, is now Table 1-3
- New text on dioxins in biosolids, sources of dioxins in biosolids, and Washington State biosolids data
- Text and Table 1-5 comparing estimated increases in dioxin soil concentrations from fertilizer products and biosolids
- Additional total metals data in fertilizer products for cobalt, molydenum, nickel and zinc
- Text describing conclusions from application rates of fertilizer products
- New information on the history of agricultural fields sampled
- New data in Table 2-4, a statistical summary of metals
- A statistical analysis of dioxin data in Chapter 3
- Table 3-4, summary of Washington State soil TEQs by land use
- New text on dioxin guidelines, standards, and source relationships
- Table 3-5, summary of soil dioxin data by region, excluding urban areas
- Figure 3-2, location of soil samples and dioxins TEQs
- Figure 3-4, dioxin profiles of different source clusters
- Figure 3-5, principal components plot of loadings
- Figure 3-6, two-dimensional plot of dioxin soils data
- Figure 3-7, dioxin signatures of soils
- Additional information in “Comparison of Dioxin Results” text
- A principal component analysis in Chapter 3 that leads to a discussion about dioxins and possible sources
- New recommendations regarding biosolids data needs

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Executive Summary

This report is a result of Washington State Executive Request 1998 legislation (SSB 6474), *The Fertilizer Regulation Act*, mandating a study of dioxins in fertilizers, soil amendments, and soils. With support from a U.S. Environmental Protection Agency (EPA) grant, the Washington State Department of Ecology (Ecology) also studied metals in fertilizers, soil amendments, and soils. The results from these studies are included in this report.

Objectives of the studies included:

1. Quantify metal and dioxin concentrations in fertilizer products
2. Determine if certain metals have accumulated in agricultural soils of the Columbia Basin
3. Provide an initial assessment of typical concentrations of dioxins in Washington soils

To satisfy these objectives, Ecology, in cooperation with the state Department of Agriculture and the state Department of Health:

1. Sampled fertilizer products to determine metal and dioxin concentrations
2. Analyzed metal concentrations of agricultural and non-agricultural soils in the Columbia Basin
3. Sampled soils in open, forest, and urban areas for dioxins

The Studies

1. Metals and Dioxins in Fertilizer Products

Fifty fertilizer products – including bulk agricultural fertilizers, home-use fertilizers, agricultural micronutrient products, and a soil amendment – were sampled for eight heavy metals and 17 types of dioxins. The most frequently analyzed products were home-use fertilizers, which include a wide variety of products.

Fertilizer products were analyzed for total metals. Leachable metals were evaluated using the Toxicity Characteristic Leaching Procedure (TCLP). TCLP is used to designate dangerous wastes under the Washington State Dangerous Waste Regulations. TCLP is being used b Ecology as a screening criterion to evaluate whether waste-derived fertilizers meet applicable standards. Results of this analysis indicate that TCLP is an adequate screening criterion for predicting whether fertilizers are in compliance with dangerous waste regulations.

Two bulk agricultural fertilizers, four home-use fertilizers, and one agricultural micronutrient product failed TCLP screening for cadmium. Concentrations of cadmium in these products ranged from 1.04 to 2.52 parts per million (ppm), compared to the federal and state criteria of 1.0 ppm for designation of dangerous waste. Two products tested had been made from steel mill flue dust (K061), which is classified as a dangerous waste under Washington State regulations. However, steel mill flue dust is currently exempt from dangerous waste rules when used in fertilizer products. Ecology proposes to eliminate the K061 exemption, through the rule-making process.

Most fertilizer products had non-detectable or extremely low levels of dioxin; 72% had less than one-tenth of one part per trillion (pptr) toxic equivalents (TEQs). Two products had relativel high dioxin TEQs: Frit F-503G (84 pptr) and NuLife All-Purpose Trace Elements (54 pptr). These two products are believed to contain steel mill flue dust, and had higher TEQs than any of the soils sampled during this study. The manufacturing process for Frit F-503G has used a non-hazardous-waste source of zinc since 1988, although it is unknown when the sample product was manufactured.

Most of the fertilizer products sampled had lower dioxin TEQs than the soils surveyed. The concentration of dioxin in soils after fertilizer products are applied depends on the application rate. When applied at recommended rates, these products add a minimal amount of dioxin to soil.

Dioxins accumulate in biosolids (sewage sludge) and have been measured in nearly all biosolids tested. The national data available on dioxin levels in biosolids are more than ten years old, and there are few biosolids data for Washington State. Review of statewide biosolids data and additional sampling are needed. Metals are also found in biosolids, but metals in biosolids were not evaluated in this report.

2. Metals in Soils

Thirty-three sites were sampled in the Columbia Basin, primarily in Grant County. To the extent possible, agricultural sites were matched with non-agricultural sites of the same soil type. Twenty agricultural soils and 13 non-agricultural soils were tested. Fields with historical applications of biosolids or lead arsenate pesticides were excluded from this study.

Zinc and cadmium concentrations in agricultural soils show small but statistically significant increases when compared to non-agricultural soils. The zinc-to-cadmium ratio suggests plants will take up zinc before cadmium. Increased cadmium levels in agricultural fields may be due to farming practices used over the last 50 years. The increased zinc and cadmium concentrations suggest no soil quality impairment, because the values found are at the lower end of the range of concentrations found in non-agricultural soils.

Levels of arsenic, copper, mercury, nickel, lead, total organic carbon, pH, total phosphorus, and cation exchange capacity in soils do not show statistically significant differences between agricultural and non-agricultural sites. The apparent increase in zinc and cadmium concentrations indicates a need to periodically monitor soils. Monitoring the rate of increase of metals in agricultural soils will provide information to allow Washington fertilizer standards to be adjusted, so concentrations of metals in agricultural soils do not reach a level of concern.

3. Dioxins in Soils

Thirty soil samples were collected from urban, open, and forested lands and tested for 17 forms of dioxins. All soil samples, including samples from remote wilderness areas, had detectable levels of dioxins. In general, average dioxin levels appear to be higher in urban areas than in forested and open areas. Dioxin concentrations ranged from 0.033 to 19.5 pptr TEQ. Sample

sites in the city of Tacoma had the two highest dioxin concentrations (9.5, 19.5 pptr TEQ). Forest soils appear to have concentrations greater than soils from open areas. Concentrations of dioxins detected in Washington State soils are comparable to the results of studies in Spain, Germany, and Austria.

The pattern of dioxin forms in biosolids and soils is similar. However, these soil "signatures" do not coincide exactly with any of the source signatures evaluated. The closest correlations appear to be with the dioxin congeners associated with pentachlorophenol (PCP) and biosolids. The apparent correlation between soils and biosolids signatures may be due to the similarity in sources contributing to these receptors. Much additional work is needed (e.g., tests of additional source types, understanding changes in signatures caused by weathering of soils) before the relative dioxin contribution of various sources can be well understood. It is likely, however, that multiple sources are involved and that air-borne dispersion, transport, and deposition are important mechanisms in the contamination of soil.

The original study design included sampling agricultural soils for dioxins. However, due to difficulties in randomly selecting agricultural sites and an inability to guarantee confidentiality to landowners, this part of the study was postponed. Ecology will sample agricultural soils for dioxin in April-May 1999. Results of that study will be published as an addendum to this report.

Recommendations and Actions

Washington State departments of Ecology, Health, and Agriculture recommend:

- Continue to implement *The Fertilizer Regulation Act* by ongoing review, sampling, and analysis of fertilizer products for metals, as specified under the Memorandum of Understanding among these agencies.
- In the biennial report to the Legislature (first report due December 1, 1999), report levels of non-nutrient substances in fertilizer products.
- Continue to monitor levels of metals and other contaminants, as appropriate, in fertilizer products, especially waste-derived materials and phosphate fertilizers.
- Monitor agricultural soils to determine a rate of increase for metals in soils.
- Review and supplement data on dioxins in biosolids from municipalities.
- Monitor EPA progress on their evaluation of dioxins in biosolids. A proposed EPA rule, due in December 1999, would provide additional direction in this matter.
- Continue to monitor the progress of EPA and other agencies and organizations in evaluating health and environmental risks associated with fertilizer use.
- Monitor and review other states or countries development of standards for metals or dioxins in fertilizers or soil amendments.
- Determine if more sampling of dioxins in fertilizers is needed.

Ecology Policy Options

Ecology policy options for managing metals and dioxins in fertilizer products, as well as a discussion of the Ecology PBT initiative, are included in this report.

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Introduction

Background

Concerns have been raised about whether metals and dioxins associated with waste-derived fertilizers and soil amendments pose a threat to human health and the environment. In response to these concerns, the Washington State Department of Agriculture and the Washington State Department of Ecology (Ecology) tested 55 fertilizers for 24 metals during the spring of 1997. Both waste-derived and non-waste-derived fertilizer products contain non-nutritive metals. This screening study (Bowha et al., 1997) concluded that the concentration of metals in most fertilizers tested met the Canadian standards[1] for metals in fertilizers. Additionally, a few waste-derived fertilizers suspected to contain dioxins were tested for dioxins. All of the waste-derived products tested contained dioxins. Naturally occurring dolomite lime was also tested and did not contain dioxins (Golding, 1997).

As of 1997, no federal or state standards existed to regulate the level of contaminants in most fertilizer products other than those derived from known waste materials. In this report, "fertilizer products" will refer to bulk agricultural fertilizers, home-use fertilizers, micronutrients, and soil amendments. During late 1997 and early 1998, information from the state screening study was given to the Fertilizer Advisory Workgroup, the Legislature, and the Governor's Office. In earl 1998, the Legislature passed Executive Request legislation (SSB 6474), *The Fertilizer Regulation Act.* The Act (1) adopted state standards, based on the Canadian standards, for metals in all fertilizers, (2) increased Ecology regulatory oversight of waste-derived fertilizers and soil amendments, and (3) mandated labeling for all fertilizers. The Act also mandated a study of dioxins in fertilizers, soil amendments, and soils as well as a crop-uptake of metals study, initiated this year. These studies will give the Legislature and others information to determine if further fertilizer regulation is needed.

Fertilizer products from natural, manufactured, and industrial by-product sources can contain "tag-along" substances that have little or no nutrient value. Additionally, some materials classified as dangerous and solid wastes under existing Ecology regulations are recycled as ingredients in fertilizer products.

- Certain elements (e.g., zinc), as constituents of fertilizers, are recognized as nutrients required for plant life. Some metals can be potentially hazardous tag-along contaminants in fertilizers. Heavy metals have been quantified in a number of fertilizers used in Washington State (Bowhay et al., 1997). These metals are naturall occurring elements, but fertilizer use over long periods of time may increase the metal concentrations in agricultural soils.

[1] "The Canadian Maximum Acceptable Cumulative Metal Additions to the Soil," Established under Trade Memorandum T-4-93, dated August 1996.

- Some polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans, together referred to as “dioxins” in this report, also pose a potential threat to human health and the environment as tag-along contaminants and have been quantified in some waste-derived fertilizers used in Washington State (Bowhay et al., 1997).

The legislation signed by Governor Locke in 1998 directed Ecology, in cooperation with the state Department of Agriculture and the state Department of Health, to "undertake a study to determine if dioxins occur in fertilizers, soils amendments and soils and, if so, at what levels." (Washington State Legislature, 1998). From May through October 1998, Ecology conducted studies to investigate (1) metals and dioxins in fertilizers and soil amendments, (2) metals in soils, and (3) dioxins in non-agricultural soils. While some conclusions may be drawn from these studies, their limited scope qualifies them as screening studies. They will help direct further research, if needed, to provide information for possible regulation of these substances.

This legislation also directed the state Department of Agriculture, which contracted with Washington State University, to conduct a crop-uptake study. That study, initiated in the fall of 1998, will evaluate the uptake of metals in certain crops in relationship to the new Washington fertilizer standards. This report does not contain results of the crop-uptake of metals study.

Study Objectives and Methods

1. Metals and Dioxins in Fertilizers

The objective of this study was to quantify metals and dioxins in bulk agricultural fertilizers, home-use fertilizers, micronutrients, and soil amendments. In addition, available information on dioxins in biosolids was reviewed as recommended in a preliminary report (Rogowski et al., 1998). This current report uses the term “fertilizer products” to refer to all products sampled, which includes one soil amendment.

Ecology randomly sampled and analyzed fertilizer products to determine dioxin and select metal concentrations. Zinc micronutrient fertilizers were also analyzed to determine heavy metal concentrations, as part of an U.S. Environmental Protection Agency (EPA) grant. Metals analyzed were arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver. These eight metals are a subset of the metals analyzed in the 1997 study (Bowha et al., 1997) and are the metals of greatest concern. The fertilizer products were also analyzed for total and leachable metals. The Toxicity Characteristic Leaching Procedure (TCLP) was used to determine leachable metals. Although the TCLP is typically used to designate hazardous and dangerous wastes, this study used TCLP as a screening tool and did not use TCLP to designate fertilizer products as hazardous or dangerous waste. Additional total metals data for cobalt, molybdenum, nickel, and zinc have been added to this report since November 1998 (Appendix G).

Results from this study will help assess the effectiveness of Ecology’s waste-derived and micronutrient fertilizer screening criteria (Washington State Register, 1998); see Appendix 1-J. As required by *The Fertilizer Regulation Act*, Ecology developed the screening criteria to review

fertilizer registration applications. This review will help ensure fertilizers meet the applicable federal hazardous waste and state dangerous waste regulations.

2. Metals in Soils

The objective of this study was to determine if certain metals have accumulated in agricultural soils of the Columbia Basin. Ecology randomly sampled and analyzed metal concentrations of agricultural and non-agricultural soils in the Columbia Basin Irrigation Project and compared these results with results from two other state soil studies. There was an attempt to match agricultural and non-agricultural samples by soil type. Metals analyzed were arsenic, cadmium, copper, lead, mercury, nickel, and zinc. These seven metals were selected for comparison with other applicable soil studies. "Agricultural" land is defined as land in active agricultural production. "Non-agricultural" land is land that has never been farmed, tilled, or grazed.

Not only are metals a concern for human health but they are also of concern for the impacts the may have on ecological systems. For example, contaminant-containing runoff from fields can enter aquatic environments. Organisms foraging in both terrestrial and aquatic environments, particularly if they are higher on the food chain, may be exposed to greater concentrations of contaminants accumulated through the food chain. Longer-lived species may bioaccumulate greater levels of certain contaminants, particularly mercury (Burger and Gochfield, 1999).

3. Dioxins in Soils

The objective of this study was to provide an initial assessment of typical concentrations of dioxins in Washington State soils. The word "typical" is used to describe the samples collected for this study, since the use of the term "background" implies a natural occurrence of these compounds. Ecology sampled soils in open, forest, and urban areas to determine if dioxins occur in these areas and, if so, at what levels. The original intent of a portion of this study included sampling and analyzing agricultural soils. However, due to difficulties in randomly selecting agricultural sampling sites and not being able to guarantee confidentiality to landowners, agricultural soil collection and analysis was not conducted in 1998. Ecology will conduct agricultural soil sampling during April-May 1999; the results will be published as an addendum to this report.

These data were analyzed to determine relationships, if any, between the dioxins found in state soils with available dioxin data from state sources using principal components analysis. Limitations of both the source and soil data sets include largely non-random sampling and small sample size. This effort is an initial step toward determining contributions of state dioxin sources to Washington State soils.

Background Information on Arsenic, Cadmium, Lead, Mercury, and Zinc[2]

Arsenic, cadmium, lead, mercury and zinc occur naturally in soils. Human activity has influenced the distribution and chemistry of these metals in the environment. Metals associated with soil contamination are not very mobile and can accumulate and persist in surface soils (Alloway, 1990a).

The toxicity of metals ultimately depends on the metal concentrations at the target tissue site which, in turn, relates to the amount of exposure (i.e. dose), route of exposure, and form of the metal. Metal bioavailability is mediated by physiological processes, including absorption, distribution, biotransformation, and elimination.

The following section presents background information on five metals. Of the five metals described, only zinc is a nutritionally essential element.

Arsenic

Arsenic is naturally elevated in ground water in some parts of Washington State (DOH, 1996a). Environmental arsenic contamination is associated with the past use of pesticides, especially lead arsenate, arsenic containing wood preservatives, and metal smelters.

Exposure to arsenic can affect many different organs in the body. The health effects from short-term arsenic exposures include effects on the heart, nervous system, liver, mucous membranes, and the gastrointestinal tract (ATSDR, 1998a). Chronic ingestion of arsenic is associated with cancers of the bladder, liver, kidneys, and skin (ATSDR, 1998a). Chronic inhalation of arsenic has been associated with lung cancer in smelter workers (Goyer, 1996).

Cadmium

Cadmium is a relatively rare metal (Alloway, 1990b). Major emissions of cadmium into the environment have resulted from zinc and lead mining and smelting, refining ores, combustion of coal and other fossil fuels, and disposal of batteries (ATSDR, 1997a). Cadmium is naturall associated with some phosphate ores, and is commonly found in phosphate fertilizers derived from phosphate ores. In general, plants take up cadmium more readily than other metals (Goyer, 1996).

Cadmium accumulates in the kidney where it can remain for many years and exposure to cadmium over a long time can cause irreversible damage to the kidneys (Goyer, 1996). Cadmium affects how calcium is used by the body and cadmium exposure has been associated with bone deformities. Occupational exposure to airborne cadmium has been associated with

[2] This section provided by the Washington State Department of Health

chronic pulmonary disease and emphysema. Cigarette smoking is a major source of cadmium exposure for the general population (Goyer, 1996).

Lead

While lead occurs naturally, most lead found in the environment is a result of human activities. The past use of leaded gasoline has resulted in widespread environmental lead contamination (ATSDR, 1997b). Other sources of lead in the environment include lead-based paint and lead arsenate pesticides.

Children are more sensitive to the toxic effects of lead than adults and absorb and retain a greater percentage of lead into their bodies than adults (Goyer, 1996). Children are most at risk from exposures to lead in soil and paint due to hand-mouth activity. Exposure to lead is associated with neurological impairment in children, including decreases in IQ scores (ATSDR, 1997b). Excessive lead exposures in adults have been associated with high blood pressure and reproductive effects (Goyer, 1996). People can have their blood tested to determine if they have had recent exposures to lead (ATSDR, 1997b).

Mercury

Natural sources of mercury are predominant, although there are some notable industrial sources. Waste incineration and disposal of industrial and domestic waste products (e.g. thermometers and batteries) are sources of mercury to the environment (ATSDR, 1994a). The burning of fossil fuels also releases mercury into the environment (Goyer, 1996)

Mercury has three major chemical forms: elemental, inorganic and organic. Methyl mercury, an organic form of mercury, is the most important form of mercury in terms of environmental exposures (Goyer, 1996). Methyl mercury is produced by bacteria in the environment from other forms of mercury. Methyl mercury accumulates in fish, where it can be a significant source of human exposures. Ingestion of methyl mercury contaminated fish has been associated with neurotoxic effects. The developing fetus is very sensitive to the toxic effects of methyl mercur (Goyer, 1996).

Zinc

Zinc is a common element in the earth's crust and is used in numerous alloys, protective coatings (e.g. oxidation protection), dry cell batteries, wood preserving, and pharmaceutical products. Because it is also a necessary plant nutrient, it is an ingredient in some fertilizers. Major releases into the environment occur during mining and smelting activities, electroplating, and metal manufacturing (ATSDR, 1994b).

Zinc is a nutritionally essential metal required for maintaining health. Excessive exposure to zinc is relatively uncommon and zinc is not biologically accumulated (Goyer, 1996). Zinc is present in most foods. The average daily dietary intake of zinc in the U.S. ranges from 12 to 15 milligrams (mg) (Goyer, 1996). The Recommended Daily Allowances (RDA) for zinc are 15

mg/day for men and 12 mg/day for women (ATSDR, 1994b). Ingestion of large doses (100-150 mg) of zinc by people over a short time can cause stomach cramps and vomiting. Zinc can interfere with the ability of the body to absorb and use other minerals such as copper and iron (DOH, 1996b).

Background Information on TCLP

The Toxicity Characteristic Leaching Procedure (TCLP) is used to determine if a solid waste is also a dangerous waste (chapter 173-303 WAC), and TCLP has recently been incorporated into Ecology's Review of Waste-Derived and Micronutrient Fertilizers. If a waste-derived fertilizer fails certain limits for TCLP (Appendix 1-I) and TCLP requirements apply to this fertilizer, Ecology will not recommend the fertilizer for registration. See Appendix 1-J for further details.

Background Information on Dioxins

Dioxins have no known industrial or commercial use. Dioxins are unintended byproducts formed during combustion of chlorinated organic compounds and the production of certain chlorinated organic compounds. They come from many sources including wood waste boilers, municipal and medical waste incinerators, and bleached pulp and paper facilities (Czuczwa and Hites, 1984,
Yake et al., 1998).

Dioxins are found in some fertilizer products made from the recycling of industrial wastes. These tend to be micronutrients (e.g., zinc) or liming products (Bowha et al., 1997). Currently, there are no state standards for dioxins in fertilizer products.

Dioxins are persistent environmental pollutants that accumulate, primarily through food webs, in the tissues of animals including humans. Dioxins are extremely stable, both to environmental and biological breakdown, leading to their persistence in the environment and bioaccumulation in the food chain (Birnbaum, 1994). Because they are lipophilic and water insoluble, dioxins concentrate both in sediments and the fatty tissues of fish, birds, reptiles, and mammals.

Dioxins exist in environmental and biological samples as complex mixtures whose relative concentrations differ across trophic levels. These differences are caused by various environmental fates, solubilities, volatilities, and rates of degradation/metabolism. As a result, these mixtures vary spatially in the environment and can change over time.

Transport of dioxins involves volatilization and long-range dispersion, primarily from combustion sources via vapors or associated with particulates. Dioxins strongly partition to soils and sediments and are generally immobile in soils and sediments due to low vapor pressure, low aqueous solubility, and strong sorption to particles, particularly organic matter (ATSDR, 1998b). The estimated half-life (time required for half a given concentration to decompose or degrade) of 2,3,7,8-tetrachloro dibenzo-*p*-dioxin (2,3,7,8-TCDD) on surface soils ranges from 9 to 15 years.

Estimated half-lifes for 2,3,7,8-TCDD in subsurface soils may range from 25 to 100 years (ATSDR, 1998b). Much of their presence in plants is due to atmospheric transport on particles, resulting in settling on the leafy tissues of plants (Birnbaum, 1994; EPA, 1994). The primar route of human exposure to dioxins is through consumption of fatty foods of animal origin such as meat, fish, and dairy products (Albers et al., 1996, Wild et al., 1994).

The effects of 2,3,7,8-TCDD on immune function have been demonstrated to be among the earliest and most sensitive indicators of TCDD-induced toxicity (Burns et al., 1996, p.374). Developmental toxicity has been shown in all laboratory species examined. Where both human and animal *in vivo* and *in vitro* data exist for enzyme induction, chloracne, immunotoxicity, developmental toxicity, and cancers, the sensitivity of humans to 2,3,7,8-TCDD appears similar to experimental animals (Birnbaum, 1994).

The International Agency for Research on Cancer has concluded that 2,3,7,8-TCDD is a "known human carcinogen" (IARC, 1997). Recent concern about the effects of dioxins on organisms has increasingly focused on endocrine disruption (hormonal disruption) and reproductive impairment (EPA, 1997).

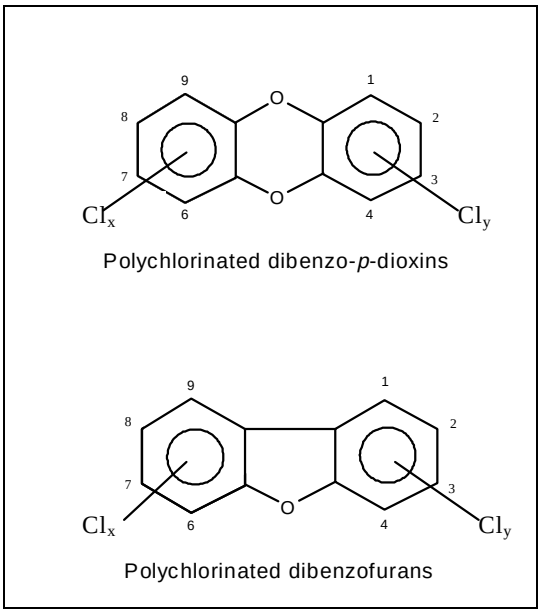
Scientific Uncertainty: Although dioxin toxicity has been studied intensively, a considerable amount of scientific uncertainty remains with respect to the human relevance of adverse effects observed in animal models. Because epidemiological studies are never definitive and the sensitivity of animals differs among species, dioxin risk to humans continues to be debated. This uncertainty, and associated controversy surrounding dioxin toxicity, are highlighted in a review of the EPA 1994 dioxin reassessment (EPA, 1994), performed by their Scientific Advisory Board (SAB, 1995).

What Are Dioxin TEFs and TEQs?

Dioxins usually occur in complex mixtures. Of the 210 forms or congeners of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans, 17 of these are considered toxic. Congeners are identified by the number and location of chlorine atoms on the molecule. The most toxic of these congeners have chlorine atoms at four specific sites (the 2,3,7, and 8 positions). In this report, the terms "dioxin" and "dioxins" refer to polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans with chlorine atoms in the 2,3,7,8, positions of the molecule. See Figure 1 for the generalized chemical structure and numbering of dioxin.

The congener 2,3,7,8-tetrachloro dibenzo-*p*-dioxin (2,3,7,8-TCDD) is assigned a TEF of 1, and the others are assigned values less than 1 (EPA, 1989; Birnbaum, 1994). Toxic equivalents (TEQs)[3] are used to express the total toxicity of dioxin congeners when the concentration of each congener is multiplied by its TEF and all of these products are summed. An example of this calculation is shown in the footnote below. See Appendix 1 for further information. The

[3] The calculation of TEQ for an environmental sample containing 5 pptr 2,3,7,8-TCDD and 23 pptr 2,3,7,8 -TCDF (considered 1/10 as toxic as TCDD, it has a TEF of 0.1) is: [5+(0.1 x 23)] = 7.3 pptr TEQ (Serdar et al., 1991).



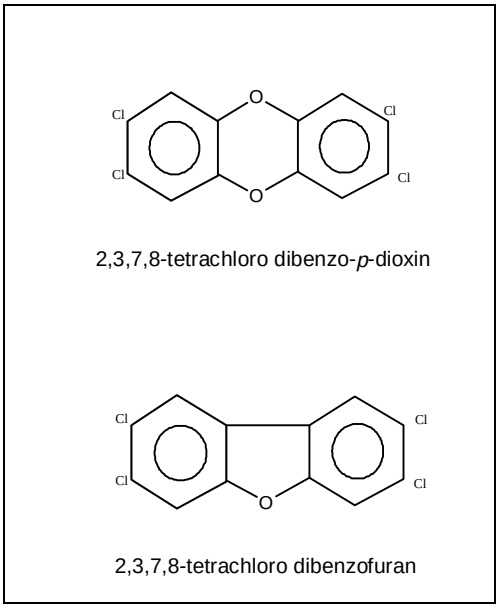


Figure 1. Chemical structure of dioxins/furans. Numbering system for chlorine atoms is indicated by the first figure. The second figure shows the structures of 2,3,7,8-TCDD and 2,3,7,8-TCDF.

Toxicity Equivalency Factor (TEF) concept is based on evidence that dioxin-like compounds share a common mechanism of action (Van den Berg et al., 1998). The basic assumption in this approach is that the combined effects of the different congeners are dose or concentration additive; the results of many studies support this assumption (Van den Berg et al., 1998).

This report uses the international convention TEFs adopted by EPA (1989). Recently, however, new internationally agreed TEFs were established by the World Health Organization (WHO) European Centre for Environment and Health and the International Programme on Chemical Safety (IPCS). Three sets of TEFs were derived to address humans and mammals, fish, and birds (Van den Berg et al., 1998).

1. Metals and Dioxins in Fertilizer Products

Purpose

The objective of this study was to quantify metals and dioxins in bulk agricultural fertilizers, home-use fertilizers, micronutrients, and soil amendments.

In this report, the term "fertilizer products" refers to all four of the above substances.

Ecology randomly sampled fertilizer products to determine their dioxin concentrations. As part of a U.S. Environmental Protection Agency (EPA) grant, the samples were also analyzed to determine heavy metal concentrations. Metals analyses of fertilizer products included total metal concentrations and leaching metal concentrations (using the Toxicity Characteristic Leaching Procedure or TCLP). Results from this study will help assess the effectiveness of Ecology's screening criteria for waste-derived fertilizers and micronutrients.

As recommended in the preliminary report (Rogowski et al., 1998), a review of information about dioxins in biosolids, and an assessment of annual increases in soil dioxin TEQ levels from selected fertilizer products and biosolids data, have been added to this chapter of this final report.

Study Design

To determine which products to sample, random selections were drawn from among products registered for use in Washington State in three fertilizer groups: bulk/packaged agricultural fertilizers, agricultural products with micronutrients, and home-use fertilizer products. Home-use fertilizer products were randomized using a random number generator, and the first 31 products were selected. Bulk/packaged agricultural fertilizers were categorized by constituent type, randomized, and the first few products per category were selected. Micronutrients were selected at random. Available fertilizer products were substituted for those that could not be obtained randomly. In all, 10 of 60 manufacturers of bulk fertilizers were selected, 12 of 44 manufacturers of micronutrients were selected, and 31 of 2296 home use products were selected.

Fertilizers are substances containing nitrogen, phosphorus, potash, calcium, magnesium, sulfur, or any of the micronutrients (boron, chlorine, cobalt, copper, iron, manganese, molybdenum, sodium, and zinc). A non-nutritive soil amendment, Ponderay Newsprint Fiberay SC, was also sampled.

Because the number of home-use products is considerably greater than the number of agricultural products, the greatest number of samples were of home-use fertilizers. This study focused on zinc as an agricultural micronutrient, because zinc micronutrients were associated with relativel high levels of dioxin and metals in some products previously tested by Ecology in 1997 (Golding, 1997; Bowhay et al., 1997). Agricultural products were sampled at distributors of agricultural chemicals. Home-use fertilizer products were obtained in the form sold to consumers

(i.e., "off-the-shelf"). Not all home-use fertilizers registered in Washington State are sold in the state, and some selected home-use fertilizer samples could not be obtained. In these cases, a commonly found product with similar constituents and usage was substituted. A list of fertilizers, soil amendments, and micronutrients sampled appears in Appendix 1-A.

Fifty-eight samples (50 different products) were analyzed for eight heavy metals and dioxins. This number included two samples each of Cozinco zinc micronutrient and Frit F-503G obtained independently from different suppliers, as well as six duplicate samples of other fertilizer products. Duplicates are samples taken from a single mixed sample in order to determine replicability of results. Fort James NutriLime was sampled twice: once in 1997 and once in this study.

Sampling Procedures

Samples were collected based on procedures described in the Washington State Department of Agriculture *Investigator's Manual*, Pesticide Management Division (WSDA, 1991). The following is a description of the modified sampling procedure.

Samples were taken using organic-free, laboratory-cleaned sample jars and pre-cleaned stainless steel ladles. Bulk solid samples were collected as grab-composite samples consisting of ten grab subsamples from discrete parts of a product being sampled. Packaged solid samples were obtained as grab samples by filling a mixing bowl approximately two-thirds full. Packaged solids were not composite sampled because of practical constraints in sampling from a container. The subsamples and grab samples were combined in a cleaned, four-quart stainless steel mixing bowl, mixed with the sampling ladle, and split into Ecology and facility sample containers. Sample jars were ultra-clean with Teflon lids. Bulk liquid was sampled by flushing a sample port and collecting the sample as a grab sample directly into a clean glass sample bottle. Bulk liquids were not composite sampled because of the limitations of sampling from a tap. The cleaning regimen is listed in Appendix 1-B. Because of the special cleaning requirements for the sampling of dioxins, cleaned stainless steel ladles were used in lieu of the triers (metal tubes) specified in the Washington State Department of Agriculture *Investigator's Manual.*

Sample jars were labeled with tags and placed in plastic bags. All samples were stored in a cooler and maintained at a temperature of 4°C until analysis. Chain-of-custody procedures followed the Manchester Environmental Laborator *Lab Users Manual* (Ecology, 1994a). The samples for this project were delivered to the Manchester Laboratory by Ecology staff.

Analytical Procedures

Analysis of total metals was carried out by either graphite furnace atomic absorption (GFAA) or inductively coupled plasma (ICP) optical emission spectroscopy, depending on analyte level and matrix interference. EPA SW-846 Method 6010 was used for ICP. For graphite furnace analyses, SW-846 Methods 7421 (lead), 7131 (cadmium), 7740 (selenium), 7761 (silver), and 7060 (arsenic) were used. Mercury analysis was carried out by cold vapor atomic absorbance, SW-846 Method 7471. Toxicity Characteristic Leaching Procedure (TCLP) analyses were

carried out in accordance with SW-846 Method 1311. Method references appear in Appendix 1-C. Detection limits for total metals are shown for non-detected total metals results in Appendix 1-G, and for non-detected TCLP results in Table 1-3.

Analysis of the 2,3,7,8-substituted dioxin congeners was conducted at MAXIM Technologies Inc./Pace Analytical, using high resolution GC/MS EPA Method 8290, with enhancements derived from Method 1613B.

Detection limits for dioxins varied depending upon the physical and chemical characteristics of the samples, with a target detection limit of 0.1 pptr (parts per trillion). EPA Method 8290, Section 7.9.5 specifies the sample specific Estimated Detection Limit (EDL) as the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. Not all the analyses for congeners were responsive enough to provide EDLs down to 0.1 pptr.

Data Quality

Established laboratory quality control procedures were adequate to estimate laboratory precision and accuracy for this project. Laboratory quality control tests were done on each set of 20 or fewer samples and consisted of blanks, duplicate samples, and spiked samples. Laborator quality control and procedures are discussed in the Manchester Environmental Laborator *Lab Users Manual* (Ecology, 1994a).

The variability of metals and dioxins in fertilizer products was not addressed for most of the products tested in this study, because only one sample was analyzed for most products. Limited data for multiple and duplicate samples indicate that variability is considerable in some cases.

Metals

Metals results can be used without qualification, except in those cases with low spike recoveries and poor duplicate precision. Qualifiers appear in the data tables included in this report. A discussion of Quality Assurance/Quality Control (QA/QC) for metals appears in Appendix 1-D.

A comparison of multiple sample metals results, as well as duplicate sample results, appears in Appendix 1-E. Duplicate sample results were in close agreement. The target relative percent difference (RPD) was 25% or lower. The average (RPD) for pairs of detected metals was 23%, within the target range; and the range of RPDs was not excessive, indicating moderate consistency in sampling and analysis. RPD, a measure of precision, is the ratio of the difference and the mean of the results expressed as a percentage. A low RPD indicates high precision.

Dioxin

Quality Assurance/Quality Control (QA/QC) measures indicate that the dioxin results are accurate. One sample (328132) exceeded the allowable 30-day holding period by one day, but

holding time is not considered critical for dioxin. Calibration standards, internal standard recoveries, ion abundance ratios, and matrix spike/matrix spike duplicates were acceptable. A more complete discussion of QA/QC appears in Appendix 1-D.

In the fall of 1997, when Ecology sampled several waste-derived fertilizer products, dolomite was sampled to serve as a blank sample. No 2,3,7,8-substituted dioxins congeners were detected in the dolomite sample, yielding a dioxin TEQ of 0 for the case where undetected congeners are assumed to have a dioxin concentration of 0 (minimum value). The TEQ (toxic equivalent) was 0.84 pptr for the "worst case" (maximum value) where the calculation of TEQ is made, assuming all undetected congeners were present at the detect limit (i.e., non-detects set to the detection limit [ND=DL] - Golding, 1997). See Appendix 1 for a discussion of dioxin TEQ calculations. Of the 50 fertilizer products sampled in this study, no dioxins were detected in 13 of the fertilizer products. These results indicate that the sampling and analysis techniques employed were capable of measuring small concentrations of dioxin without significant field or laborator contamination.

Field quality assurance for this project consisted of six duplicate split samples. The differences in duplicate sample results reflect combined sampling and laboratory variability. All duplicate sample dioxin TEQs (for ND=0) were within 0.34 pptr (Appendix 1-F). The RPD between the duplicate split sample results was not calculated, because RPDs are not meaningful when results approach zero. Because the dioxin TEQs of duplicated samples were low, conclusions cannot be drawn concerning the replicability of samples with larger TEQs.

Results and Discussion

Total Metals

Metals analyses results are shown in Appendix 1-G. Each value represents the result of a single composite or grab sample of a product.

Table 1-1 shows the dry fertilizer products with the five highest total metal concentrations for each metal tested and the products' metal concentrations. None of the ten liquid fertilizers tested was among the five highest metals, but liquid fertilizers were reported in terms of wet weight and are not comparable with dry weight results.

From Table 1-1, the fertilizer products with the highest concentrations of metals were NuLife All-Purpose Trace Elements (75.2 mg/kg-dw arsenic), Fort James NutriLime (543 mg/kg-dw barium), Agrium Ammonium Phosphate Sulfate (160 mg/kg-dw cadmium), McLendon Weed and Feed 15-5-5 (5,060 mg/kg-dw chromium), Frit F-503G (3,490 mg/kg-dw lead), Frit F-503G (10.06 mg/kg-dw mercury), Thrifty Pay-Less Tomato and Vegetable Food (5.71 mg/kg-dw selenium), and Frit F-503G (9.27 mg/kg-dw silver), NuLife All-Purpose Trace Elements (222 mg/kg-dw cobalt), NuLife All-Purpose Trace Elements (553 mg/kg-dw molybdenum), NuLife All-Purpose Trace Elements (383 mg/kg-dw nickel), and Western Farm/Monteray 9% Zinc (657,000 mg/kg-dw zinc).

Table 1-1. Five highest rank ordered total metal concentrations in dry fertilizer products - 1998 sampling results.

Arsenic (As)

Abbreviated Product Description	mg/kg-dw
NuLIfe All-Purpose Trace Elements	75.2
Frit F-503G Sample #2	32.6
Fort James NutriLime	28.5
Frit F-503G Sample #1	21.7
Whitney Farms Jersey Green Sand	11.4

Lead (Pb)

Abbreviated Product Description	mg/kg-dw
Frit F-503G Sample #2	3490
Gaia's Own Cottonseed Meal* Sample #1	2550
NuLIfe All-Purpose Trace Elements	1940
Frit F-503G Sample #1	588
Hydro-Feed with Polyon 20-10-10	434

*(Lead was undetected in Gaia's Sample #2 at 3 mg/kg-dw detection limit)

Barium (Ba)

Abbreviated Product Description	mg/kg-dw
Fort James NutriLime	543
NuLIfe All-Purpose Trace Elements	205
Osmocote Vegetable and Bedding	141
Frit F-503G Sample #2	137
Frit F-503G Sample #1	124

Mercury (Hg)

Abbreviated Product Description	mg/kg-dw
Frit F-503G Sample #2	11.9
Frit F-503G Sample #1	8.22
Terosa Rose Food	1.13
Pursell Sta-Green Nursery Special	0.652
Pursell Sta-Green Azalea	0.364

Cadmium (Cd)

Abbreviated Product Description	mg/kg-dw
Agrium Ammonium Phosphate Sulfate	160
UAP 0-45-0	106
Frit F-503G Sample #2*	92.0
Pace NuLife 10-20-20	89.3
Webfoot Rhododendron	70.4

*(The cadmium concentration of Frit F-503G Sample #1 was 10.9 mg/kg-dw)

Selenium (Se)

Abbreviated Product Description	mg/kg-dw
Thrifty Pay-Less Tomato & Veg.	5.71
Terosa Rose Food	2.6
NuLIfe All-Purpose Trace Elements	1.9
Whitney Farms 100% Organic Citrus	1.1
Whitney Farms Jersey Green Sand	0.94

Chromium (Cr)

Abbreviated Product Description	mg/kg-dw
McLendon Weed and Feed 15-5-5	5060
Webfoot Rhododendron	612 J
NuLIfe All-Purpose Trace Elements	417
UAP 0-45-0	378
Pace NuLife 10-20-20	254

Silver (Ag)

Abbreviated Product Description	mg/kg-dw
Frit F-503G Sample #2*	9.27
NuLIfe All-Purpose Trace Elements	5.28
Tech-Flo Zeta Zinc 22	3.2
Cozinco Sample #1**	3.0
Thrifty Pay-Less Tomato & Veg.	2.88

*The silver concentration of Frit F-503G Sample #1 was 2.0 mg/kg-dw
**The silver concentration of Cozinco Sample #2 was 2.7 mg/kg-dw

J - estimated value

(continued on next page)

Table 1-1 - (cont'd) - 1998 sampling results.

