THESIS

LEAD, CADMIUM AND ZINC: EVALUATION OF CONTAMINATION USING THE NH4HCO3-DTPA SOIL TEST

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In partial fulfillment of the requirements for the Degree of Master of Science Colorado State University Fort Collins, Colorado Spring 1985

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WE HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER OUR SUPERVISION BY ______ DAVID Y. BOON ENTITLED _____LEAD, CADMIUM AND ZINC: EVALUATION OF CONTAMINATION USING THE NH4HCO3-DTPA SOIL TEST BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF ______MASTER OF SCIENCE



Committee on Graduate Work

ABSTRACT OF THESIS

LEAD, CADMIUM AND ZINC: EVALUATION OF CONTAMINATION USING THE NH₄HCO₃-DTPA SOIL TEST

The NH₄HCO₃-DTPA (AB-DTPA) soil test of Soltanpour and Schwab was developed for the simultaneous determination of P, K, Z, Fe, Cu and Mn in calcareous soils. However, its use for evaluating other elements has been demonstrated. The objective of the present research was to evaluate the AB-DTPA soil test for Pb, Cd, Zn and Ni on contaminated soils.

Use of the AB-DTPA soil test for evaluating contaminated soils was examined using two laboratory studies. The first study compared the AB-DTPA with the DTPA soil test for Pd, Cd, Zn and Ni on 26 contaminated garden soils from Aspen, Colorado. The second study correlated the AB-DTPA soil test with total soil digests for Pb, Cd and Zn on 21 contaminated soils from Aspen, Colorado.

The results indicate that the AB-DTPA soil test was highly correlated with the DTPA test for Pb, Cd, Zn and Ni. Correlation coefficients (r) were 0.96 for Pb, 0.99 for Cd, 0.99 for Zn and 0.90 for Ni. The results of the total soil digests demonstrate that the AB-DTPA soil test is highly correlated with total element concentrations for Pb,

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Cd and Zn. Correlation coefficients (r) were 0.92 for Pb, 0.93 for Cd and 0.89 for Zn.

Additional laboratory studies were conducted to evaluate the nitric acid plant digest procedure of Havlin and Soltanpour for plant analysis of Pb, Cd, Zn, Ni and Mo. Results obtained from digestion of National Bureau of Standards (NBS) Reference materials (1571, 1573 and 1575) demonstrated that the nitric acid digestion procedure compared well with NBS certified values.

Field sampling of Aspen soils and plants from Aspen resulted in high levels of Pb, Cd and Zn in both soils and plants. Soil Pb levels in excess of 100 ug/g AB-DTPA Pb may pose potential health hazards from the ingestion of contaminated soil. Plant concentrations of Pb, Cd and Zn were highest in leafy vegetables. Root crops were intermediate and took up less metals than leaves but more than vegetable fruits. The $\rm NH_4HCO_3$ -DTPA soil test was a good predictor of Pb and Cd concentrations in lettuce (<u>Lactuca sativa</u>) and spinach (<u>Spinacia oleracea</u>). Correlation coefficients (r) were (0.95) and (0.86) for Pb and Cd, respectively.

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CHAPTER 1

INTRODUCTION

Increasing populations in mountain resorts has resulted in the expansion of many communities onto historic mine tailings and dumps. This increased rapid development has raised concern over heavy metal contamination in soils and the possible contamination of vegetables grown on these soils. Heavy metal contamination of soils from mining activities is localized and often intense.

In the summer of 1981 several soil samples from Aspen, Colorado were submitted to the Colorado State University Soil Testing Laboratory (CSU-STL) for routine garden soil analysis. It was noticed, upon analysis, that many of the soils were contaminated with high levels of lead (Pb), cadmium (Cd), and zinc (Zn). The discovery of the contaminated soils was a fortuitous one since the CSU-STL utilizes a multielement extraction procedure followed by simultaneous multielement analysis using inductively coupled plasma atomic emission spectrometry (ICP-AES).

Soil tests were traditionally developed to differentiate between nutrient deficient and nondeficient soils and predict the yield response from nutrient additions. Many soil tests developed with these criteria are not adequate for soil testing on drastically disturbed lands where the concern is not deficiencies but more often toxicities. With the increased cost of reagents and labor, soil test development has been aimed at developing extraction procedures which will simultaneously extract macro- and micronutrients. Multielement extractants are especially useful for conducting screening programs for elements of environmental concern.

The ammonium bicarbonate - DTPA soil test (Soltanpur and Schwab, 1977) as modified by Soltanpur and Workman (1979) was developed for simultaneous extraction of P, K, Zn, Fe, Mn and Cu from calcareous soils. This soil test (AB-DTPA) is currently being used in conjunction with ICP-AES for the simultaneous determination of macro- and micronutrients (Soltanpour et al., 1979). The AB-DTPA soil test has been shown to be highly correlated with the ammonium carbonate soil test for Mo (Boon and Soltanpour, 1983; Boon, 1984; Soltanpour, 1983). Boron (B) and seleium (Se) have also been evaluated in soils using the AB-DTPA soil test (Gestring and Soltanpour, 1981; Soltanpour and Workman, 1980). The advantages of the AB-DTPA soil test are:

- 1) one extracting solution
- 2) short extracting time
- 3) rapid multielement analysis possible with ICP-AES
- 4) reproducible results
- 5) savings in time, labor and reagents.