Cobalt (Co)

Abbreviated Product Description	mg/kg-dw
NuLIfe All-Purpose Trace Elements	222
Frit F-503G Sample #1	155
Frit F-503G Sample #2	149
Osmocote Vegetable and Bedding	83.9
QC 30% Iron	44.8

Nickel (Ni)

Abbreviated Product Description	mg/kg-dw
NuLIfe All-Purpose Trace Elements	383
Frit F-503G Sample #2	229
Agrium Ammonium Phosphate Sulfate	219
Frit F-503G Sample #1	202
UAP 0-45-0	167

Molybdenum (Mo)

Abbreviated Product Description	mg/kg-dw
NuLIfe All-Purpose Trace Elements	553
Frit F-503G Sample #2	401
Frit F-503G Sample #1	234
Whitney Farms Iron Sulfate	73.4
Hydro-Agri/Viking Ship FS/31	47.9

Zinc (Zn)

Abbreviated Product Description	mg/kg-dw
Western Farm/Monteray 9% Zinc	657,000
Tech-Flo Zeta Zinc 22	348,000
Cozinco Sample #1	310,000
Cozinco Sample #2	286,000
Monteray 10% Zinc	96,600

The appearance of a product in this list does not necessarily indicate that the concentrations are of concern. Zinc is intentionally added as a micronutrient in some fertilizer products. The fertilizer products sampled were in the channels of trade prior to the 1998 registration. As a result, some of these products may no longer be available or may have been reformulated.

The source of the metals in Frit 503-G is industrial by-products (Schauble, 1998). NuLife All-Purpose Trace Elements contains Frit 503-G as its primary ingredient. The source of the cadmium in Agrium Ammonium Phosphate Sulfate is naturally occurring cadmium in western rock phosphate. The source of chromium in McLendon Weed and Feed appears to be chromium sulfate from leather tanning by-products.

Table 1-2 compares the estimated annual loading of metals for five fertilizer products with the highest total metal concentrations for arsenic, cadmium, lead, and mercury to the Washington standards (Washington State Legislature, 1998).

From Table 1-2, Fort James NutriLime exceeds the standard for arsenic, Pace NuLife 10-20-20 and Webfoot Rhododendron exceed the standard for cadmium, and Sample 1 of Gaia's Own cotton seed meal exceeds the standard for lead. The Washington standards adopted in RCW 15.54.820 are the maximum annual metal additions to soil allowed in Washington. The application rates in this study are not necessarily those used by the Washington State Department of Agriculture to regulate heavy metals in fertilizers.

Table 1-2. Selected Washington standard comparison for fertilizer products with highest total metal concentrations - 1998 sampling results.

Arsenic (As)

Abbreviated Product Description	*Conc.*	*Application Rate*	*metal applied*	*Wa std.*
	mg/kg-dw	*lbs/acre/yr*	*lbs/acre/yr*	*lbs/acre/yr*
NuLIfe All-Purpose Trace Elements	75.2	41 **	0.003	0.297
Frit F-503G Sample #2	32.6	138	0.004	0.297
Fort James NutriLime	28.5	24000 ***	**.684**	0.297
Frit F-503G Sample #1	21.7	138	0.003	0.297
Whitney Farms Jersey Green Sand	11.4	2178 **	0.025	0.297

Cadmium (Cd)

Abbreviated Product Description	*Conc.*	*Application Rate*	*metal applied*	*Wa std.*
	mg/kg-dw	*lbs/acre/yr*	*lbs/acre/yr*	*lbs/acre/yr*
Agrium Ammonium Phosphate Sulfate	160	250	0.040	0.079
UAP 0-45-0	106	200	0.021	0.079
Frit F-503G Sample #2*	92.0	138	0.013	0.079
Pace NuLife 10-20-20	89.3	871 ***	0.078	0.079
Webfoot Rhododendron	70.4	1167	**.092**	0.079

*(The cadmium concentration of Frit F-503G Sample #1 was 10.9 mg/kg-dw)

Lead (Pb)

Abbreviated Product Description	*Conc.*	*Application Rate*	*metal applied*	*Wa std.*
	mg/kg-dw	*lbs/acre/yr*	*lbs/acre/yr*	*lbs/acre/yr*
Frit F-503G Sample #2	3490	138	0.482	1.981
Gaia's Own Cottonseed Meal* Sample #1	2550	4356 **	**11.1**	1.981
NuLIfe All-Purpose Trace Elements	1940	41 **	0.080	1.981
Frit F-503G Sample #1	588	138	0.081	1.981
Hydro-Feed with Polyon 20-10-10	434	544 **	0.236	1.981

*(Lead was undetected in Gaia's Sample #2 at 3 mg/kg-dw detection limit)

Mercury (Hg)

Abbreviated Product Description	*Conc.*	*Application Rate*	*metal applied*	*Wa std.*
	mg/kg-dw	*lbs/acre/yr*	*lbs/acre/yr*	*lbs/acre/yr*
Frit F-503G Sample #2	11.9	138	0.002	0.019
Frit F-503G Sample #1	8.22	138	0.001	0.019
Terosa Rose Food	1.13	7259 **	0.008	0.019
Pursell Sta-Green Nursery Special	0.652	1500 **	0.001	0.019
Pursell Sta-Green Azalea	0.364	239 **	9×10^{-5}	0.019

** Application rates extrapolated from per plant or per square foot rates for home use

*** Application rates based on label submittal for 1998 registration

bold - exceeds Washington standard

The adoption of the Fertilizer Regulation Act in 1998 has had an impact on the fertilizer products being registered for sale and distribution in Washington. A number of products registered prior to passage of the Fertilizer Regulation Act, which includes the Washington Standards for Metals, will not be re-registered for the 1999 registration cycle. The standards are shown in Appendix 1-H. To date, the state departments of Agriculture and Ecology are aware of 139 fertilizer products from 45 manufacturers that have been voluntarily withdrawn from consideration for the 1999 registration cycle. It is unclear what is causing companies not to re-register their products (i.e., standards, labeling requirements, or regulatory requirements).

Two of the five fertilizer products with the highest cadmium concentrations are phosphate fertilizers: Agrium ammonium phosphate sulfate and UAP 0-45-0. As noted in the 1997 screening survey (Bowha et al., 1997), phosphate fertilizers had relatively high amounts of product applied per acre (loading rates). More phosphate fertilizer is applied in the state than micronutrient fertilizer. Cadmium was found to be elevated in agricultural soils in the Metals in Soils study (Chapter 2). The study found a small but significant increase in cadmium in the agricultural soils sampled, as opposed to background non-agricultural soil samples.

TCLP Metals

Sources of metals in fertilizer products include natural elements found in raw materials, and impurities in wastes or industrial by-products from manufacturing. Beginning July 1, 1999, waste-derived and micronutrient fertilizers must undergo an evaluation required by law (RCW 15.54.820) to determine if those products meet solid waste and dangerous waste regulations.

A primary dangerous waste regulation is that metal concentrations are limited in fertilizer products derived from dangerous waste. These limits, known as Land Disposal Restrictions (LDR), vary according to the type of dangerous waste used to make the fertilizer products but generally are equal to the Toxicity Characteristic Leaching Procedure (TCLP) limits listed in Appendix 1-I. The TCLP limits are also used to determine if a waste is subject to regulation as a dangerous waste. Generally, the TCLP is the test method used to evaluate the metal concentrations for both the LDR and dangerous waste designation.

Ecology intends to use the TCLP limits as a screening criterion in the fertilizer evaluation process. An effective screening criterion would differentiate between dangerous-waste-derived fertilizers (those in compliance with LDR standards) that pass fertilizer review criteria and dangerous-waste-derived fertilizers (those out of compliance with LDR standards) that fail the Ecology fertilizer review criteria. (See Appendix 1-J for a description of criteria used in Ecology's fertilizer review process.) If TCLP limits are exceeded, the manufacturer must submit information about whether dangerous wastes were used in manufacturing the fertilizer products. This information is then used to determine which LDR standards apply and whether the fertilizer meets the standards.

A high total metals level for a fertilizer product indicates (1) an increased likelihood that the fertilizer will exceed TCLP limits and (2) that the fertilizer may be a waste-derived product. In this study Ecology conducted TCLP testing on 16 fertilizer products with relatively high total metal concentrations[4]. The testing helped assess the effectiveness of this waste-derived and micronutrient fertilizer screening criterion, by determining if waste-derived fertilizers would fail the TCLP screening criterion and be subject to review for compliance with LDR standards. Furthermore, the testing helped determine whether waste-derived fertilizers that failed the TCLP also failed appropriate LDR standards.

In accordance with guidance provided by the EPA RCRA Hotline[5], all samples for which total metal concentrations equaled or exceeded 20 times the dangerous waste limit for a TCLP metal (WAC 173-303-090) were tested using the TCLP analysis Method 1311. The *20 times rule* does not apply to liquid samples. The liquid sample serves as the leaching extract directly, and the total metals of the liquid sample are compared with the TCLP limits. The results of these tests are shown in Table 1-3. Fertilizers not exceeding the *20 times rule* for a particular metal were not tested, and there is a corresponding blank place in Table 1-3. Appendix 1-I shows the TCLP limits and 20 times these limits. Appendix I-J describes the Ecology fertilizer review process.

Seven of the 16 products tested in 1998 exceeded TCLP limits for cadmium (Table 1-4). These products were (1) Agrium Ammonium Phosphate Sulfate, (2) United Agri Products 0-45-0, (3) Frit F-503G, (4) Webfoot Rhododendron, Camellia, and Azalea Food, (5) NuLife 10-20-20, (6) NuLife Agro 10-15-10, and (7) Thrifty Payless Tomato and Vegetable Food. Two of the seven were bulk or packaged agricultural phosphate fertilizers, one was an agricultural micronutrient, and four were home-use packaged fertilizer products.

Ecology contacted the companies that manufacture these products to determine if any of these products are waste-derived. Only two products are thought by the manufacturers to be waste-derived. Frit F-503G was made from a hazardous waste, steel mill flue dust, prior to 1988 and manufactured from a non-hazardous waste after 1988 (Schauble 1998). It is not known when the sampled Frit product was manufactured. NuLife All-Purpose Trace Elements has Frit F-503G as a principal ingredient (Shaffer, 1998). Two containers of Frit F-503G were sampled and onl one sample exceeded the TCLP limits. The NuLife All-Purpose Trace Elements sample did not fail the TCLP test.

From these results one might conclude that the TCLP test is not completely effective as a screening criterion since the NuLife All-Purpose Trace Elements product would not have been subject to further review. However, NuLife All-Purpose Trace Elements is in compliance with LDR regulations; therefore, the TCLP screening criterion appears to accurately predict

[4] The fertilizer products tested for TCLP metals were chosen based on their total metal concentrations and ***not*** because they were determined to be waste-derived fertilizers. Some or all of these products may have elevated metal concentrations due to naturally occurring metals in raw materials.

[5] Elsevier Science Inc. 1996. *Use of total waste Analysis in Toxicity Characteristic Determinations.* RCRA Regulations and Keywords Index. pp 1162.

Table 1-3. TCLP metals test results of fertilizers - 1998 sampling results (units in ppm).

	As	Ba	Cd	Cr*		Pb		Hg	Se	Ag	Lab Log#
TCLP Limit	**5.0**	**100**	**1.0**	**5.0**		**5.0**		**0.2**	**1.0**	**5.0**	
Abbreviated Product Description											
Frit F-503G Sample #1				0.055		0.536		0.0007			318086
Webfoot Rhododendron duplicate			**1.53**	2.49							328126
Agrium Ammonium Phosphate Sulfate			**2.25**	0.208							328131
Webfoot Rhododendron			**1.50**	2.30							328140
NuLife All-Purpose Trace Elements			0.907	0.008		0.111	J				328144
Terosa Rose Food			0.277	0.040		0.053	J				328146
Gaia's Own Cottonseed Meal						0.02	U				338183
Hydro-Feed with Polyon 20-10-10						0.02	U				338187
McLendon Weed and Feed 15-5-5				4.57							338190
Pace NuLife 10-20-20			**2.23**	0.258							338194
NuLife Agro 10-15-10			**1.36**	0.142							338195
NuLife Agro 10-15-10 duplicate			**1.04**	0.118							338196
Winter Green 15-10-25			0.032	0.075							338197
J.R. Simplot Best 6-20-20XB			0.903	0.171							338198
Thrifty Pay-Less Tomato and Veg.			**1.26**	0.101							338205
A.H. Hoffman Ace Tomato and Veg.				0.175							348209
United Agri Products 0-45-0			**2.16**	0.491							348210
Frit F-503G Sample #2			**2.52**	0.05	U						348214

bold - Value exceeds TCLP limit.

U - Analyte was not detected at or above the reported result.

J - Analyte was positively identified. Associated numerical result is an estimate.

UJ - Analyte was not detected at or above the reported estimated result.

* Total chromium includes chromium III and chromium VI.

For values not reported there was no analysis performed.

compliance of this waste-derived fertilizer with LDR standards.[6] All of these products, including NuLife All-Purpose Trace Elements, exceeded the *20 times rule*. This suggests the *20 times rule* can also be an effective screening criterion. Either the TCLP test or the total metals test may be an effective screening criterion for products that warrant further examination by Ecology due to high metal levels.

Comparison of Metals Results with the Findings of Previous Ecology Sampling Events

Three of the 50 fertilizer products sampled in July-August 1998 for this study were previousl sampled in January 1998: Kelly Green Fresh Fish Fertilizer, Cozinco, and QC 30% Zinc. Although these products have elevated levels of cadmium, chromium, and lead, they do not exceed the TCLP limit by 20 times, so no TCLP testing was warranted. Results between both

[6] In actuality, neither NuLife All-Purpose Trace Elements nor FRIT F-503G are subject to the LDR requirements because there is a federal exemption for steel mill flue dust that is used to manufacture fertilizer.

Table 1-4. Summary of fertilizer samples failing TCLP tests for cadmium.

Bulk/Packaged Agricultural Fertilizers

Abbreviated Product Description	TCLP *ppm*
Agrium Ammonium Phosphate Sulfate	2.25
United Agri Products 0-45-0	2.16

Agricultural Micronutrients

Abbreviated Product Description	TCLP *ppm*
Frit F-503G	2.52

Home-Use Packaged Fertilizer Products

Abbreviated Product Description	TCLP *ppm*
Webfoot Rhododendron	1.53
Webfoot Rhododendron	1.5
Pace NuLife 10-20-20	2.23
NuLife Agro 10-15-10	1.36
NuLife Agro 10-15-10	1.04
Thrifty Payless Tomato and Veg.	1.26

sampling dates differed somewhat, with an average relative percent difference (RPD) for detected pairs of metals of 32%, exceeding the target range of 25% or lower. This is an indication that products differed in composition between the two sampling dates. Appendix 1-K shows a comparison between the metals results. Appendix 1-L shows the January 1998 results. Appendix 1-M lists the materials or product names and manufacturers of the products shown in Appendix 1-L.

Metals results obtained in a 1997 sampling survey of several waste-derived fertilizer product sources are shown in Appendix 1-N. Four of the products sampled in the fall of 1997 (Golding, 1997) were also sampled earlier in 1997 (Bowha et al., 1997). In the Bowhay study, a Holnam cement kiln dust soil amendment sample was found to have 150 mg/kg-dw of total lead. In the fall 1997 study, Holnam cement kiln dust had 230 mg/kg-dw of total lead. TCLP tests of Holnam cement kiln dust have shown no exceedance of TCLP limits (Stone, 1998).

Bay Zinc Company, Inc. has produced several zinc micronutrient products from several sources of zinc-containing material. A comparison of metals results shows that Bay Zinc 18% Blu-Min micronutrient samples obtained for the 1997 metals screening study, as well as the 1997 dioxin and metals study, had close results, with an average RPD for paired detected metals of 9%. Bay Zinc 18% Blu-Min was derived from K061 steel mill flue dust. "K061" is a RCRA waste code for dangerous waste designation. When K061 is recycled into zinc micronutrient fertilizer it is currently exempt from dangerous waste regulations (WAC 173-303-071).

Dioxin

A few fertilizer products were found to contain relatively high levels of dioxin. Two fertilizer products had dioxin TEQs of greater than 50 pptr. Of these, Frit F-503G (140 pptr), had the highest dioxin TEQ (Figure 1-1; Appendix 1-O). In a separate sample, however, Frit F-503G had a dioxin TEQ of 27 pptr. The Frit product is a micronutrient believed to be derived from steel mill flue dust (Bowhay, 1998). NuLife All-Purpose Trace Elements had a dioxin TEQ of 54 pptr. All other fertilizer products had TEQs of less than 10 pptr. The Cozinco micronutrient product and other zinc micronutrient products had low TEQs compared with the Frit sample results. The Cozinco product is derived from galvanizing waste (Bowhay, 1998).

The results of analyses for two independently collected samples of the Cozinco 35.50% zinc micronutrient from different suppliers were close, with TEQs within 0.1 pptr. (Appendix 1-F). This shows good agreement between the two samples and their analyses. The results for the two independently collected Frit F-503G samples differed by a factor of 5. Metals results for these two samples also varied considerably, indicating that the product as sampled was not consistent with respect to the metals tested (Appendix 1-E).

Figures 1-1 and 1-2 show dioxin TEQs for individual product samples, rank-ordered by TEQ. Figure 1-3 shows a frequency distribution of TEQs for dioxin results of the fertilizer products tested. Figure 1-3 and Appendix 1-O show that 36 of the 50 products sampled (72%) had TEQs of less than 0.1 pptr. (There are 37 total samples with TEQs of less than 0.1 pptr, but two of these are multiple samples of Cozinco micronutrient product). Fertilizer products with low TEQs tend to have many non-detected congeners, and for this reason, their calculated TEQs ma range widely depending on the method of TEQ calculation, as seen in supplemental appendix 1-N.

A summary of dioxin TEQs for fertilizers sampled in 1998 appears in Appendix 1-O, and TEQ calculations are found in Appendices 1-P and 1-Q. When a compound being analyzed is not detected, the result is termed a "non-detect" and the true sample concentration of that compound is not known, falling somewhere between zero and the detection limit (DL) of the analysis. In this study, unless otherwise noted, TEQs are calculated based on non-detects set to 0 (ND=0), so that calculated TEQs are minimum TEQs. The three methods of calculating the TEQs that appear in Appendix 1-O are explained in Appendix 1. Each value represents the results of a single grab or composite sample of a product. See Appendix 1-R for a summary of results for fertilizer products and micronutrients sampled in 1997 (Golding, 1997).

In 1997, seven waste-derived fertilizer products were tested for dioxin. One of these products, 18% Blu-Min micronutrient, had a dioxin TEQ of 340 pptr (Figure 1-2; Appendix 1-R). The product was marketed by Bay Zinc Company, Inc. and was derived from steel mill flue dust. Fort James NutriLime was tested in 1997 and again in 1998. NutriLime is fly ash from a Fort James hog fuel boiler. The dioxin TEQ for the Fort James NutriLime sampled in October 1997 (35 pptr) was greater than the TEQ for the August 1998 sample (7.4 pptr) by almost a factor of 5. This may be the result of differences in hog fuel boiler fuel or operating conditions (Young, 1998).

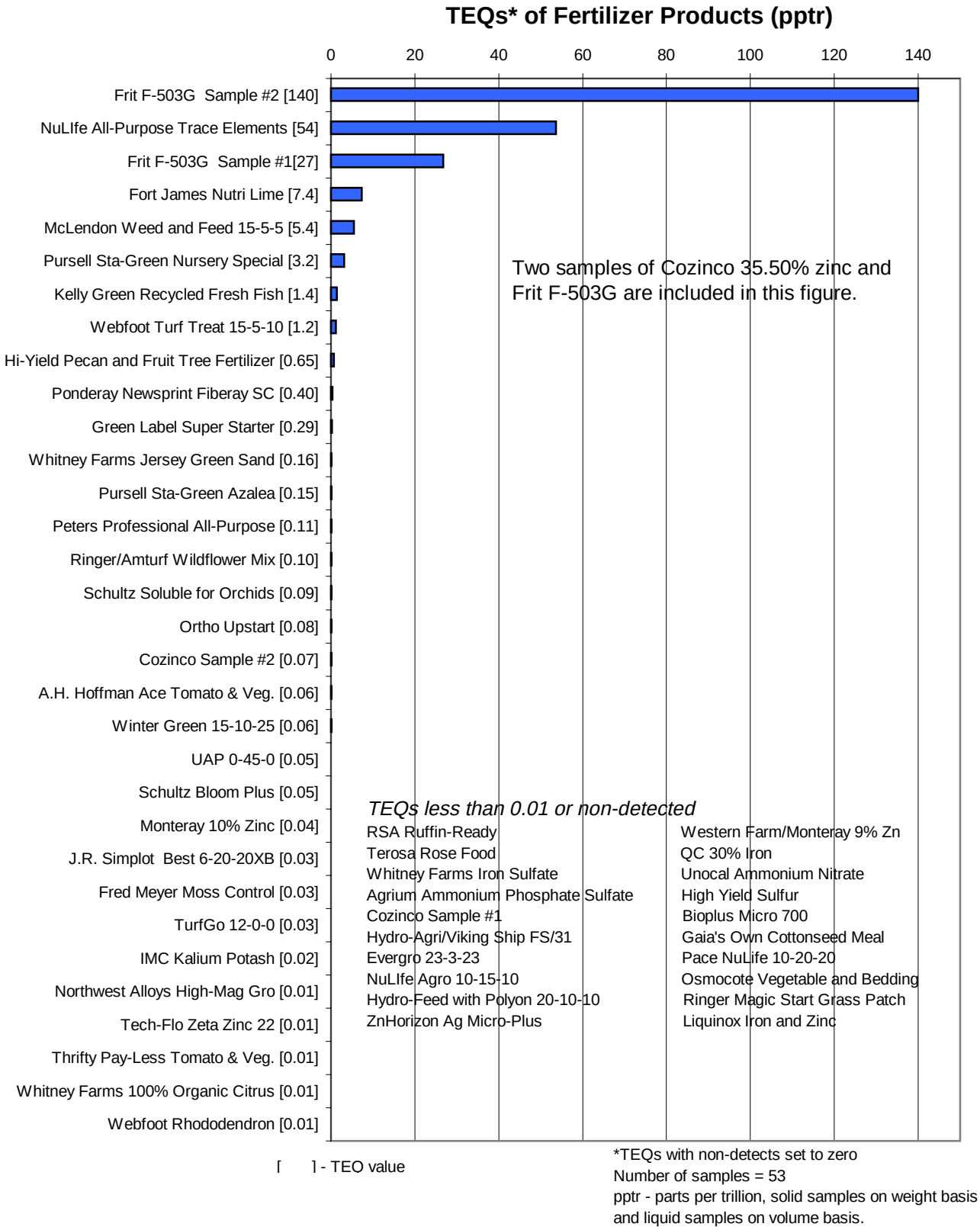


Figure 1-1. Rank-ordered dioxin TEQs in fertilizer products -1998 sampling results.

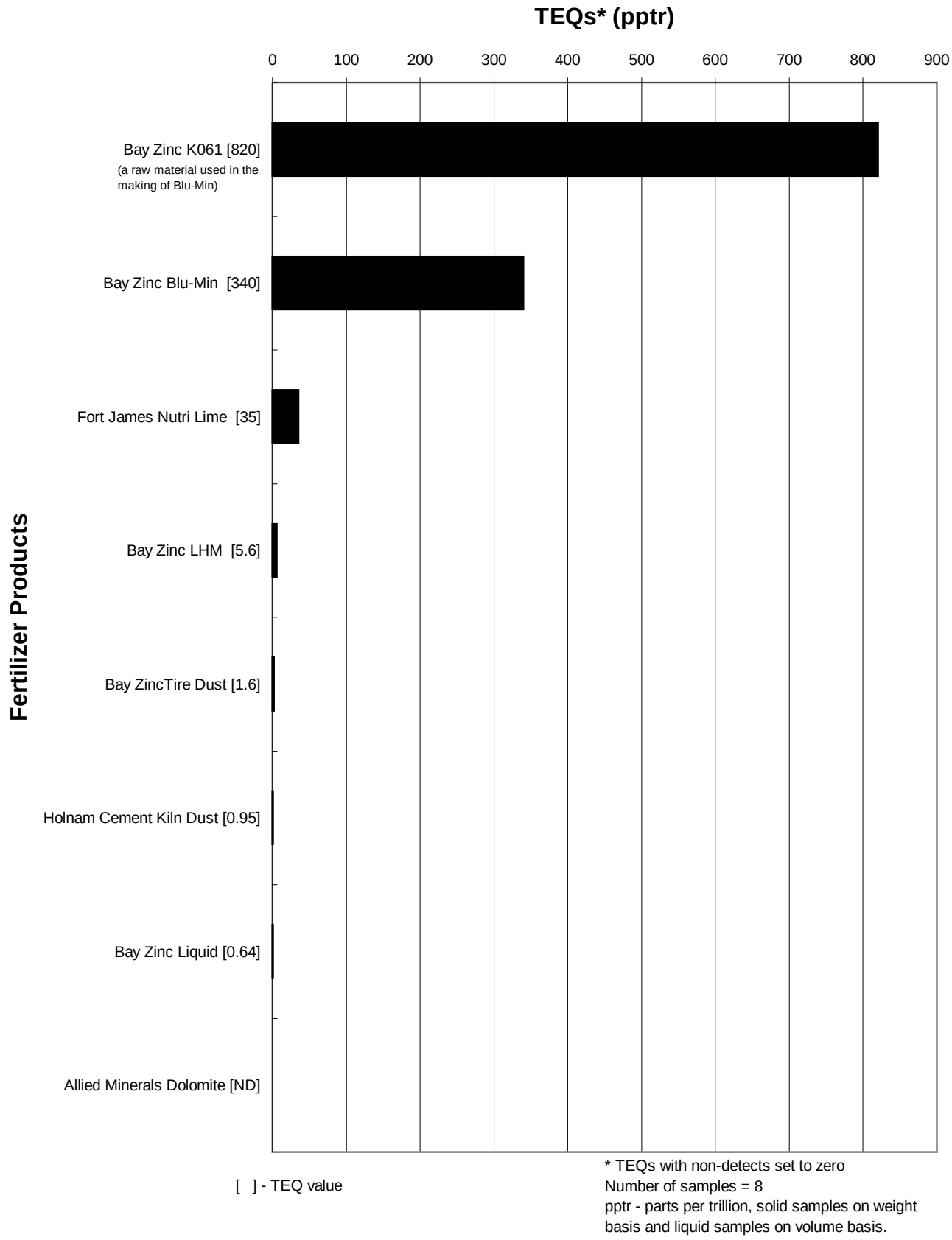


Figure 1-2. Rank-ordered dioxin TEQs in fertilizer products and fertilizer source materials - 1997 sampling results.

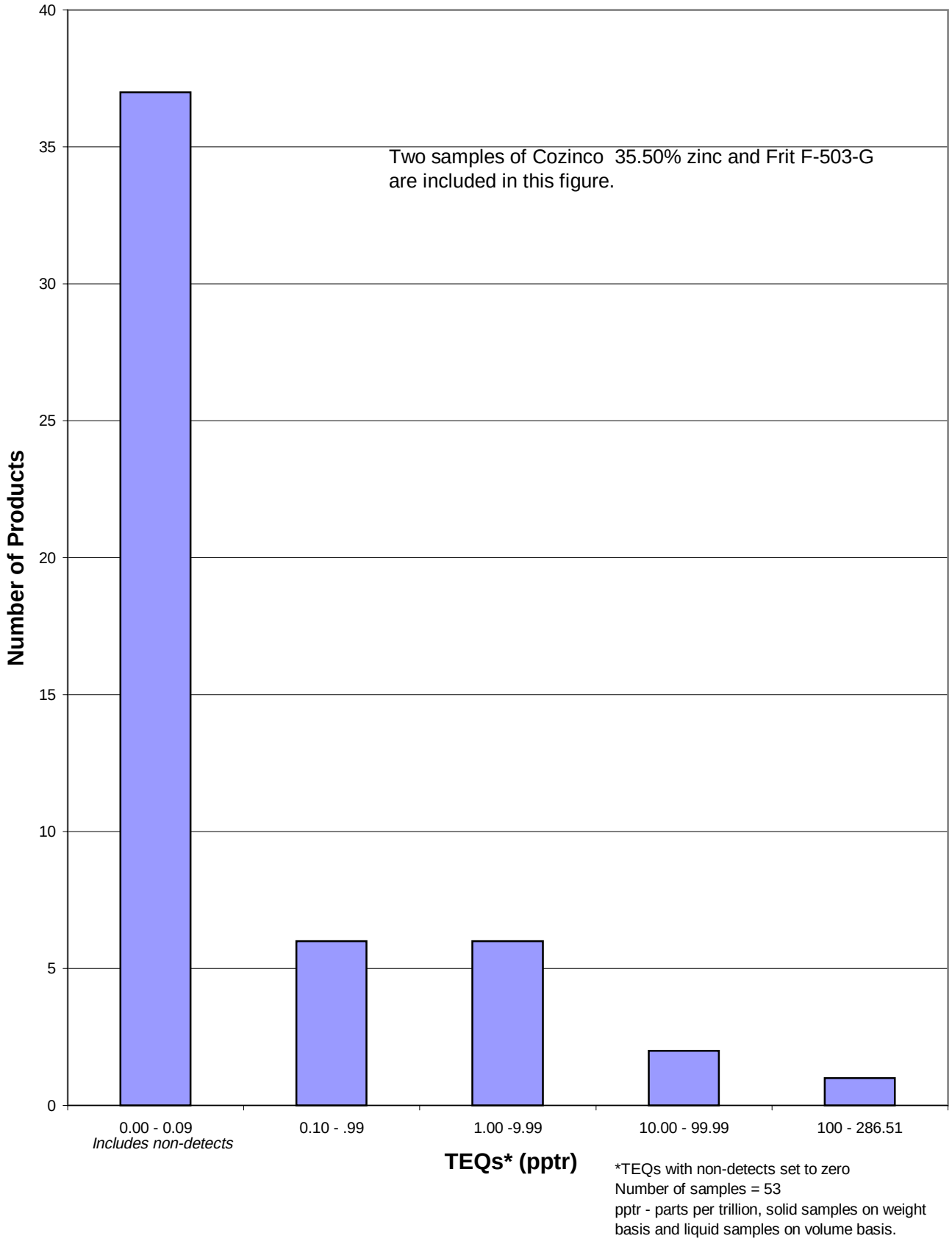


Figure 1-3. Frequency distribution: dioxin TEQs in fertilizer products - 1998 sampling results.

The selection process also differed between the 1997 and 1998 studies. The products tested in 1997, with the exception of dolomite, were selected because they were waste-derived products associated with known or reported sources of dioxin, whereas most products tested in 1998 were randomly selected from all registered fertilizers.

In order to give perspective to the dioxin data, following is a comparison of dioxin results with guidelines and findings of other studies, and dioxins in biosolids. A comparison of estimated increases in soil concentrations of dioxins from the application of selected fertilizer product is also included.

Comparison of Dioxin Results with Guidelines and the Findings of Other Studies

A literature review found no studies of dioxin levels in fertilizers. While no applicable standards for dioxins in fertilizers were found at this time, Germany has adopted guidelines for dioxins in soil (Schulz, 1993). The German guidelines state that fruits, legumes, and forage plants must not be cultivated when the dioxin TEQ of soils is greater than 40 pptr.

Fertilizer dioxin levels can be compared with the results of the Dioxins in Soils study (Chapter 3). Most fertilizer products tested in 1998 had low dioxin levels, with 72% of the products sampled having dioxin TEQs of less than 0.1 pptr. The Dioxin in Soils study found only 17% of soil samples in Washington State with a dioxin TEQ of less than 0.1pptr. The reason for the higher soil levels of dioxin may be that soil is more subject to atmospheric deposition of dioxin than are fertilizers. (Czuczwa et al., 1984; Czuczwa and Hites, 1986; Creaser et al., 1989; Rotard et al., 1994).

Dioxins in Biosolids

Fertilizer products are not the only nutritive materials applied to agricultural lands with the potential for containing dioxins. Compost, farmyard manures, and biosolids may contain dioxins (Duarte-Davidson et al., 1997). Municipal wastewater treatment plants (WWTPs) generate large quantities of sewage sludge, which when properly treated is known as biosolids. Biosolids are a valuable soil amendment due to their organic material and nutrient content, and their beneficial use is seen as an environmentally sound alternative to disposal. However, some contaminants present in municipal wastewater can accumulate in biosolids (McLachlan et al., 1996). EPA has adopted standards for several pollutants in biosolids in 40 CFR Part 503, and the state has equivalent requirements in Chapter 173-308 WAC. There are currently no federal or Washington State standards for dioxins in biosolids.

Dioxins are among the compounds that have been found to accumulate in biosolids after passing through municipal WWTPs. Volatilization and photodegradation have a negligible influence on the fate of dioxins in biosolids applied to soil (McLachlan et al., 1996).

Sources of Dioxins in Biosolids

Dioxins have been measured in nearly all biosolids tested, although the concentrations var widely (EPA, 1988). EPA (1998) cites the work of McLachlan, Horstmann, and Hinkel (1996), who have investigated potential sources of dioxins to WWTPs in Germany. While usually a negligible source, industrial wastewater contributions can sometimes be an important source of dioxins to municipal WWTPs and the biosolids they produce. While pulp and paper mills ma be potential sources of dioxins, they generally treat their wastewater on site for discharge and do not typically contribute industrial wastewater to municipal WWTPs. Surface runoff entering WWTPs through combined sewers, and by inflow and infiltration, also contribute dioxins in biosolids.

The washing of dioxin contaminated clothing has been found in one study to be a principal source of dioxins in biosolids (McLachlan et al., 1996). The pattern of dioxins in some new textiles was found to have the signature of dioxins associated with pentachlophenol (PCP), with certain dyestuffs making a lesser contribution (McLachlan et al., 1996). Using several data sets, including summary results of the EPA Sewage Sludge Survey, the multivariate principal component analysis in Chapter 3 of this report demonstrated an association between biosolids and PCP in terms of dioxin congener patterns (Figure 3-5, Figure 3-6). However, the magnitude and variation of the contribution of dioxin in biosolids remains to be established in Washington State and nationwide.

Typical Concentrations of Dioxins in Biosolids

Jones and Sewart (1997) have reviewed concentrations of dioxins found in biosolids from data collected worldwide. The range of dioxin TEQ values for biosolids reported in the worldwide literature is 0.5 to 4,100 pptr. Biosolids with particularly high TEQs are likely associated with industrial wastewater contributors having high concentrations of dioxins. The mean dioxin TEQ for biosolids from nine studies conducted in Europe ranged from 23.3 pptr to 357 pptr. The median dioxin TEQ from these studies ranged from 21 to 90 pptr. For the 239 samples obtained during the EPA Sewage Sludge Survey (1988), the mean dioxin TEQ was found to be 83 pptr. The median dioxin TEQ, a better indicator of typical concentrations, was found to be 37 pptr. These TEQ calculations were made based on non-detected congeners being represented by values set at one-half of the detection limit. The calculations were based on data derived in part from analyses that had relatively higher limits of detection. If more current data for biosolids can be collected, detection limits may decline because of improved analytical capabilities, likel lowering calculated dioxin TEQs.

Dioxin levels in fertilizer products sampled in this study can be compared with biosolids dioxin levels by using the same dioxin TEQ calculation method as was used in the EPA Sewage Sludge Survey (with non-detected congeners set at one-half of the detection limit). The mean dioxin TEQ for fertilizer products calculated on this basis is 5.4 pptr, and the median is 1.2 pptr. Comparisons between the different data sets are approximate.

Washington State Biosolids Dioxins Data

One of the 239 sample results reported by the EPA in the 1988 National Sewage Sludge Surve was from a sample collected at the METRO Renton WWTP (Renton). The Renton facilit serves a major portion of the King County metropolitan area. Approximately 60 industrial users collectively discharge more than 2.5 MGD of wastewater to the facility, approximately four percent of the dry weather flow (Ecology, 1997). With non-detected congeners set at a concentration of zero (ND=0), the dioxin TEQ was 9.5 pptr. With non-detected congeners set at a concentration of one-half the detection limit (ND=1/2 DL), the dioxin TEQ was 42 pptr. The detection limits for the data were considerably higher than the detection limits of this fertilizer screening study. As a result, the Renton reported TEQ tends to be inflated when compared to the fertilizer results on the basis of one-half detection limit. METRO has provided Ecology with the results of a second sample of biosolids from the Renton facility, collected in 1997. Detection limits were lower in the more recent data. For ND=0, the dioxin TEQ was 14 pptr. For ND=1/2DL, the dioxin TEQ was 23 pptr.

Other than the results from the METRO Renton WWTP, no dioxin data for biosolids in Washington State were available at the time this report was prepared. Ecology believes it is good policy for operators to obtain information on dioxins in their biosolids, in view of potential federal regulations that may be proposed later this year. Currently there is no requirement for operators to provide this information. Ecology has expressed an interest in obtaining additional data on dioxins in biosolids with the cooperation of the Northwest Biosolids Management Association. The Association has indicated a willingness to work with Ecology on this subject and has assigned a committee to that task.

Biosolids Data Needs

The national data collected by EPA in 1988 may not represent conditions in Washington State today, and Ecology needs to obtain data on dioxins concentrations in biosolids representative of Washington State. The EPA 1988 Sewage Sludge Survey can serve as a model of the approach to be taken.

Comparison of Estimated Increases in Soil Concentrations of Dioxins

The concentrations of dioxins in soils from the application of fertilizer products can be estimated. Expected increases in the concentrations of dioxins in soils with the application of fertilizer products containing dioxins depends upon the application rates of the products. Micronutrients have lower application rates than other fertilizer products, as reflected in Table 1-5. The estimated annual increase in soil dioxin TEQ level in the table below is calculated using a simple soils mixing equation: Annual increase in soil TEQ level (pptr) = (annual application rate in kg/ha) X (TEQ) X (5×10^{-7} ha/kg). The equation assumes uniform mixing of fertilizer products containing dioxins to a uniform depth and no degradation of dioxins over time.

Table 1-5. Estimated increase in soil concentration of dioxins from selected agricultural fertilizer products.

Product	Annual Application Rate* (kg/ha)	TEQ (pptr) (non-detects set at 1/2 Detect Limit)	Annual increase in soil TEQ level** (pptr)
Bay Zinc LHM (Granular Zinc from Tire Ash)	25	9.0	**0.0001**
Holnam Cement Kiln Dust	2,970	1.9	**0.003**
Bay Zinc 18% Blu-Min (from steel mill flue dust)	25	340	**0.004**
Fort James NutriLime (1997 sample)	54,800	36	**0.99**
Fort James NutriLime (1998 sample)	54,800	7.4	**0.20**
Frit F-503G sample #1	80.4	29	**0.001**
Frit F-503G sample #2	80.4	150	**0.006**
METRO Renton Biosolids (1988 sample)	15,000	42	**0.32**
METRO Renton Biosolids (1997 sample)	15,000	23	**0.17**
Biosolids (1988 national median value)	15,000	37	**0.28**

* Application rates selected are the top of the reported range of application rates for these products in WA. The Hog Fuel Boiler Fly Ash Product is reported to be applied only once per field. Estimated maximum biosolids application rates for Washington State are fro Dorsey, 1999. Other application rates are fro *Fact Sheet: Controlling Metals and Dioxins in Fertilizers*, Ecology January 1988. Bay Zinc and Frit F-503G application rates are based on zinc application.