A nitric acid digestion procedure for plant analysis was developed for use in conjunction with an ICP-AES for simultaneous determination of P, K, Ca, Mg, Na, Zn, Fe, Mn and Cu (Havlin and Soltanpour, 1980). This same nitric acid digestion procedure has been used to evaluate B (Gestring and Soltanpour, 1981).

The objectives of this study were to evaluate the AB-DTPA soil test for evaluating soils contaminated with Pb, Cd and Zn, and to evaluate the nitric acid digestion procedure for Pb, Cd and Zn in plant tissue. This study has been conveniently divided into the following four sections which comprise Chapters 2 through 5:

 review of the literature concerning Pb, Cd and Zn in soils, plants and various analytical methods;

2) laboratory experiments to correlate the AB-DTPA soil test with the DTPA soil test and total soil analysis for Pb, Cd and Zn. Additional laboratory experiments compared the nitric acid digestion procedure with standard plant analysis methods;

3) evaluation of the AB-DTPA soil test and the nitric acid plant digestion procedure for identifying Pb, Cd and Zn contaminated garden soils and plants;

4) concluding remarks.

CHAPTER 2

LITERATURE REVIEW

Metals in Soils

Lead (Pb), cadmium (Cd), zinc (Zn), and other heavy metals often occur together in mineralized outcrops. Shacklette and Boerngen (1984) found that soils of the Rocky Mountain region tend to have high concentrations of Cd, copper (Cu), Pb and Zn. The contribution of these metals to environmental contamination is significant. Anthropogenic sources of these metals include: automobile emissions, tires, paints, pesticides, fertilizers, mining and smelting of metaliferous ores.

The average values and common ranges for metals in soils have been reported (Swaine, 1955; Lindsay, 1979; Shacklette and Boerngen, 1984). Selected values reported by Lindsay (1979) are summarized in Table 2.1. The average concentrations of elements in soils, coal and overburden in the western United States are given in Table 2.2.

Lead

Lead is the most abundant of the naturally occurring heavy metals. The primary form of Pb in nature is galena (PbS). Other forms of Pb in nature include plattnerite

Element	Common Range (ug/g)	Average Value (ug/g)	
Pb	2 - 200	10.0	
Cd	0.01 - 0.70	0.06	
Ni	5 - 500	40.0	
Мо	0.2 - 5.0	2.0	
Zn	10 - 300	5.0	

Table 2.1 Common ranges and average values for the elemental composition of soils

Table 2.2 Average concentrations of elements in soils, coal and overburden in the western United States

Element	Bighorn ¹ Basin	Wind River ¹ Basin	Fort Unio Shale - (ug/g)	n Formation ² Sandstone	Roland ³ Coal Seam
Pb	8.6	13.0	15.0	5.2	13.0
Cđ	-	-	-	-	1.4
Ni	22.0	21.0	31.0	16.0	8.0
Мо	4.8	5.0	8.1	5.0	4.0
Zn	55	43.0	80	44.0	26

¹ Severson (1979)

² Ebens and McNeal (1977)

³ Trace metal analysis for the Anderson (Roland) Coal Seam, Campbell County, Wyoming (PbO_2) , cerussite $(PbCO_3)$, and anglesite $(PbSO_4)$. Galena and cerussite have been reported to occur with the silver ore zones in Aspen, Colorado (Volin and Hild, 1950).

Total soil lead levels in suspected ore areas can range from 5000-45,000 ug/g (Huff, 1952; Swaine, 1955; Mudge et al., 1968). Davies and Roberts (1975) have reported values as high as 50,000 ug/g total Pb. An area in Montana where soil developed through weathering of Devonian carbonate contained greater than 5000 ug/g Pb (Mudge et al., 1968). Soil Pb values of 6500 ug/g have been reported for the Helena Valley, Montana (Miesch and Huffman, 1972). Nriagu (1978) reported remote areas near ore outcrops as containing greater than 100,000 ug/g total Pb. Total soil Pb in many urban soils and street dust may easily contain Pb concentrations exceeding 10,000 ug/g (Barltrop et al., 1974; Duggan and Williams, 1977).

Mean Pb values for the conterminous United States and the western United States were 16 and 17 ug/g respectively (Shacklette and Boerngen, 1984). The most striking observation is the high percentage (49%) of sampling sites in Colorado containing lead levels in excess of 30 ug/g. These authors report that 20% of the U.S. samples contained more than 30 ug/g Pb.

Total Pb in soils and overburden from the Great Plains varies from 10-30 ug/g (Munshower et al., 1978; Severson et al., 1978). Extractable Pb (DTPA) concentrations ranged from 0.2-2 ug/g. Munshower (1983) reported that DTPA

extracted 5-12% of the total Pb in undisturbed alkaline soils of southwestern Montana.

Cadmium

In natural conditions, Cd is usually associated with zinc and iron minerals. The only natural concentrations of commercial importance are those in sulfide deposits, espęcially those containing Zn, Pb and Cu (Gough et al., 1979). Street (1976) lists six Cd minerals which are known to occur in nature: greenockite (CdS), cadmoselite (CdSe), monteponite (CdO), and otavite (CdCO₃). In most minerals and soils a ratio of 1:100 to 1:1000 of Cd to Zn have been reported (Schroeder et al., 1967).

Farmer et al. (1976) reported that "hot spots" at the Blackbird Mine in southern Idaho contain 10-20 ug/g total Soils near a lead smelter complex in Kellogg, Idaho Cd. contain total Cd concentrations of 140 ug/g (Ragiani et al., 1977). Munshower (1977) reported total Cd concentrations in the soil two kilometers from a smelter as 29 ug/g. The average Cd concentration in a phosphate ore from Idaho was reported as 90 ug/g (U.S.G.S., 1978). Total Cd concentrations of soils in a mineralized limestone area of Wales, Great Britain ranged 1.0-540 ug/g (Davies and Roberts, 1975). Topsoil Cd concentrations of 28 ug/g resulted from a derelict Pb-Zn mine (Johnson and Eaton, 1980). Soil Cd values of 150 ug/g have been reported for the Helena Valley, Montana (Miesch and Huffman, 1972). Pasture soils have been

reported as contaminated with Cd (12 ug/g) as a result of a New Zealand base-metal mine (Ward et al., 1977).

Munshower et al. (1978) reported that DTPA extractable Cd rarely exceeded 0.1 ug/g for southeastern Montana topsoils. Severson et al. (1978) reported DTPA extractable Cd in surficial soils of the Great Plains up to 0.3 ug/g with an average value of 0.1 ug/g.

Zinc

The most abundant geological source of Zn is the sulfide mineral, sphalerite (ZnS). Zinc concentrations of 4000-100,000 ug/g have been reported for New York peat soils (Staker and Cummings, 1941). As a rule, Zn-rich soils (1000-100,000 ug/g) are distinguished by also having a high content of Pb (1000-32,000 ug/g) (Gough et al., 1979). Maximum Zn concentrations in the soil near a Pb smelter in Kellogg, Idaho were reported up to 29,000 ug/g (Ragiani et al., 1977). Zinc concentrations in soils from a mineralized limestone in Wales, Great Britain was 49,394 ug/g (Davies and Roberts, 1975). Values for soil Zn from Alaska have been reported as high as 7,000 ug/g (Chapman and Shacklette, Zinc values of up to 5000 ug/g have been reported 1960). for the Helena Valley, Montana (Miesch and Huffman, 1972).

Total Zn concentrations in soils of the Northern Great Plains ranged from 23-94 ug/g (Tidball and Severson, 1976). Total Zn concentrations in the Northern Great Plains have also been reported to range from 14-174 ug/g (Severson et

al., 1977). Subsurface soils of the Powder River Basin, Wyoming have been reported to range from 34-110 ug/g (Anderson et al., 1975).

Topsoils from southeastern Montana contain 0.3-4.2 ug/g DTPA extractable Zn (Munshower et al., 1978). These concentrations are well below plant inhibitory levels and closer to deficiency levels. Yamamoto (1975) reported marginal Zn values for regraded coal overburden from Wyoming. Severson et al. (1978) reported DTPA extractable Zn from soil A horizons in the Northern Great Plains ranging from 0.2-5.3 ug/g.

Soil Testing on Disturbed Lands

As a result of increased environmental concern over anthropogenic contamination of heavy metals and increased restrictions on reclamation of lands affected by mineral extraction, many soil tests developed for agronomic crops are being applied to reclamation work or environmental monitoring in assessing "plant available" levels of various elements. Berg (1978) pointed out the limitations of soil testing on drastically disturbed lands. Mining affects the mobilization and availability of elements in soils and may change their rates of uptake by plants. Very little work has been done on the calibration of soil tests on disturbed lands.

The results of interlaboratory testing programs should awaken us to the inadequacies common in analytical procedures. The nature of the analytical problem encompasses all

phases of soils testing: sample collection, sample preparation, extraction procedure, analysis, and interpretation of results. Soil testing in mined areas offers many unique problems not yet encountered in agricultural soil testing.

There is widespread discrepancy in the number of samples required for soil testing on mined lands (Limstrom, 1960; Davis, 1971; Berg, 1969; Barnhisel, 1975). Soil sampling may be conducted in a systematic approach, completely random manner, or a stratified random manner. Composite recommended sampling has been agricultural on soils (Soltanpour and Workman, 1981). A composite sample is obtained by taking soil samples from several areas and thoroughly mixing the samples together. This is a form of physical averaging and is more economical than analyzing The number of samples taken to form a comeach sample. posite sample depends on the heterogeneity of the soil. Berg (1978) does not recommend composite sampling on disturbed lands due to the heterogeneity of the soils.