** Formula to calculate soil concentration based on a soil mixing depth of 15 cm (6 inches) and a soil densit of 1.33 g/cc. The annual increase in soil concentrations assumes a starting dioxin soil concentration of zero. Calculated annual increases are initial increases. Because dioxins degrade over time, soils TEQs would be expected to level off over a period of years. The constant in the equation, 5E-7 ha/kg =(c ^{3}/1.33g)(^{2}/1E4 cm^{2}) (1/15 cm)(ha/1E4 ^{2})(1E3 g/kg).

***Extracted from 1997 and 1998 data and from the 1988 EPA Sewage Survey (median TEQ value).

The estimated annual increases in soil TEQ levels for the fertilizer products in Table 1-5 ranged from 0.0001 pptr to 0.99 pptr. While dioxin TEQ levels for the Bay Zinc and Frit micronutrients were the highest tested, they contribute relatively low estimated increases in soils dioxin levels. Estimated soils dioxin TEQ increases associated with those products are less than one-twentieth of the estimated increases from the Fort James NutriLime samples and biosolids.

Conclusions

Cadmium was found in relatively high concentrations in two phosphate fertilizers tested. Cadmium was also elevated in agricultural soils as compared with background soils in the Metals in Soils Study (Chapter 2).

The TCLP metals limits appear to be an adequate screening criterion for predicting whether fertilizers are in compliance with the current LDR standards. If the LDR standards are lowered as a result of ongoing state and federal rulemaking efforts, the TCLP screen will be less effective. It will then be important to consider using the *20 times rule* as a screening criterion. The alternative screen will ensure that fertilizers with a lower range of total metals content will be reviewed against the lower LDR standards.

Seventy-two percent of the 50 fertilizer products tested in this 1998 study had dioxin TEQs of less than 0.1 pptr. Most of the fertilizers sampled had lower dioxin TEQs than did the soils surveyed (Chapter 3). Two of the fertilizer products sampled in 1998 and two of the fertilizer products sampled in 1997 had dioxin TEQs higher than any of the TEQs found in the soils dioxin study. However, the dioxin level in soils after fertilizer products are applied is dependent on application rate. The four products with high TEQs are micronutrients that are applied to soils at very low rates, and calculations of soil concentrations after mixing found that they add a minimal amount of dioxins to soil. A literature review found no studies of dioxin levels in fertilizers. There are no applicable standards for dioxin in fertilizers at this time.

While dioxin TEQ levels for the Bay Zinc and Frit micronutrients were the highest tested, the contribute relatively low estimated increases in soils TEQ levels. Estimated soils dioxin TEQ increases associated with those products are less than one-twentieth of the estimated increases from the Fort James NutriLime samples and biosolids.

Of the fertilizer products sampled in 1998, fertilizer products having dioxin TEQs greater than 50 pptr were Frit F-503G (84 pptr mean value) and NuLife All-Purpose Trace Elements (54 pptr). By comparison, of all waste-derived fertilizer products and micronutrients sampled in 1997, the highest dioxin TEQ found was Bay Zinc's 18% Blu-Min micronutrient, with a TEQ of 340 pptr. The Fort James NutriLime sample in 1997 was found to have a dioxin TEQ of 35 pptr.

Available nationwide data on dioxin levels in biosolids are limited to data collected over ten years ago in the EPA Sewage Sludge Survey, and there is little data for Washington State. Review of statewide biosolids data and additional sampling are needed.

A multivariate analysis using principal component analyses is consistent with the literature that indicates pentachlorophenol may be a source of dioxin in municipal biosolids.

2. Metals in Soils

Purpose

The objective of the metals in soils study was to determine if certain metals have accumulated in agricultural soils of the Columbia Basin of Washington State.

Ecology randomly sampled and analyzed seven metal concentrations in agricultural and non-agricultural (background) soils from the Columbia Basin Irrigation Project and compared the results with three other soil studies. Agricultural lands are defined as lands in active agricultural production. Non-agricultural lands are lands that have never been farmed, tilled, or grazed.

Sampling Procedures

The Columbia Basin Irrigation Project was selected for soil sampling because of the agricultural diversity and potential availability of historical information. The study area included portions of Adams, Franklin, and Grant counties within the Columbia Basin Irrigation Project. An important aspect of this study area is that historical agricultural practices (e.g., cropping patterns and agricultural chemical use) can be documented.

Fields with historical use of biosolids (sewage sludge) and/or lead arsenate pesticides were excluded from this study, and sampling was limited to irrigated agricultural fields. Background sites were non-irrigated, non-agricultural areas. Twenty agricultural sites and 13 matched background non-agricultural sites were sampled.

Site History

Within the Columbia Basin Irrigation Project in central Washington State, Grant County was the primary sampling location (Figure 2-1). One sample was taken from Adams County, and no samples were taken from Franklin County. Grant County covers approximately 691,175 hectares (1,707,870 acres). The Columbia River flows in a deep valley along the southwestern boundar of the county. The southern portion of the county contains Saddle Mountains and Frenchman Hills. Babcock Ridge and Beezly Hills border the northern part of the plain (Gentry, 1984).

Grant County has approximatel 62 types of soil with a wide range of texture and natural drainage (Gentry, 1984). Wind and water erosion are major soil-related problems in the southern part of the county. Agriculture is the main economic enterprise in the county. About 19 percent of the total area is irrigated cropland, about 18 percent is non-irrigated cropland, and about 62 percent is rangeland. Rangeland includes natural grasslands, savannas, wetlands, deserts, and areas that support certain forb and shrub communities (Gentry, 1984). Only 971 hectares

Figure 2-1. Map showing location of Grant County in Washington State.

(2,400 acres or 0.1% of the county) are classified as urban. The county's main irrigated crops are winter wheat, alfalfa hay, potatoes, corn, and beans (Gentry, 1984). The main non-irrigated crop is winter wheat.

Landowners of the 20 agricultural fields sampled were surveyed about the history of each field. Each owner was asked:

1. The year the field was originally cultivated, and
2. If row crops, hay, small grains, pasture, orchard, or other crop had ever been grown on the field and, if so, for how many years.

Historical site information is summarized in Appendix 2-A1. When sampled, the crops present were alfalfa, apples, beans, corn, pasture, potato, primrose, sugar beet, and wheat (Table 2-1). Compared with the USDA Soil Survey (Gentry, 1984), the crop types encountered are representative of the area.

The majority of these fields had been cultivated with combinations of row crops, hay, and small grains. Two fields had previously been pasture, and two other fields had previously been fruit orchard. Three fields had been cultivated at one time with asparagus, seed, and peppermint. Initial cultivation of most fields began when the Columbia Basin Irrigation Project began in the

Table 2-1. Crops present on fields sampled.

Crops Present on Fields Sampled	Number of Fields Sampled	Main Irrigated Crops (Gentry, 1984)
Alfalfa	7	Alfalfa
Apples	3	---
Beans	2	Beans
Corn	1	Corn
Pasture	1	---
Potato	1	Potato
Primrose*	1	---
Sugar Beet	1	---
Wheat	3	Winter Wheat

*Cultivated for primrose oil

early 1950s. Two fields had been dry land farmed before the Columbia Basin Irrigation Project began. The historical diversity of the crops on the fields sampled indicate that a variety of farming practices have been used over the past 40 to 50 years. Because of this diversity, a wide range of fertilizer types has likely been applied to these soils.

Site Selection

The Columbia Basin Irrigation Project is divided into uniquely numbered farm units. Each farm unit represents one or more fields owned by an individual. Computer-generated numbers and a random number table (Steel and Torrie, 1960) were used to create a list of potential farm unit numbers representing the unique identification numbers associated with the farm units. Ecolog verified that these numbers corresponded to farm fields using farm unit maps (USDI, 1982).

Landowners were contacted and asked to participate in the study. Before owners were contacted, fields were roughly compared to selection criteria and U.S. Department of Agriculture (USDA) soil survey maps (Gentry, 1984). Selection criteria for agricultural field sampling followed Holmgren site selection criteria (Holmgren et al., 1993). See Appendix 2-A2 for selection criteria.

If a farm unit did not meet the selection criteria, it was eliminated from the list of potential sampling locations before contact with the owner. When owners were contacted, selection criteria were confirmed. Sites not meeting the criteria were excluded from the study before participation was requested. If available, the historical agricultural use of acceptable sites was recorded. See Figure 2-2 for map of generalized sampling areas. From these seven general locations, twenty agricultural samples and thirteen background samples were taken. Nineteen sites were located in Grant County, and one was located in Adams County. No sites meeting the criteria and landowner approval were found in Franklin County.

Figure 2-2. Map of general sampling locations (round shaded areas).

Participation in the sampling program was voluntary. As owners were asked to participate, their responses were recorded (Appendix 2-B). The predetermined rejection rate to constitute an unacceptable, unquantifiable bias was twenty rejections, prior to obtaining 20 participants. Had 20 rejections been obtained, this study would have been terminated.

At the time the twentieth landowner agreed to participate, eight had rejected the opportunity. Landowners did not exhibit a bias related to knowledge about metal concentrations in the agricultural soil. Several participants acknowledged some reservation about the sampling, because the heavy metal content of their soil was unknown to them, although they routinel tested the soil for nutrient content.

Matching Background Sites with Agricultural Fields

The U.S. Geological Survey (USGS) Soil Survey for Grant County (Gentry, 1984) was used to classify soil types for all sites. Table 2-2 summarizes the soil types by sample site. The table also lists the percent of that soil type found in Grant County. A brief description of each soil type can be found in Appendix 2-E.

All of the agricultural sites selected had potential background sites in close proximity. However, in several cases, additional background sites were located because access could not be obtained for sampling. Some background sites were farther from the agricultural sites than originall planned. As a result, agricultural and background sites were not uniquely paired one to one. Appendix 2-C lists soil types and the distances separating the agricultural sites from the background sites. In all cases soil types of the selected agricultural and background sites were

Table 2-2. Soil types of fields sampled in the Columbia Basin.

Percent (%) of Grant County	Soil Type and Number of Samples	Percent (%) of Total Sample Sites
5%	Ephrata-Malaga Ephrata fine sandy loam (3)	9%
11%	Kennewick-Warden-Sagemoor Kennewick fine sandy loam (2) Kennewick silt loam (4) Warden silt loam (3) Sagemoor silt loam (2) Novark silt loam (2)	40%
12%	Quincy Quincy fine sand (4)	12%
6%	Taunton-Scoon Scoon silt loam (2)	6%
4%	Shano Shano silt loam (3) Prosser very fine sandy loam (2)	15%
4%	Timmerman-Quincy Timmerman coarse sandy loam (4) Royal very fine sandy loam (2)	18%

identified using USDA soil maps. Sample sites included 20 agricultural sites and 13 background sites.

The background sites were selected based on landowners' site history, as well as visual evidence that the sites had not been cultivated. Ten background sites had sagebrush (*Artemesia sp.*) and cryptobiotic crusts present, suggesting undisturbed soils (Katona et al., 1996). Two sites had 1.83 m (6 foot) tall sagebrush specimens and steep topography that suggested no historical cultivation. One site was within an historic railroad right-of-way and had been plowed for weed control by the second-generation landowner but never planted. A more certain background site could not be found for this soil type due to its presence in prime farmland. Variability in soil particle size distribution between and within soil types was noted. See Appendix 2-D for soil particle size distribution per sample and soil type.

Sampling Procedures

For each site sampled, large-scale maps of the selected fields were obtained, and 0.4 hectare (one-acre) grid was used with a global positioning system (GPS) to identify the latitude and longitude of the starting point in each one-acre sampling unit.

Five samples were taken within the identified one-acre sampling unit and combined to create one composite sample per sampling unit or field. The starting point was one sample, with the other four samples collected in a radius originating from the starting point at a distance of approximately 27.4 meters (30 yards) at equal intervals of 90°.

The surface layer of vegetative or organic material was removed and a 30.5-cm (12-inch) deep hole was dug. A depth of 30.5 cm was used to account for local tilling and farmers nutrient-sampling practices. Equal portions of soil were collected with a clean stainless steel trowel, between the surface and a depth of 30.5 cm, from an uncontaminated side of the hole. An equal amount of material was removed from each sample site and combined in a clean stainless steel mixing bowl. Samples were thoroughly mixed and placed in pre-cleaned sample jars.

Sample jars were labeled with an Ecology seal, a sample number, date, and the investigator's initials. All samples were stored in a cooler and maintained at a temperature of 4°C until analyses. Chain-of-custody procedures followed Manchester Environmental Laborator (Ecology, 1994a) guidelines. The samples for this project were delivered to the Manchester Laboratory by Ecology staff.

Field quality assurance consisted of four "blind" replicate samples taken from the same agricultural field. Blind replicate samples are identical samples submitted to the laboratory with different identification numbers. An estimate of the combined sampling and laboratory precision can be determined by calculating the relative percent difference (RPD) between the duplicate sample results. The RPD is the ratio of the difference and the mean of the results expressed as a percentage.

Analyses

Appendix 2-F summarizes the analyses and methods used on each sample. Analyses conducted on all samples included pH, soil particle size (or grain analysis), total organic carbon (TOC), total phosphorus, and cation exchange capacity (CEC). In addition to total metals analyses (As, Cd, Cu, Pb, Hg, Ni, Zn), an extraction procedure and analysis to help determine metal concentrations available to plants was performed (diethylene triamine pentaacetic acid [DTPA] extractable metals, As, Cd, Cu, Pb, and Zn). The intent of the DTPA procedure was to determine the portion of metals present that may be available to plant life (Spielman and Shelton, 1989).

Data Quality

Precision and Accurac

Routine laboratory quality control procedures were adequate to estimate laboratory precision and accuracy for this project. Laboratory quality control tests were done on each set of 20 or fewer samples and consisted of blanks, duplicate samples, and spiked samples.

One sample in each set of evaluations was analyzed in duplicate in order to assess precision. Precision and accuracy for all analyses was also assessed through the analysis of two matrix spikes and matrix spike duplicates. Method criteria were applied to results to ensure acceptable accuracy and precision.

Representativeness

Because a comprehensive analysis of area soils was not cost-effective at the time of this study, the results are considered a screening survey of the area and not a characterization of the Columbia Basin Irrigation Project soils. The sample size determination was arbitrary.

Comparability

Samples were analyzed using standard analytical methods (EPA, 1986) at the Manchester Environmental Laboratory and state-accredited laboratories. Samples were analyzed for metal concentrations at the 1.0 mg/kg detection level, or lower. Metal analytes not detected ("non-detects") were identified as such in Appendix 2-I.

General Chemistry Quality Assurance

The data generated by the analysis of these samples can be used with the qualifications discussed in Appendix 2-G.

Metals Analysis Quality Assurance

The data generated by the analysis of these samples can be used noting data qualifications discussed in Appendix 2-H.

Data Limitations

Field variability (variability within a single field) was not addressed in this study. Only one composite sample per field was taken. Limitations, particularly for site matching, in these analyses are due to:

- differences in soil properties
- limited resources to look at cursory soil properties
- differing irrigation practices
- small sample size

Results and Discussion

Results

Data Summary

Table 2-3 summarizes the results of the metal analyses in Columbia Basin Irrigation Project Agricultural soils. Arithmetic and geometric mean calculations used one-half the detection limit

Table 2-3. Summary of Columbia Basin soil analyses results.

Analysis	Agricultural Field Results (n=20)				Background Site Results (n=13)			
	Arithmetic Mean[4]	Geometric Mean[4]	Range	Standard Deviation	Arithmetic Mean[4]	Geometric Mean[4]	Range	Standard Deviation
Total Metals (mg/kg d [1])								
Arsenic	3.35	3.21	2.10-5.68	1.04	3.13	2.98	1.50-5.56	0.977
Cadmium	0.103	0.096	0.050-0.210	0.040	0.050	0.042	<0.030[8]-0.098	0.022
Copper	14.3	14.1	9.49-19.0	2.23	13.5	13.3	9.89-20.2	2.39
Lead	7.28	7.20	5.78-9.59	1.12	6.92	6.80	4.60-9.97	1.64
Mercury	0.007	0.007	<0.003[8]-0.013	0.003	0.011	0.007	<0.0032[8]-0.066	0.014
Nickel	11.3	11.1	7.90-15.7	2.30	10.5	10.4	8.00-14.1	2.05
Zinc	53.1	52.8	43.6-65.0	5.86	45.3	44.6	32.5-56.2	7.79
DTPA Extraction (mg/kg dw)								
Arsenic	0.280[5]	0.207[5]	<0.480[8]-0.740	0.068	0.150[6]	0.133[6]	<0.480[8]-0.530	0.018
Cadmium	0.060	0.050	<0.040[8]-0.130	0.027	0.020[7]	0.013[7]	<0.040[8]-0.080	0.012
Copper	2.84	2.74	1.43-4.85	0.793	2.48	1.90	0.072-4.71	1.14
Lead	0.797	0.729	0.230-1.52	0.327	0.630	0.496	<0.160[8]-1.36	0.363
Zinc	3.91	3.37	0.320-6.97	1.65	1.34	0.925	0.0670-3.64	1.09
Total Organic Carbon (TOC)								
@ 104C (%)	0.660	0.621	0.330-1.14	0.252	0.530	0.477	0.210-1.06	0.236
@ 70C (%)	0.630	0.587	0.300-1.06	0.237	0.510	0.460	0.190-1.06	0.235
pH	6.94	6.90	5.50-7.95	0.769	7.51	7.49	6.40-8.20	0.529
Total Phosphorus (mg/kg dw)	804	793	618-1060	140	846	809	587-1460	285
Cation Exchange Capacity(CEC) (g/kg ww[2])	3.63	3.57	2.52-5.33	0.727	3.45	3.40	2.21-4.92	0.609
CEC meq/kg[3] soil	158		110-231		150		96.1-214	

[1] Dry weight
[2] Wet weight
[3] Milliequivalents per kilogra
[4] Arithmetic and geometric mean calculations used ½ detection limit for all non-detect values
[5] Only seven values above detection limits
[6] Only one value above detection limits
[7] Only three values above detection limits
[8] Detection limit

for all values not detected. Results include 20 agricultural samples and 13 background samples. For the complete data set, see Appendix 2-I.

Statistical Summary

The sample collection design for analyzing metals in agricultural soils attempted to provide "paired" or matched samples from agricultural fields and non-farmed background fields. A paired sampling design is beneficial to the degree that it controls for extraneous variability that

tends to mask the effects of a targeted variable. The pairing of samples needs to control for the extraneous factors that could affect measurements, by making the members of each pair "equal" on most traits. To detect an effect without controlling extraneous variability, much larger sample sizes may be required. A paired sampling design allows for a smaller sample size while maintaining statistical power to detect effects, or (equivalently) greater power can be achieved for a fixed number of samples.

The ideal method for a paired soil sampling design would be to sample in the same fields before and after application of fertilizer products. That design could not be implemented for this screening study. Instead, the pairing of soil samples in this study was based on matching of soil types and spatial proximity between paired background and agricultural fields. While many of the background samples were adjacent to the agricultural field samples, several were located at a considerable distance relative to the overall study area dimensions (Appendix 2-C). It is also uncertain in some cases whether or not the agricultural field samples and matched background samples are identical in soil type. These factors raise some concerns about the strength of the pairing in the study as carried out, even though the two data sets (agricultural fields and background fields) are far from independent. The study design as carried out probably represents an intermediate condition between independent and a paired sample design.

Given the reasonable questions about the strength of pairing between samples, statistical analyses were first performed using an approach with minimal assumptions about the data sets. All statistical analyses were conducted using SYSTAT 7.01 (SPSS Inc., 1997). Non-parametric, unpaired statistical tests comparing agricultural field results and background field results were first performed using the Mann-Whitney (Wilcoxon) rank sum test. This approach assumes the two data sets are independent and does not require that data be normally distributed. The non-parametric test is based on the ranks of the measurements in the combined data sets. The null hypothesis that there is no difference between agricultural and background fields was tested against the alternative hypothesis that there is a difference (two-tailed test). The results are provided in Table 2-4.

Statistically significant differences (*p* less than 0.05) are shown for total cadmium and zinc and also extractable (DTPA) cadmium and zinc. Cadmium and zinc total metals and DTPA were higher in agricultural soils than in background soils. Although zinc concentration differed significantly between agricultural and background fields (with alpha set at 0.05), the statistical significance is equivocal, since repeated tests were performed, raising the potential for false positives (Stevens, 1986).

A second set of statistical analysis was performed assuming that the data are paired, using the two-tailed, non-parametric Wilcoxon signed rank paired test. For these tests, whenever more than one agricultural field was paired with a background field, the data from the multiple matched agricultural fields were averaged. This produced 13 pairs of matched results. A statistically significant difference was found between agricultural and background fields for cadmium and zinc, as well as DTPA zinc and DTPA cadmium (results not shown here).

Table 2-4. Statistical summary of data.

Analysis	Mann-Whitney U Test Statistic	Probability
Total Metals (mg/kg dw[1])		
Arsenic	114.0	0.56
Cadmium	30.5	**0.00026**
Copper	100.0	0.27
Mercury	119.5	0.70
Nickel	106.5	0.39
Lead	100.5	0.28
Zinc	60.0	**0.010**
DTPA Extraction (mg/kg dw)		
Arsenic	93.0	0.070
Cadmium	43.0	**0.0010**
Copper	96.5	0.22
Lead	94.0	0.19
Zinc	30.0	**0.00025**
Total Organic Carbon (TOC)		
@ 104C (%)	104.5	0.35
@ 70C (%)	109.0	0.44
pH	170.0	0.14
Total Phosphorus (mg/kg dw)	119.5	0.67
Cation Exchange Capacity (CEC) (g/kg ww[2])	118.0	0.66

[1]Dry weight
[2]Wet weight
Bolded numbers indicate a statistically significant difference

Discussion

Cadmium and zinc concentrations show a small but statistically significant increase in agricultural samples compared to concentrations in background samples (Tables 2-3 and 2-4). Increased concentrations of cadmium and zinc in agricultural fields suggest agricultural practices may have impacted soils over the past 50 years. No statistically significant differences were found for arsenic, copper, lead, mercury, and nickel between agricultural and background sites. Soil concentrations of all metals in this study were typically less than or at the lower ranges of the comparison studies data. See figures in Appendix 2-J for a graphical comparison of these data to the studies discussed below.

In order to put these results in context, the data were compared to three studies:

- Natural Background Soil Metal Concentrations in Washington State (Ecology, 1994b)
- Background Concentrations of Metals in Soils from Selected Regions in the State of Washington (Ames and Prych, 1995)
- Cadmium, Lead, Zinc, Copper, and Nickel in Agricultural Soils of the United States of America (Holmgren et al., 1993)

It is important to understand the differences in these studies in order to evaluate the results. Numerical comparisons of these studies are found in Table 2-5. Ames and Prych (1995) and Ecology (1994b) may not be entirely comparable to this study because of varying sampling depths. The depth sampled in this study (surface to 30.5 cm) may capture effects of agricultural practices. The deeper depths used by Ames and Prych (61 to 96.5 cm) and Ecology (1994b) (surface to 91 cm) may represent agricultural practices differently. Although Ames and Prych sampling depths were different, arithmetic means for each metal were similar to all studies. The range of values in the Ames and Prych study was greatest.

Table 2-5. Comparison of arithmetic and geometric means of metal concentrations in soils.

Soil Studies	Arithmetic Mean (mg/kg)						
	As	**Cd**	**Cu**	**Pb**	**Hg**	**Ni**	**Zn**
Agricultural Soils[1,4] (n=20)	3.35	0.103	14.3	7.28	0.007	11.3	53.1
Background Soils[1,4] (n=13)	3.13	0.050	13.6	6.92	0.011	10.6	45.3
Ecology (1994b)[4] Yakima Basin (n=32)	3.73	0.550	20.2	7.03	0.030	24.8	57.5
Ecology (1994b)[4] Group "E" (n=21)	2.70	<0.200[2]	17.7	6.92	0.010	13.8	45.7
Ames and Prych (1995)[5] (n=60)	3.40	<0.200[2]	20.0	7.00	0.027	25.0	50.0
Holmgren et al. (1993)[3,4] (n=122)	NA	0.170	22.7	7.44	NA	20.5	63.5
	Geometric Mean (mg/kg)						
Agricultural Soils[1,4] (n=20)	3.21	0.096	14.1	7.20	0.007	11.1	52.8
Background Soils[1,4] (n=13)	2.98	0.042	13.3	6.80	0.007	10.4	44.6
Holmgren et al.[4] (n=122)	NA	0.184	26.7	8.50	NA	26.4	66.0
Ames and Prych[5] (n=60)	<2.80	<0.200	17.0	7.00	<0.016	17.0	47.0

[1]This current stud
[2]All values below detection limit of 0.20 mg/kg
[3]Grant and Adams counties onl
[4]Non-detect (ND) = ½ detection limit (DL)
[5]ND = lab's minimum reporting level

The Ecology (1994b) study determined "natural background" concentrations of metals in Washington State soils. To determine natural background concentrations of metals, the stud tried to avoid impacts from agricultural practices by using deeper sampling depths. Samples were collected statewide, by region. The two most comparable regions to this study were:

- Yakima Basin (Yakima, Kittitas, Chelan, and Grant counties)
- Group "E" (Benton, Spokane, Lincoln, Adams, Okanogan, and Whitman counties)

Soil samples were collected from predominant soil series, and efforts were made to collect samples from undisturbed or undeveloped areas. Samples were collected from the ground surface to a depth of about 91 cm (3 feet) (Ecology, 1994b). This is a distinct sampling difference with this current study which sampled to a depth of about 30.5 cm (12 inches). The same analytical methods were used in both studies. For data analysis, Ecology (1994b) used one-half the detection limit value for non-detect values, per MTCA specifications (WAC 173-340-708(11)(e)).

Ecology and the U.S. Geological Survey investigated the magnitude and variability of background metal concentrations in state soils (Ames and Prych, 1995). Samples in Ames and Prych were collected between 61 and 96.5 cm. Soil series sampled were Quincy, Shano, and Taunton. Region R (central Columbia Basin) in the Ames and Prych study was used for comparison to this study. The same methods and analyses were used in the Ames and Prych study as in this study. For data analysis, Ames and Prych used the laboratory's minimum reporting level for those values smaller than the minimum reporting level.

The Holmgren et al. (1993) study analyzed 3,045 surface soil samples from 307 different soil types for several metals, including cadmium and zinc, throughout the United States. The primar purpose of their study was to assess the background levels of cadmium and lead in major food crops and in the soils of their major growing areas. Samples for Holmgren et al. were taken from surface soils (commonly 0-15 cm or 0-20 cm), compared to a depth of 30.5 cm used in this study. Ecology obtained county level data from Dr. Rufus Chaney, the corresponding author of Holmgren et al. (Chaney, 1998). Although arithmetic mean concentrations for these metals are relatively similar, their ranges vary considerably. The arithmetic and geometric means for Grant and Adams county data are presented in Table 2-5 and arithmetic means are graphicall compared with the other studies in Appendix 2-J. For data analysis, Holmgren et al. used one-half the detection limit value for non-detect values.

In this study, cadmium levels were less than 0.21 mg/kg in all agricultural sites and less than 0.098 mg/kg in all background sites. This corresponds with the Ecology (1994b) study in which all Group "E" cadmium values were below detection limits (0.2 mg/kg); Yakima Basin mean cadmium values were 0.55 mg/kg (Ecology, 1994b). Ames and Prych (1995) also found all cadmium concentrations below detection limits (0.2 mg/kg). Cadmium values in the Holmgren data from Grant and Adams counties ranged from 0.1 to 0.26 mg/kg and were closer to the results of this study. These studies imply that cadmium soil concentrations in the Columbia Basin are typically below 0.6 mg/kg.

Zinc concentrations in this study ranged from 43.6 to 65.0 mg/kg in agricultural fields, with an arithmetic mean of 53.1 mg/kg. The Ecology (1994b) study reported similar values for Group E and the Yakima Basin. Ames and Prych (1995) found zinc concentrations from 21.0 to 116 mg/kg with an arithmetic mean of 50.0 mg/kg. Zinc concentrations in Grant and Adams counties (Chaney, 1998) were also very similar to this study. See Table 2-5 for a comparison of means between studies and Appendix 2-J for graphical representations of data ranges in these studies. Metal concentrations for arsenic, copper, lead, mercury, and nickel from this study were also comparable with the above studies (see Table 2-5 and Appendix 2-J) with similar mean values, but ranges varied considerably.

Zinc is a plant nutrient and necessary for normal plant growth (Amrani et al., 1997). Historically, eastern Washington calcareous soils were extremel zinc deficient, strongly limiting such crops as potatoes and beans. Because significant amounts of zinc have been added to agricultural soils – increasing concentrations to levels above background – crops such as potatoes and beans can successfully be grown in eastern Washington (Stevens, 1999; Chaney, 1998).

Certain pairs of metals, such as zinc and cadmium, compete with one another for plant absorption (Chaney et al., 1996). Although the presence of zinc is not a primary factor in crop cadmium uptake, under the right circumstances zinc soil concentrations could influence crop uptake of cadmium. Generally, when zinc soil concentrations are 100 times greater than cadmium soil concentrations (e.g., when the zinc to cadmium ratio is high), crops take up zinc before cadmium. Also, the phytotoxicity of zinc can limit a crop's uptake of cadmium to levels far below that tolerated by the crop . (Chaney et al., 1996).

Holmgren et al. (1993) noted that the crustal ratio of zinc to cadmium is often determined for comparison; that study used a value of 270 for the crustal ratio of zinc to cadmium. In this current study, the zinc-to-cadmium ratio was 516 for agricultural fields and 906 for background sites using arithmetic means. Using geometric means, the agricultural field zinc to cadmium ratio is 550 and the background site ratio is 1062. The data from this study agrees with that of Holmgren et al. (1993) that the zinc-to-cadmium ratio is high (>350) for those agricultural and non-agricultural fields tested in central Washington.

Data from this current study suggest that over the last 50 years agricultural practices may have increased cadmium concentrations over background levels in the Columbia Basin, although further investigation is necessary to confirm this. The metal concentrations of the fertilizers used in the past are unknown, however, the highest cadmium levels in the fertilizer products sampled were found in phosphate fertilizers (Chapter 1). Cadmium is a known contaminant of phosphate fertilizers (Mortvedt, 1987; Holmgren, et al., 1993; Chaney and Oliver, 1996).

Although standards adopted in the past year by Washington State limit the amount of cadmium in fertilizers, the standards allow for the addition of metals in the soil. The current rate of increase or how many years are required before these metals, particularly cadmium, could approach levels of concern is not known, but will vary with farming practices, soil conditions, and other site specific considerations.

Typical U.S. cadmium levels in agricultural soil pose little risk to human and ecosystem health, although cadmium is ubiquitous in the environment, (Gavi et al., 1997). Chaney et al. (1996) states "excessive transfer of environmental cadmium to humans has no basis in actual cases of high cadmium+zinc contamination except in rice paddies and in tobacco production." That stud also noted that "there is no evidence that bioavailable cadmium transfer in food and feed-chains is higher today than in 1900 before cadmium became more widely dispersed by industrial and urban processes."

To determine the portion of metals present in soil that may be available to growing plant life, single-extraction tests such as DTPA have been used (Speilman and Shelton, 1989; Quevauviller et al., 1998). Higher values indicate a metal is more available to growing plant life. A statistically significant difference was shown between agricultural DTPA-zinc and -cadmium values and background DTPA-zinc and -cadmium values (Table 2-4). This indicates that relatively more zinc and cadmium is available to plants on the agricultural sites sampled than on the background sites sampled. DTPA-arsenic, DTPA-copper, and DTPA-lead were not significantly different between agricultural and non-agricultural soils.

In the original study design, the measurement of cation exchange capacity (CEC; the ability of a soil to adsorb and desorb micronutrient elements) was to be used to help identify soil series (Table 2-2). In this study, CECs (Table 2-3) averaged 158 meq/kg soil for agricultural soils and 150 meq/kg soil for background soils. No statistical differences were found between agricultural CEC and background site CEC. No statistical differences were found for pH and total phosphorus between agricultural and background sites. Total phosphorus and pH are commonl recorded parameters for soil analyses. Total phosphorus results from this study will aid in further investigations of (1) the relationship between soil cadmium and phosphorus and (2) possible correlations of cadmium to phosphate fertilizers.

Conclusions

Cadmium and zinc concentrations show small but statistically significant increases in agricultural fields over background sites. DTPA-cadmium and DTPA-zinc values also show small but statistically significant increases in agricultural soils compared to background soils. No statistically significant differences were found between agricultural and background sites for arsenic, copper, lead, mercury, nickel, DTPA-arsenic, DTPA-copper, DTPA-lead, total organic carbon (TOC), pH, total phosphorus, and cation exchange capacity (CEC).

The data suggest that increased cadmium in agricultural fields may be due to farming practices used over the last 50 years. Further investigation is necessary to confirm this possibility. The increased zinc levels were purposefully established to correct nutrient deficiencies affecting crop production. The zinc-to-cadmium ratio suggests plants will preferentially uptake zinc over cadmium. The increased cadmium and zinc soil concentrations in agricultural fields sampled suggest no potential soil quality impairment because the values detected are within the lower range of background comparison studies.

All of the studies addressed above, including this study, yielded similar results for most metals with the exception of cadmium in the Yakima Basin. Overall, the similarities are more striking than the differences. Although the other studies typically reported greater soil concentration ranges than this study, arithmetic mean metal concentrations were similar.

Washington fertilizer standards allow for the addition of metals in agricultural soils. It is important to determine (1) if metal concentrations increase in agricultural soils and (2) *if* they do, the rate of increase. State agricultural soils should be periodically monitored to determine a rate of increase and if this rate has been limited since the implementation of Washington State fertilizer standards.

In particular, increased agricultural cadmium levels over background levels indicate a need to periodically monitor cadmium concentrations in soils to determine any rate of increase and ensure levels do not become a concern. Arsenic, copper, lead, mercury, nickel, and zinc concentrations should also be periodically monitored in soils to determine any rate of increase and ensure levels do not become a concern.

To this end, sources of cadmium in fertilizer products should be further investigated. Total phosphorus results from this study will aid in further investigations of (1) the relationship between soil cadmium and phosphorus and (2) possible correlations of cadmium to phosphate fertilizers. As an example, fertilizers with high levels of cadmium – including United Agricultural Products (UAP) 0-45-0, Frit F-503G, Agrium Ammonium Phosphate Sulfate, and NuLife Agro 10-15-10 – should be further reviewed.

Knowing the rate of increase, if any, of metals in agricultural soils would assist in revising the Washington fertilizer standards, if needed, so concentrations of metals in agricultural soils do not reach a level of concern.

A state Department of Agriculture/Washington State University crop-uptake study was initiated in the fall of 1998. It will evaluate the uptake of metals in certain crops in relationship to the new fertilizer standards. This report is due June 2001.

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3. Dioxins in Soils

Purpose

The objective of this study was to provide an initial assessment of typical dioxin concentrations in soils in Washington State, particularly agricultural soils.

Low levels of dioxin are pervasive in the environment, probably due in large part to long-range transport and deposition of aerial particles from various combustion activities.[7]

Ecology sampled soils in open, forested, and urban areas to determine if dioxins occur in these areas and at what levels. A data analysis technique called "principal component analysis" was conducted to examine potential associations between the dioxin "signatures" in soil samples to the signatures of potential dioxin sources.

The original study design included sampling and analyzing agricultural soils for dioxins. However, due to difficulties in randomly selecting agricultural sites and an inability to guarantee confidentiality to landowners, this part of the study was postponed until the spring of 1999.

Study Design

Thirty soil samples were allocated to open, forested, and urban areas (Table 3-1). To evaluate possible associations between soil sampling results and potential dioxin sources, a correlation analysis called principle component analysis (PCA) was conducted. In addition to the soil sample results, 35 dioxin source sample results, along with data from nine fertilizer products that contained dioxin (reported in Chapter 1), were obtained for this evaluation. Dioxin source information was obtained from the literature (Appendix 3-A) and data obtained for the *Washington State Dioxin Source Assessment* (Yake et al., 1998).

Open Areas

Eight samples were collected from open areas. For this study "open areas" were defined as historically non-forested, non-agricultural, and located away from large urban areas. Sites were chosen based on spatial distribution (four samples each, from east and west sides of the state) and ability to gain site access. Because only eight sites were located in open areas, no attempt was made to choose the samples randomly. Four of these eight samples were collected from grazed land, and the other four from conservation areas and reserves.

[7] The word "typical" is used to describe the samples collected for this study, since the use of the term "background" implies a natural occurrence of these compounds.

Table 3-1. Number of samples allocated by land use.

Land Use	East	West	Total
Open	4	4	8
Grazed	2	2	
Non-grazed	2	2	
Forest	4	4	8
Managed (Commercial)	2	2	
Parks (Non-commercial)	2	2	
Urban	3	11	14
Seattle Area		9	
Tacoma		2	
Tri-Cities	2		
Spokane	1		
Total	11	19	30

Two sites in eastern Washington were sampled to represent grazed land (rangeland). Both sites were on state lands managed by the state Department of Natural Resources. One site was located near Palouse Falls, and the other sample was collected from rangeland northeast of Ellensburg. In western Washington a sample was collected from a horse ranch in Clark County, and the other sample was collected from a dairy farm in Pierce County.

Two sites on each side of the state were sampled to represent open, non-grazed land. Three of these sites were from national wildlife refuges, and the fourth sample was collected from a national park.

Forest Land

Eight soil samples were collected from forested areas. "Forested sites" were defined as areas with an extensive canopy composed primarily of mature trees. Sites were chosen based on spatial distribution (e.g., east and west sides of the state) and ability to gain site access. Because a total of only eight sites were located in forested areas, no attempt was made to choose the samples randomly.

Four samples were collected from areas actively managed for silviculture (e.g., sites that have been logged and are slated for future logging). Soil samples were obtained from both private and public forests. Two samples were collected from public forests: Wenatchee National Forest and Olympic National Forest. The other two samples were from private forests, one near the town of Newport and one near the town of Rainier.

Four soil samples were obtained from forested areas that had not been managed for timber harvest. Collection sites were (1) a state park in the southeast corner of the state, (2) Olympic National Park, (3) Willapa National Wildlife Refuge, and (4) Pasayten Wilderness in the Okanogan National Forest.

Urban Areas

Fourteen of the 30 soil samples collected were allocated to urban areas. As defined by the U.S. Census Bureau (1997), an urbanized area comprises one or more places (central place) and the adjacent densely settled surrounding territories (urban fringe) that together have a minimum of 50,000 persons. The urban fringe generally consists of contiguous territory having a density of at least 1,000 persons per 256 hectares (one square mile). According to the U.S. Census Bureau (1998), Washington has 10 urbanized areas, comprising a total of 3,394 square kilometers.

To allocate 14 sites within the urban areas, a random number generator was used on a database of 3,394 units, based on one-kilometer square grids representing the total urban area. Random numbers were used to allocate the sample count among the 14 urban areas. Sequential numbers were used to represent the one kilometer square grids, but not specific locations, within the 14 listed urban areas of the state. The database was then sorted by these random numbers. The first 14 units selected by this method determined the number of sites assigned to each urban area selected for this study (Appendix 3-B).

The greater Seattle area is the largest urban area in Washington State, both in terms of size and population. The majority (9) of the urban samples were assigned to this area. Using maps that defined urbanized areas, Ecology randomly selected public sites such as parks and other similar grass-covered landscapes for this study. Parks were used because they are generally not in industrial areas or close to point sources of dioxins; they tend to be in residential areas and at least one-acre (0.4-hectare). Approximately 300 sites listed as parks in the Seattle urban area were entered into a database (Thomas Brothers Maps, 1989).