Sample preparation involves air drying the soil sample with subsequent crushing to break clods and aggregates. After air drying, soils are ground to pass a 2-mm sieve. The CSU-STL currently uses a Nasco-Asplin grinder with a porcelain mortar, a high density aluminum oxide auger and a 2-mm stainless steel sieve. The auger was made by the Coors Porcelain Company especially for the CSU-STL to prevent contamination of soils with Zn, Fe, Mn, and Cu.

A standardized grinding pressure is needed since excesmay sive arinding influence the analytical results. Soltanpour et al. (1976, 1979) have shown that increased time and force of grinding significantly increases Fe and Zn levels in soil extracts. Iron levels were increased more than twofold with excessive grinding. Severson et al. (1979) noted changes in Fe, Mn, Zn, Cu and Pb levels with disaggregating, grinding and sieving. Sieving through a 2mm sieve may create problems on disturbed land since a large portion of the materials from disturbed lands may contain 80-90 percent coarse fragments that are greater than 2-mm Laboratories must use a standardized soil (Berg, 1978). preparation procedure to obtain reproducible results. The method should eliminate operator bias, provide a sample that is readily homogenized and increases analytical precision (Severson et al., 1979).

Mining affects the mobilization and availability of elements in mined soils. In soil testing a plant availability level of the element is most often measured. Available nutrients refer to that portion in the soil which can be readily taken up by the plant. The measurement of extractable levels has been traditionally used to estimate plant element concentrations. Obtaining reproducibility in extractable element analysis is more difficult than in total element analysis. In total analysis the complete dissolution of the sample can be determined visually. The use of reference materials whose homogeneity and elemental content

are reasonably well known is essential for determining extractable elements (Crock and Severson, 1980).

Interpretation of results obtained from soil extracts must be backed by sound uptake research. Cope and Rouse (1973) point out that values obtained from soil extracts reflect plant available levels only when they have been correlated with plant growth or nutrient uptake. Melsted and Peck (1973) recognize the limitations in using soil test results in areas lacking adequate plant correlations or field calibration. A great void has developed due to the lack of soil and plant correlations on disturbed lands. This area of soil testing and plant analysis awaits future researchers.

Soil Tests

A variety of extractants have been employed for determining Pb, Cd, Zn and Ni in soils. Most often the extraction technique consists of using a standardized procedure that was developed for elements other than those listed above. Some of the extractants employed include: HCl, H_2SO_4 , HNO_3 , HAC, NH_4OAC , CaCl, NH_4Cl , EDTA and DTPA (Burau, 1982; Baker and Amacher, 1982).

Most soil tests have been developed for predicting deficiencies of nutrients. These same soil tests are now being applied to research involved with heavy metal loading of soils through sewage sludge applications. In addition, several of these soil tests (DTPA and AB-DTPA) are recommended by State and Federal Agencies for Environmental monitoring of topsoil, overburden and regraded spoils on surface-mined lands (Berg, 1983). The methods most commonly used to extract "available" trace elements include the DTPA method, the 0.1 N HCL method and the double-acid method (Baker and Amacher, 1982).

A great deal of emphasis has been placed on the need for all soil testing laboratories to use the same procedure. This would minimize the number of procedures used thus simplifying the process of comparing results on similar soils analyzed in different labs. However, a more pressing need is to establish a relationship between different procedures. How the results are obtained is less important than how well they correlate to each other.

A good soil test should extract nutrients or metals from the same labile pool in the soil that plants do. In addition, a soil test should be cheap, reproducible in different labs, and easily adapted to routine lab procedures. If a soil test can extract more than one element simultaneously then it has a distinct advantage. The DTPA and AB-DTPA soil tests meet these criteria

DTPA Soil Test --

The DTPA soil test was developed to assess Cu, Zn, Mn and Fe deficiencies in calcareous soils (Lindsay and Norvell, 1969, 1978). The theoretical basis for the DTPA soil test has been described in detail (Lindsay and Norvell,

1978). Sommers and Lindsay (1979) have demonstrated that the DTPA soil test has a sound basis for extracting Cd, Ni and Pb in addition to the micronutrients it was originally designed to extract. The DTPA soil test with additional computer programming to account for the effect of pH is predicted to gain popularity for routine application for Ni, Cu, Zn, Cd, and several other trace metals that are chelated by this compound (Baker and Amacher, 1982). Sommers and Lindsay (1979) demonstrated that, in addition to DTPA, several other ligands (EGTA, HEDTA, and EDTA) could be used to extract metals from soils.

The DTPA (diethylenetriaminepentacetic acid) extracting solution consists of 0.005 M DTPA, 0.01 M calcium chloride, and 0.1 M triethanolamine adjusted to a pH of 7.30. The soil test consists of shaking 10 gm of air-dry soil with 20 ml of the extractant in a 125 ml Erlenmeyer flask for two hours on a reciprocal shaker at 180 cycles/minute. The sample solutions are then filtered through Whatman no. 42 filter paper and are ready for analysis.

AB-DTPA Soil Test ---

Soltanpour and Schwab (1977) developed the ammonium bicarbondate-DTPA (AB-DTPA) soil test for simultaneous extraction of macro- (P, K) and micronutrients (Fe, Mn, Cu and Zn) in calcareous soils. The AB-DTPA soil test was modified by Soltanpour and Workman (1979) to omit carbon black which sometimes contaminated the sample and absorbed

metal chelates. The AB-DTPA soil test is based on the NH_4OAc soil test for K, the DTPA soil test for the micronutrients Fe, Mn, Cu and Zn, and the $NaHCO_3$ soil test for P.

The AB-DTPA extraction solution consists of 1.0 M NH_4HCO_3 , 0.005 M DTPA adjusted to a pH of 7.6. The soil test consists of shaking 10 gm of air-dry soil with 20 ml of the extraction solution in a 125 ml Erlenmeyer flask for 15 minutes on a recipricating shaker at 180 cycles/minute. The extracts are filtered through Whatman no. 42 filter paper and are then ready for analysis by ICP-AES. The theoretical basis for the AB-DTPA soil test has been described (Havlin and Soltanpour, 1981) and is repeated here for completeness.

In the development of any soil-extracting solution, two criteria should be considered. First, the extraction of nutrients should be from the same labile pool that supplies those nutrients to plant roots. Secondly, the soil test procedure should be rapid, reproducible and economical.

The theoretical development of DTPA as a micronutrient soil test has been well documented (Lindsay and Norvell, 1969, 1978; Lindsay, 1974, 1979; Lindsay et al., 1967; Norvell, 1972). Plant uptake of micronutrients is related to the activity of the metal cations in solution and to the ability of the solid phases in the soil to resupply the solution with those cations. Once added to the soil solution, chelates (such as DTPA) form stable soluble complexes with the various metal cations. The binding strength of a chelate for a metal cation depends on the stability constant

of the metal-chelate complex and the metal concentration in the soil solution. The higher the stability constant, the stronger the metal-chelate complex. As free metal cations are removed from solution through this complexation (or through root uptake) labile solid phases dissolve or surface cations desorb to replenish the solution. Rule and Graham (1976) using labeled 59 Fe, 54 Mn, and 65 Zn calculated soil labile pools of these nutrients and obtained similar results between plant uptake and soil equilibration with DTPA for Fe, Mn and Zn. Lauer (1971) also obtained similar results with Zn.

The primary purpose of the HCO_3 anion in the extracting solution is to extract P. Olsen et al. (1954) demonstrated that the NaHCO3 soil test is a good measure of plantavailable P. As CO₂ gas evolves during extraction with AB-DTPA, the pH of the soil-extractant mixture rises from its initial value (7.6) to values of about 8.5. At this pH with 1.0 M carbonate-bicarbonate, CaCO₃ precipitates, allowing the labile phases of calcium phosphates to dissolve, resulting in increased solution P. Previous studies (Soltanpour and Schwab, 1977) have shown that AB-DTPA extracts about one-half the P compared with NaHCO3. This mainly results from a 20:1 solution/soil ratio for the NaHCO3 test and a 2:1 ratio for the AB-DTPA soil test.

As plants absorb K from solution, the resulting shifts in exchangeable-solution K equilibrium cause the solution K to be replenished. For many years, 1.0 M NH_4OAc has been

the standard method for determining plant available K and was first introduced by Praivishnikov (1913). The same concentration of NH_4^+ is used in the AB-DTPA soil test which extracts similar levels of K (Soltanpour and Schwab, 1977).

The AB-DTPA extracting solution satisfies the theoretical criteria necessary to separate deficient from nondeficient soils for P, K, Fe, Mn, Cu and Zn and is highly correlated with field-tested soil tests. More recently, the AB-DTPA soil test has been used to evaluate selenium uptake into plants (Soltanpour and Workman, 1980). The AB-DTPA soil test was as effective as the hot water soluble soil test for Se. Soltanpour (1983), Boon and Soltanpour (1983), and Boon (1984) demonstrated that the AB-DTPA soil test was highly correlated with the ammonium carbonate (Vlek, 1975) soil test for molybdenum. Boon (1984) used the AB-DTPA soil test in contaminated mining soils to assess Pb, Cd, Ni and Mo in barley. The AB-DTPA soil test was highly correlated to plant metal concentrations. The AB-DTPA soil test has also been used for assessing the boron availability to alfalfa (Gestring and Soltanpour, 1984).

The Colorado State University Soil Testing Laboratory commonly uses the AB-DTPA soil test in conjunction with inductively coupled plasma atomic emission spectroscopy (ICP-AES) to evaluate the potential contamination of soils for various elements of environmental concern including: Mn, Cu, Zn, Pb, Cd, Ni, Mo, B, As, Se and Hg.

Plant Analysis

Decontamination

Plant tissue samples are almost always contaminated with soil, especially if samples are obtained from grazed pastures (Fleming, 1965; Healy et al., 1974). In areas of high levels of soil contamination significant differences in plant metal concentrations can occur due to soil contamination (Boon, 1984).