To select these nine sites within the Seattle urban area, a random number generator function was used on the database. Each park was assigned a random number and the database was then sorted by these random numbers. The first nine parks (excluding parks within Seattle city limits) in the list that met the selection criteria were the sites selected for soil sampling. Seattle parks were not sampled due to difficulty in getting timely information, as well as a lengthy permit process.

Due to the small sample sizes allocated to the other urban areas (1-2 soil samples), no attempt was made to randomize site selection in these areas. Sites selected were in residential areas within the urban boundaries.

Agricultural Soils

Ecology encountered significant problems obtaining samples from agricultural lands and found it impossible to gain permission to sample randomly selected agricultural sites within study time constraints. Ecology could not guarantee confidentiality of sampling results, so property owners were reluctant to have their soils tested. As a result, sampling of agricultural land was postponed.

Sampling of agricultural soils will take place during April and May 1999. Data from this phase of the study, sampling agricultural soils, will be published as an addendum to this report.

Soil Sampling Procedures

A global positioning system (GPS) was used to identify the starting point and sampling locations on the selected property. An attempt was made to avoid locating sampling sites near roads, railroad tracks, treated wood utility poles or fences, or areas of significant erosion.

A sampling unit of one-acre (0.4-hectare) was selected; this was the largest practical unit that allowed for representative composite sampling. For example, finding an urban area of ten acres (4.05 hectares) suitable for sampling proved difficult. A one-acre (0.4-hectare) site allowed for uniform sized sampling units across all land uses.

Samples were collected based, in part, upon guidelines developed for the EPA National Dioxin Study (EPA, 1984) and other published studies (Schuhmacher et al., 1997; Jiménez et al., 1996; Creaser et al., 1990; Creaser et al., 1989). Each sample was a composite of ten samples collected within the sampling unit. The initial sample was collected at a starting point (center), with nine additional samples collected at the end of a radius originating from the starting point, extending a distance of 36 m (39 yards), and rotated at equal intervals of 40°. The surface layer of organic vegetative material was removed, and a sample was collected from a depth of 0-5 cm below the surface to include an equal amount of material throughout the depth of the sample. Dioxins are relatively immobile substances and do not appreciably leach through the soil. Each sample contained approximately 120 cm^3 (6 ounces) of material, and was collected using dedicated utensils. Sampling apparatus was appropriately cleaned prior to sampling (Appendix 1-B).

Samples were collected with a stainless steel scoop, placed in a stainless steel mixing bowl, and thoroughly mixed. Composite soil samples were mixed until the entire sample was uniforml consistent. Rocks, vegetation, and debris were removed from the samples in the field using stainless steel tweezers. Samples were placed in ultra-clean sample jars with a Teflon lid for transport and analyses. Each sample was analyzed for dioxin, total organic carbon (TOC), and grain size. All samples were stored in a cooler and maintained at a temperature of 4ºC until analysis. A summary of sample handling procedures for dioxin is found in Table 3-2.

Table 3-2. Dioxin analyses, container, and holding summary.

Target Analyses	Minimum Sample Size	Holding Requirements
2,3,7,8-substituted PCDD/PCDF Method 8290 (EPA 1994)	10g sample in ultra clean glass jars with Teflon lids	Cool to 4°C and keep dark; max. hold 30 days[8]; analyze within 45 days of extraction

Sample labeling, shipping, and chain-of-custody procedures as defined in the Manchester Environmental Laboratory *Lab Users Manual* (Ecology, 1994a) were followed.

[8] The holding time of 30 days from collection to extraction is a recommendation. PCDDs and PCDFs are very stable in a variety of matrices, and holding times for samples stored at 4ºC in the dark may be as high as a year for certain matrices.

Analytical Procedures

Analysis of 2,3,7,8-substituted PCDD/PCDF congeners (forms) was conducted at MAXIM Technologies Inc./Pace Analytical, using high resolution GC/MS EPA Method 8290, with enhancements derived from Method 1613B.

Detection limits varied depending on the physical state (e.g., moisture content and organic content) of the samples, but the target detection limit was 0.1 pptr. EPA Method 8290, Section 7.9.5, specifies the sample specific Estimated Detection Limit (EDL) as the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level. Not all the congeners were responsive enough to provide EDLs
at 0.1 pptr.

Data Quality

This project is designed to provide data on *typical* concentrations of dioxins in Washington State surface soils. It is primarily for informative and descriptive purposes and does not test an specific hypothesis. The study was not designed to test whether specific land uses are associated with significant differences in dioxin levels, although general comparisons are made among land uses.

For the comparison analysis, dioxin source data from the *Washington State Dioxin Source Assessment* were not reviewed in extensive detail, "however, every attempt was made to use published data or data that were available for the public record." (Yake et al., 1998). The source data were used qualitatively, and not to determine dioxin loading in the environment.

Representativeness

This study was designed to provide an initial assessment of dioxin levels in surface soils. A combination of random and non-random sampling using spatial stratification (e.g., samples taken from locations across the state and across several land uses) provides adequate coverage and data consistent with pilot study objectives. However, conclusions based on data generated by this pilot study are limited, due primarily to small sample size and non-random sampling.

Quality Control Procedures

Established laboratory quality control procedures for this project met data quality objectives for laboratory precision and accuracy. Laboratory quality control tests were done on each set of 20 or fewer samples and consisted of blanks, duplicate samples, and spiked samples. Manchester Laboratory quality control samples and procedures are discussed in Manchester Environmental Laboratory *Lab Users Manual* (Ecology, 1994a).

Quality assurance and quality control measures indicate dioxin results are reliable. A number of the 17 congeners were detected in the associated method blank at concentrations below the lowest calibration standard. According to the method, re-analysis is not required when a target congener is detected below the lowest calibration standard. If the concentration of a congener in a sample was less than five times the method blank, a qualifier was added to the result specifying that the analyte was not detected at or above the (estimated) reported result. In cases where the sample concentration for a congener was greater than five times that of the method blank, the blank result is considered insignificant relative to the concentrations detected in the samples.

Field quality assurance for this project consisted of two duplicate split samples. The differences in duplicate sample results reflect combined sampling and laboratory variability. The Richland split samples were relatively close, with dioxin TEQs of 4.5 and 4.8 pptr. The split sample from Spokane had TEQs of 0.33 and 0.98 pptr.

Sample 98328339 was re-analyzed because only one of the 15 internal standards met the recovery criteria.

For further details on quality control procedures, see Appendix 3-C.

Data Analysis

Principal component analysis (PCA) is a qualitative technique that was used to examine correlations between the dioxin signature (fingerprint) of the soil samples and potential dioxin sources. PCA is a data reduction tool used to reduce a number of variables (in this case, the ten dioxin and furan congener groups in Table 3-3) to a few variables (linear components) that describe the data with a minimum loss of information (Scheiner and Gurevitch, 1993). This process is called ordination. PCA is the oldest ordination technique and perhaps most widel known (Sparks et al., 1999), and is a common tool used to identify relationships among samples and possible sources of dioxins. Dioxin samples are composed of a mixture of various dioxins and furans. The ratio of the different congeners results in a particular signature that is identifiable to the source. Similar processes result in a similar signature. The soil and source samples can be plotted graphically using "score plots." Similarities and differences can then be seen as distances between points. Clusters of points represent similarities in composition. The closer that samples are to one another, the greater the similarity.

There are limitations to PCA. This analysis does not take into account environmental degradation of dioxins. Dioxins can be transported long distances once released into the atmosphere (Baker and Hites, 1999; Brzuzy and Hites, 1996; Tysklind et al., 1993). The dioxin signature of a source may change over time and distance due to differences in volatilization, solubility, and rate of photodegradation of the different congeners, resulting in a dioxin signature different than from its source of origin (McPeters and Overcash, 1993; Podoll et al., 1986). Despite these limitations, PCA has been successfully used to interpret data and make comparisons between signatures of dioxin sources and environmental samples (Bonn, 1998; Grundy et al., 1997; Jimenez et al., 1996).

Table 3-3. Dioxin and furan congener groups (homologues).

Congener Group	Abbreviation	Degree of Chlorination (# of chlorine atoms per molecule)
Tetrachlorinated dibenzofurans	TCDF	4
Tetrachlorinated dibenzo-*p*-dioxins	TCDD	4
Pentachlorinated dibenzofurans	PeCDF	5
Pentachlorinated dibenzo-*p*-dioxins	PeCDD	5
Hexachlorinated dibenzofurans	HxCDF	6
Hexachlorinated dibenzo-*p*-dioxins	HxCDD	6
Heptachlorinated dibenzofurans	HpCDF	7
Heptachlorinated dibenzo-*p*-dioxins	HpCDD	7
Octachlorinated dibenzofurans	OCDF	8
Octachlorinated dibenzo-*p*-dioxins	OCDD	8

A data matrix was created containing the analytical data of five groups of congeners (homologues) of the polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs) according to the degree of chlorination (Appendix 3-D,-E). These ten congener group results listed in Table 3-3 were used for PCA. In order to maximize information content, the entire tetra- through octa-CDD/CDF congener data set was employed in the PCA. This facilitated characterization of dioxin in soils and sources; PCA was not used to characterize TEQ.

PCA was conducted using the statistical software package, SYSTAT 7.01 (SPSS, Inc., 1997). Percentages were used in PCA to remove biases due to concentration differences among samples. For congener groups that were not detected, a concentration equal to half the value of the detection limit was assumed. The data set was transformed prior to analysis to approximate a near normal distribution. Percentages or proportions form a binomial rather than a normal distribution (Zar, 1984). Results were transformed using an equation based on an arcsine transformation developed by Freeman and Tukey (Zar, 1984).

$$p' = \frac{1}{2}\left[\arcsin\sqrt{\frac{X}{n+1}} + \arcsin\sqrt{\frac{X+1}{n+1}}\right]$$

Where: n = number of congener groups (10)
X = original analytical value (percent)
p' = transformed analytical value

Results and Discussion

Dioxin TEQs

TEQ refers to the *toxic equivalents* of dioxin congeners (different forms of dioxins and furans present) calculated as shown in Appendix 3-F. Unless otherwise specified, TEQ values reported here assume that if a specific congener is not detected in a sample its concentration is zero (ND = 0). See Appendix 1 for a discussion on dioxin TEQs and how they are calculated.

A summary of the dioxin TEQ data is listed in Table 3-4. TEQs for each sample are listed in Appendix 3-G. Complete analytical results for the 17 congeners of concern for dioxins and furans can be found in Appendix 3-F. The ten congener group results for the soil analyses can be found in Appendix 3-D; TOC and grain-size results are located in Appendix 3-H. Dioxin concentrations are often correlated to organic content. In this study the correlation coefficient between dioxin (TEQ) and TOC of 0.34 (log-log correlation) approached, but did not meet, statistical significance at the 0.05 level ($p = 0.066$).

Table 3-4. Summary of Washington State soil dioxin TEQs (pptr) by land use.

Land Use		Range	Mean	Median	Geometric Mean	n
Urban		0. 13 – 19	4.1	1.7	1.9	14
	Tri-Cities	1.4 - 4.8	3.1	3.1	2.3	2
	Spokane	0.98	--	--	--	1
	Tacoma	9.5 - 19	15	15	14	2
	Seattle	0.13 – 6.0	2.4	1.4	1.3	9
Open		0.040 – 4.6	1.0	0.27	0.24	8
	Grazed	0.040 – 4.6	1.32	0.33	0.26	4
	Non-grazed	0.046 – 2.4	0.71	0.21	0.23	4
Forest		0.033 – 5.2	2.3	2.2	1.2	8
	Commercial	0.033 – 2.4	1.4	1.5	0.62	4
	Non-commercial	0.45 – 5.2	3.3	3.8	2.3	4
Total		0.033 – 19	2.8	1.2	0.98	30

n = number of samples

Figure 3-1 shows TEQs of the dioxin soil analyses by land use, and Figure 3-2 shows the approximate location and range of TEQ values for soil samples. Every sample had detectable levels of dioxins, even samples from remote wilderness areas. Dioxins are ubiquitous; they are found throughout the state, most likely as a result of aerial deposition (Czuczwa et al., 1984; Czuczwa and Hites, 1986; Creaser et al., 1989; Rotard et al., 1994).

The appropriate statistical measure of central tendency used to describe a distribution of data is based on what is known or suspected about the shape of the distribution. If data are distributed

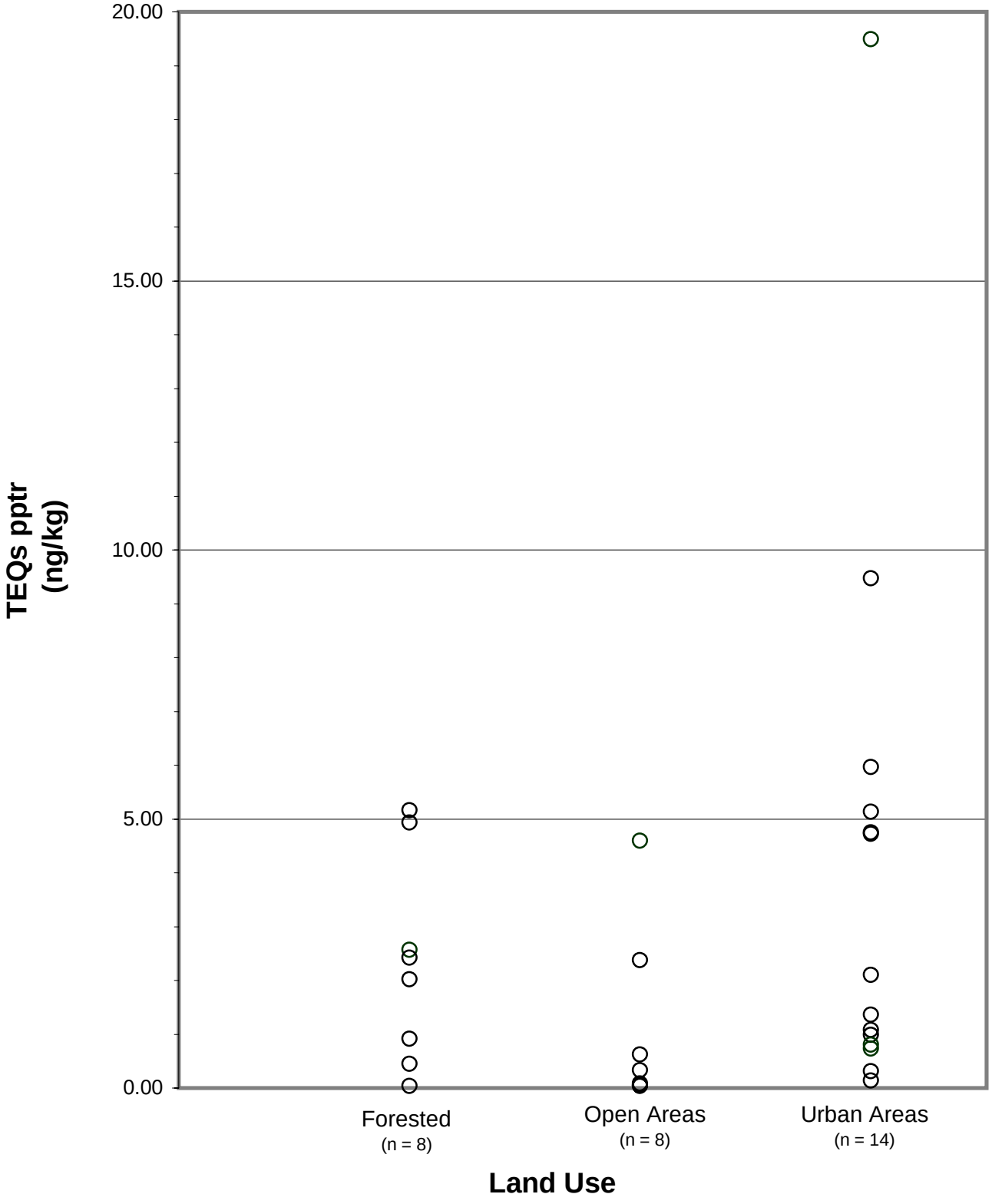
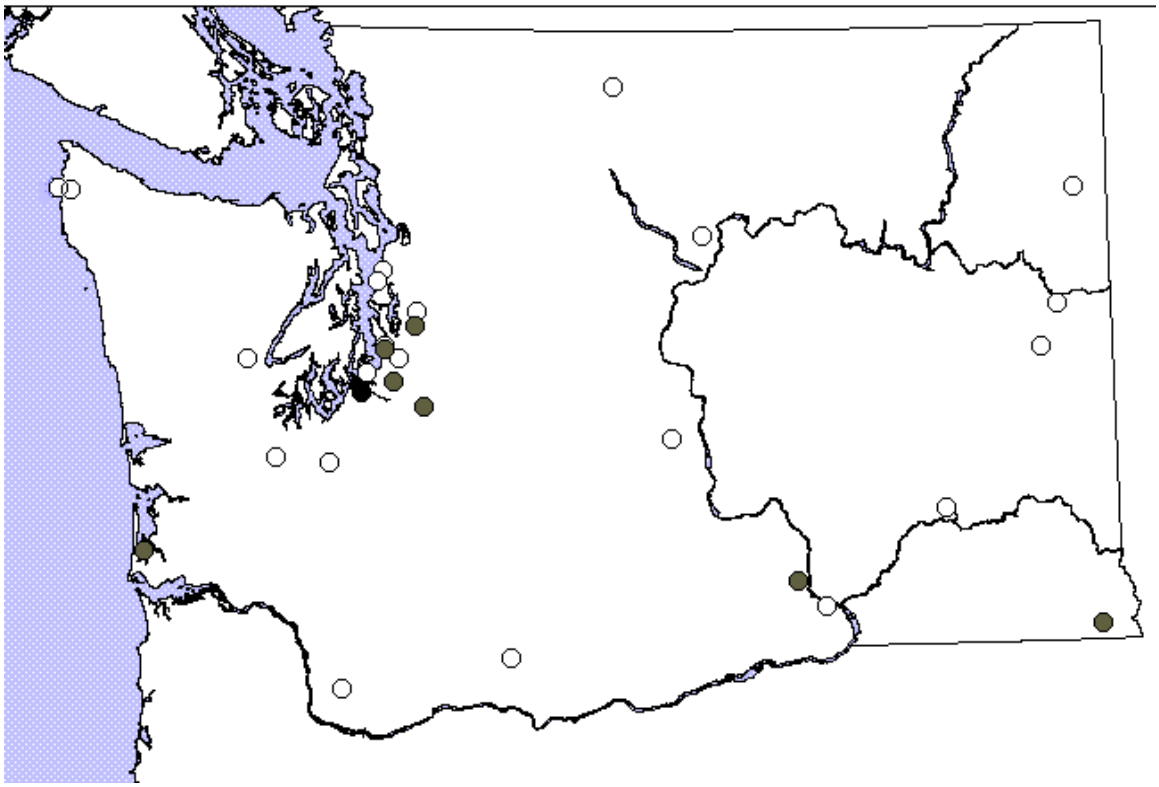


Figure 3-1. Dioxin TEQs of select soils in Washington State by land use.



Range of dioxin TEQs (ng/kg)

- **0.03 – 2.9**
- **3.0 – 9.4**
- **9.5 - 19**

Figure 3-2. Approximate locations of soils samples and range of dioxin TEQs in Washington State.

normally, the arithmetic mean is a good measure of the central tendency of data. If data are skewed to the right, the geometric mean is often used to describe the central tendency.

For the soil dioxin data, most data are centered around the low end of the range (i.e., skewed to the right) with a few higher levels. Because this type of data distribution results in a mean that is not truly representative of the central tendency of the data, the geometric mean or the median may be the most appropriate measure of central tendency of the data presented in Table 3-4.

The range of results from urban areas is greater than the range of the other two land use areas. Urban areas also include the three sites with the highest soil dioxin TEQs. These results are consistent with other studies comparing dioxin TEQs of urban lands to rural lands in Austria (Boos et al., 1992), Britain (Creaser et al., 1990), and Spain (Schuhmacher et al., 1997). Additional sources of dioxin data can be found in EPA (1994) and ATSDR (1998).

No accepted (regulatory) background standard for dioxin levels exists for comparison to these data. In 1994, EPA released a draft report estimating a mean TEQ soil background level of 8 pptr in the U.S. (EPA, 1994) assuming that non-detects were equal to half the detection limit. This was not based on any study or sampling that EPA conducted to determine typical or background levels, but was based on the mean of selected available data. Using half the detection limit for calculating the average and median dioxin TEQs for this study, the results are 4.2 and 2.9 pptr respectively. Some similar studies conducted in Europe can be used as a rough comparison to this study. The dioxin TEQ soil levels found in this study are within the range of similar studies conducted in Spain, Germany, and Austria (Figure 3-3).

The data plotted for Spain come from two studies (Jiménez et al., 1996; Schuhmacher et al., 1997). The dioxin TEQ values near an incinerator in Spain were calculated using half the value of the detection limit for congeners not detected (Jiménez et al., 1996). Median values from Germany (Rotard et al., 1994) are based on international dioxin TEFs. The report does not state whether congeners below the detection limit were given a value of zero for dioxin TEQ calculations. The sites sampled in Germany were outside of industrial and urban areas.

Dioxins are unintended byproducts from processes such as combustion (Czuczwa and Hites, 1986; Creaser et al., 1990; Alcock and Jones, 1996); therefore, the sites closest to these sources (e.g., incinerators, industrial boilers, and cement kilns) have some of the highest dioxin concentrations. A comparison between the east and west side of the state (Table 3-5), excluding urban samples, shows that the sites sampled in eastern Washington tend to have lower levels of dioxin in the soils (Figure 3-4). This is not a conclusive statement, as the study was not designed to test differences between east and west sides of the state, nor were the sites randomly selected. However, this effect may be attributed to more people and greater development (i.e., urban areas) in western Washington.

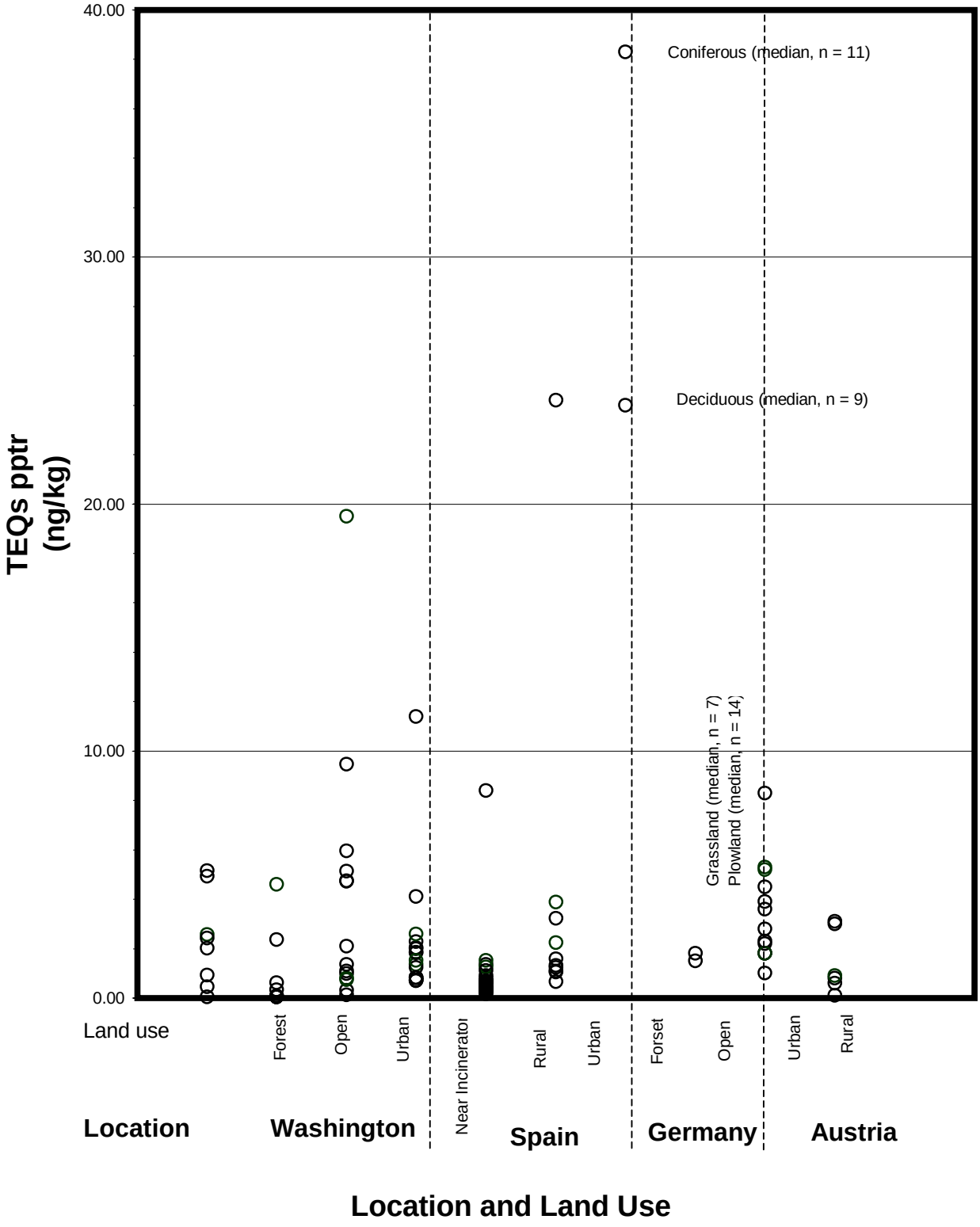


Figure 3-3. Dioxin TEQs of soil by select land uses in Washington State, Spain (Jiménez et al., 1996; Schuhmacher et al., 1997), and Germany (Rotard et al., 1994) and Austria (Boos et al., 1992).

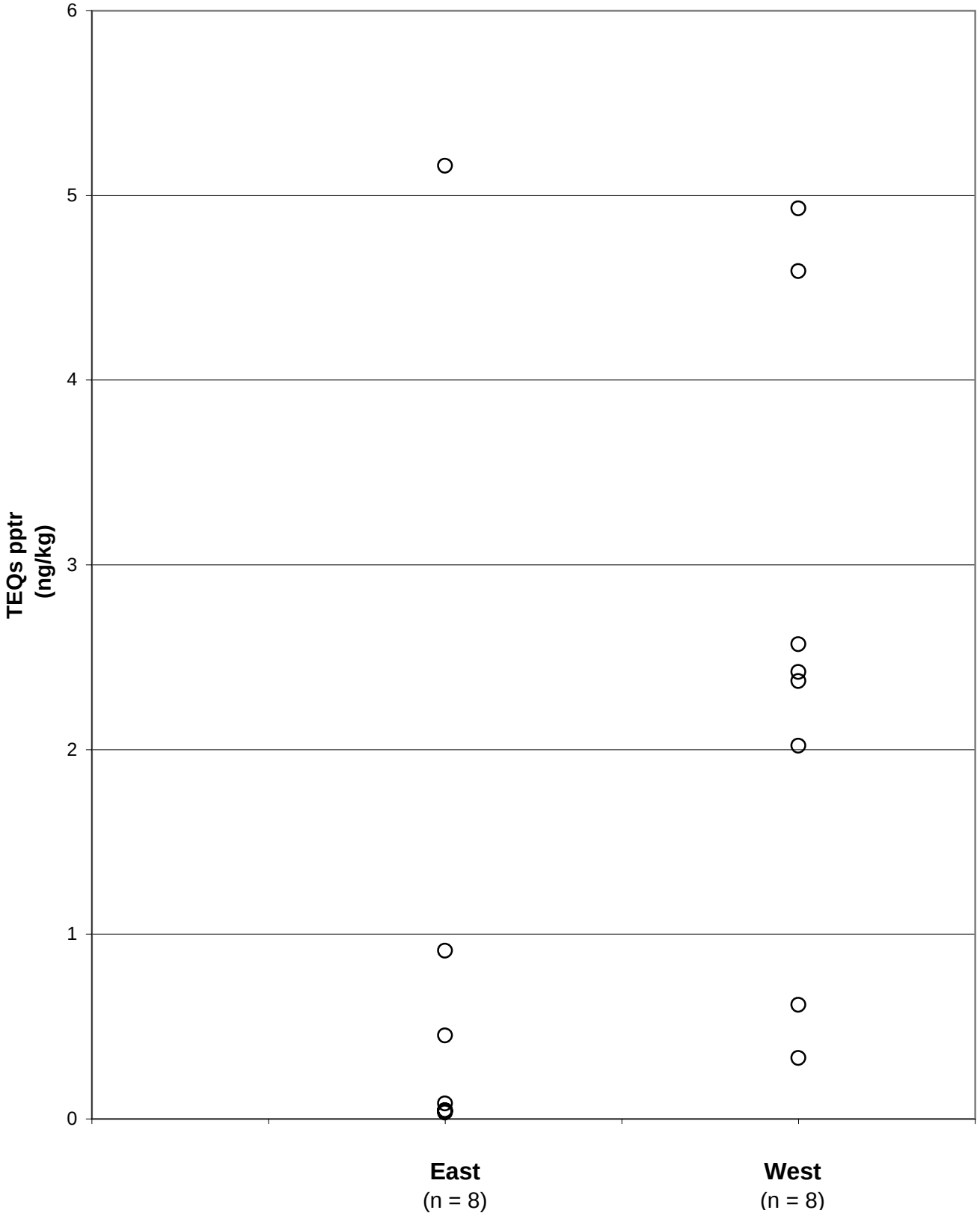


Figure 3-4. Dioxin TEQs of soil samples in eastern and western Washington State excluding urban areas.

Table 3-5. Summary of soil dioxin data (expressed as TEQs) by east and west side of the state, excluding urban samples (pptr).

Land Use	Range	Median	Mean	Geometric Mean	n
East	0.033 – 5.2	0.064	0.85	0.16	8
West	0.33 – 4.9	2.4	2.5	1.9	8

n = number of samples

The two soil samples collected from Tacoma have the highest levels of dioxin detected (19 and 9.5 pptr TEQ) in this study. Although the Tacoma sites are located in residential areas, they ma be closer to industrial areas than the other urban sites sampled. Possible historical sources of dioxin in Tacoma include hog fuel boilers, smelters, pulp and paper mills, as well as municipal and other incinerators. Tacoma has several cleanup sites with confirmed dioxin contamination (Yake et al., 1998).

Forest sites appear to have dioxin levels greater than open areas. In Germany, forests have some of the highest levels of dioxins (Rotard et al., 1994) (Figure 3-3). Trees and vegetation may act as a large filter (Rotard et al., 1994; Horstmann et al., 1997) resulting in a greater surface area available for dioxin absorption and deposition than in open grassy areas. The leaves and needles accumulate volatile and particulate dioxins from the atmosphere, resulting in greater deposition of dioxins on the forest floor (Horstmann et al., 1997). In addition, organic matter in a forest is not harvested or removed as frequently as it is in areas managed for timber or agriculture. This may account for the apparent difference between commercial forests and the wilderness areas (geometric mean = 0.62 and 2.3 pptr respectively, Table 3-4), although a small sample size and non-random sampling precludes making a definitive statement.

Average dioxin TEQ values for grazed lands and non-grazed lands appear in Table 3-4. There are too few samples, and the median values are too similar, to speculate about potential differences in dioxin levels of grazed and non-grazed lands.

Guidelines and Standards

Few guidelines or standards exist for dioxins in soil. Germany has guidelines (Schulz, 1993) for dioxin in soils based on dioxin TEQs[9]. The guidelines recommend that no restrictions be placed on use of soil with dioxin levels below 5 pptr (ng/kg). At levels between 5-20 pptr (ng/kg) management systems should be implemented to reduce dust and pollution. At levels greater than 40 pptr (ng/kg) it is recommended that fruits, legumes, and forage plants not be cultivated. At levels above 100 pptr (ng/kg) in playgrounds, soils should be removed (0 to 10-cm depth), decontaminated, or sealed. In residential areas "measures should be taken to reduce soil contact, such as planting lawns, etc." (Schultz, 1993). In soils with dioxin levels above 10,000 pptr (ng/kg), the same measures should be taken to reduce soil contact as with residential areas; this also applies to levels above 10,000 (ng/kg), independent of location.

[9] German guidelines for TEQs use half the value of the detection limit for congeners not detected at or above the detection limit.

The Agency for Toxic Substances and Disease Registry (ATSDR) has adopted an interim policy guideline to assess public health implications of dioxins in residential soils on or near hazardous waste sites (DeRosa et al., 1997). Evaluation levels for dioxins are concentrations greater than 50 pptr (0.05 ppb), and action levels are set at greater than 1 ppb. This policy provides a framework for evaluating the health implications of exposure to dioxins in residential soils on a site-specific basis.

Within Washington State, three methods are used to determine cleanup levels under the Model Toxics Control Act: MTCA Methods A, B, and C (Ecology, 1996). These are based upon contaminant concentrations designed to protect human health and the environment (cleanup levels). Method A levels are appropriate for routine sites or sites that involve relatively few contaminants. Method B is the standard method for determining cleanup levels and may be applicable to all sites. Method C is the conditional level where Method A or B may be impossible to achieve, may cause greater environmental harm, or for industrial sites.

No specific Method A level is listed for dioxins (PCDDs and or PCDFs); therefore, Method B or C would be used to determine cleanup levels at a site with dioxin. The Method B residential soil cleanup standard for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) is 6.67 pptr (ng/kg) (Ecology, 1996). This standard is applied to cleanup or remediation sites known to be contaminated with dioxins. The calculated dioxin level for Method B cites a specific congener, 2,3,7,8-TCDD (CAS 1746-01-6). It is the policy of the Ecology Toxics Cleanup Program to apply the dioxin TEQ when determining site cleanup levels. The cleanup level does not apply to an area unless it is classified as a cleanup site.

None of the samples in this study had levels of 2,3,7,8-TCDD above the Method B cleanup level. Only four of the 30 soil samples had detectable levels of 2,3,7,8-TCDD, all in urban areas. The samples with TEQs above 6.67 pptr were the two urban sites from Tacoma.

A proposed MTCA rule revision that addresses dioxins more specifically has been published for public comment (Ecology, 1998). The proposed change requires the use of TEFs (EPA, 1989) for assessing the potential carcinogenic risk of mixtures of chlorinated dibenzo-*p*-dioxins and chlorinated dibenzofurans, or assume the entire mixture is as toxic as 2,3,7,8-TCDD.

Relationship between Dioxins in Soil and Dioxin Sources

Data from 35 dioxin sources and nine fertilizer products containing dioxin were compared to the results from the 30 soil samples of this study. A PCA analysis was conducted to evaluate an potential relationship between the dioxin signature of soil samples with that of dioxin sources.

The dioxin source raw data are tabulated in Appendix 3-E. This is not an inclusive list of dioxin sources. Other sources of dioxin were not included in this report, because there were no reliable data available. Potential dioxin sources not included in this analysis were emissions from motor vehicles, oil combustion, wood burning (fireplaces), and trash barrels. Pesticides such as 2,4-D

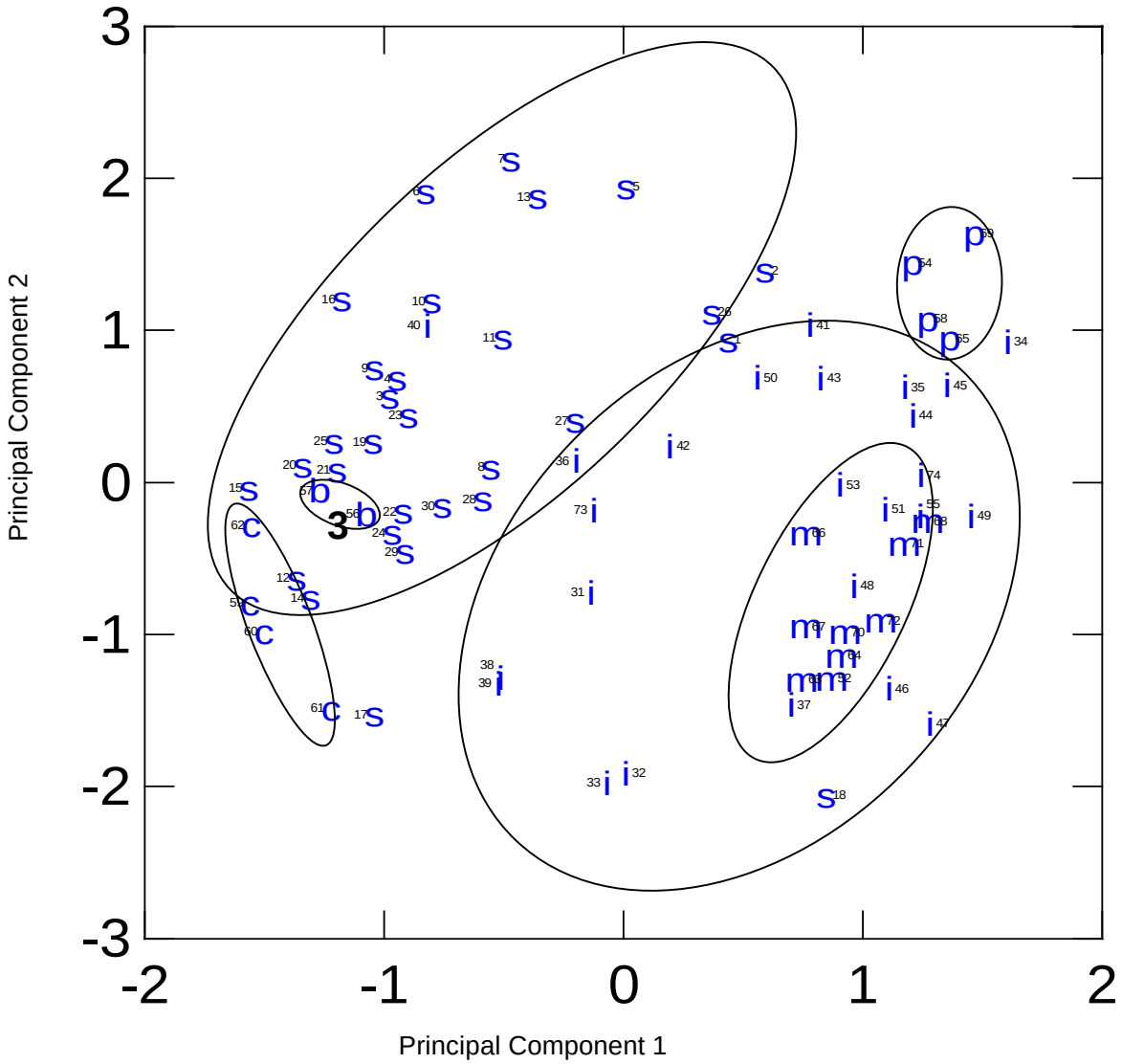
(2,4-dichlorophenoxyacetic acid) and 2,4,5-T (2,4,5- trichlorophenoxyacetic acid) known to be contaminated with dioxins were not included either (Schecter et al., 1997). Many of the Washington dioxin source data were obtained from the *Washington State Dioxin Source Assessment* (Yake et al., 1998). The data used from the Source Assessment were primarily aerial emission data from combustion sources, including municipal and hospital waste incinerators, a cement kiln, and a remelt furnace from an aluminum plant. A detailed data quality review was not conducted on the data obtained from the Source Assessment (Yake et al., 1998). However, only data reporting complete results for the ten dioxin congener groups were used. The fertilizer information was obtained from Chapter 1, *Metals and Dioxins in Fertilizer Products*, of this report. Only those materials containing dioxin at levels above 5 pptr TEQ were included.

None of the pulp and paper mill samples was from aerial emissions. Of the three samples from pulp and paper mills included in this analysis, one was wood ash, one was fly ash, and one was effluent from a Kraft mill.