Peterson (1978) suggests that high Pb concentrations in leafy portions of vegetables may be subject to dust and soil contamination. Gordon (1972) compared Pb and Cd concentrations in washed versus unwashed lettuce. Unwashed plant tissue contained up to a ten-fold increase in Pb over plants washed with copious amounts of cold running water. Cadmium values dropped two-fold following washing while in three cases Cd concentrations increased with washing. Johnson and Eaton (1980) demonstrated that Pb, Cd and Zn levels dropped significantly when plants were washed with a 0.2% detergent followed by 0.05% EDTA.

Since air-borne metals often settle on plant surfaces, the leaf size, shape, location and the presence or absence of leaf hairs are critical factors in determining the extent of contamination from atmospheric sources (Peterson, 1978). The metal content of many plants may be mainly one of surface contamination. The amount of Pb which can be washed from leaves has been reported to be around 50% (Daines et

al., 1970) but may be as high as 80% (Little, 1973) or may be as low as 8% (Haney et al., 1974). Little (1973) reports that water and detergents only remove a small portion of surface lead but dilute acid (0.01% HNO_3) removed up to 80% of the total Pb suggesting that it may be ionically bound to the leaf surface.

Steyn (1959) showed that washing plant tissue with 0.1 to 0.3% detergent solution was satisfactory in removing soil contamination. A variety of detergents and dilute acids have been evaluated for removing soil contamination prior to plant analysis (Askley et al., 1960; Baher et al., 1964; Labanauskas, 1968; Ashby, 1969). More recently, Zimdahl and Foster (1976) developed a plant washing procedure for removing Pb contaminated soil from plant roots prior to analysis. Previous studies (Arvik and Zimdahl, 1974) demonstrate that this procedure does remove surface Pb but not absorbed Pb. Their procedure consists of washing the plant material with tap water followed by a 30 second rinse in distilled water plus 0.5% detergent. The plant material is then rinsed in distilled water for 30 seconds followed by a 30 second wash in 3 N nitric acid. The plant material is then placed in a final distilled water rinse for 30 seconds, blotted dry as is ready for drying or ashing.

Soil contamination of plant samples can be identified by using any element which is present in relatively large concentrations in soils and relatively low concentrations in plants. Elevated levels of iron (Fe) and titanium (Ti) are commonly used to identify soil contamination in plant samples (Fleming, 1965; Cherney and Robinson, 1983). Any plant analysis in excess of 10 ug Ti/g must be strongly suspected of being contaminated with soil. Cherney and Robinson (1983) suggested that the nitric acid digestion procedure of Havlin and Soltanpour (1980) is ineffective in determining soil contamination by titanium analysis. However, their suggestion is based on digesting soil with various plant digestion procedures and is not based on analysis of plant tissue contaminated with various amounts of soil.

Plant Digestion Procedures

The two most common digestion procedures for the oxidation and dissolution of plant tissue for element analysis are the dry and wet methods. A controversy exists between which method is the best. The choice is limited by the element being determined since volatile elements (Hg, Cd, As, Se, and Pb) may be lost during dry ashing. Piper (1942) and Johnson and Ulrich (1959) describe wet and dry ashing techniques in detail. Advantages of wet ashing are: 1) low temperature which limits volatilization; 2) speed of oxidation; and 3) less elemental retention because of liquid condition during digestion.

Wet ashing can be accomplished by using a variety of different mixtures of acids including HNO_3 , $HClO_4$ and H_2SO_4 . Caution should be exercised when using H_2SO_4 for lead

analysis due to the possible precipitation of PbSO₄. Nitric-perchloric acids have been widely used for the digestion of plant tissue (Blanchar et al., 1965; Behan and Kincaide, 1970; Zososki and Borau, 1977). Wet digestion procedures utilizing perchloric acid have two disadvantages: first, HClO₄ requires special hoods and very careful handling due to its explosive nature and, secondly, needlelike $KClO_A$ crystals often form during digestion due to high plant potassium concentrations. To overcome these problems a wet digestion procedure using nitric acid was developed by Havlin and Soltanpour (1980) for simultaneous analysis of P, K, Ca, Mg, Na, Zn, Fe, Mn and Cu using ICP-AES. The nitric acid digestion procedure may not completely oxidize organic matter. Any incomplete oxidation of organic matter is overcome due to the high temperature (6000-10,000 K) of the argon plasma (Fassel and Knisley, 1974). More recently this same procedure has been used in assessing boron concentrations in plants (Gestring and Soltanpour, 1981a, 1981b).

Plant Metal Concentrations

Lead

High concentrations of Pb have been reported for leafy green vegetables such as lettuce (<u>Lactuca sativa</u>), spinach (<u>Spinacia oleracea</u>) and chard (<u>Beta vulgaris</u>). Most of these plants have been used extensively in research due to their easy growth in greenhouses. In addition, these plants seem to accumulate more Pb than fruiting crops.

Several studies have reported Pb contents of leafy vegetables. Values for greenhouse leaf lettuce range from 5.7-10.0 ug/g (Motto et al., 1970; Ter Haar, 1970). Cannon and Bowles (1962) estimated that normal Pb values in produce was 5-20 ug/g. Peterson (1978) reported the "normal" Pb concentration of lettuce as 20 ug/g with a range of 2-620 ug/g. Cabbage Pb concentrations were reported to be significantly lower (2-40 ug/g). Lead concentrations in lettuce grown on soils contaminated by a smelter in Japan have been reported as high as 370 ug/g (Kobayashi, 1972).

Hindawi and Neely (1972) conducted a study in the Helena Valley to determine how the vegetation was being contaminated and at what concentrations were the heavy metals being accumulated in the vegetables. Contaminated soils were used in ambient-air greenhouses and purified air shelters. These experiments demonstrated that arsenic (As), Cd, Pb and Zn can be assimulated into the plant tissue through the plant root system. The metal concentration in the vegetables varied directly with the metal concentration found in the soil. The highest Pb values were reported for lettuce. In general, leafy green portions of the plant took up more Pb than roots and roots took up more lead than fruits.

Spitler and Feder (1979) conducted a study of soil contamination and plant Pb in Boston urban gardens. The amount of Pb found in the plant tissue was generally related to the soil lead concentrations but was also organ or tissue

related: fruits took up less Pb than roots and roots took up less than tops. MacLean and Langille (1973) found that tissue Pb followed the same general trend with above ground plant portions having the higher metal content than the below ground portions.

Nicklow et al. (1983) studied the influence of varying soil Pb levels on Pb uptake by leafy and root vegetables. Turnip (Brassica rapa) and lettuce leaf tissue accumulated highest Pb concentration while collard (Brassica the oleracea) and kale (B. oleracea) accumulated the lowest concentration. The authors point out that collard and kale belong to the same genus and species; Brassica oleracea. Gordon (1972) conducted a study in the Helena Valley of Montana to evalute the Pb and Cd contamination of soils and vegetables grown in the area of a lead smelter. Lead values in lettuce range from 10-460 ug/g. Cabbage (Brassica oleracea) grown on a soil with 1100 ug/g total Pb contained Pb in the plant below detection limits. Purves and MacKenzie (1970) reported that the inner leaves of cabbage did not contain a significantly higher Pb concentration even when grown on soils seven times the Pb concentration of the control soils. Cabbage is from the same genus and species as collard and kale.

Roberts et al. (1974) reported that tomato (Lycopersicon lycopersicum) fruits grown on highly contaminated garden soils were not significantly different than those in an

urban control area. The highest Pb concentrations were found in lettuce leaf followed by radish roots.

Cadmium

Hindawi and Neely (1972) reported higher cadmium concentrations in the leafy portions of plants than in root crops or fruits. Lettuce accumulated the highest cadmium concentrations with the next highest in beets (<u>Beta</u> <u>vulgaris</u>). Gordon (1972) reported cadmium concentrations of up to 28 ug/g from unwashed lettuce and 13 ug/g in washed lettuce from an area contaminated by a lead smelter.

Literature values for Cd content of leaf lettuce range from 0.5-2.1 ug/g (Hemphill et al., 1973). Values as high as 34.5 ug/g were reported for leaf lettuce grown near a lead smelter (Hemphill et al., 1973). Cadmium concentrations of leafy vegetables grown on Boston contaminated soils 0.8-9.1 uq/q ranged from (Preer and Rosen, 1977). Beavington (1973) reported the mean Cd concentration in lettuce as 4.5 ug/g when plants were grown on domestic gardens around a smelter complex in Wollongong, Australia. Cadmium values as high as 61 ug/g were reported for lettuce grown on contaminated soils in Japan (Kobayashi, 1972).

Zinc

Chapman (1966) summarized the zinc content of plant tissue for nutritional deficiency and toxicity. Values below 25 ug/g were indicative of deficiencies while values greater than 400 ug/g indicate zinc excess.

Kobayashi (1972) reported Zn concentrations as high as 7010 ug/g in lettuce grown in an area contaminated by a smelter in Japan. Potato (Solanum tuberosum) plants contained up to 530 ug/g while tomato plants contained a maximum of 150 ug/g. Langerwerff and Brower (1974) reported Zn concentration in lettuce of 197 ug/g. Root crops and fruits contained less Zn in general than the leafy green portions of plants. Hutchinson et al. (1974) reported the highest Zn concentration in cabbage root. However, the highest concentration in the above ground portion was in lettuce (84.3 ug/g). Beavington (1975) reported Zn concentrations as being the highest in lettuce with a mean of 316 ug/g.

Analytical Techniques for Soil and Plant

Walsh (1971) reviewed the instrumental methods for analysis of soils and plant tissue. Walsh and Beaton (1973) further reviewed methods for soil testing and plant analysis. More recently, the methods for analysis of soil extracts and soil digests have been reviewed in detail (Page et al., 1982). The reader is referred to these sources for a more comprehensive review of the literature.

The most commonly used instrument for metal analysis of plant tissue, soil digests and extracts is atomic absorption spectroscopy (AA). The determination of Ni, Cu, Zn and Cd by AA in soil extracts and soil digest have been outlined (Baker and Amacher, 1982). The determination of Pb in soil
digests and extracts by AA has also been reviewed recently (Burau, 1982). Although AA is the most commonly used method for quantifying these elements, other methods have been used including anodic stripping voltammetry, polography, optical emission spectroscopy, neutron activation and in some cases colorimetry.