No useable dioxin source data from pentachlorophenol (PCP), sodium pentacholorphenate (PCP-Na), or biosolids were available within Washington, so this information was obtained from the literature. Commercial formulations of PCP chemicals were analyzed for dioxin content (Hagenmaier and Brunner, 1987). One of the two biosolids samples is a median value from the National Sewage Sludge Survey (EPA 1989). The other biosolids sample was reported as a typical or representative sample from the United Kingdom (Duarte-Davidson et al., 1997).

Due to the limited source data available from Washington, some of the data included were multiple measurements from the same source under different operating conditions at different times. Only data believed to be representative of normal operating conditions were included in the database, with the exception of an activated carbon regenerating facility (Cameron-Yakima). The Cameron-Yakima emissions data are thought to be a "moderate worst case" test using prepared feed material (Yake et al., 1998); however, the facility ceased operation in 1997. The Cameron-Yakima facility was included because it was the only facility of its type in the state, and one of the few on the east side of the state. When it was operating it had the highest dioxin loading in the state of the facilities that had available dioxin information (Yake et al., 1998).

PCA was used to examine the association between the dioxin signature of the soil samples and those of potential dioxin sources. PCA reduced the ten original variables derived from the sample results to three main principal components, based on a criteria of having the principal components account for at least 70% of the original variance of the data set. The first three principal components accounted for about 73% of the total variation of the original data set. The component "loadings" are correlations of the ten original variables with the principal components (Appendix 3-I). A comparison of the loadings within a principal component indicates which variables have the greatest influence on that particular component. Figure 3-5 is a plot of the first two principal component scores for each sample. Several dioxin signature patterns can be recognized by the grouping of various samples.



s = soil sample
I = incinerator
p = pulp and paper, including NutriLime
m = metal associated, including fertilizer products
b = biosolids
c = PCP

Figure 3-5. Two dimensional component scores of the soils and source samples. Ellipses represent closely related groups, and the small numbers refer to the identification of the sample (see Appendices 3-E, 3-H).

The first principal component, and the one that accounted for the most variability (42%), was a combination of the tetra- through hexa- CDDs and CDFs (Appendix 3-I). Samples with a high score for this principal component had high levels of the lower chlorinated congener groups and low levels of the higher chlorinated congeners. The second principal component accounted for approximately 19% of the variability. For samples scoring high on principal component 2, at each level of chlorination, furans (PCDFs) contributed more to the dioxin percentage of the sample than the corresponding dioxin groups (PCDDs). The third principal component was characterized by samples with relatively high levels of penta- through hepta- CDDs and CDFs.

A plot of the two main principal component scores for each sample is shown in Figure 3-5. Although the first two principal components account for only 61% of the total variance, it is much easier to represent graphically than using the three main principal components. A slight random "jitter" was introduced to the plotting program to counteract overlapping values. The closer a sample is to another, the more closely related their signatures are to one another. Based on the analysis, approximately six clusters or groups emerged: soils, biosolids, PCP, pulp and paper mills, incinerators, and metal associated materials. Figure 3-6 shows a dioxin profile (signature) for six groups. The incinerator and soil groups have relatively variable congener signatures and, as a result, encompass a portion of the other groups.

Soil samples showed a high degree of variability but tended to cluster in the upper left quadrant of Figure 3-5. Soil samples are represented by an S and are numbered 1 through 30. With the exception of the incinerators, there was a distinct grouping of the "dioxin signatures" from each of the dioxin sources.

The two biosolid samples are located within the grouping for soil samples (Figure 3-5). The dioxin signature for biosolids is somewhat intermediate between the signatures of soils and PCP (Figure 3-6).

The four PCP samples (59-62) clustered together, overlapping somewhat with the soil grouping. PCP samples are also close to the biosolids; this may be due to PCPs being a primary source of dioxins in biosolids, possibly contaminants in cotton clothing produced from raw materials that have been treated with PCP (Broman et al., 1990; Horstmann and McLachlan, 1995; Jones and Sewart, 1997). Chapter 1 of this report discusses in more detail the potential sources of dioxins in biosolids. Both PCP and biosolid signatures were dominated by the higher level chlorinated dioxins, hepta- and octa-CDDs and CDFs (Figure 3-6).

Dioxin signatures of wastes from pulp mills clustered together, even though samples were collected from different facilities and different media (effluent 54, fly ash 69, wood ash 58). Another sample was pulp mill fly ash; this is used as a fertilizer product marketed as NutriLime (65). The pulp mill samples had relatively high scores for all three principal components. The were dominated by tetra- to penta- CDDs and CDFs (component 1), as well as overall low values of PCDFs compared to PCDDs (component 2), with the exception of TCDF (Figure 3-6).

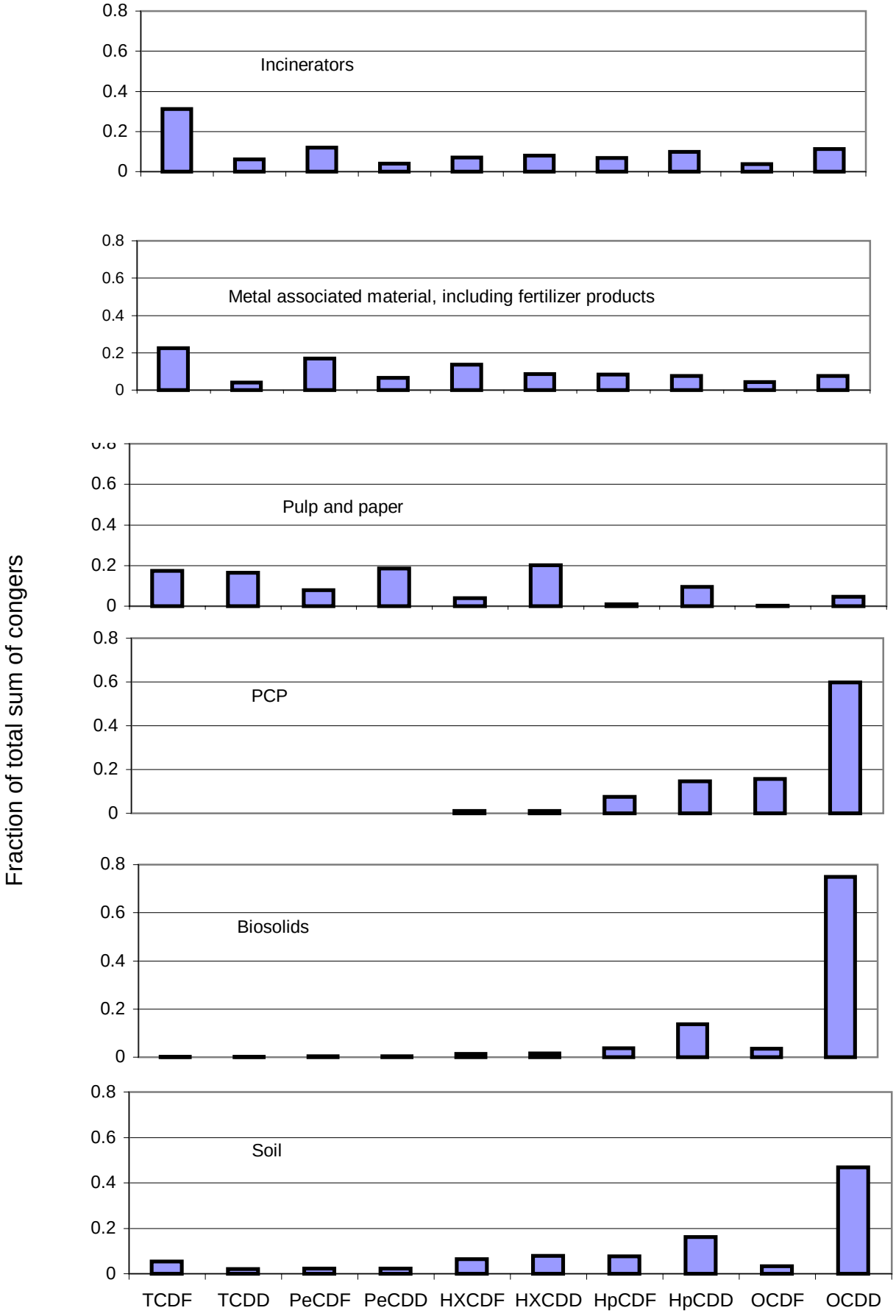


Figure 3-6. Dioxin signatures of various groups.

Incinerators (hospitals, municipal, and the cement kiln) were highly variable in terms of dioxin signatures. There was some overlap between patterns for incinerators and materials associated with metals processing (Figure 3-6). Materials associated with metals processing included (1) fertilizer products (samples 63-72) composed of Frit products, Bay Zinc products, NuLife All Purpose Trace Elements, and McLendon Weed and Feed (2) emissions from the aluminum remelt furnace (sample 52), and (3) a sample from Cameron-Yakima (sample 37). These samples grouped together because they have a common source signature. They all are derived from similar processes, with an association to metal processing or combustion of metal materials. The fertilizer products are discussed in more detail in Chapter 1. It is believed these fertilizers have, as a component, material that is derived from steel mill flue dust.

Conclusions

This report is not a conclusive analysis of the source of dioxins in Washington State soils; however, it does provide some insights.

Due to limitations in data quality (i.e., non-random sampling and small sample numbers), this screening survey did not statistically compare dioxin soil levels among different land uses; however, several observations were made.

Dioxins are found in surface soils throughout Washington State. They were detected in all samples, including samples from remote wilderness areas. Dioxin TEQs in soils sampled ranged from 0.033 to 19 pptr, with a median value of 1.2 pptr.

The three highest values of dioxins were from urban areas. Urban areas also had the greatest range of TEQ values (0.13- 19 pptr). Soils in forested areas appear to have a higher level of dioxins than soils in open areas; however, more samples would be required to verify this. The results of this study indicate that the levels of dioxins detected in these selected Washington State soils are comparable to the results of studies in Spain, Germany, and Austria.

An analysis of the soil samples and potential dioxin sources using principal component analysis clearly showed differences among the dioxin signatures of soil and source samples. Furthermore, dioxin signatures differed considerably within soil samples, as well as between soils and source samples. None of the soil samples is clearly linked to any specific dioxin source.

In summary, soil signatures do not coincide exactly with any of the source signatures evaluated. The closest correlations appear to be with the dioxin congeners associated with PCP and biosolids. The apparent correlation between soils and biosolids signatures may be due to the similarity in sources contributing to these receptors. Much additional work is needed (e.g., tests of additional source types, understanding changes in signatures caused by weathering of soils) before the relative dioxin contribution of various sources can be well understood. It is likely, however, that multiple sources are involved and that air-borne deposition is an important mechanism in the contamination of soil.

Summary of Conclusions

This final report includes a description and findings for three studies (1) metals and dioxins in fertilizer products, (2) metals in soils, and (3) dioxins in soils. These studies provide a better understanding of contaminants in fertilizer products and how some fertilizer components may be affecting Washington State soils.

1. Metals and Dioxins in Fertilizer Products

The objective of this study was to quantify metals and dioxins in fertilizer products. Ecolog randomly sampled and analyzed fertilizer products including 50 bulk agricultural and home-use fertilizers, and micronutrients, to determine their dioxin concentrations. The samples were also analyzed to determine heavy metal concentrations.

Metals in Fertilizer Products

Fertilizer products were analyzed for total metals and leachable metals using the Toxicit Characteristic Leaching Procedure (TCLP). TCLP is used to designate dangerous wastes under the Washington State Dangerous Waste Regulations. TCLP is being used by Ecology as a screening criterion to evaluate whether waste-derived fertilizers meet applicable standards.

Of the 50 products tested, seven failed the TCLP. Two bulk or packaged agricultural fertilizers, one agricultural micronutrient fertilizer, and four home-use packaged fertilizers failed the test for cadmium. Concentrations of cadmium ranged from 1.04 to 2.52 ppm, compared to a federal and state criterion of 1.0 ppm for designation of dangerous waste.

The TCLP metals limits appear to be an adequate screening criterion for predicting whether fertilizers are in compliance with the current land disposal restriction (LDR) standards. Dangerous-waste-derived fertilizers must meet the LDR standards before they are registered as fertilizers in Washington.

Two of the seven fertilizers with high levels of cadmium (relative to the others tested) are potentially hazardous-waste-derived from steel mill flue dust (K061). One of these products (Frit F-503G) has used a non-hazardous waste source of zinc since 1988. K061 is currentl exempt from hazardous waste regulations if it is used to make zinc-containing fertilizer; however, through the rule-making process Ecology will propose the elimination of the K061 exemption.

Dioxins in Fertilizer Products

Most of the fertilizer products tested contained non-detectable or extremely low levels of dioxin. Seventy-two percent (or 36) of the 50 fertilizer products tested had dioxin TEQs of less than 0.1 pptr. A few bulk agricultural fertilizers contained relatively high levels of dioxin. Two fertilizer products had dioxin TEQs greater than 50 pptr: Frit F-503G (84 pptr) and NuLife All-Purpose Trace Elements (54 pptr).

Most of the fertilizers that were sampled had lower dioxin TEQs than the soils surveyed. Onl two of the fertilizer products sampled in 1998 and two of the fertilizer products sampled in 1997 had dioxin TEQs higher than any of the TEQs found in the soils dioxin study. However, the dioxin level in soils after fertilizer products are applied is dependent on application rate. The four products with high TEQs are micronutrients that are applied to soils at very low rates. Calculations of soil concentrations after mixing found that the micronutrients add a minimal amount of dioxins to soil.

A literature review found no studies of dioxin levels in fertilizers. There are no applicable standards for dioxin in fertilizers at this time.

Dioxins in Biosolids

Dioxins have been found to accumulate in biosolids and have been measured in nearly all biosolids tested.

The national data available on dioxin levels in biosolids are more than ten years old, and there are few biosolids data for Washington State. Review of statewide biosolids data and additional sampling are needed.

Initial data interpretation using principal component analyses (PCA) is consistent with the published data suggesting that pentachlorophenol (used to treat cotton for clothing) may be a source of dioxin in municipal biosolids.

2. Metals in Soils

The objective of this study was to determine if certain metals have accumulated in agricultural soils of the Columbia Basin in Washington State. Ecology analyzed agricultural and non-agricultural (background) soils from the Columbia Basin Irrigation Project for seven metal concentrations and compared the results with two other state soil studies. The 33 sites were located primarily in Grant County. Twenty samples came from agricultural soils and 13 from non-agricultural soils. To the extent possible, agricultural and non-agricultural soils were matched.

Zinc and cadmium concentrations show small but statistically significant increases in agricultural fields when compared to background sites. Increased cadmium levels on agricultural fields ma be due to the farming practices used over the last 50 years. Further investigation is necessary to confirm this possibility. The increased zinc levels were purposefully established to correct nutrient deficiencies affecting crop production. The zinc-to-cadmium ratio in this study suggests plants will take up zinc before cadmium. The increased cadmium and zinc soil concentrations in agricultural fields sampled suggest no potential soil quality impairment because the values detected are within the lower range of background comparison studies.

The levels of arsenic, copper, mercury, nickel, lead, total organic carbon, pH, total phosphorus, and cation exchange capacity in soils do not show statistically significant differences between agricultural fields and background sites.

The increased agricultural cadmium levels warrant monitoring over a period of time to determine their rate of increase and to ensure that the levels do not become a concern. To this end, sources of cadmium in fertilizers should be investigated (e.g., phosphate or zinc fertilizer products). Arsenic, copper, lead, mercury, nickel, and zinc concentrations in soils should also be periodically monitored to determine any rate of increase and ensure that levels do not become a concern. Data on the rate of increase of metals in agricultural soils will provide information so that Washington fertilizer standards could be adjusted, if needed, so concentrations of these metals in agricultural soils do not reach a level of concern.

3. Dioxins in Soils

The objective of this study was to provide an initial assessment of typical dioxin concentrations in soils in Washington State. Ecology obtained 30 soil samples in open, forested, and urban areas to determine if dioxins occur in these areas and at what levels.

Testing showed that dioxins are found in surface soils throughout Washington State with values ranging from 0.033 to 19 pptr. All samples had detectable levels of dioxin, including samples from remote wilderness areas. In general, average dioxin levels appear to be higher in urban areas than forested and open areas. Three of the highest detected values of dioxins were from urban areas. This was expected since the primary source of dioxins is from combustion processes. The results of this study indicate that the levels of dioxins detected in these selected Washington State soils are comparable to the results of studies in Spain, Germany, and Austria.

A principal component analysis (PCA) was performed on the soil samples and several potential dioxin sources. This PCA is not a conclusive analysis of the source of dioxins in Washington State soils; however, it does provide some insights. The analysis clearly showed differences between the dioxin signatures of soil and source samples. None of the soil samples is clearl linked to any specific dioxin source. Soil signatures do not coincide exactly with any of the source signatures evaluated. The closest correlations appear to be with the dioxin congeners associated with PCP and biosolids. The apparent correlation between soils and biosolids signatures may be due to the similarity in sources contributing to these receptors.

Much additional work is needed (e.g., tests of additional source types, understanding changes in signatures caused by weathering of soils) before the relative dioxin contribution of various sources can be well understood. It is likely, however, that multiple sources are involved and that air-borne deposition of particulates from combustion sources is an important mechanism in the contamination of soil.

Ecology is sampling agricultural soils for dioxin during April-May 1999. The results of that study will be published as an addendum to this report.

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Recommendations and Actions

Washington State departments of Ecology, Health, and Agriculture recommend

- Continue to implement the Fertilizer Regulation Act by ongoing review, sampling, and analysis of fertilizer products for metals as specified under the Memorandum of Understanding among these agencies.
- In the biennial report to the Legislature (first report due December 1, 1999), report levels of non-nutrient substances in fertilizer products.
- Continue to monitor the levels of metals and other contaminants, as appropriate, in fertilizer products, especially waste-derived materials and phosphate fertilizers.
- Monitor agricultural soils to determine a rate of increase for metals in soils.
- Continue to monitor the progress of EPA and other agencies and organizations in evaluating health and environmental risks associated with fertilizer use.
- Continue to encourage EPA to:
  - ◊ Complete and release the dioxin risk assessment report and the cement kiln dust report that is expected to have standards for dioxin in cement kiln dust.
  - ◊ Adopt metals and dioxin standards for hazardous-waste-derived fertilizers and cement kiln dust used as fertilizers or soil amendments.
  - ◊ Conduct an assessment of all fertilizer products, as well as related research, and develop risk-based metals and dioxin standards.
- Monitor EPA progress on their evaluation of dioxins in biosolids. A proposed EPA rule, due in December 1999, would provide additional direction in this matter.
- Monitor and review other states or countries development of standards for metals or dioxins in fertilizers or soil amendments.
- Ecology complete the study of dioxins in agricultural soils during the spring of 1999.
- Determine if more sampling of dioxins in fertilizers is needed.
- Review and supplement data on dioxins in biosolids from municipalities.

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Ecology Policy Options for Managing Persistent, Bioaccumulative, and Toxic Chemicals in Fertilizers

In August 1998, Ecology announced an agency-wide initiative to address certain contaminants in our environment that are persistent, bioaccumulative, and toxic (PBT). Ecology is developing a strategy to address the following challenges:

1. Prevent the generation of PBT chemicals
2. Virtually eliminate the release of PBTs in the environment
3. Effectively manage or clean up PBT contamination where possible

Ecology's proposed PBT initiative is included in this discussion because of the overlap between PBTs and waste-derived fertilizer products. At least three PBTs were found in some fertilizer products: dioxins, cadmium, and mercury. While Washington recently adopted standards for cadmium and mercury in fertilizer products, it does not have standards for dioxins. In addition, no standards exist for dioxins in fertilizer products in other states or countries (Schultz, 1993).

The options listed below for addressing PBTs are included in this report to provide a more complete picture of the regulatory and non-regulatory alternatives under consideration b Ecology to address the issue of contaminants in fertilizer products. These options are potential actions and interim steps for addressing PBTs in fertilizer products. Ecology will consult with the Departments of Agriculture and Health as issues related to addressing PBTs in fertilizer products unfold.

Ecology options for PBTs in fertilizer

- Eliminate the steel mill flue dust (K061) exclusion in the Washington State Dangerous Waste Regulations (chapter 173-303 WAC) to reduce a source of metals and dioxins in waste-derived fertilizers.
- Re-evaluate the wood ash exclusion in the state Dangerous Waste Regulations (chapter 173-303 WAC) to determine the impact of the exclusion as a possible contributor to dioxin in soils.
- Amend the state Dangerous Waste Regulations and set a dioxin standard for waste-derived fertilizers. Possible standards are:
  - ◊ Non-detectable level of dioxins
  - ◊ "Background" or "typical" levels based on existing levels of dioxin in soil
  - ◊ Levels based on reasonable available technology to remove dioxins from fertilizers and their component sources
  - ◊ Levels that would eliminate the top 10% of highest dioxin concentrations found
  - ◊ Use of the EPA standard from the cement kiln dust report (when final)

- Set a standard for dioxins in all hazardous waste.
- Encourage EPA to address the issue of persistent, bioaccumulative and toxic chemicals in fertilizers nationally.
- Address and eliminate sources of the highest releases of PBTs to the environment.
- Examine sources other than fertilizer products to determine if they have higher releases of PBTs to the environment.
- Ask the Legislature to (1) set strict standards for PBTs in all fertilizer products or (2) ban all dangerous waste from being made into fertilizer products.
- Require fertilizer companies with waste-derived fertilizers to test and report levels of dioxins to Ecology without mandating a standard, to obtain more information about current levels before considering establishing a standard.
- Reward companies with publicity/awards for manufacturing and selling fertilizer products with negligible concentrations of dioxins or PBTs.

Ecology recommendations for PBTs in fertilizers and biosolids

- Work with stakeholders to develop a strategy to minimize PBTs and other metals of concern in fertilizer products.
- Continue to determine the levels of PBTs in fertilizer products, as well as levels of PBTs in agricultural soils, and share that information with the public in a timely manner.
- Commit to a regulatory process to eliminate the steel mill flue dust (K061) exemption in the state Dangerous Waste Regulations in order to reduce a source of metals and dioxins in waste-derived fertilizers.
- Actively engage the biosolids regulated community in investigating the significance of PBTs in biosolids, and in developing appropriate policy and direction.
- Conduct a complete sampling program of dioxins in biosolids in Washington State, or review data from municipalities in the state and supplement these data, as needed.

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Appendices

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Appendix
for
Introduction

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Appendix 1. Conventions used in calculating TEQs

Dioxins occur in many forms or congeners. Of the 210 congeners of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs), only 17 with chlorine atoms in the 2,3,7,8 positions are considered highly toxic (Birnbaum, 1994). Seven PCDDs and ten PCDFs have this configuration. 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) is the most toxic. While PCDDs and PCDFs with chlorine atoms in the 2,3,7,8 positions are considered the most toxic, 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) is considered 1/10 as toxic as 2,3,7,8-TCDD. The ratios adopted by international convention (EPA, 1989) are the basis for the calculation of TEQs as shown in the table below and in Appendices 1-P, 1-Q, and 3-C. TEQ is the sum of the toxicity of the forms present.

Table 1. Toxicity equivalent factors (TEF) for the 17 PCDDs and PCDFs.

	Congener	TEFs (EPA, 1989)
1	2,3,7,8-TCDD	1
2	1,2,3,7,8-PCDD	0.5
3	1,2,3,4,7,8-HxCDD	0.1
4	1,2,3,6,7,8-HxCDD	0.1
5	1,2,3,7,8,9-HxCDD	0.1
6	1,2,3,4,6,7,8-HpCDD	0.01
7	OCDD	0.001
8	2,3,7,8-TCDF	0.1
9	1,2,3,7,8-PCDF	0.05
10	2,3,4,7,8-PCDF	0.5
11	1,2,3,4,7,8-HxCDF	0.1
12	1,2,3,6,7,8-HxCDF	0.1
13	2,3,4,6,7,8-HxCDF	0.1
14	1,2,3,7,8,9-HxCDF	0.1
15	1,2,3,4,6,7,8-HpCDF	0.01
16	1,2,3,4,7,8,9-HpCDF	0.01
17	OCDF	0.001

When one or more of the 2,3,7,8-substituted dioxins or furans is not detected in the sample, the calculation of the toxicity equivalent (TEQ) for that sample can be ambiguous. Three approaches to this dilemma are often used:

A. One approach assumes that if a congener is not detected, its concentration is zero. The TEQ is calculated assuming no contribution from the undetected congeners (ND = 0). This approach yields the *minimum* value for the calculated TEQ.

B. A second approach assumes the congener(s) may have been present at concentrations as high as the detection limit. The TEQ is calculated assuming undetected congeners are present at the detection limit (ND = DL). This approach yields the *maximum* value for the calculated TEQ.

C. A third approach takes the intermediate path and assumes undetected congeners are present at half the detection limit (ND = ½ DL). This approach yields a value for the calculated TEQ intermediate between the first and second method.

The tables in the report text are based on TEQ values calculated using method A described above (e.g., concentrations of undetected congeners are assumed to equal zero). Full analytical results and TEQ calculations for soil and fertilizer samples using these three methods are listed in Appendices 1-P, 1-Q, and 3-C

The difference between minimum and maximum results <u>for a single sample</u> (methods A and B) ranged from 0 to 11 pptr for fertilizer samples, and 0 to 8 pptr for soils. The largest differences are generally found where the detection (or quantification) limits are relatively high. High detection limits are often associated with samples high in complex organic matter, from which it is difficult to extract dioxins. The fertilizer samples with the highest differential between minimum and maximum calculated TEQ were Ponderay Newsprint Fiberay SC (consisting of paper fibers and wood chips) and Kelly Green Recycled Fresh Fish. Both of these materials would be expected to have high concentrations of complex organic matter.

Appendices

for

1. Metals and Dioxins in Fertilizers

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Appendix 1-A. Soil amendments, fertilizers, and micronutrients - products sampled, 1998

Soil Amendments

Manufacturer	*Product Name*	*Grade/Constituents*
Ponderay Newsprint	Fiberay SC	N/A

Bulk/Packaged Agricultural Fertilizers

Manufacturer	*Product Name*	*Grade/Constituents*
Northwest Alloys	High-Mag Gro Powder	1-0-8 + 18% Magnesium* *(Magnesium analysis not guaranteed)
Fort James	NutriLime	12% equiv. CaCO3 (OSU Method)
Unocal	Ammonium Nitrate	34-0-0
Agrium	Ammonium Phosphate Sulfate	16-20-0 + 14% Sulfur
IMC Kalium	Potash	0-0-62.4
Global Recycling and Research	Kelly Green Recycled Fresh Fish	3-2-1
United Agri Products	UAP 0-45-0	0-45-0
High Yield Chemical Company	Sulfur	90% Sulfur

Agricultural Products with Micronutrients

Manufacturer	*Product Name*	*Grade/Constituents*
Frit	F-503G	2.40% Boron
	Sample #1	2.40% Copper
	Sample #2	14.40% Iron
		6.00% Manganese
		0.06% Molybdenum
		5.60% Zinc
RSA	Ruffin-Ready Zn	10% Zinc
Nutrient Technologies	Tech-Flo Zeta Zinc 22	22% Zinc
Stoller	Green Label Micronutrient II Super-	1% Magnesium
	Starter	2% Copper
		1% Manganese
		4% Zinc
Cozinco	Zinc Sulfate Monohydrate Sample #1 (Lab Log# 318085) Sample #2 (Lab Log# 338201)	35.50% Zinc

Appendix 1-A (cont'd) - products sampled, 1998

Agricultural Products with Micronutrients (cont'd)

Manufacturer	*Product Name*	*Grade/Constituents*
Bioplus	Micro 700 Chelated Micronutrients	1-0-3 +
		1.00% Sulfur
		0.025% Boron
		0.07% Copper
		0.10% Iron
		0.70% Manganese
		0.0007% Molybdenum
		0.20% Zinc
Horizon Ag	Micro-Plus	2.00% Iron
		1.00% Manganese
		3.00% Zinc
Western Farm/Monteray	9% EDTA Zinc	9.00% Zinc
Monteray	Premium Zinc 10%	10.00% Zinc
Hydro-Agri/Viking Ship	FS/31 Ferrous Sulfate	31.00% Iron

Home-Use Packaged Fertilizer Products

Manufacturer	*Product Name*	*Grade/Constituents*
J.R. Simplot -	Best 6-20-20XB Premium Plant Food	6-20-20 +
Best Professional Products Division		1.50% Iron
		5.50% Sulfur
		0.75% Zinc
I.F.M.	Gaia's Own Cottonseed Meal	6-2-1
A.H. Hoffman	Ace Tomato & Vegetable Food	8-10-8 +
		8% Calcium
		4% Magnesium
		3% Sulfur
		1% Iron
		0.2% Manganese
Northwest Chemical Corporation dba	Fred Meyer Moss Control-	12-2-4 +
United Horticultural Supply	Plus Lawn Food	18% Sulfur
		10% Iron
Northwest Chemical Corporation dba	Winter Green 15-10-25	15-10-25 +
United Horticultural Supply		3.60% Sulfur
		2% Iron

Appendix 1-A (cont'd) - products sampled, 1998

Home-Use Packaged Fertilizer Products (cont'd)

Manufacturer	*Product Name*	*Grade/Constituents*
Northwest Chemical Corporation dba	Webfoot Turf Treat 15-5-10	15-5-10 +
United Horticultural Supply		2.60% Sulfur
		0.0225% Boron
		3% Iron
		0.05% Manganese
		0.0006% Molybdenum
		0.055% Zinc
Terosa	Rose Food	5-8-2 +
		7.40% Calcium
		2.10% Magnesium
		3.70% Sulfur
		0.03% Boron
		0.40% Iron
		0.12% Manganese
		0.0012% Molybdenum
		0.10% Zinc
Evergro Products	Evergro 23-3-23	23-3-23 +
		2.10% Iron
Pursell Industries	Sta-Green Azalea, Camelia and	14-7-7 +
	Rhododendron Food	0.02% Boron
		0.05% Copper
		1.00% Iron
		0.05% Manganese
		0.005% Molybdenum
		0.05% Zinc
Schultz	Schultz Bloom Plus	10-60-10 +
		0.10% Iron
		0.05% Manganese
		0.05% Zinc

Appendix 1-A (cont'd) - products sampled, 1998

Home-Use Packaged Fertilizer Products (cont'd)

Manufacturer	*Product Name*	*Grade/Constituents*
Northwest Chemical Corporation dba	TurfGo	12-0-0 +
United Horticultural Supply		5.00% Sulfur
		0.50% Magnesium
		6.00% Iron
		2.00% Manganese
Pace International	NuLife 10-20-20	10-20-20
Liquinox	Fully Chelated Iron and Zinc	0.20% Iron
		0.20% Zinc
Pace International	McLendon Weed and Feed 15-5-5	15-5-5
Pace International	NuLIfe Agro 10-15-10	10-15-10 +
		0.08% Zinc
		4.05% Magnesium
		10.00% Sulfur
		0.03% Boron
		0.03% Copper
		0.21% Iron
		0.09% Manganese
		0.0009% Molybdenum
Pursell Industries	Sta-Green Nursery Special	12-6-6 +
		0.02% Boron
		0.05% Copper
		0.25% Iron
		0.05% Manganese
		0.0005% Molybdenum
		0.05% Zinc
QC	Ferrous Sulfate Monohydrate	30% Iron
Ampro Industries/Ringer	AmTurf Wildflower Mix/ Ringer Magic Start	1-1-1
Schultz	Schultz Soluble for Orchids	19-31-17 +
		0.02% Boron
		0.07% Copper
		0.33% Iron
		0.05% Manganese
		0.0005% Molybdenum
		0.07% Zinc
Scotts-Sierra Horticultural Products	Osmocote Vegetable and Bedding Plant Food	14-14-14

Appendix 1-A (cont'd) - products sampled, 1998

Home-Use Packaged Fertilizer Products (cont'd)

Manufacturer	*Product Name*	*Grade/Constituents*
Spectrum Group Division of	Peter's Professional All-Purpose	20-20-2 +
United Industries Corp.	Plant Food	0.50% Magnesium
		0.02% Boron
		0.05% Copper
		0.10% Iron
		0.05% Manganese
		0.0005% Molybdenum
		0.05% Zinc
Chas. H. Lilly Co.	Thrifty Pay-Less Tomato and Vegetable Food	5-10-10
The Garden Grow Company	Whitney Farms 100% Organic Citrus, Berry & Vine Food	7-4-2
Solaris Group of the Monsanto Company	Ortho Upstart Vitamin B-1 Plant Starter with 3-10-3 Fertilizer	3-10-3
Pace International	NuLife All-Purpose Trace Elements	2.40% Boron
		2.40% Copper
		14.40% Iron
		6.00% Manganese
		0.06% Molybdenum
		5.60% Zinc
The Garden Grow Company	Whitney Farms Jersey Green Sand	0-0-3
The Garden Grow Company	Whitney Farms Iron Sulfate	11% Sulfur
		31% Iron
J.R. Simplot Co.	Hydro-Feed with Polyon 20-10-10 Specialty Plant Food	20-10-10
		6.00% Sulfur
Voluntary Purchasing Groups, Inc.	Hi-Yield Pecan and Fruit Tree Fertilizer	12-4-4 +
		1.00% Sulfur
		1.00% Zinc
Northwest Chemical Corporation dba United Horticultural Supply	Webfoot Rhododendron, Camelia, Azalea Food	7-15-10 +
		2% Calcium
		1% Magnesium
		4% Sulfur
		0.0225% Boron
		0.05% Copper
		0.10% Iron
		0.050% Manganese
		0.0005 Molybdenum
		0.060% Zinc
Ringer	Ringer Magic Start Grass Patch	0.5-1-1

Appendix 1-B. Cleaning procedures for metals and PCDD/PCDF sampling

Sampling equipment cleaning procedures

1. Wash with laboratory detergent
2. Rinse several times with tap water
3. Rinse with 10% nitric acid solution
4. Rinse three times with distilled/deionized water
5. Rinse with high purity acetone
6. Rinse with high purity hexane
7. Allow to dry, and seal with aluminum foil

Appendix 1-C. Methods bibliography

All methods are taken from Test Methods for Evaluating Solid Waste, SW-846, EPA, Office of Solid Waste and Emergency Response. Particular methods are as follows.

Laboratory Analysis	Method Used for Analysis
Acid Digestion of Sediments, Sludges, and Soils	Method 3050A. 1996
Inductively Coupled Plasma-Atomic Emission Spectroscopy	Method 6010A. 1996
Arsenic. Atomic Absorption Furnace Technique	Method 7060A. 1996
Selenium. Atomic Absorption Furnace Technique	Method 7740. 1996
Silver. Atomic Absorption Furnace Technique	Method 7761. 1996
Cadmium. Atomic Absorption Furnace Technique	Method 7131A. 1996
Lead. Atomic Absorption Furnace Technique	Method 7421. 1996
Mercury in solid or semi-solid waste (Cold Vapor Technique)	Method 7471A. 1996
Toxicity Characteristic Leaching Procedure (TCLP)	Method 1311. 1996
PCDD's and PCDF's by Hi-Res Mass Spectrometry	Method 8290. 1994

Appendix 1-D. Quality assurance memos

Appendix 1-D is included in a supplemental report, Ecology Publication 99-310:

Supplementary Appendices: Final Report, Screening Survey of Metals and Dioxins in Fertilizer Products and Soils in Washington State

Appendix 1- E. Metals data for multiple and duplicate samples - 1998 sampling results

Variations in product, as well as analyses, can be determined by comparing the results of two samples of several products collected independently. The analyses for Samples #1 and #2 of the Cozinco zinc micronutrient product gave similar results. Note that these samples were obtained from different sources and are not duplicate samples.

Although the average RPD for detected pairs of like metals was 57%, the results for each metal agreed within 5.4 mg/kg-dw. Analyses for total metals were expressed in terms of dry weight (dw), so that the concentration of metals reported represents the concentration in a dried sample.

The two Fort James NutriLime sample results were also similar, with an average relative percent difference of 24% for detected pairs of like metals. The two samples of Frit F-503G gave divergent results, with an average RPD of 78%. Cadmium, lead, and silver concentrations for those samples differed considerably.

Multiple Samples	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	
	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	Lab
Abbreviated Product Description	- dw	- dw	- dw	- dw	- dw	- dw	- dw	- dw	Log#
Fort James Nutri Lime 08/98	**28.5**	**543**	**1.44**	**39**	**89.3**	**0.158**	0.3 U	**0.444**	338181
Fort James Nutri Lime 10/97			**0.93**	**47.5**	**92.3**	**0.210**	0.3 UJ	0.3 U	448081
Cozinco Sample #1	0.3 U	**0.37**	**10.2**	**7.6**	**51.5**	0.005 U	0.3 U	**3.0**	318085
Cozinco Sample #2	0.3 U	**0.13**	**5.0**	**2.2**	**52.2**	0.005 U	0.3 U	**2.7**	338201
Frit F-503G Sample #1	**21.7**	**124**	**10.9**	**184**	**588**	**8.22**	**1.0**	**2.0**	318086
Frit F-503G Sample #2	**32.6**	**137**	**92.0**	**251**	**3490**	**11.9**	**0.45**	**9.27**	348214

Duplicate Samples	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Lab
	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	Log#
Abbreviated Product Description	- dw	- dw	- dw	- dw	- dw	- dw	- dw	- dw	
Cozinco Sample #2	0.3 U	**0.13**	**5.0**	**2.2**	**52.2**	0.005 U	0.3 U	**2.7**	338201
Cozinco Sample #2 duplicate	0.3 U	**0.11**	**4.9**	**1.9**	**53.9**	0.005 U	0.3 U	**2.6**	338202
Hydro-Agri/Viking Ship FS/31	0.3 U	**2.86**	0.03 U	**6.95**	**35.3**	0.005 U	0.3 U	0.05 U	328139
Hydro-Agri/Viking Ship FS/31 dupe.	0.3 U	**3.07**	0.03 U	**6.9**	**37.7**	0.005 U	0.3 U	0.05 U	328125
Webfoot Rhododendron	1.8 J	**19.0 J**	**70.4**	**612 J**	**12**	**0.0077**	0.3 UJ	0.05 U	328140
Webfoot Rhododendron duplicate	**1.1**	**13.7 J**	**69.4**	**844 J**	**6.20 J**	**0.0064**	0.3 UJ	**0.061**	328126
Whitney Farms 100% Organic Citrus	**0.96**	**40.9**	**0.497**	**4.5**	**1.5**	0.005 U	**1.1**	0.05 U	328138
Whitney Farms 100% Organic dupl.	**0.75**	**36.7**	**0.443**	**5.12**	**1.6**	**0.0055**	**0.73**	0.05 U	328127
Evergro 23-3-23	**0.90**	**4.16**	**5.98**	**24.5**	**10.4**	**0.026**	0.3 U	0.05 U	338188
Evergro 23-3-23 duplicate	**0.80**	**3.25**	**5.95**	**24.5**	**35.2**	0.005 U	0.3 U	0.05 U	338189
NuLIfe Agro 10-15-10	**1.8**	**12.7**	**58.9**	**175**	**52.4**	**0.0745**	0.3 U	0.05 U	338195
NuLIfe Agro 10-15-10 duplicate	**2.0**	**8.66**	**47.1**	**138**	**22.3**	**0.0928**	0.3 U	0.05 U	338196

bold detected value

U - The analyte was not detected at or above the reported result.

J - The analyte was postively identified. The associated numerical result is an estimate.

UJ - The analyte was not detected at or above the reported estimated result.

Appendix 1-F. Dioxin data for multiple and duplicate samples - 1998 sampling results

	TEQ ND=0	**TEQ** ND=1/2DL	**TEQ** ND=DL
Multiple Samples			
Abbreviated Product Description	pptr*	pptr*	pptr*
Fort James Nutri Lime (two sample times)			
sampled 10/20/97	35.4	35.8	36.1
sampled 08/10/98	7.35	7.39	7.42
Cozinco 35.50% zinc (two distributors)			
Sample #1 (sampled 7/31/98)	ND	1.13	2.27
Sample #2 (sampled 8/14/98)	0.07	1.12	2.17
Frit F-503G (two distributors)			
Sample #1 (sampled 8/17/98)	26.8	28.8	30.8
Sample #2 (sampled 8/31/98)	145	148	152
Duplicate Samples			
Abbreviated Product Description			
Cozinco 35.50% zinc			
Sample #2	0.07	1.12	2.17
Sample #2 duplicate	0.06	0.67	1.28
Hydro-Agri/Viking Ship FS/31			
Sample	ND	0.81	1.63
Sample duplicate	<0.01	0.54	1.08
Webfoot Rhododendron Food			
Sample	0.01	1.04	2.06
Sample duplicate	0.35	1.19	2.03
Whitney Farms Citrus, Berry, and Vine			
Sample	0.01	1.92	3.83
Sample duplicate	0.01	1.64	3.28
Evergro 23-3-23			
Sample	ND	1.37	2.73
Sample duplicate	ND	1.71	3.43
NuLIfe 10-15-10			
Sample	ND	2.52	5.03
Sample duplicate	0.02	3.69	7.37

ND = non-detect < = less than * = parts per trillion

Appendix 1-G. Total metals in soil amendments, fertilizers, and micronutrients - 1998 sampling results

Soil Amendments

Abbreviated Product Description	As mg/kg-dw*	Ba mg/kg-dw*	Cd mg/kg-dw*	Cr mg/kg-dw*	Pb mg/kg-dw*	Hg mg/kg-dw*	Se mg/kg-dw*	Ag mg/kg-dw*	Lab Log#
Ponderay Newsprint Fiberay SC	**0.45**	**53.0**	**0.586**	**6.3**	**2.73**	**0.044**	0.3 U	0.05 U	318082

Bulk/Packaged Agricultural Fertilizers

Abbreviated Product Description	As mg/kg-dw*	Ba mg/kg-dw*	Cd mg/kg-dw*	Cr mg/kg-dw*	Pb mg/kg-dw*	Hg mg/kg-dw*	Se mg/kg-dw*	Ag mg/kg-dw*	Lab Log#
Northwest Alloys High-Mag Gro	0.3 U	**27.6**	0.03 U	**1.7**	**4.21**	0.005 U	0.3 U	**1.1**	318081
Fort James Nutri Lime	**28.5**	**543**	**1.44**	**39**	**89.3**	**0.158**	0.3 U	**0.444**	338181
Unocal Ammonium Nitrate	0.3 U	**0.83**	**0.042**	0.5 U	0.74	0.005 U	0.3 U	0.05 U	318084
Agrium Ammonium Phosphate Sulfate	**0.60**	**5.52**	**160**	**196**	**2.90**	**0.019**	0.3 U	0.05 U	328131
IMC Kalium Potash	0.3 U	0.1 U	0.03 U	0.5 U	**0.28 J**	0.005 U	0.3 U	0.05 U	338184
Kelly Green Recycled Fresh Fish**	**1.9**	0.1 U	**4.3**	**13.0**	0.2 U	**0.0768**	**0.32**	0.05 U	338182
UAP 0-45-0	**1.0**	**8.01**	**106**	**378**	**3.19**	0.005 U	0.3 U	0.05 U	348210
High Yield Sulfur	0.3 U	**1.21**	0.03 U	0.5 U	**0.40**	0.005 U	0.3 U	0.05 U	348207

Agricultural Micronutrients

Abbreviated Product Description	As mg/kg-dw*	Ba mg/kg-dw*	Cd mg/kg-dw*	Cr mg/kg-dw*	Pb mg/kg-dw*	Hg mg/kg-dw*	Se mg/kg-dw*	Ag mg/kg-dw*	Lab Log#
Frit F-503G Sample #1	**21.7**	**124**	**10.9**	**184**	**588**	**8.22**	**1.0**	**2.0**	318086
Frit F-503G Sample #2	**32.6**	**137**	**92.0**	**251**	**3,490**	**11.9**	**0.45**	**9.27**	348214
RSA Ruffin-Ready Zn**	0.3 U	**0.60**	**0.095**	0.5 U	**0.42**	0.005 U	0.3 U	0.05 U	318083
Tech-Flo Zeta Zinc 22	0.3 U	**0.68 J**	**1.9**	**3.8**	**8.92**	0.005 U	0.3 U	**3.2**	328132
Green Label Super Starter**	**0.57**	**18.1**	**11.1**	**56.3**	**19.0**	0.005 U	0.3 U	**0.071**	338185
Cozinco Sample #1	0.3 U	**0.37**	**10.2**	**7.6**	**51.5**	0.005 U	0.3 U	**3.0**	318085
Cozinco Sample #2	0.3 U	**0.13**	**5.0**	**2.2**	**52.2**	0.005 U	0.3 U	**2.7**	338201
Bioplus Micro 700*	**2.5**	**0.30**	**0.676**	0.5 U	0.2 U	0.005 U	0.3 U	0.05 U	328133
Horizon Ag Micro-Plus**	**0.56**	**0.27**	**0.34**	**0.53**	**4.14**	0.005 U	**0.37**	0.05 U	328135
Western Farm/Monteray 9% Zn**	0.3 U	0.1 U	**0.13**	0.5 U	**1.8**	**0.0068**	**0.34**	0.05 U	328134
Monteray 10% Zinc**	0.3 U	**0.17**	**1.6**	1 U	**0.32**	0.005 U	0.3 U	0.05 U	338186
Hydro-Agri/Viking Ship FS/31	0.3 U	**2.86**	0.03 U	**6.95**	**35.3**	0.005 U	0.3 U	0.05 U	328139

* For fertilizers in liquid form (as indicated by **), metals results are reported in wet weight.

** Fertilizer in liquid form **bold -** detected value

Appendix 1-G (cont'd) - 1998 sampling results

Soil Amendments

Abbreviated Product Description	Co mg/kg-dw*	Mo mg/kg-dw*	Ni mg/kg-dw*	Zn mg/kg-dw*	Lab Log#
Ponderay Newsprint Fiberay SC	**0.56**	**2.7**	**1.9**	**43.6**	318082

Bulk/Packaged Agricultural Fertilizers

Abbreviated Product Description	Co mg/kg-dw*	Mo mg/kg-dw*	Ni mg/kg-dw*	Zn mg/kg-dw*	Lab Log#
Northwest Alloys High-Mag Gro	**0.93**	**0.15**	1.5 U	6 U	318081
Fort James Nutri Lime	**9**	**9.85**	**26.3**	**348**	338181
Unocal Ammonium Nitrate	0.5 U	0.5 U	1.5 U	6 U	318084
Agrium Ammonium Phosphate Sulfate	**3.7**	**7.1**	**219**	**2,110**	328131
IMC Kalium Potash	0.5 U	0.5 U	1.5 U	1 U	338184
Kelly Green Recycled Fresh Fish**	0.5 U	**0.58**	**6.1**	**54**	338182
UAP 0-45-0	**2.7**	**10.7**	**167**	**1,350**	348210
High Yield Sulfur	0.5 U	0.5 U	1.5 U	**9.9**	348207

Agricultural Micronutrients

Abbreviated Product Description	Co mg/kg-dw*	Mo mg/kg-dw*	Ni mg/kg-dw*	Zn mg/kg-dw*	Lab Log#
Frit F-503G Sample #1	**155**	**234**	**202**	**36,100**	318086
Frit F-503G Sample #2	**149**	**401**	**229**	**80,100**	348214
RSA Ruffin-Ready Zn**	0.5 U	4 U	1.5 U	**62,400**	318083
Tech-Flo Zeta Zinc 22	0.5 U	10 U	**6.4**	**348,000**	328132
Green Label Super Starter**	**11.4**	**15.4**	**9.2**	**43,800**	338185
Cozinco Sample #1	0.5 U	0.5 U	**26.2**	**310,000**	318085
Cozinco Sample #2	0.5 U	0.5 U	**2.7**	**286,000**	338201
Bioplus Micro 700**	**0.97**	0.5 U	1.5 U	**4790**	328133
Horizon Ag Micro-Plus**	**8.9**	2 U	**21.9**	**27,700**	328135
Western Farm/Monteray 9% Zn**	0.5 U	4 U	1.5 U	**657,000**	328134
Monteray 10% Zinc**	0.5 U	3 U	**27**	**96,600**	338186
Hydro-Agri/Viking Ship FS/31	**18.2**	**47.9**	**6.9**	**236**	328139

* For fertilizers in liquid form (as indicated by **), metals results are reported in wet weight.

** Fertilizer in liquid form **bold -** detected value

Appendix 1-G (cont'd) - 1998 sampling results

Home-Use Packaged Fertilizer Products

Abbreviated Product Description	As mg/kg-dw*	Ba mg/kg-dw*	Cd mg/kg-dw*	Cr mg/kg-dw*	Pb mg/kg-dw*	Hg mg/kg-dw*	Se mg/kg-dw*	Ag mg/kg-dw*	Lab Log#
J.R. Simplot Best 6-20-20XB	**3.03**	**9.96**	**43.5**	**189**	**85.6**	0.005 U	0.3 U	0.05 U	338198
Gaia's Own Cottonseed Meal (Sample #1)	**1.0**	**25.6**	0.03 U	0.5 U	**2,550**	0.005 U	0.3 U	**0.051**	338183
Gaia's Own Cottonseed Meal (Sample #2)					3 U				43805
A.H. Hoffman Ace Tomato & Veg.	**1.4**	**20.6**	**1.24**	**139**	**4.16**	**0.0555**	0.3 U	0.05 U	348209
Fred Meyer Moss Control	**0.62**	**1.58**	**9.83**	**28.6**	**5.97**	0.005 U	0.3 U	0.05 U	348211
Winter Green 15-10-25	**1.7**	**1.45**	**26.9**	**106**	**2.67**	0.005 U	0.3 U	0.05 U	338197
Webfoot Turf Treat 15-5-10	**1.6**	**13.8**	**15.7**	**52.1**	**28.3**	**0.257**	**0.46**	**0.19**	348213
Terosa Rose Food	**7.05**	**25.1**	**30.1**	**103**	**8.03**	**1.13**	**2.6**	**0.567**	328146
Evergro 23-3-23	**0.90**	**4.16**	**5.98**	**24.5**	**10.4**	**0.026**	0.3 U	0.05 U	338188
Pursell Sta-Green Azalea	**1.4**	**14.5**	**1.78**	**29.9**	**76.0**	**0.364**	0.3 U	0.05 U	338200
Schultz Bloom Plus	**0.58**	**1.15**	0.03 U	**11.2**	0.2 U	**0.045**	0.3 U	0.05 U	328143
TurfGo 12-0-0**	0.3 U	**0.49**	**0.048**	**2.6**	**0.42**	0.005 U	0.3 U	0.05 U	338191
Pace NuLife 10-20-20	**1.3**	**3.44**	**89.3**	**254**	**14.8**	**0.0865**	0.3 U	0.05 U	338194
Liquinox Iron and Zinc**	0.3 U	**0.14**	0.03 U	0.5 U	**0.22**	0.005 U	0.3 U	0.05 U	328142
McLendon Weed and Feed 15-5-5	**1.6**	**59.5**	**15.2**	**5060**	**10.9**	**0.017**	0.3 U	0.05 U	338190
NuLIfe Agro 10-15-10	**1.8**	**12.7**	**58.9**	**175**	**52.4**	**0.0745**	0.3 U	0.05 U	338195
Pursell Sta-Green Nursery Special	**1.3**	**7.27**	**2.5**	**26.0**	**32.6**	**0.652**	0.3 U	**0.16**	348206
QC 30% Iron	**0.3 U**	**2.26**	**2.8**	**5.77**	**16**	0.005 U	0.3 U	0.05 U	348212
Ringer/Amturf Wildflower Mix	**0.34**	**26.0**	**0.161**	**4.9**	**1.5**	**0.014**	0.3 U	0.05 U	328137
Schultz Soluble for Orchids	0.3 U	**1.14**	0.03 U	**4.4**	**0.35 J**	0.005 U	0.3 U	0.05 U	338204
Osmocote Vegetable and Bedding	0.3 U	**141**	0.03 U	**4.8**	**1.2**	0.005 U	0.3 U	0.05 U	328145
Peters Professional All-Purpose	**0.33**	**1.00**	0.03 U	**3.0**	0.2 U	0.005 U	0.3 U	0.05 U	338203
Thrifty Pay-Less Tomato & Veg.	**1.9 J**	**23.6**	**62.1**	**231**	**6.58**	**0.139**	**5.71 J**	**2.88**	338205
Whitney Farms 100% Organic Citrus	**0.96**	**40.9**	**0.497**	**4.5**	**1.5**	0.005 U	**1.1**	0.05 U	328138
Ortho Upstart**	0.3 U	**0.15**	0.03 U	**1.2**	**0.22**	0.005 U	0.3 U	0.05 U	338193
NuLIfe All-Purpose Trace Elements	**75.2**	**205**	**45.9**	**417**	**1940**	**0.206**	**1.9**	**5.28**	328144
Whitney Farms Jersey Green Sand	**11.4**	**16.0**	**0.12**	**79.2**	**4.26**	**0.0054**	**0.94**	0.05 U	338199
Whitney Farms Iron Sulfate	0.3 U	**2.0**	0.03 U	**17**	**29.8**	0.005 U	0.3 U	0.05 U	328141
Hydro-Feed with Polyon 20-10-10	**1.4**	**3.04**	**18.9**	**72.4**	**434**	**0.103**	0.3 U	0.05 U	338187
Hi-Yield Pecan and Fruit Tree Fertilizer	**1.1**	**43.7**	**1.30**	**37.8**	**2.26**	0.005 U	0.3 U	0.05 U	348208
Webfoot Rhododendron	1.8 J	**19.0 J**	**70.4**	**612 J**	**12**	**0.0077**	0.3 UJ	0.05 U	328140
Ringer Magic Start Grass Patch	0.3 U	**7.96**	**0.189**	**15.3**	**17**	0.005 U	0.3 U	0.05 U	338192

U - The analyte was not detected at or above the reported res

J - The analyte was postively identified. The associated numerical result is an estim

UJ - The analyte was not detected at or above the reported estimated res

* For fertilizers in liquid form (as indicated by **), metals results are reported in wet wei

bold - detected value

** fertilizer in liquid form

Appendix 1-G (cont'd) - 1998 sampling results

Home-Use Packaged Fertilizer Products

Abbreviated Product Description	Co mg/kg-dw*	Mo mg/kg-dw*	Ni mg/kg-dw*	Zn mg/kg-dw*	Lab Log#
J.R. Simplot Best 6-20-20XB	**4.2**	**5**	**103**	**6,510**	338198
Gaia's Own Cottonseed Meal (Sample #1)	0.5 U	**1.5**	**1.8**	**46.1**	338183
Gaia's Own Cottonseed Meal (Sample #2)					43805
A.H. Hoffman Ace Tomato & Veg.	**3**	**3.1**	**15.3**	**160**	348209
Fred Meyer Moss Control	**7.8**	2 U	**16.2**	**198**	348211
Winter Green 15-10-25	**3.6**	**2.8**	**40.8**	**386**	338197
Webfoot Turf Treat 15-5-10	**1.6**	**2**	**23.7**	**698**	348213
Terosa Rose Food	**12**	**8.83**	**46.2**	**1,600**	328146
Evergro 23-3-23	**2.1**	**1**	**13**	**228**	338188
Pursell Sta-Green Azalea	**11**	**26.4**	**22.1**	**1,160**	338200
Schultz Bloom Plus	0.5 U	**1.9**	1.5 U	**428**	328143
TurfGo 12-0-0**	**6.9**	**16**	**27.4**	**124 J**	338191
Pace NuLife 10-20-20	**2.1**	**7.87**	**107**	**3,790**	338194
Liquinox Iron and Zinc**	0.5 U	0.5 U	1.5 U	**1,790**	328142
McLendon Weed and Feed 15-5-5	**1.1**	**2**	**17.5**	**251**	338190
NuLIfe Agro 10-15-10	**4.3**	**6.9**	**81.4**	**2,230**	338195
Pursell Sta-Green Nursery Special	**6.7**	**2.9**	**12**	**1,350**	348206
QC 30% Iron	**44.8**	10 U	**32.6**	**340**	348212
Ringer/Amturf Wildflower Mix	0.5 U	**0.89**	1.5 U	**443 J**	328137
Schultz Soluble for Orchids	0.5 U	**6.08**	1.5 U	**740**	338204
Osmocote Vegetable and Bedding	**83.9**	**1.1**	**2.3**	**43**	328145
Peters Professional All-Purpose	**2.5**	**4.8**	1.5 U	**589**	338203
Thrifty Pay-Less Tomato & Veg.	**1.2**	**6.6**	**52.5**	**1,110**	338205
Whitney Farms 100% Organic Citrus	0.5 U	**4**	**4.6**	**736**	328138
Ortho Upstart**	0.5 U	0.5 U	1.5 U	**25.6 J**	338193
NuLIfe All-Purpose Trace Elements	**222**	**553**	**383**	**72,700**	328144
Whitney Farms Jersey Green Sand	**4.6**	0.5 U	**12**	**63.9**	338199
Whitney Farms Iron Sulfate	**41.7**	**73.4**	**27.3**	**196**	328141
Hydro-Feed with Polyon 20-10-10	**1.3**	**1.9**	**35**	**288**	338187
Hi-Yield Pecan and Fruit Tree Fertilizer	**2.3**	**0.52**	**8**	**5,390**	348208
Webfoot Rhododendron	**3.4**	**11.9**	**83**	**1,070**	328140
Ringer Magic Start Grass Patch	0.5 U	**0.76**	1.5 U	**45.7**	338192

U - The analyte was not detected at or above the reported resu

J - The analyte was postively identified. The associated numerical result is an estima

UJ - The analyte was not detected at or above the reported estimated res

* For fertilizers in liquid form, as indicated by **, metals results are reported in wet weig

bold - detected value

** fertilizer in liquid form

Appendix 1-H. Standards for the maximum addition of metals to soils by the application of commercial fertilizers

The Washington Standards for Metals were adapted from an existing set of Canadian standards for metals in fertilizers as directed by law RCW 15.54.820.

Constituent	Canadian Standards[1]	Washington Standards[2]
Arsenic (As)	15. kg/ha	.297 lbs./acre/year
Cadmium (Cd)	4.	.079
Cobalt (Co)	30.	.594
Lead (Pb)	100.	1.981
Mercury (Hg)	1.	.019
Molybdenum (Mo)	4.	.079
Nickel (Ni)	36.	.713
Selenium (Se)	2.8	.055
Zinc (Zn)	370.	7.329

[1] Long-term (45 year) cumulative metals additions to the soil in kilograms/hectare (Canadian Trade Memorandum T-4-93, August 1996).

[2] Maximum acceptable metals additions to soils in Washington obtained by dividing the Canadian Standards by 45 and converting to pounds/acre (WAC 16-200-7064).

Appendix 1-I. TCLP limits

Metal	TCLP Limit, mg/L	20X TCLP Limit mg/kg dw
Arsenic	5.0	100
Barium	100.0	2,000
Cadmium	1.0	20
Chromium	5.0	100
Lead	5.0	100
Mercury	0.2	4.0
Selenium	1.0	20
Silver	5.0	100

TCLP analyses were run for samples with total metals concentrations greater than 20X TCLP limit. When total metals are below 20X the TCLP limit, TCLP is, by definition, not exceeded.

Appendix 1-J. The Ecology fertilizer review process

Beginning July 1, 1999, the fertilizer review process required by law (RCW 15.54.820) states that the Washington State Department of Ecology will:

- Review waste-derived and micronutrient fertilizers to determine if products pass dangerous waste criteria.
- Advise if these products should be registered by the Washington State Department of Agriculture for use as a fertilizer in Washington State (Washington State Register, 1998).

Ecology review criteria for waste-derived and micronutrient fertilizers require fertilizer manufacturers to provide information in addition to that required by the Department of Agriculture for the annual registration of fertilizer products to be distributed and sold in Washington. That additional information will enable Ecology to determine if these products meet the state Dangerous Waste (DW) Regulations for dangerous wastes to be applied to the land. If these products are unable to meet Ecology's review criteria, or the manufacturers are unable to otherwise prove that the DW Regulations do not apply, Ecology will not recommend the product for registration by the Department of Agriculture.

The Ecology review criteria are:

- Toxicity Characteristic Leaching Procedure (TCLP) analyses for arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver.
- Total Halogenated Organic Compounds (HOCs).
- Total Polycyclic Aromatic Hydrocarbons (PAHs).

If a fertilizer product exceeds the regulatory limit for any of these criteria, the manufacturer must provide documentation to Ecology showing the product is not subject to the state DW Regulations or showing that the product is in compliance with the DW Regulations.

Appendix 1-K. Comparison of January and July-August metals in fertilizer products -

Abbreviated Product Description	As	Ba	Cd	Cr	Pb	Hg	Se	Ag	Lab Log#
	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw	
Kelly Green Fresh Fish Fert. 8/98	**1.9**	0.1 U	**4.3**	**13.0**	0.2 U	**0.0768**	**0.32**	0.05 U	328182
Kelly Green Fresh Fish Fert. 1/98	**2 U**	**0.14**	**4.20**	**20.2**	1 U	**0.111**	2 U	0.25 U	
Cozinco Sample #1 7/98	0.3 U	**0.37**	**10.2**	**7.6**	**51.5**	0.005 U	0.3 U	**3.0**	318085
Cozinco Sample #2 8/98	0.3 U	**0.13**	**5.0**	**2.2**	**52.2**	0.005 U	0.3 U	**2.7**	338201
Cozinco 1/98	4 U	**0.51**	**10.3**	**2.1**	**119**	0.005 U	4 U	**2.9**	058156
QC 30% Iron 8/98	0.3 U	**2.26**	**2.8**	**5.77**	**16**	0.005 U	0.3 U	0.05 U	
QC 30% Iron 1/98	100 UJ	**2.1**	**2.1**	**6.18**	**23.1**	0.005 U	200 UJ	2 UJ	058172

bold **detected value**

U - The analyte was not detected at or above the reported result.

J - The analyte was postively identified. The associated numerical result is an estimate.

UJ - The analyte was not detected at or above the reported estimated result.

Appendix 1-L. Fertilizer metals data - January 1998 samples*

Lab Log#:	058155	058156	058157	058158	058159	058160	058161	058162
Field ID:	H0939	H1924	H0762	H1255	H1253	H1251	H1257	H0950
	mg/L**	mg/kg-dw	mg/L**	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw
Aluminum	3.7	82.6	1.2 U	795	16	4.2	95.8	2 U
Antimony	2.7 U	4 U	2.5 U	4 U	4 U	8.2	4 U	4 U
Arsenic	2.7 U	4 U	2.5 U	4 U	4 U	4 U	4 U	4.2
Barium	0.07 U	0.51	0.065	31.5	85.5	0.5	3.41	2.44
Beryllium	0.07 U	0.1 U	0.062 U	0.19	0.1 U	0.1 U	0.1 U	0.1 U
Cadmium	1.5	10.3	0.31 U	0.5 U	0.5 U	8.19	0.5 U	0.5 U
Calcium	26.5	299	8.7	1190	190000	657	32000	845
Chromium	0.34 U	2.1	0.31 U	0.5 U	10.5	1.2	1.4	1.1
Cobalt	0.35	0.5 U	0.31 U	0.5 U	0.5 U	0.5 U	0.5 U	288
Copper	2.2	3.8	0.62 U	1 U	1 U	3.9	15.5	15400
Iron	1.4 U	2130	6.0	430	11	29.4	524	35500
Lead	1.4 U	119	1.2 U	3.5	2 U	13	2.0	2 U
Magnesium	3.4 U	50.3	3.1 U	218	87.1	261	4950	51000
Manganese	3.10	291	0.28	42.9	3.27	10.2	15.4	36400
Molybdenum	0.34 U	0.5 U	0.43	0.5 U	0.5 U	0.5 U	0.5 U	846
Nickel	60.7	4.3	0.62 U	1.1	1 U	8.2	1.6	1.5
Potassium	1400	100 U	2020	140	100 U	580	45300	1680
Selenium	2.7 U	4 U	2.5 U	4 U	4 U	4 U	4 U	4 U
Silver	2.0	2.9	0.31 U	0.5 U	0.5 U	2.7	0.5 U	0.76
Sodium	843	502	3430	1270	128	11600	4210	23400
Strontium	0.068 U	0.92	0.11	26.4	3050 J	4.82	132 J	11.3 J
Thallium	3.4 U	5 U	3.1 U	5 U	5 U	5 U	5 U	5 U
Titanium	0.34 U	0.57	0.31 U	17	4.4	0.5 U	4.5	55.8
Vanadium	0.14 U	0.2 U	0.12 U	0.2 U	0.2 U	0.2 U	0.37	0.2 U
Zinc	258000	348000	1.29	13	15	339000	64.8	13900
Mercury	3.3**	0.005 U	3.1** U	0.005 U	0.005 U	0.005 U	0.077	0.005 U

* Fertilizers are listed in Appendix 1-M.

** Liquid samples. Mercury as ug/L for these samples

Appendix 1-L (cont'd) - January 1998 samples

Lab Log	058163	058164	058165	058166	058167	058168	058169	058170
Field ID	H0761	H1256	G3682	G3683	G3684	G3685	G3687	G3688
	mg/kg-dw	mg/kg-dw	mg/L**	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw
Aluminum	2 UJ	1530	346	751	126	7.2	5500	186
Antimony	4 UJ	4 U	2 U	5.4	4 U	4 U	4 U	4 U
Arsenic	4 UJ	4 U	2 U	4 U	4 U	4 U	14	20
Barium	0.94	9.87	0.14	11.5	0.84	0.16	53	7.56
Beryllium	0.1 U	0.15	0.19	0.1 U	0.1 U	0.1 U	4.2	0.1 U
Cadmium	2.5	0.5 U	4.20	0.5 U	0.5 U	0.5 U	115	0.5 U
Calcium	753	232000	551	267000	399000	111	289000	30100
Chromium	3.9	11.5	20.2	11.5	0.5 UJ	0.5 U	454	1.1
Cobalt	64.6	0.5 U	0.25 U	0.95	0.5 U	0.5 U	1.6	0.96
Copper	5 UJ	1.6	2.0	15.6	6.4	3.7	79.0	3.2
Iron	2 UJ	893	251	2310	209	51.2	5300	433
Lead	2 UJ	2 U	1 U	7.0	2 U	2.4	8.1	2 U
Magnesium	533	18400	262	478	1710	17	2750	8020
Manganese	303000	39.5	20.2	46.8	28.3	0.92	86.6	34.2
Molybdenum	34.5	0.5 U	0.56	0.5 U	0.5 U	0.5 U	16.1	0.58
Nickel	66.2	1.1	5.1	2.7	1.3	1 U	119	1.4
Potassium	2690	510	2160	150	100 U	100 U	3420	20000
Selenium	4 U	4 U	2 U	4 U	4 U	4 U	27	4 U
Silver	17.9	0.5 U	0.25 U	0.5 U	0.5 U	0.5 U	4.9	0.5 U
Sodium	681	1170	1290	98.2	27	23	3370	26200
Strontium	16	883 J	2.77	1130 J	838	1.86	752 J	605 J
Thallium	5 UJ	5 U	2.5 U	5 U	5 U	5 U	5 U	5 U
Titanium	0.5 U	18.2	4.70	67.2	0.5 U	0.5 U	56	6.75
Vanadium	0.2 U	0.98	35.9	2.77	0.4	0.2 U	848	2.32
Zinc	430	11	70.5	15	4.4	6.7	1320	34.7
Mercury	0.005 U	0.005 U	111**	0.005 U	0.005 U	1.25 J	0.315	0.024

** Liquid samples. Mercury as ug/L for these samples

Appendix 1-L (cont'd) - January 1998 samples

Lab Log	058171	058172	058173	058174	058175	058176	058177
Field ID	G3689	G3489	G3490	G3491	G3492	H0947	G3690
	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw
Aluminum	13000 J	134	538	5110	23.3	6.9	12600
Antimony	4 U	4 U	4 U	4 U	4.1	4 U	22 J
Arsenic	7.0	100 UJ	4 U	15	4 U	4 U	4460
Barium	13.8	2.1	14	194	0.42	1.81	17.1 J
Beryllium	1.79	0.1 U	0.18	0.13	0.1 U	0.1 U	0.22
Cadmium	2.0	2.1	0.70	2.3	0.5 U	0.5 U	18.9
Calcium	177000 J	4870	20100	15300	11600	226	33700
Chromium	59.4 J	6.18	5.11	339	10	0.59	17.2
Cobalt	2.5	49.5	0.5 U	3.6	0.5 U	0.5 U	12.6
Copper	2.0	25	50.8	229	4.0	1.1	289
Iron	11900	299000	957	37800	101	32.7	112000
Lead	2 U	23.1	5.8	64.2	2 U	2 U	2420
Magnesium	14200 J	9090	7470	4530	110	51.3	18400
Manganese	208 J	1050	54.2	210	16.9	5.31	722
Molybdenum	3.9	0.5 UJ	1.5	7.63	0.5 U	0.5 U	4.7
Nickel	8.8	60	3.1	31	1.1	1.9	9.4
Potassium	2630	100 U	113000	5060	100	6480	180
Selenium	4 U	200 UJ	4 U	4 UJ	4 U	4 U	4 UJ
Silver	0.5 U	2 UJ	0.5 U	13.2	0.5 U	0.5 U	16
Sodium	1150	163	1230	1270	33	103000	58.1
Strontium	272.0	1.91	45.9	232	4.95	2.65 J	37.5 J
Thallium	5 U	50 UJ	5 U	7.4	5 U	5 U	13
Titanium	176	2250	11.5	44.8	0.91	0.5 U	53 J
Vanadium	92	30	6.82	8.57	0.2 U	0.2 U	40.0
Zinc	43	291	96.5	477	4.6	11	8760
Mercury	0.005 U	0.005 U	0.005 U	0.778	0.005 U	0.005 U	13.7

Appendix 1-M. Fertilizer products - January 1998 samples

Lab Log #	Field I.D.	Material	Company
058155	H0939	Zinc	UAP Northwest
058156	H1924	Granular zinc sulfate monc	Cozinco
058157	H0762	Trisert CB	Tessenderlo-Kerley
058158	H1255	Sulfur	Montana Sulfur
058159	H1253	Calcium nitrate	Hydro-Agri
058160	H1251	Zinc sulfate monohydrate	Chemical and Pigment Company
058161	H1257	Organic turf fertilizer	BioProducts
058162	H0950	Microplex	Miller Chemical Company
058163	H0761	Manganese	American Microtrace
058164	H1256	Gypsum	Greenacres Gypsum
058165	G3682	Organic fish fertilizer	Global Recycling
058166	G3683	Gypsum	U.S. Gypsum
058167	G3684	Limestone	Chemical Lime of Canada
058168	G3685	Ammonium sulfate	Agrium
058169	G3687	Rock phosphate	Garden Grow Company
058170	G3688	Kelp meal	Garden Grow Company
058171	G3689	Super phosphate	Voluntary Purchasing Group
058172	G3489	Ferrous sulfate	QC Corporation
058173	G3490	Organic turf fertlizer	Ecosoil Systems
058174	G3491	Biosolid fertilizer	Milorganite
158175	G3492	Diammonium phosphate	Monsanto
058176	H0947	Solubor	U.S. Borax
058177	G3690	Ironite	Ironite Company

Appendix 1-N. Metals results for waste-derived fertilizers and soil amendments - October 1997

Source	Product	As	Cd	Cu	Pb	Hg	Ni	Zn
		mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw
Fort James	**hog fuel boiler ash**							
	Dioxin study:	49.3	0.93	91.5J	92.3	0.210	33.1	381J
	Metals screening study:	66	2.1U	159	171	0.414	32	581
Holnam	**cement kiln dust**							
	Dioxin study:	18.8	2.4	172J	230	0.772	19.4	1380J
	Metals screening study:	37	3.6	158	150	0.041	18	1770
Bay Zinc	**Zinc micronutrient**							
	18% Blu-Min							
	Dioxin study:	27.0	269	1730J	11,700	4.32	70.0	184000J
	Dioxin study duplicate:	28.1	267	1750J	11,600	4.56	68.8	189,000J
	Metals screening study:	34U	275J	1680J	11,300J	3.36J	83J	178,000J
	LHM							
	Dioxin study:	29.5	21.5	419J	738	1.89	33.2	225000J
	Metals screening study:	35U	52.1	672	1400		61.6	203,000
	Liquid product*							
	Dioxin study:	46.2J*	25400*	9020*	13300*	20.5*	3570*	81000000*

Dioxin study - Ecology sampling of waste-derived fertilizer products and micronu
(unpublished).

Metals screening study - Department of Agriculure sampling of fertilizers and industrial by-p
fertilizers (Bowhay et al, 1997.)

* Liquid product as µg/L. Liquid density = 1.33

J - estimated value

U - The analyte was not detected at or above the reported result.

Appendix 1-N (cont'd) - October 1997

Source	Product	Sb	Be	Cr	Se	Ag	Tl
		mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw	mg/kg-dw
Fort James	**hog fuel boiler ash**						
	Dioxin study:	5UJ	0.65	47.5J	0.3UJ	0.3U	0.3UJ
	Metals screening study:	21UJ	0.7U	46.7	27U	2.1UJ	27U
Holnam	**cement kiln dust**						
	Dioxin study:	5UJ	0.31	29.8J	0.3UJ	0.97	0.3UJ
	Metals screening study:	30UJ	1U	73.2	40U	3UJ	40U
Bay Zinc	**Zinc micronutrient**						
	18% Blu-Min						
	Dioxin study:	30UJ	0.32	529J	7.88J	37.4	0.3UJ
	Dioxin study duplicate:	30UJ	0.34	525J	7.90J	38.1	0.3UJ
	Metals screening study:	42J	1.1U	580J	45U	38.5J	45U
	LHM						
	Dioxin study:	30UJ	0.14	29.9J	2.2J	2.6	0.3UJ
	Metals screening study:	44J	1.2U	67.8	50U	5.4	100U
	Liquid product*						
	Dioxin study:	10,000UJ*	168J*	3170*	62.3J*	735*	6UJ*

* Liquid product as µg/L. Liquid density = 1.33

utrients, fall 1997

J - estimated value

product

U - The analyte was not detected at or above the reported result.

Appendix 1-O. Dioxin TEQs in soil amendments, fertilizers, and micronutrients – 1998 sampling results

Soil Amendments	**TEQ** ND=0	**TEQ** ND=1/2DL	**TEQ** ND=DL	
	pptr*	pptr*	pptr*	
Abbreviated Product Description				*Lab Log#*
Ponderay Newsprint Fiberay SC	0.40	6.0	12	318082

Bulk/Packaged Agricultural Fertilizers

Abbreviated Product Description				Lab Log#
Northwest Alloys High-Mag Gro	0.01	0.46	0.91	318081
Fort James Nutri Lime	7.4	7.4	7.4	338181
Unocal Ammonium Nitrate	0.0	2.0	4.1	318084
Agrium Ammonium Phosphate Sulfate	0.0	1.1	2.2	328131
IMC Kalium Potash	0.02	0.73	1.4	338184
Kelly Green Recycled Fresh Fish	1.4	5.2	9.4	338182
UAP 0-45-0	0.05	0.49	0.93	348210
High Yield Sulfur	0.0	2.0	4.1	348207

Agricultural Products with Micronutrients

Abbreviated Product Description				Lab Log#
Frit F-503G Sample #1	27	29	31	318086
Frit F-503G Sample #2	140	150	150	348214
RSA Ruffin-Ready Zn	<0.01	0.49	0.98	318083
Tech-Flo Zeta Zinc 22	0.01	0.74	1.5	328132
Green Label Super Starter	0.29	1.5	2.6	338185
Cozinco Sample #1	0.00	1.1	2.3	318085
Cozinco Sample #2	0.07	1.1	2.2	338201
Bioplus Micro 700	0.00	0.50	1.0	328133
Horizon Ag Micro-Plus	<0.01	1.7	3.3	328135
Western Farm/Monteray 9% Zn	<0.01	0.34	0.68	328134
Monteray 10% Zinc	0.04	0.54	1.0	338186
Hydro-Agri/Viking Ship FS/31	0.00	0.81	1.6	328139

* parts per trillion. Solid samples on dry-weight basis. Liquid samples on volume basis. TEQs with non-detects set at zero.

Appendix 1-O (cont'd) - 1998 sampling results

Home-Use Packaged Fertilizer Products	**TEQ** ND=0	**TEQ** ND=1/2DL	**TEQ** ND=DL	
	pptr*	pptr*	pptr*	
Abbreviated Product Description				Lab Log#
J.R. Simplot Best 6-20-20XB	0.03	1.2	2.3	338198
Gaia's Own Cottonseed Meal	0.0	0.67	1.3	338183
A.H. Hoffman Ace Tomato & Veg.	0.06	1.4	2.8	348209
Fred Meyer Moss Control	0.03	1.0	2.0	348211
Winter Green 15-10-25	0.06	1.4	2.6	338197
Webfoot Turf Treat 15-5-10	1.2	2.1	3.0	348213
Terosa Rose Food	<0.01	1.4	2.9	328146
Evergro 23-3-23	0.0	1.4	2.7	338188
Pursell Sta-Green Azalea	0.15	1.8	3.3	338200
Schultz Bloom Plus	0.05	0.85	1.6	328143
TurfGo 12-0-0	0.03	0.54	1.0	338191
Pace NuLife 10-20-20	0.0	1.8	3.6	338194
Liquinox Iron and Zinc	<0.01	0.42	0.83	328142
McLendon Weed and Feed 15-5-5	5.4	6.6	7.8	338190
NuLife Agro 10-15-10	0.0	2.5	5.0	338195
Pursell Sta-Green Nursery Special	3.2	4.1	5.0	348206
QC 30% Iron	<0.01	1.0	2.1	348212
Ringer/Amturf Wildflower Mix	0.10	2.4	4.8	328137
Schultz Soluble for Orchids	0.09	0.90	1.7	338204
Osmocote Vegetable and Bedding	0.00	1.2	2.3	328145
Peters Professional All-Purpose	0.11	0.93	1.8	338203
Thrifty Pay-Less Tomato & Veg.	0.01	2.4	4.7	338205
Whitney Farms 100% Organic Citrus	0.01	1.9	3.8	328138
Ortho Upstart	0.08	0.58	1.1	338193
NuLife All-Purpose Trace Elements	54	54	54	328144
Whitney Farms Jersey Green Sand	0.16	0.85	1.5	338199
Whitney Farms Iron Sulfate	<0.01	1.1	2.2	328141
Hydro-Feed with Polyon 20-10-10	0.00	1.2	2.5	338187
Hi-Yield Pecan and Fruit Tree Fertilizer	0.65	1.4	2.0	348208
Webfoot Rhododendron	0.01	1.0	2.1	328140
Ringer Magic Start Grass Patch	0.00	0.70	1.4	338192

* parts per trillion. Solid samples on dry-weight basis. Liquid samples on volume basis. TEQs with non-detects set at zero.
ND = non-detect DL = detection limit
ND = 0: if congener not detected, concentration assumed = 0
ND = 1/2 DL: if congener not detected, concentration assumed = 1/2 detect limit
ND = DL: if congener not detected, concentration assumed = detect limit

Appendix 1-P. Dioxin data and TEQ calculations - 1997 sampling results

Appendix 1-P is included in a supplemental report, Ecology Publication 99-310:

Supplementary Appendices: Final Report, Screening Survey of Metals and Dioxins in Fertilizer Products and Soils in Washington State

Appendix 1-Q. Dioxin data and TEQ calculations – 1998 sampling results

Appendix 1-Q is included in a supplemental report, Ecology Publication 99-310:

Supplementary Appendices: Final Report, Screening Survey of Metals and Dioxins in Fertilizer Products and Soils in Washington State

Appendix 1-R. Dioxin TEQs in fertilizers and micronutrients - 1997 sampling results

	TEQ ND=0	TEQ ND=1/2DL	TEQ ND=DL	*Lab Log#*
Bulk/Packaged Agricultural Fertilizers	pptr**	pptr	pptr	
Allied Minerals Dolomite	ND	0.42	0.84	448080
Fort James Nutri Lime	35	36	36	448081
Holnam Cement Kiln Dust	0.95	1.9	2.9	448083
Agricultural Micronutrients				
Bay Zinc K061	820	830	840	448084
Bay ZincTire Dust	1.6	2.7	3.8	448085
Bay Zinc Blu-Min	340	340	340	448087
Bay Zinc LHM	5.6	9.0	12	448088
Bay Zinc Liquid	0.64	0.64	0.64	448089

* Groupings by fertilizer type are tentative and may change.
** Parts per trillion. Solid samples on weight basis (ng/kg = pg/g). Liquid samples on volume basis (ng/L = pg/mL).
ND = non-detect DL = detection limit
ND = 0: if congener not detected, concentration assumed = 0
ND= 1/2 DL: if congener not detected, concentration assumed = 1/2 detect limit
ND = DL: if congener not detected, concentration assumed = detect limit

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Appendices
for
2. Metals in Soils

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Appendix 2-A1. Field cultivation history by crop

Sample #	1998 Crop	Initial Cultivation	Years in Production by Crop					
			Row Crops	***Hay***	***Small Grains***	***Pasture***	***Orchard***	***Other***
707	Alfalfa	1955	4 (Bean 1, Corn 3)	10	6 (Wheat)			# Years Unknown (Carrot seed)
719	Alfalfa	NA[1]						
711	Alfalfa	1955	3	20+	3			
725	Alfalfa	1958	8	18	8	6		
723	Alfalfa	1960		# Years Unknown	# Years Unknown			
731	Alfalfa	1954						
709	Alfalfa	Before 1951	5 (Bean, corn)	5	5			
703	Apples	Early 1950's	45				3	
705	Apples	NA[1]						
701	Apples	1954	# Years Unknown (Corn, Potato, Bean, Pea)		# Years Unknown (Wheat)		4	
713	Bean							
740	Bean	At CBIP[2] Start (1950's)	# Years Unknown	# Years Unknown	# Years Unknown			
717	Corn	1973	5 (Corn)	17	3			
715	Wheat	Unknown Before 1980	10-15	4	# Years Unknown			
742	Pasture	Late 1950's			# Years Unknown	# Years Unknown		
738	Potato	1956	20	10	8			4 (Asparagus)
728	Primrose	1910	30	20	80			16 (Seed)
739	Sugar Beet	At CBIP[2] Start (1950's)	# Years Unknown	# Years Unknown	# Years Unknown			
733	Wheat	1957	24		7			10 (Peppermint)
737	Wheat	1956	10	3	30			

[1]NA=information not available
[2] Columbia Basin Irrigation Project

Appendix 2-A2. Site selection criteria for metals in soils study

Selection criteria for agricultural field sampling included (Holmgren et al., 1993):

- No obvious aerial deposition from industrial or automotive sources. Sites selected should be at least:
  - ◊ 8 km downwind from any stack emitter such as coal-fired generators, smelters, and foundries,
  - ◊ 200 m from US or state highways such as I-90,
  - ◊ 100 m from rural roadways,
  - ◊ 100 m from current, abandoned, or known obliterated building sites, and
  - ◊ 50 m from field boundaries.
- No known use of orchard pesticides such as lead arsenate; sites should be at least 8 km downwind of active orchard pesticides to minimize drifting.
- No known applications of biosolids or sewage sludge.
- If an appropriate matched non-agriculture site cannot be located, an agriculture site will be excluded.

Appendix 2-B. Landowners' reasons for rejecting study participation

None of the landowners contacted had heard of this study before our initial contact. Each contacted landowner was given the same information about the study and given the opportunity to ask questions or consult with others before deciding. Only two of the eight landowners who rejected the opportunity to participate opted to consult with other people prior to rejecting the opportunity. The other six rejections occurred during the initial contact. Those contacts were short, lasting only several minutes, with few questions from the landowners.

Listed below are the reasons given for not choosing to participate in this study.

- "I don't trust the Government."
- "I don't like Ecology and this is against Cenex and the Farmers."
- "I don't like the idea of it."
- "This hits me cold, I don't have enough information about it, I might say yes if I had heard about it before."
- "I don't trust the government and I don't like some of the things they are doing like the nitrogen in the groundwater issue and talking about removing the dams for the salmon."
- "I have leased the farm and I don't think the operator would want you to trample the corn (unharvested corn field)."

Neither of the two landowners who took several days to decide gave a reason for not participating.

Appendix 2-C. Distance between agricultural sites and background sites

Sample Number	Soil type	Proximity to Background site	Background Site Number
709	Warden silt loam	Adjacent	710
701	Warden silt loam	9.65 km	
703	Shano silt loam	Adjacent	702
705	Shano silt loam	1.61 km	
723	Scoon silt loam	6.44 km	745
728	Novark silt loam	Adjacent	729
733A	Kennewick silt loam	Adjacent	730
737	Kennewick silt loam	3.22 km	
719	Kennewick silt loam	33.8 km	
739	Sagemoor silt loam	8.05 km	744
707	Ephrata fine sandy loam	3.22 km	746
717	Ephrata fine sandy loam	24.1 km	
738	Kennewick fine sandy loam	9.65 km	747
740	Royal very fine sandy loam	Adjacent	741
742	Prosser very fine sandy loam	Adjacent	743
711	Quincy fine sand	Adjacent	712
725	Quincy fine sand	Adjacent	726
731	Timmerman coarse sandy loam	Adjacent	732
715	Timmerman coarse sandy loam	37.0 km	
713	Timmerman coarse sandy loam	40.2 km	

Appendix 2-D. Soil particle size distribution by soil type

Sample Number	Soil Type	Soil Particle Size Distribution			
		% Gravel	*% Sand*	*% Silt*	*% Clay*
710	Warden silt loam	0.0	42.1	54.1	3.8
709	Warden silt loam	0.0	48.4	44.8	6.8
701	Warden silt loam	0.0	25.0	64.4	10.6
702	Shano silt loam	0.0	36.0	63.2	0.8
703	Shano silt loam	0.0	34.2	60.9	4.9
705	Shano silt loam	0.0	38.1	58.8	3.1
745	Scoon silt loam	0.9	65.3	33.7	0.1
723	Scoon silt loam	0.3	45.3	51.8	2.6
729	Novark silt loam	0.7	74.0	23.6	1.7
728	Novark silt loam	2.8	67.9	26.2	3.1
730	Kennewick silt loam	5.5	47.8	44.8	1.9
733A	Kennewick silt loam	0.0	45.0	49.4	5.5
737	Kennewick silt loam	0.0	50.0	45.8	4.2
719	Kennewick silt loam	0.8	65.3	31.3	2.5
744	Sagemoor silt loam	0.0	36.4	60.0	3.6
739	Sagemoor silt loam	0.0	48.2	48.7	3.1
746	Ephrata fine sandy loam	4.7	37.6	54.6	3.1
707	Ephrata fine sandy loam	10.2	45.2	40.6	4.0
717	Ephrata fine sandy loam	14.9	46.1	35.1	3.8
747	Kennewick fine sandy loam	0.1	57.8	41.6	0.5
738	Kennewick fine sandy loam	0.0	42.8	50.8	6.3
741	Royal very fine sandy loam	0.5	39.5	59.2	0.9
740	Royal very fine sandy loam	0.0	35.3	61.4	3.2
743	Prosser very fine sandy loam	1.5	35.9	61.1	1.5
742	Prosser very fine sandy loam	0.4	32.2	64.3	3.1
712	Quincy fine sand	0.5	72.4	26.3	0.8
711	Quincy fine sand	0.0	85.7	12.9	1.3
726	Quincy fine sand	0.0	85.2	14.6	0.2
725	Quincy fine sand	0.0	82.8	15.6	1.6
732	Timmerman coarse sandy loam	0.0	71.6	26.7	1.7
731	Timmerman coarse sandy loam	0.4	66.4	29.4	3.8
715	Timmerman coarse sandy loam	2.2	53.4	40.4	3.9
713	Timmerman coarse sandy loam	2.2	68.7	25.3	3.9

Appendix 2-E. USGS soil type descriptions (Gentry, 1984)

Kennewick-Warden-Sagemoor Soil Unit

This unit is located in the southern part of the county. The native vegetation is mainly grasses and shrubs. This unit makes up about 11% of the county. It is about 40% Kennewick soils, 20% Warden soils, and 10% Sagemoor soils. The remaining 30% is components of minor extent, such as Novark soils. This unit is used mainly for irrigated crops, rangeland, and wildlife habitat. The main limitations for irrigated crops are the hazards of soil blowing and water erosion and steepness of slope. The production of forage is limited by the low annual precipitation.

Timmerman-Quincy Soil Unit

This unit is located in the southern part of the county. The native vegetation is mainly grasses and shrubs; however, some areas are barren of vegetation. This unit makes up about 4% of the county. It is about 70% Timmerman soils and 15% Quincy soils. The remaining 15% is components of minor extent, such as Royal soils. This unit is used mainly for irrigated crops and wildlife habitat. The main limitations for irrigated crops are the hazards of soil blowing and water erosion, restricted available water capacity, and steepness of slope.

Ephrata-Malaga Soil Unit

This unit is in the southern part of the county. Native vegetation is grasses and shrubs. It makes up about 5% of the county, with 60% Ephrata soils, 35% Malaga soils, and the remaining 5% is components of minor extent. This unit is mainly used for irrigated crops and wildlife habitat. The main limitations for irrigated crops are restricted available water capacity, the hazard of water erosion, and steepness of slope.

Quincy Soil Unit

This unit is in the southern part of the county. This unit supports little if any native vegetation. This unit makes up about 12% of the county; 90% are Quincy soils and the remaining 10% is components of minor extent. This unit is used mainly as rangeland and for irrigated crops and wildlife habitat. The production of forage is limited by restricted available water capacity. The main limitations for irrigated crops are the hazard of soil blowing, restricted available water capacity, and steepness of slope.

Taunton-Scoon Soil Unit

This unit is in the southern part of the county. The native vegetation is mainly grasses and shrubs. This unit makes up about 6% of the county. It is about 50% Taunton soils, 40% Scoon soils, and the remaining 10% is components of minor extent. This unit is used mainly as rangeland and for irrigated crops and wildlife habitat. The production of

forage is limited by restricted available water capacity. The main limitations for irrigated crops are the hazards of soil blowing and water erosion, restricted available water capacity, and steepness of slope.

Shano Soil Unit

This unit is in the southern part of the county. The native vegetation is mainly grasses and shrubs. The unit makes up about 4% of the county. It is about 95% Shano soils. and the remaining 5% is components of minor extent. Shano soils are on hills. The unit is used mainly for nonirrigated and irrigated crops and wildlife habitat. The main limitations for nonirrigated crops are the low annual precipitation and the hazard of water erosion. The main limitations for irrigated crops are the hazard of water erosion and steepness of slope.

Appendix 2-F. Methods summary

Target Analysis	Method Reference
Cation Exchange Capacity	EPA SW-846 Method 9081
Total Available Phosphorus	EPA SW-846 Method 3050/6010
Extractable Metals (As, Cd, Cu, Pb, Zn)	Plant Available As, Cd, Cu, Pb, & Zn using DTPA Extraction followed by ICP Analysis (Spielman And Shelton, 1989)
Soil Particle Size	Conventional Sediment Variables: Particle Size (Puget Sound Estuary Program 1986)
pH	EPA SW-845 Method 9045C
Total Organic Carbon (TOC)	EPA SW-846 Method 415.1
Total Metals (Cd, Cu, Pb, Ni, Zn)	EPA SW-846 Methods 6010/6020 (analysis) Method 3050 (digestion)
Total Metals (As)	EPA SW-846 Method 7060 (GFAA)
Total Metals (Hg)	EPA SW-846 Method 7471 (CFAA)

Appendix 2-G. General chemistry quality assurance

Sample Information

Samples from the Metals in Soils study were received by the Manchester Laboratory on 8/l 8 and 8/26/98 in good condition. Analysis for percent solids was performed immediately after sample arrival. The samples were not stored in the freezer until TOC analysis could be performed due to the shorter turnaround time for this project.

Holding Times

Soil TOC analysis, as well as pH analysis, was not performed within laboratory accepted holding times. The TOC method in the Conventional Sediment Variables of the Puget Sound Protocols of March 1986 recommends that the samples should be stored frozen and can be held for up to 6 months. There is no known established regulatory holding time for TOC sediment for samples that are stored at 4°C. Due to pH probe drifting problems, the pH samples also were analyzed outside the laboratory established holding times. There is also no known established regulatory holding time for this parameter.

Instrument Calibration

Where applicable, instrument calibration was performed before each analysis, and verified by initial and verification standards and blanks. All initial and continuing calibration verification standards were within the relevant EPA control limits. All balances are calibrated yearly with calibration verification occurring monthly.

Procedural Blanks

All procedural blanks were within acceptable limits.

Precision Data

The results of the duplicate and triplicate analysis of samples were used to evaluate the precision on this sample set. Relative percent differences (RPD) were within their acceptance windows of +/- 20%. The relative standard deviations (RSD) were within their acceptance windows of +/- 20%.

Laboratory Control Sample (LCS) Analyses

LCS and standard reference materials (SRM) analyses were within their acceptance windows of +/- 20%.

Other Quality Assurance Issues

The results for the three pH duplicates have been qualified as estimates. These samples were analyzed from leftover supernatant that was left on the counter overnight.

Appendix 2-H. Metals analysis quality assurance summary

Data quality for this project met all quality assurance and quality control criteria with the exceptions that (1) recoveries of ICP and furnace elements were high for one of the three LCS samples, (2) recovery of lead from one of the spiked samples was low, and (3) replication of DTPA extractable copper and zinc from one sample was outside limits.

Because of several miscommunications at Manchester Laboratory, the mercury soil samples were not analyzed within the recommended holding time (28 days) for mercury in solid matrices. The lab does not feel that any mercury was lost from these samples before analysis, as the great majority of the samples are very dry and do not appear to have much biological or chemical activity associated with them. Additionally, the storage that these samples received (4ºC, sealed, dark), indicate that loss of mercury would probably be minimal. However, we are qualifying the sample with J, denoting estimated values, recognizing that there is a possibility that some mercury may have been lost in storage.

To verify the stability of the samples and their mercury content, the lab will re-analyze the samples toward the end of October. This re-analysis will be free of charge. If the concentration has not substantially changed at this re-analysis, the lab will recommend that the J qualifiers be removed from the data set.

No other significant quality assurance issues were noted with the data. No certified reference materials were available for either DTPA extractable metals or for the cation exchange capacity (CEC). Spiked samples were not analyzed with these two methods.

Sample Information

The samples from the Metals in Soils study were received by the Manchester Laboratory on 08/l 8/98 and 8/26/98 in good condition.

Holding Times

All analyses, except those for mercury, were performed within the specified method holding times for metals analysis, 180 days for all metals except mercury. Mercury was analyzed at a time in excess of the 28-day holding time due to laboratory error. Mercury data were qualified J, as estimated, or UJ, as undetected at estimated detection level.

Instrument Calibration

Instrument calibration was performed before each analytical run and checked by initial calibration verification standards and blanks. Continuing calibration standards and blanks were analyzed at a frequency of 10% during the run and again at the end of the analytical run. All initial and continuing calibration verification standards were within the relevant method control limits. PLA calibration gave a correlation coefficient (r) of 0.995 or greater, also meeting method calibration requirements.

Procedural Blanks

The procedural blanks associated with these samples showed no analytically significant levels of analyte except zinc. Zinc was present in two of the three ICP procedure blanks. Sample zinc results were greater than ten times the blank results, so the data were not qualified.

Spiked Samples Analysis

Spiked and duplicate spiked sample analyses were performed on this data set. All spike recoveries, with the exception of that for the lead spike on sample 98338710, were within the acceptance limits of +/- 25%. Recovery of the noted spike was 63%. Recovery from the duplicate spiked sample was acceptable and the average recovery, 74%, from this sample was marginal. Data were not qualified based on this result on one out of three spiked samples; spiked samples were not analyzed for DTPA extractable metals or with the CEC analysis.

Precision Data

The results of the spiked and duplicate spiked samples and duplicate sample results were used to evaluate precision on this sample set. The relative percent difference (RPD) for all analytes was within the 20% acceptance window for duplicate analysis. Mercury results for sample 98338710 had acceptable precision based on spiked sample results but not on duplicate sample results. The duplicate may have been contaminated or the sample matrix non-homogenous. Data for this sample was qualified J as estimated based on poor result precision.

Serial Dilution

Serial dilutions were not analyzed with these samples.

Laboratory Control Sample (LCS) Analysis

LCS analyses were within the windows established for each certified parameter, with the exception of results for elements other than arsenic and zinc, on one of the three LCS samples (M8245SL2) analyzed by ICP and GFAA. The recoveries of cadmium, copper, nickel, and lead were - 134%, 126%, 127%, and 127% respectively, on the noted LCS sample. Recovery of phosphorous was also higher from this sample, and phosphorous precision from this sample was poor. Phosphorous level was not certified for the LCS sample. Recoveries on these elements for this sample, were within 20% of the manufacturer's made to value level. Data were not qualified based on the result on one out of three of the LCS samples for ICP and GFAA analysis.

Appendix 2-I. Analytical results of metals in soils study

Lab #	Crop	Soil Type	pH	CEC	TOC-104ºC	TOC-70ºC	Phosph	As	Cd	Cu	
				g/kg	%	%	mg/Kg	mg/Kg	mg/Kg	mg/Kg	m
		Detection Limits		**0.050**	**0.002**	**0.002**	**10.0**	**0.300**	**0.030**	**0.500**	**0**
Background Samples											
338710	NA	Warden silt loam	7.1	3.79	0.62	0.56	701	2.5	0.08	15.9	
338702	NA	Shano silt loam	7.7	3.46	0.68	0.61	616	2.5	0.084	14.6	
358745	NA	Scoon silt loam	7.3	3.78	1.06	1.06	853	5.56	0.03 U	20.2	
348729	NA	Novark silt loam	8.2	3.15	0.54	0.53	699	4.45	0.03 U	11.5	
348730	NA	Kennewick silt loam	8.2	2.92	0.28	0.28	694	3.19	0.044	12.7	
358744	NA	Sagemoor silt loam	6.5	4.51	0.83	0.82	734	2.4	0.039	10.9	
358746	NA	Ephrata fine sandy loam	7.8	3.77	0.76	0.76	671	3.14	0.98	13	
358747	NA	Kennewick fine sandy loam	7.2	2.97	0.59	0.59	587	2.7	0.061	10.3	
348741	NA	Royal very fine sandy loam	6.4	3.93	0.46	0.46	805	3.51	0.062	14.6	
358743	NA	Prosser very fine sandy loam	6.9	4.92	0.67	0.66	938	3.03	0.032	16.7	
338712	NA	Quincy fine sand	7.4	3.3	0.21	0.19	987	2.4	0.042	13.1	
338726	NA	Quincy fine sand	7.7	2.21	0.33	0.32	873	3.81	0.042	9.89	
338732	NA	Timmerman coarse sandy loam	7.6	3.16	0.3	0.27	1460	1.5	0.05	12.7	
Field Samples											
338701	Apples	Warden silt loam	6.1	3.32	0.53	0.5	618	2.3	0.21	14.5	
338703	Apples	Shano silt loam	6	3.21	0.42	0.4	695	3	0.13	15.6	
338705	Apples	Shano silt loam	6.3	3.21	0.55	0.49	712	2.6	0.15	14.4	
338707	Alfalfa	Ephrata fine sandy loam	6.1	3.93	0.99	0.9	873	2.2	0.14	14.5	
338709	Alfalfa	Warden silt loam	6.4	5.21	0.72	0.66	693	3.26	0.13	19	
338711	Alfalfa	Quincy fine sand	6.7	2.52	0.33	0.3	944	3.23	0.069	10.7	
338713	Bean	Timmerman coarse sandy loam	6.2	3.4	0.91	0.84	1050	2.1	0.092	13.4	
338715	Oats	Timmerman coarse sandy loam	6.6	3.49	0.84	0.77	819	2.5	0.089	13.3	
338717	Corn	Ephrata fine sandy loam/ Malaga gravelly sandy loam	5.5	3.91	1.14	1.05	656	2.5	0.13	13.4	
338719	Alfalfa	Kennewick silt loam	7.8	3.53	0.56	0.52	750	3.9	0.09	13.3	
338723	Alfalfa	Scoon silt loam	7	3.72	0.97	0.89	636	2.4	0.15	13.6	
338725	Alfalfa	Quincy fine sand	6.7	2.56	0.41	0.37	852	3.67	0.088	9.49	
338731	Alfalfa	Timmerman coarse sandy loam	7.6	3	0.44	0.41	1010	2.6	0.079	15.5	
338733	Wheat	Kennewick silt loam	7.95	3.63	0.47	0.46	811.5	3.87	0.1	14.48	
348728	Primrose	Novark silt loam	7.5	3.01	0.59	0.58	776	5.68	0.05	12.6	
348737	Wheat	Kennewick silt loam	7.8	3.78	0.48	0.47	733	3.61	0.1	13.9	
348738	Potato	Kennewick fine sandy loam	7.4	3.5	1.06	1.06	714	4.51	0.059	13.4	
348739	Sugar	Sagemoor silt loam	7.9	4.39	0.6	0.59	1060	4.48	0.051	17.7	
348740	Bean	Royal very fine sandy loam	7.6	5.33	0.48	0.48	974	5.39	0.086	17.7	
359742	Pasture	Prosser very fine sandy loam	7.7	4.05	0.89	0.89	696	3.16	0.081	15.7	
348733R	Wheat	Kennewick silt loam	7.9	3.74	0.48	0.47	796	3.86	0.12	14.2	
348734R	Wheat	Kennewick silt loam	8	3.77	0.45	0.45	834	3.91	0.13	14.6	
348735R	Wheat	Kennewick silt loam	8	3.55	0.46	0.46	827	3.87	0.15	14.7	
348736R	Wheat	Kennewick silt loam	7.9	3.45	0.47	0.47	789	3.82	0.10	14.4	

R= Replicate sample

U = The analyte was not detected at or above the reported result.

J = The analyte was positively identified; the associated numerical result is an estimate.

UJ = The analyte was not detected at or above the reported estimated result.

Appendix 2-I. Analytical results of metals in soils study

Lab #	Crop	Soil Type	pH	CEC	TOC-104ºC	TOC-70ºC	Phosph	As	Cd	Cu	Pb	Hg	Ni	Zn
				g/kg	%	%	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
		Detection Limits		**0.050**	**0.002**	**0.002**	**10.0**	**0.300**	**0.030**	**0.500**	**0.200**	**0.003**	**1.00**	**1.00**
Background Samples														
338710	NA	Warden silt loam	7.1	3.79	0.62	0.56	701	2.5	0.08	15.9	8.36	0.0065 J	12.2	56.2
338702	NA	Shano silt loam	7.7	3.46	0.68	0.61	616	2.5	0.084	14.6	5.47	0.008 J	14.1	38.7
358745	NA	Scoon silt loam	7.3	3.78	1.06	1.06	853	5.56	0.03 U	20.2	9.97	0.066 J	13.6	53.4
348729	NA	Novark silt loam	8.2	3.15	0.54	0.53	699	4.45	0.03 U	11.5	5.65	0.011 J	9.1	36.9
348730	NA	Kennewick silt loam	8.2	2.92	0.28	0.28	694	3.19	0.044	12.7	6.34	0.0047 J	11	38.2
358744	NA	Sagemoor silt loam	6.5	4.51	0.83	0.82	734	2.4	0.039	10.9	6.01	0.009 J	10	35.9
358746	NA	Ephrata fine sandy loam	7.8	3.77	0.76	0.76	671	3.14	0.98	13	9.21	0.012 J	10.4	46.5
358747	NA	Kennewick fine sandy loam	7.2	2.97	0.59	0.59	587	2.7	0.061	10.3	6.77	0.0045 J	9.5	32.5
348741	NA	Royal very fine sandy loam	6.4	3.93	0.46	0.46	805	3.51	0.062	14.6	8.21	0.008 J	10.1	47.9
358743	NA	Prosser very fine sandy loam	6.9	4.92	0.67	0.66	938	3.03	0.032	16.7	7.54	0.007 J	12.7	48.3
338712	NA	Quincy fine sand	7.4	3.3	0.21	0.19	987	2.4	0.042	13.1	5.76	0.0032 J	8.4	55.7
338726	NA	Quincy fine sand	7.7	2.21	0.33	0.32	873	3.81	0.042	9.89	6.12	0.004 UJ	8	46.1
338732	NA	Timmerman coarse sandy loam	7.6	3.16	0.3	0.27	1460	1.5	0.05	12.7	4.6	0.0032 J	8	52.7
Field Samples														
338701	Apples	Warden silt loam	6.1	3.32	0.53	0.5	618	2.3	0.21	14.5	8.23	0.009 J	13.6	53
338703	Apples	Shano silt loam	6	3.21	0.42	0.4	695	3	0.13	15.6	7.3	0.013 J	15.7	49.5
338705	Apples	Shano silt loam	6.3	3.21	0.55	0.49	712	2.6	0.15	14.4	7.16	0.008 J	14.9	53.3
338707	Alfalfa	Ephrata fine sandy loam	6.1	3.93	0.99	0.9	873	2.2	0.14	14.5	6.53	0.007 J	10.1	52.8
338709	Alfalfa	Warden silt loam	6.4	5.21	0.72	0.66	693	3.26	0.13	19	9.02	0.01 J	14.8	59.9
338711	Alfalfa	Quincy fine sand	6.7	2.52	0.33	0.3	944	3.23	0.069	10.7	6.81	0.003 UJ	8.1	57
338713	Bean	Timmerman coarse sandy loam	6.2	3.4	0.91	0.84	1050	2.1	0.092	13.4	5.78	0.0042 J	9.4	65
338715	Oats	Timmerman coarse sandy loam	6.6	3.49	0.84	0.77	819	2.5	0.089	13.3	6.21	0.0043 J	9.2	58.1
338717	Corn	Ephrata fine sandy loam/ Malaga gravelly sandy loam	5.5	3.91	1.14	1.05	656	2.5	0.13	13.4	6.14	0.005 J	9.2	53.2
338719	Alfalfa	Kennewick silt loam	7.8	3.53	0.56	0.52	750	3.9	0.09	13.3	6.56	0.011 J	11.2	45
338723	Alfalfa	Scoon silt loam	7	3.72	0.97	0.89	636	2.4	0.15	13.6	6.29	0.008 J	12.7	43.8
338725	Alfalfa	Quincy fine sand	6.7	2.56	0.41	0.37	852	3.67	0.088	9.49	5.94	0.003 UJ	7.9	51.4
338731	Alfalfa	Timmerman coarse sandy loam	7.6	3	0.44	0.41	1010	2.6	0.079	15.5	6.34	0.007 J	9.9	57.8
338733	Wheat	Kennewick silt loam	7.95	3.63	0.47	0.46	811.5	3.87	0.1	14.48	8.2	0.009 J	12.65	48.88
348728	Primrose	Novark silt loam	7.5	3.01	0.59	0.58	776	5.68	0.05	12.6	6.93	0.008 J	8.8	47.8
348737	Wheat	Kennewick silt loam	7.8	3.78	0.48	0.47	733	3.61	0.1	13.9	8.23	0.009 J	12.3	48.5
348738	Potato	Kennewick fine sandy loam	7.4	3.5	1.06	1.06	714	4.51	0.059	13.4	7.7	0.006 J	12.3	43.6
348739	Sugar	Sagemoor silt loam	7.9	4.39	0.6	0.59	1060	4.48	0.051	17.7	9.59	0.009 J	11.8	59.2
348740	Bean	Royal very fine sandy loam	7.6	5.33	0.48	0.48	974	5.39	0.086	17.7	8.95	0.01 J	10.5	59
359742	Pasture	Prosser very fine sandy loam	7.7	4.05	0.89	0.89	696	3.16	0.081	15.7	7.66	0.008 J	10.7	55.2
348733R	Wheat	Kennewick silt loam	7.9	3.74	0.48	0.47	796	3.86	0.12	14.2	8.06	0.0089 J	13	48
348734R	Wheat	Kennewick silt loam	8	3.77	0.45	0.45	834	3.91	0.13	14.6	8.5	0.011 J	13.2	49.4
348735R	Wheat	Kennewick silt loam	8	3.55	0.46	0.46	827	3.87	0.15	14.7	8.48	0.0088 J	12.1	50
348736R	Wheat	Kennewick silt loam	7.9	3.45	0.47	0.47	789	3.82	0.10	14.4	7.77	0.0081 J	12.3	48.1

R= REPLICATE SAMPLE

U = The analyte was not detected at or above the reported result.

J = The analyte was positively identified; the associated numerical result is an estimate.

UJ = The analyte was not detected at or above the reported estimated result.

Appendix 2-I. Analytical results of metals in soils study (cont'd)

Lab #	Crop	Soil Type	As - DTPA	Cd - DTPA	Cu - DTPA	Pb - DTPA	Zn - DTPA
			mg/Kg	mg/Kg	mg/Kg	mg/Kg	mg/Kg
		Detection Limits	**0.48**	**0.04**	**0.048**	**0.16**	**0.04**
Background Samples							
338710	NA	Warden silt loam	0.48 U	0.08	4.71	1.36	3.64
338702	NA	Shano silt loam	0.48 U	0.04 U	2.76	0.28	0.52
358745	NA	Scoon silt loam	0.48 U	0.044	2.25	0.89	1.86
348729	NA	Novark silt loam	0.48 U	0.04 U	2.82	0.57	1.03
348730	NA	Kennewick silt loam	0.53	0.04 U	2.47	0.42	0.4
358744	NA	Sagemoor silt loam	0.48 U	0.04 U	2.12	0.69	1.25
358746	NA	Ephrata fine sandy loam	0.48 U	0.04 U	2.8	1.07	1.93
358747	NA	Kennewick fine sandy loam	0.48 U	0.04 U	0.072	0.16 U	0.067
348741	NA	Royal very fine sandy loam	0.48 U	0.052	2.69	0.53	1.47
358743	NA	Prosser very fine sandy loam	0.48 U	0.04 U	4.69	0.78	0.74
338712	NA	Quincy fine sand	0.48 U	0.04 U	1.75	0.6	3.05
338726	NA	Quincy fine sand	0.48 U	0.04 U	1.13	0.63	0.958
338732	NA	Timmerman coarse sandy loam	0.48 U	0.04 U	1.92	0.29	0.49
Field Samples							
338701	Apples	Warden silt loam	0.48 U	0.13	2.89	1.52	6.12
338703	Apples	Shano silt loam	0.48 U	0.063	2.73	0.72	3
338705	Apples	Shano silt loam	0.48 U	0.08	3.33	1.15	4.2
338707	Alfalfa	Ephrata fine sandy loam	0.48 U	0.089	2.36	0.86	6.2
338709	Alfalfa	Warden silt loam	0.48 U	0.04 U	2.01	0.58	1.83
338711	Alfalfa	Quincy fine sand	0.48 U	0.04 U	1.97	0.23	0.32
338713	Bean	Timmerman coarse sandy loam	0.48 U	0.057	2.21	0.44	5.02
338715	Oats	Timmerman coarse sandy loam	0.48 U	0.052	2.35	0.6	3.33
338717	Corn	Ephrata fine sandy loam/ Malaga gravelly sandy loam	0.48 U	0.105	2.47	0.55	3.69
338719	Alfalfa	Kennewick silt loam	0.48 U	0.056	3.13	0.76	3.99
338723	Alfalfa	Scoon silt loam	0.56	0.094	3.31	1.08	3.36
338725	Alfalfa	Quincy fine sand	0.48 U	0.04U U	1.43	0.57	3.29
338731	Alfalfa	Timmerman coarse sandy loam	0.49	0.068	3.42	0.58	3.58
338733	wheat	Kennewick silt loam	0.49	0.09	3.38	1.15	4.93
348728	Primrose	Novark silt loam	0.62	0.048	2.48	0.88	4.2
348737	Wheat	Kennewick silt loam	0.54	0.058	4.22	0.74	5.31
348738	Potato	Kennewick fine sandy loam	0.6	0.051	2.57	0.965	3
348739	Sugar	Sagemoor silt loam	0.48	0.04 U	2.59	0.39	1.19
348740	Bean	Royal very fine sandy loam	0.74	0.113	4.85	1.31	6.97
358742	Pasture	Prosser very fine sandy loam	0.48 U	0.084	3.19	0.86	4.67
348733R	Wheat	Kennewick silt loam	0.48 U	0.095	3.34	1.11	4.92
348734R	Wheat	Kennewick silt loam	0.48 U	0.093	3.44	1.12	5.04
348735R	Wheat	Kennewick silt loam	0.53	0.104	3.56 J	1.16	5.22 J
348736R	Wheat	Kennewick silt loam	0.48 U	0.08	3.16	1.19	4.53

R= REPLICATE SAMPLE

U = The analyte was not detected at or above the reported result.

J = The analyte was positively identified; the associated numerical result is an estimate.

UJ = The analyte was not detected at or above the reported estimated result.

Appendix 2-J. Graphical comparisons of other metals in soils studies

The following graphs are comparisons of range and mean values of metal concentrations in soils from four studies: This study; Ecology, 1994b; Ames and Prych, 1995; and Holmgren et al., 1993.

Legend:

This Study:

◊ **Ag Field**: agricultural sample results

◊ **Background**: background sample results

Natural Background Soil Metals Concentrations in Washington State (Ecology, 1994b):

◊ **TCP-YB**: Yakima Basin results (Yakima, Kittitas, Chelan, and Grant counties)

◊ **TCP-GE**: Group E results (Benton, Spokane, Lincoln, Adams, Okanogan, and Whitman counties)

Background Concentrations of Metals in Soils from Selected Regions in the State of Washington (Ames & Prych, 1995):

◊ **Ames & Prych**: results from "total-recoverable" method

Cadmium, Lead, Zinc, Copper, and Nickel in Agricultural Soils of the United States of America (Holmgren et al., 1993):

◊ **Holmgren**: results from Grant and Adams counties only

Vertical lines represent the range of values for that study.
Boxes (■) represent arithmetic means.

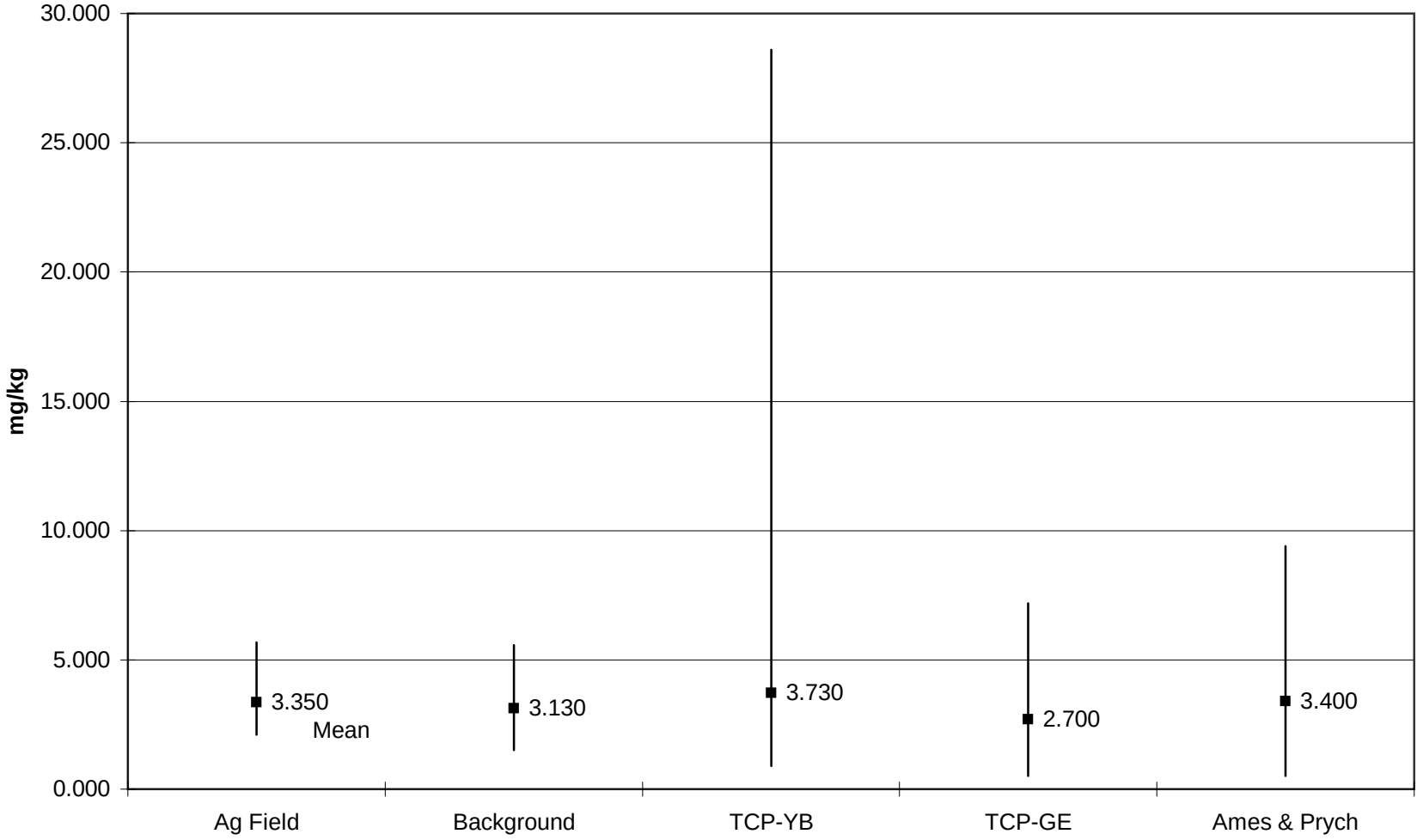

Figure 2J-1. Arsenic soil concentrations comparison.

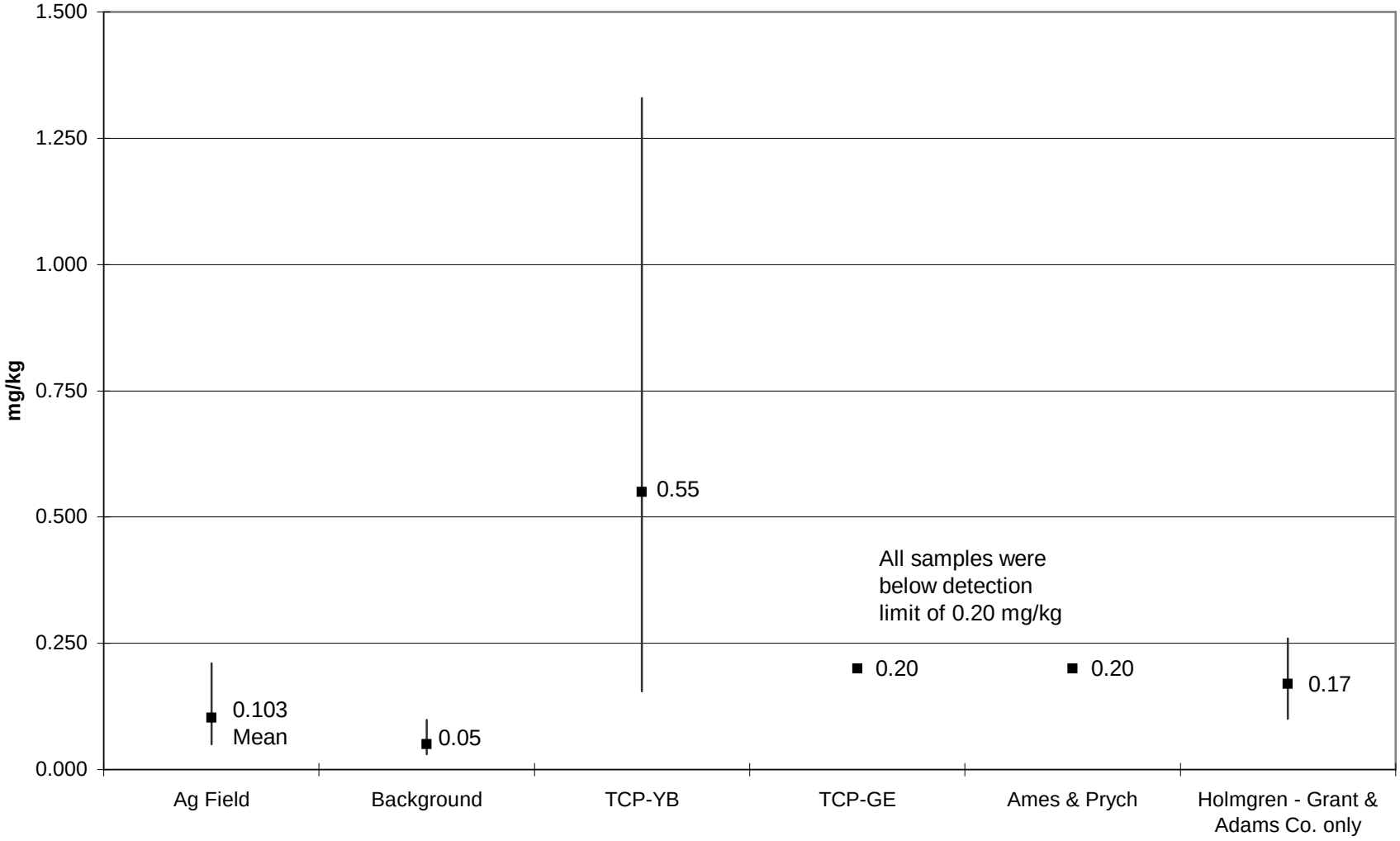

Figure 2J-2. Cadmium soil concentrations comparison

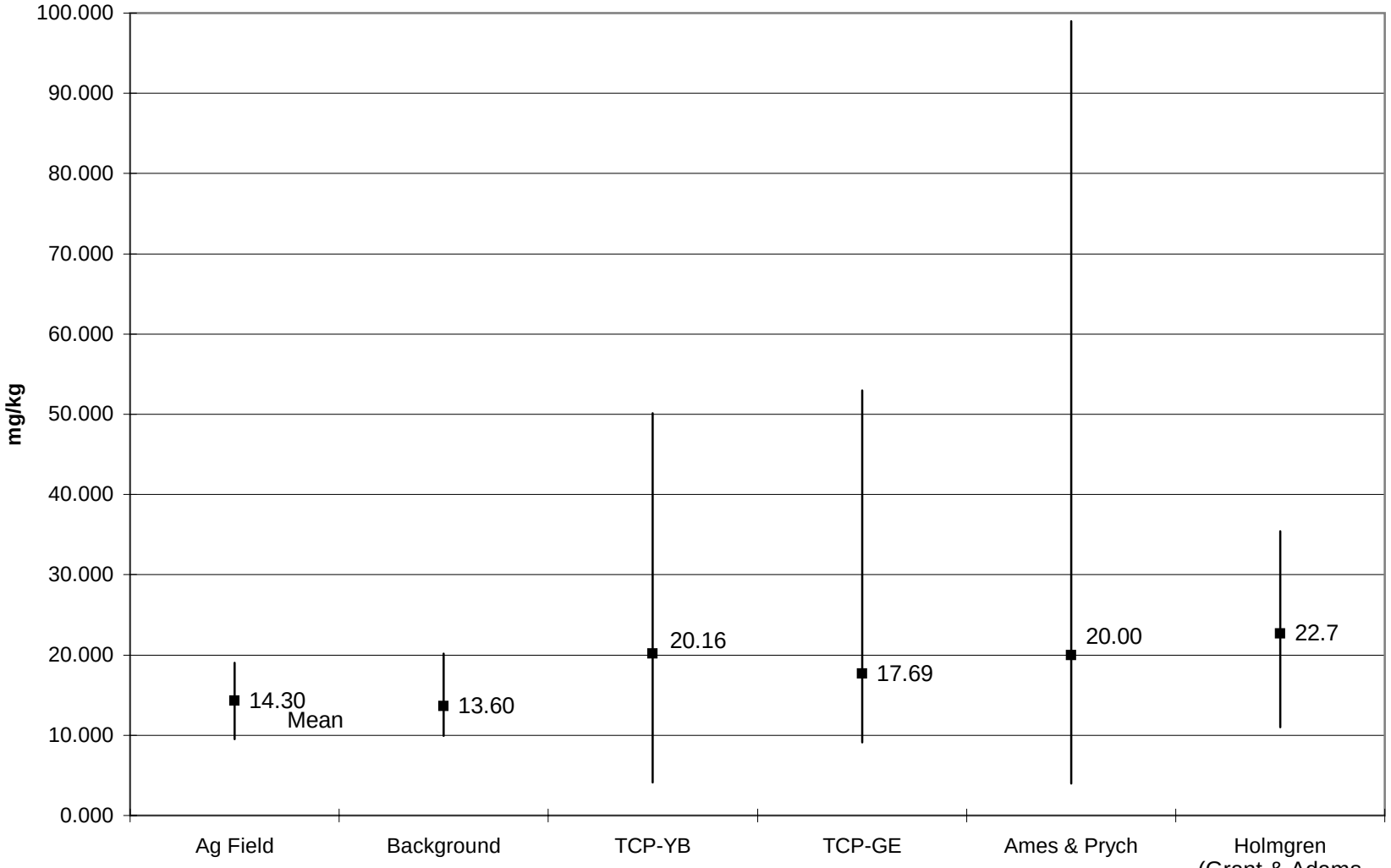

Figure 2J-3. Copper soil concentrations comparison

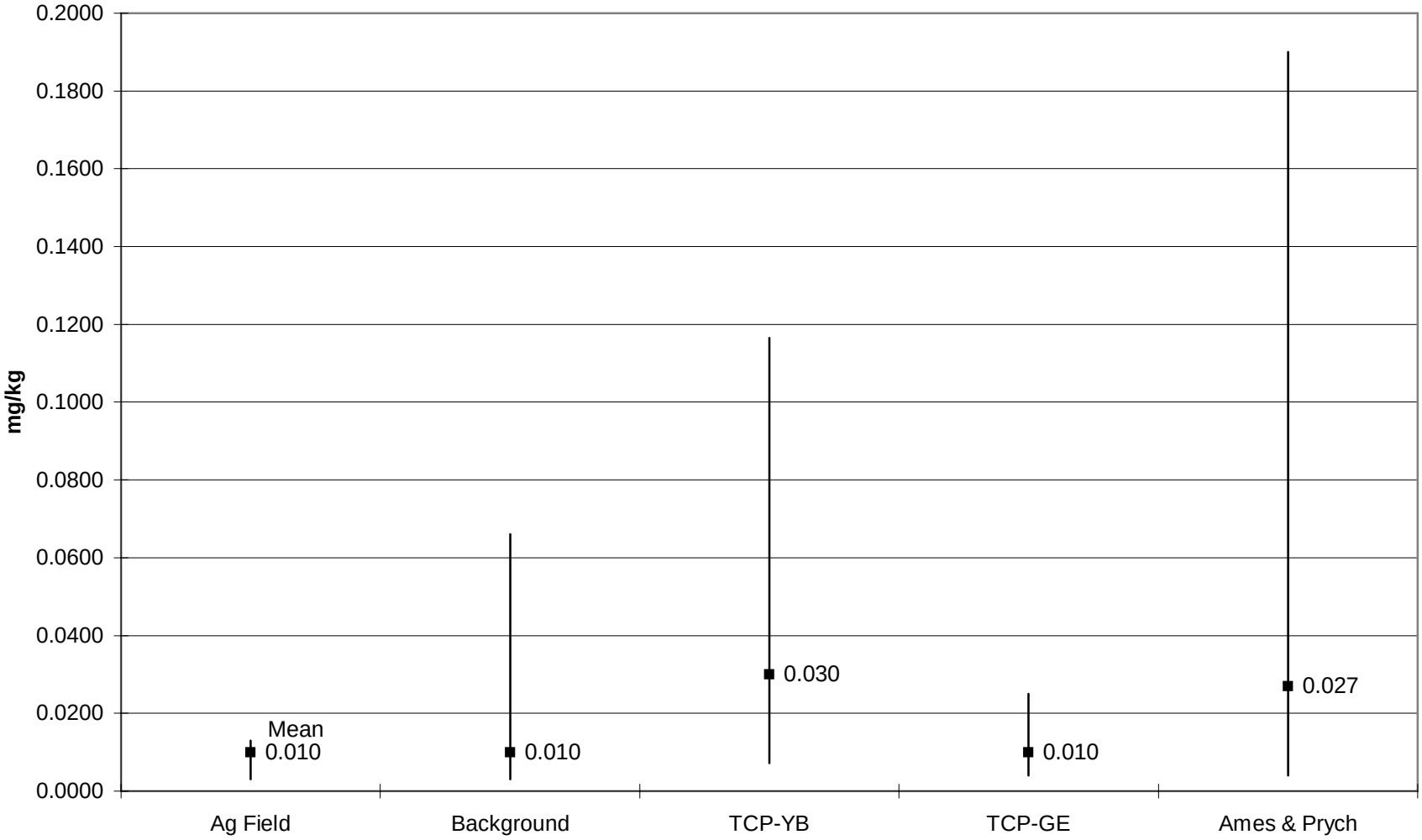

Figure 2J-4. Mercury soil concentrations comparison

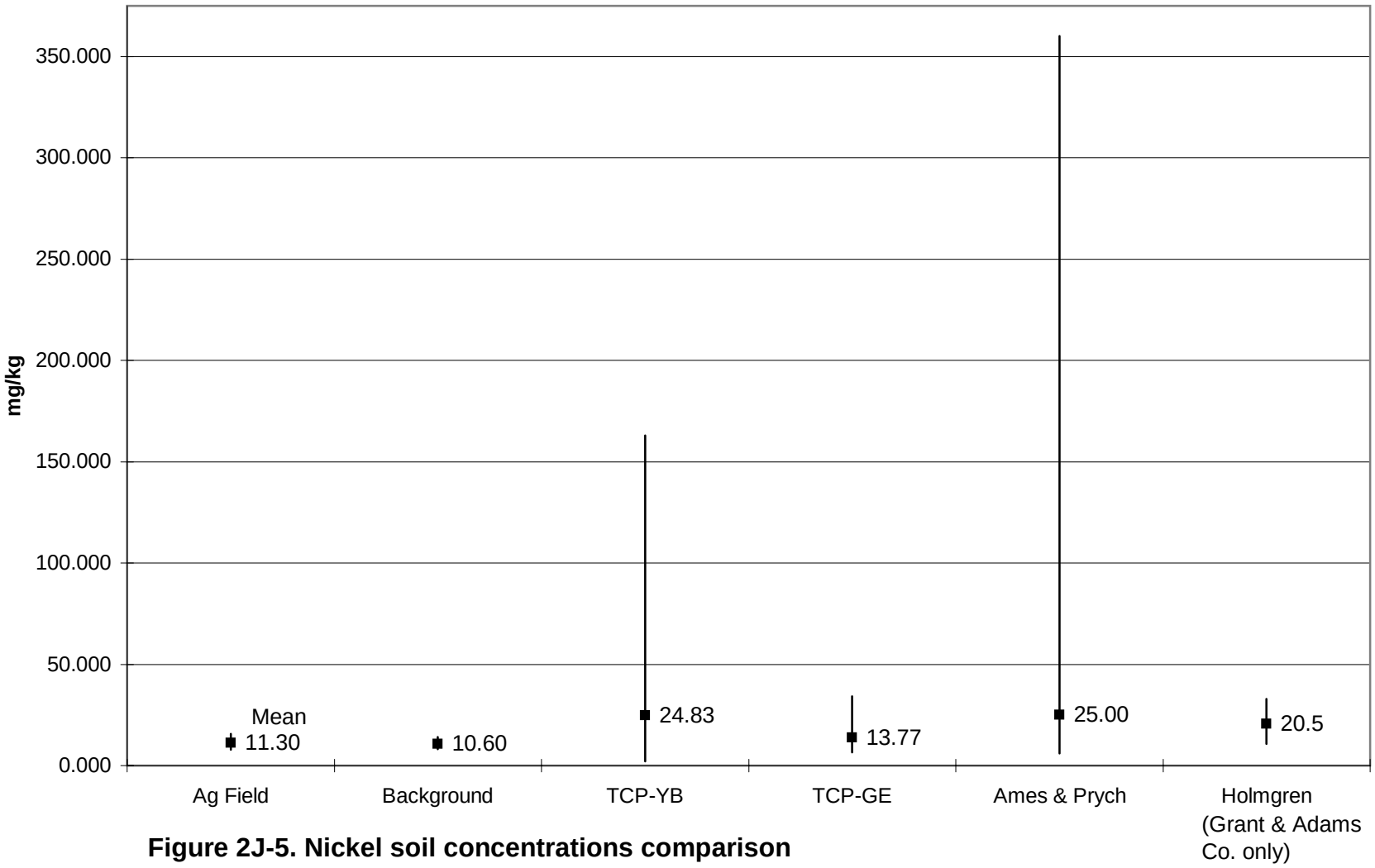

Figure 2J-5. Nickel soil concentrations comparison

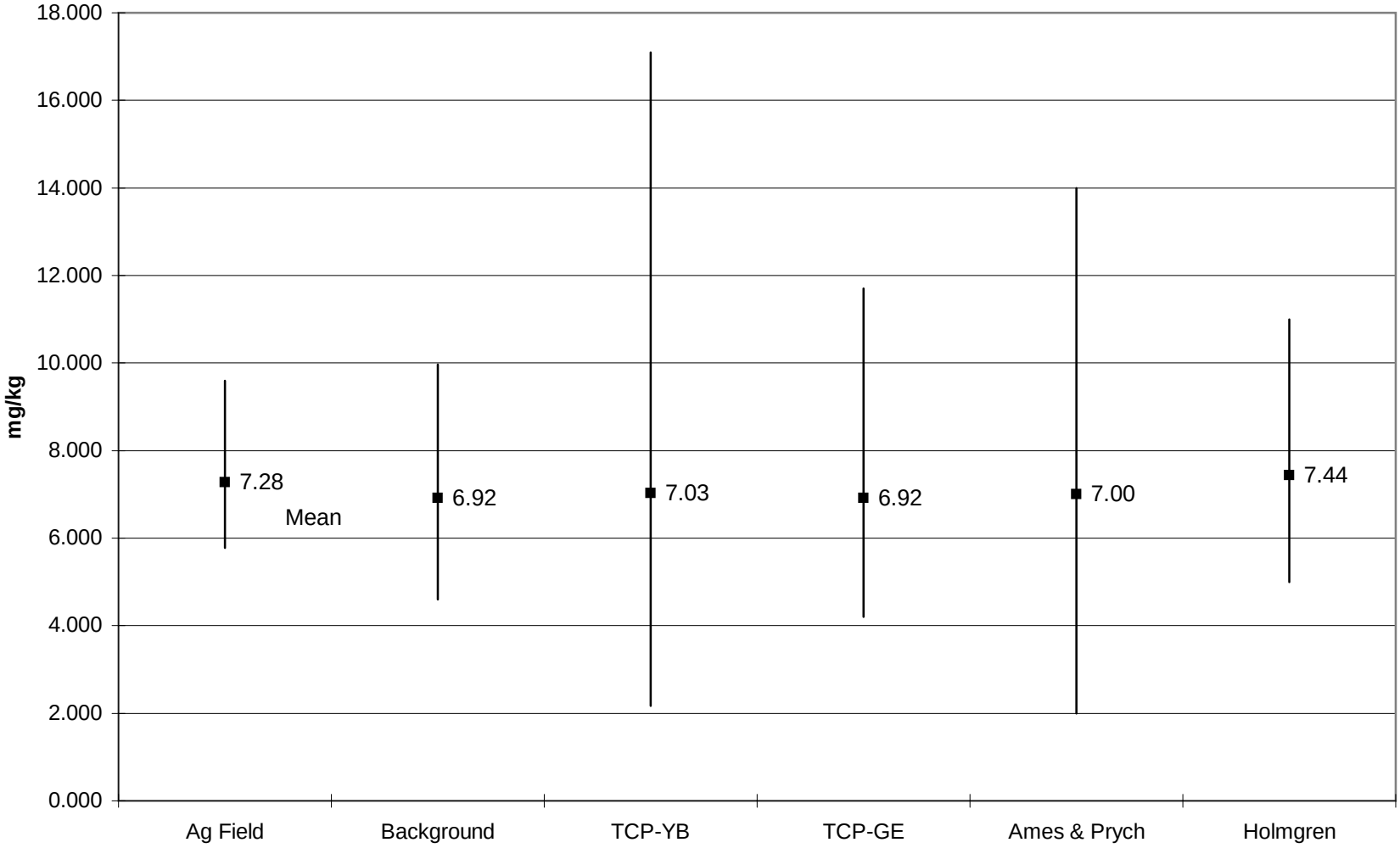

Figure 2J-6. Lead soil concentrations comparison

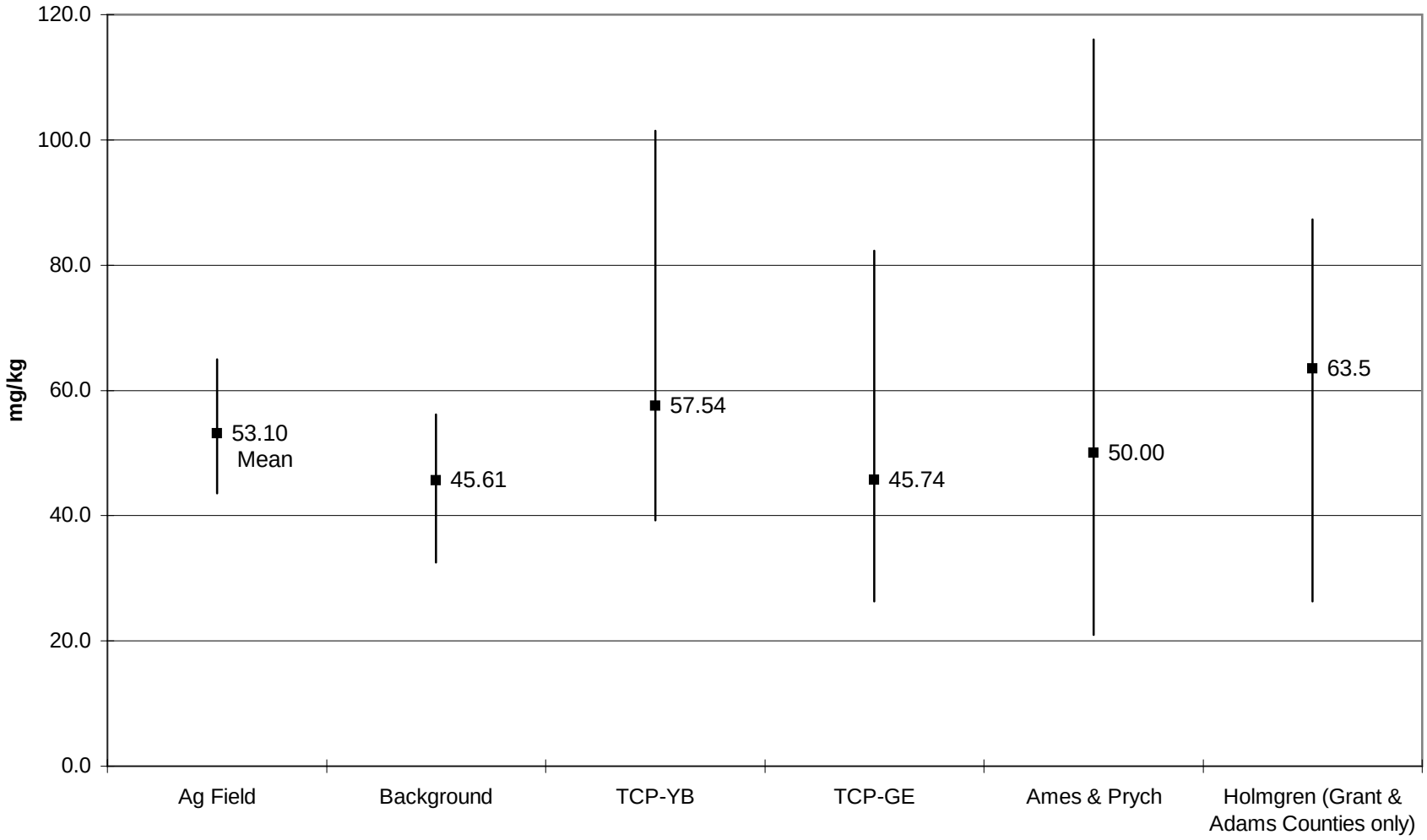

Figure 2J-7. Zinc soil concentrations comparison

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Appendices
for
3. Dioxins in Soils

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Appendix 3-A. Dioxin sources and additional dioxin data included in principal component matrix and analysis

Data Source	# of Samples	Medium	Process	Location
Rappe & Oberg, 1997	1 (median value)	Biosolid	Sewage sludge	NSSS, USA
Duarte-Davidson et al., 1997	1 (median value)	Biosolid	Sewage sludge	United Kingdom
Hagenmaier & Brunner, 1987	4	PCP, PCP-Na	Products	Germany
Washington State Sources				
VA Medical center	2	Air emissions	Incinerator-Hospital	Seattle
Kennewick Hospital	1	Bottom ash	Incinerator-Hospital	Kennewick (closed)
Northwest Hospital	2	Air emissions	Incinerator-Hospital	Seattle
Olivine Corp.	1	Air emissions	Incinerator-Municipal	Bellingham)
Spokane Municipal Incinerator	3	Air emissions & fly ash	Incinerator-Municipal	Spokane
Fort Lewis Incinerators # 1,2,3	3	Air emissions	Incinerator-Municipal	Tacoma
Fort Lewis Incinerator	1	Fly ash	Incinerator-Municipal	Tacoma
Tacoma City Light	2	Air emissions	Incinerator-Municipal	Tacoma (closed)
Recomp-TRC	1	Air emissions	Incinerator-Municipal and medical waste	Bellingham
Kaiser Aluminum & Chemical Corp.	1	Air emissions	Aluminum Rolling Mill, aluminum remelt furnace	Trentwood
Cameron-Yakima Inc.	2	Air emissions	Incinerator-multi-hearth and rotary kiln	Yakima (closed)
Holnam, Cement Kiln	6	Air emissions	Incinerator-Cement kiln	Seattle
Fort James Pulp and Paper	1	Fly ash	Hog fuel boiler	Camas
Simpson Kraft Mill	1	Effluent	Wastewater	Tacoma
Washington State Fertilizer Products				
Frit F-503G_#1, #2	2	Micronutrient	Product	
Fort James Pulp and Paper, NutriLime	1	Fertilizer	Product	
McLendon Weed and Feed 15-5-5	1	Fertilizer	Product	
Pace NuLife All-Purpose Trace Elements	1	Fertilizer	Product	
Bay Zinc K061	1	Micronutrient	Source material	
Kimberly Clark	1	Wood ash	Potential Product	
Bay Zinc 18% (zinc) Blu-Min	1	Micronutrient	Product	
Bay Zinc LHM	1	Raw material is tire dust	Product	
Bay Zinc Liquid	1	Brass ingot dust	Product	

Appendix 3-B. Urban area dioxin soil sampling random allocation

Urban Name	Land area (sq km)	Population	Number of Samples Allocated
Bellingham	77.69	59,317	0
Bremerton	143.04	112,977	0
Longview	86.57	54,985	0
Olympia	143.42	95,471	0
Vancouver	174.23	167,482	0
Richland-Kennewick-Pasco	251.78	116,118	2
Greater Seattle (incl. Everett)	1,522.63	1,744,086	9
Spokane	294.19	279,038	1
Tacoma	603.04	497,210	2
Yakima	96.92	88,054	0
Total	3,393.51	3,214,738	14

Appendix 3-C. Quality assurance memos for dioxin in soils data

Appendix 3-C is included in a supplemental report, Ecology Publication 99-310:

Supplementary Appendices: Final Report, Screening Survey of Metals and Dioxins in Fertilizer Products and Soils in Washington State

Appendix 3-D. Soil samples results for dioxin congener groups, pptr (ng/kg)

Sample	Lab #	Land use	TCDF	TCDD	PeCDF	PeCDD	HxCDF	HxCDD	HpCDF	HpCDD	OCDF	OCDD
1	308000	FOREST	66	11	14	26	12	31	4.3	41	2.8	76
2	318241	FOREST	160	16	14	20	10	71	7.85*	36	1.9*	89
3	318243	FOREST	5.1	0.75*	0.91	1.35*	9	9.7	4.8	28	4.9*	51
4	328332	FOREST	4.9	0.65*	1.7	5.9	5.3	27	6.1	59	3.8	150
5	328341	FOREST	4.2	3.5	5.3	25	5.1	120	5.165*	65	4.5	43
6	338330	FOREST	0.3	0.84	0.4	0.39*	0.325*	1.8	4.0*	5.4	1.05*	10
7	338331	FOREST	5.3	4.4	2.4	1.2	0.525*	8.5	2.1*	21	0.7*	33
8	338333	FOREST	15	3.7	1	6.7	6.3	19	28	47	3.3	160
9	308004	OPEN	0.65*	0.5*	1.3	2.1	2.9	10	9.25*	21	3.3	59
10	318242	OPEN	6.8	1.1*	0.31	0.475	1.9	8.4	5.875*	9.8	0.95*	25
11	328330	OPEN	14	2.95*	4	9.3	6.4	32	7.5*	49	3	130
12	328331	OPEN	3.8	1*	0.62	4.2	18	56	160	190	93	1000
13	328335	OPEN	0.52	0.46	0.235*	0.195*	0.265*	0.24*	2.63*	1.1	0.75*	2.8*
14	328336	OPEN	1.1	0.22*	0.475*	0.75*	48.5*	0.61*	0.1175*	2.4	2.8	3.5*
15	328340	OPEN	0.465*	0.37*	0.835*	0.485*	0.415*	1	3.4	10	2.4	28
16	338332	OPEN	0.6	0.38	0.36*	0.39*	0.34*	0.535*	3.11*	2.3	0.7*	9.1
17	318230	URBAN	0.085*	0.65*	0.18*	0.35	1.6	0.33	17	3.5	0.9*	14
18	318231	URBAN	0.65*	0.65*	0.415*	0.27	2.4	0.26*	1.44*	0.95*	0.145*	0.265*
19	318232	URBAN	8.6	1.25*	10	2.7	17	18	8.5*	96	17	280
20	318233	URBAN	5.9	1.2*	1.4	0.395*	4.1	11	8.1	43	6.5	170
21	318234	URBAN	4.3	2*	5.3	6.1	23	50	47	250	23	890
22	318235	URBAN	0.145*	1*	2.2	0.79	3.6	7.5	5.4	16	3.2	55
23	318236	URBAN	35	2*	7	7.1	11	27	7.6*	66	15	330
24	318237	URBAN	11	2.7*	11	5.3	12	17	23	66	24	320
25	318238	URBAN	5.2	1.6*	1.7	13	19	68	29	160	43	570
26	318239	URBAN	190	190	150	230	45	300	29	300	31	820
27	318240	URBAN	86	53	31	23	30	100	68	160	30	580
28	328333	URBAN	6.7	2.6	14	0.6*	9.5	8.7	3.7	23	6.8	67
29	328337	URBAN	13	3.3	38	0.89	33	15	20	87	55	430
30	328339	URBAN	11	2.4	5.6	0.365*	7.9	5.2	4.9	26	12	130

* = non-detect, the value listed is half the detection level.

Appendix 3-E. Source and fertilizer product dioxin congener group results, pptr (ng/kg).

#	Sample	Type	Units	TCDF	TCDD	PeCDF	PeCDD	HxCDF	HxCDD	HpCDF	HpCDD	OCDF	OCDD
	Medical Waste Incinerators												
32	VA Medical	Emission	ng/m^3	11	1.65	28	5.04	53.2	13.2	63	28.7	28.8	39.4
33	VA Medical	Emission	ng/m^3	20.2	3.05	51.7	9.29	98.1	24.4	116.2	53	53.1	72.6
38	NW Hospital	Emission	ng/m^3	1.14	0.372	3.23	1.45	5.64	4.46	9.99	12.3	8.41	14.8
39	NW Hospital	Emission	ng/m^3	1.99	0.652	5.63	2.54	9.82	7.8	17.4	21.5	14.7	26
49	Kennewick Hosp.	Bottom ash	ng/kg	1800	580	1400	800	970	810	450	430	76	270
	Incinerators												
40	Fort Lewis 1	Emission	ng/dscm	0.178	0.082	0.027*	0.0265*	0.027*	0.305	0.126	0.555	0.074	0.605
41	Fort Lewis 2	Emission	ng/dscm	0.518	0.197	0.091	0.12	0.061	0.254	0.081	0.248	0.014*	0.183
42	Fort Lewis 3	Emission	ng/dscm	0.392	0.016	0.105	0.0165*	0.078	0.152	0.116	0.269	0.019*	0.172
53	Fort Lewis	Fly ash	ppb	21.3	11.8	35.6	22.9	22.4	26.7	15.2	26.1	3.4	16.2
34	Tacoma Steam Plant	Emission	ng/min	7179.8	2847	2052.3	1917.8	726.3	2976.8	304.4	670.4	56.1	484.5
35	Tacoma Steam Plant	Emission	ng/min	1037.5	217	313.6	109.3	53.4	140.9	16.5	68.6	18.4	219.1
31	RECOMP	Emission	ng/sec	169.8	33.4	124.87	42.4	127.3	101.6	173.7	236.7	77.2	513.2
50	Olivine	Emission	pg/sample	10400	3966	9266	7800	8200	18666	7933	20666	2500*	21333
51	Olivine	Emission	pg/sample	216333	81333	263333	153000	200000	326667	144667	276667	19200	19300
73	Spokane Muni	Emission	ng/sample	0.15	0.04	0.28	0.12	0.18	0.31	0.19	0.48	0.08	0.94
74	Spokane Muni	Emission	ng/sample	4.23	1.79	4.93	4.27	3.8	5.63	1.39	3.4	0.38	1.07
55	Spokane Muni	Fly ash	ppt	2780	250	1420	288	594	324	156	270	26.5	194
	Pulp and Paper												
54	Simpson Kraft	Effluent	pg/l	283	459	158	530	43	706	43	276	7	190
69	Ft James Paper	Fly ash	pg/g	360	540	170	600	63	580	23	280	1.4*	99
58	Kim-Clark	Wood Ash	pg/g	257	118	90.2	117	49.9	146	12.1	70.4	1.69	33.8
	Other Sources												
36	Cameron	Multihearth	pg/sample	2E+06	220000	3300000	390000	3E+06	710000	1900000	1200000	310000	2E+06
37	Cameron	Rotary Kiln	pg/sample	2E+06	330000	2000000	680000	2E+06	2200000	1500000	5000000	350000	7E+06
43	Holnam w/ Sterifuel	Cement Kiln	ng/m^3	4.39	0.947	1.09	0.177	0.296	0.691	0.051	0.751	0.063	1.43
44	Holnam	Cement Kiln	ng/m^3	22.1	3.45	4.54	0.598	1.17	1.01	0.18	0.674	0.032*	0.47

45	Holnam	Cement Kiln	ng/m^3	9.01	1.69	2.03	0.22	0.346	0.407	0.097	0.328	0.032*	0.266
46	Holnam Baseline	Cement Kiln	ng/m^3	12.9	2.1	4.66	0.63	2.61	0.41	2.18	0.32	2.2	0.13*
47	Holnam w/ Sterifuel	Cement Kiln	ng/m^3	13.1	2.01	4.36	0.58	2.72	0.23	2.22	0.075	2.67	0.11*
48	Holnam afterSteri	Cement Kiln	ng/m^3	8.6	1.92	0.358	0.93	0.85	0.54	0.99	0.25	1.17	0.098
52	Kaiser	Aluminum	ng/m^3	1.03	0.054	0.667	0.083	0.709	0.292	0.521	0.271	0.167	0.086
56	NSSS Biosolid	Sludge	ng/kg	16	17	35	24	100	120	190	780	210	3600
57	Biosolid	Sludge	ng/kg	50	15	41	67	144	134	675	2290	556	15231
59	PCP1	Product	mg/kg	0.0008	0.002	0.141	0.0065	4.3	1.7	74	154	118	733
60	PCP2	Product	mg/kg	0.0004	0.0004	0.343	0.0152	13.9	3.3	127	198	137	790
61	PCP NA	Product	mg/kg	0.082	0.027	0.137	0.213	3	3.9	13.2	18.5	37.2	41.6
62	PCP NA2	Product	mg/kg	0.012	0.052	0.027	0.031	0.09	0.23	0.86	5.8	4.25	32.4
	Fertilizer Products												
63	Frit F-503G #1	Product	ng/kg	240	32	220	82	200	96	120	70	110	130
64	Frit F-503G #2	Product	ng/kg	1400	260	1200	350	1100	550	620	480	460	570
65	Ft James Nutrilime	Product	ng/kg	68	41	36	51	27	50	0.9*	29	2.15*	15
66	MclendonWeed	Product	ng/kg	93	2.6	62	2.35*	1.1*	2.1*	1.4*	5.3	2.6*	22
67	NuLifeallpurpose	Product	ng/kg	460	64	380	200	380	210	200	160	170	210
68	Bayzinc K061	Product	ng/kg	9400	2100	7400	4700	4300	5400	2400	2700	610	780
70	Bayzinc Bluemin	Product	ng/kg	3500	700	3400	1000	2100	1200	1500	1200	780	540
71	Bayzinc LHM	Product	ng/kg	220	57	47	44	46	49	37	29	27	15
72	Bayzinc Brass Ingo	Product	ng/l	7400	2000	6500	2600	4800	2900	4000	2300	2800	1500

* = non-detect, the value listed is half the detection level.
# = sample number
dscm = dry standard cubic meter (of gas sampled)

Appendix 3-F. Dioxin in soils results and TEQ calculations

Appendix 3-F is included in a supplemental report, Ecology Publication 99-310:

Supplementary Appendices: Final Report, Screening Survey of Metals and Dioxins in Fertilizer Products and Soils in Washington State

Appendix 3-G. TEQ values of soil samples collected from selected Washington State land use areas (ng/kg)

Land Use	TEQ ND = 0	TEQ ND = 1/2 DL	TEQ ND = DL	Lab #
Forested Lands				
East non-commercial	5.16	5.57	6.04	328341
East non-commercial	0.449	1.60	2.76	338331
West non-commercial	4.93	5.69	6.46	308000
West non-commercial	2.57	4.86	7.15	318241
East commercial	0.0330	1.05	2.06	338330
East commercial	0.914	3.84	6.76	318243
West commercial	2.02	2.70	3.38	328332
West commercial	2.42	2.80	3.17	338333
Open Areas				
East rangeland grazed	0.0431	0.891	1.74	338332
East rangeland grazed	0.0400	1.31	2.59	328336
West rangeland grazed	0.617	1.40	2.19	308004
West rangeland grazed	4.59	5.87	7.15	328331
East non-grazed	0.0460	0.631	1.22	328335
East non-grazed	0.0834	1.36	2.64	328340
West non-grazed	2.37	2.87	3.37	328330
West non-grazed	0.330	1.09	1.84	318242
Urban Areas				
Richland	4.75	7.09	9.44	328337
Kennewick	1.08	1.92	2.76	328339
Spokane	0.984	3.00	5.01	328333
Tacoma 1	19.5	21.9	24.4	318239
Tacoma 2	9.47	11.7	13.9	318240
Seattle 1	0.313	0.699	1.08	318230
Seattle 2	5.13	5.47	5.81	318238
Seattle 3	4.72	5.78	6.84	318236
Seattle 4	0.133	0.639	1.14	318231
Seattle 5	0.804	1.21	1.62	318235
Seattle 6	2.10	3.02	3.94	318232
Seattle 7	0.729	1.52	2.30	318233
Seattle 8	5.96	6.31	6.66	318234
Seattle 9	1.36	2.81	4.26	318237
Duplicate Samples				
Spokane	0.326	4.36	8.39	328334
Richland	4.50	8.26	12.0	328338

ND = Non-detect
DL = Detection limit
ND = 0: if congener not detected, concentration assumed = 0
ND = ½ DL: if congener not detected, concentration assumed = ½ detection limit
ND = DL: if congener not detected, concentration assumed = detection limit

Appendix 3-H. Apparent percent grain size and percent total organic carbon (TOC) of soil samples from selected Washington State land use areas

Land Use	Gravel	Sand	Silt	Clay	TOC 70	TOC 40	Lab #
Forested Lands							
East non-commercial	11.2	59.5	26.9	2.4	8.06	9.48	328341
East non-commercial	13.8	72.7	12.0	1.5	22.9	25	338331
West non-commercial	0.0	91.4	8.4	0.2	43.6	60.6	308000
West non-commercial	10.3	66.8	17.6	5.2	41.1	45.9	318241
East commercial	2.7	56.1	39.3	1.8	6.23	6.81	338330
East commercial	2.8	53.5	42.1	1.6	6.58	7.69	318243
West commercial	40.6	51.1	7.8	0.5	8.16	9.45	328332
West commercial	37.7	60.0	1.4	0.9	11.7	13.5	338333
Open Areas							
East rangeland grazed	10.8	50.1	36.7	2.3	1.32	1.42	338332
East rangeland grazed	3.3	32.6	60.9	3.2	1.95	2.27	328336
West rangeland grazed	1.3	53.7	43.4	1.6	6.54	7.83	308004
West rangeland grazed	16.7	74.6	8.4	0.3	7.92	8.98	328331
East non-grazed	0.0	53.9	43.9	2.2	3.91	4.52	328335
East non-grazed	15.4	67.1	15.3	2.2	9.05	11.5	328340
West non-grazed	25.6	63.6	10.4	0.3	11.1	12.5	328330
West non-grazed	1.8	77.2	16.3	4.7	39.5	44.5	318242
Urban Areas							
Richland	0.1	67.3	30.5	2.2	3.97	4.69	328337
Kennewick	2.6	69.3	26.4	1.7	2.51	2.76	328339
Spokane	0.8	54.2	43.0	2.0	5.56	6.21	328333
Tacoma	5.1	78.4	16.1	0.4	5.50	6.13	318239
Tacoma	5.6	73.5	19.7	1.2	7.08	7.86	318240
Seattle 1	4.2	89.9	5.4	0.5	0.95	1.03	318230
Seattle 2	4.1	77.4	18.1	0.4	5.77	6.45	318238
Seattle 3	0.7	77.6	21.5	0.2	3.82	4.25	318236
Seattle 4	10.8	87.7	1.1	0.5	0.17	0.18	318231
Seattle 5	5.6	89.0	5.3	0.1	4.17	4.35	318235
Seattle 6	10.8	78.8	10.1	0.2	5.61	6.23	318232
Seattle 7	13.4	76.6	9.6	0.4	2.47	2.75	318233
Seattle 8	3.8	85.9	10.0	0.4	4.64	5.17	318234
Seattle 9	7.9	79.9	10.4	1.7	3.28	3.63	318237
Duplicate Samples							
Spokane	3.4	55.9	39.2	1.6	5.95	6.91	328334
Richland	4.9	64.8	28.2	2.2	4.07	4.37	328338

Appendix 3-I. Loadings for the three main principal components and their corresponding explained variation of the original data set