The development of inductively coupled plasma-atomic emission spectroscopy (ICP-AES) provides a new technique for simultaneous multielement analysis of soil digests, soil extracts and plant digests. Although the ICP-AES is a relatively new analytical tool in emission spectroscopy it does provide several distinct advantages over atomic absorption and colorimetric procedures (Fassel and Kniseley, 1974). Three of the most important advantages are: 1) simultaneous multielement determinations, 2) a higher dynamic concentrations range, and 3) reduced or eliminated matrix problems due to the high temperature argon plasma. A comprehensive review of ICP-AES has recently been published (Soltanpour et al., 1982).

The ICP-AES has been used for geochemical analysis (Floyd et al., 1980; Walsh and Howie, 1980) for analysis of extractable nutrient levels in soils (Jones, 1977; Dalquist and Knoll, 1978; Soltanpour et al., 1979; Hoult et al., 1980; Soltanpour and Workman, 1980; Gestring and Soltanpour, 1981a) and for plant tissue analysis (Jones, 1977; Havlin and Soltanpour, 1980; Soltanpour and Workman, 1980; Gestring and Soltanpour, 1981a, 1981b).

The instrumental conditions and procedures for multielement analysis of soils and plant tissue by ICP-AES has been outlined (Jones, 1977; Soltanpour et al., 1982). The main advantages of ICP-AES for multielement analysis of soils and plants are the speed and simplicity of the operation which produces data of high accuracy and reproducibility. Multielement analysis of soils and plants by ICP-AES is a boon to research involved with monitoring for environmental contamination.

CHAPTER 3

LABORATORY EXPERIMENTS

Lead, Cadmium, Zinc and Nickel Analysis of Soil Extracts and Soil Digests by Plasma Emission Spectroscopy

Abstract

Twenty-six contaminated soils were extracted with DTPA and AB-DTPA. Total soil digests were carried out on 21 contaminated soils. All soil extracts and digests were analyzed for Pb, Cd, Zn and Ni using ICP-AES.

A high degree of correlation (r) was found between DTPA and AB-DTPA extracts for Pb (0.96), Cd (0.99), Zn (0.99) and Ni (0.90). Total soil digests exhibited a high degree of correlation (r) with AB-DTPA extracts for Pb (0.92), Cd (0.93) and Zn (0.89).

Introduction

Numerous researchers are currently using the DTPA soil test to evaluate Pb, Cd, Zn, and Ni on mined lands and soils treated with sewage sludge. Most western mining regulatory agencies that require analysis of these elements recommend the DTPA soil test for evaluating plant availability (Berg, 1983). The AB-DTPA soil test has been recommended for assessing the revegetation potential when concerned with lead and molybdenum on surface coal mine overburden (Sutton et al., 1981). Colorado allows the AB-DTPA soil test for a wide variety of elements during overburden characterization including Pb, Cd, Ni, Se, and Mo (Berg, 1983).

Although the ICP-AES is a relatively new analytical tool in emission spectroscopy it does provide several distinct advantages over atomic absorption and colorimetric procedures (Fassel and Kniseley, 1974). Two of the most important advantages are 1) simultaneous multielement determinations, and 2) a higher dynamic concentration range.

Jones (1977) and Soltanpour et al. (1979) have demonstrated that the ICP-AES technique compares well with standard methods of analysis of macro- and micronutrients (P, K, Zn, Fe, Mn and Cu). More recently, ICP-AES has been used for evaluating boron (Gestring and Soltanpour, 1981) and Se (Soltanpour and Workman 1980) in soil extracts.

The objectives of this study were to compare the DTPA soil test with the AB-DTPA soil test for analysis of Pb, Cd, Zn, and Ni. In addition, total soil digests were compared to the AB-DTPA soil test for Pb, Cd, and Zn.

Materials and Methods

Twenty-six soils of varying degrees of contamination were air-dried, ground and passed through a 2-mm stainless steel sieve. Selected chemical properties of the soils used in this study are included in Table 3.1. All soils were

					рН ^а		EC (mm)	hos/cm)	b	OM	\$ ^C			
			Max.		7.80)		2.7		6.	9			
			Min.		6.60)		0.2		2.	2			
			Mean		7.22	:		0.9		5.	7			
			a Satu b Satu c Modi	arated aration fied W	paste n extra Walkley	ct -Black								
	Fe	Mn	Cu	PA Ext	Cd	Zn	Ni	Fe	Mn	Cu	Pb	Cd	Zn	Ni
							ug	/g						
Max.	242	24.5	30.8	484	14.2	384	1.5	184	47	16.5	417	16.0	349	1.2
Min.	29.9	2.9	2.7	4.1	0.3	9.8	0.2	22.2	5.9	0.9	2.3	0.2	3.3	0.2
Mean	68.0	11.0	7.9	147	2.1	98.0	0.7	50.2	15.4	4.0	107	1.9	71	0.7

Table 3.1 Selected chemical properties of the twenty-six soils used to compare AB-DTPA and DTPA extracts.

then extracted with DTPA and AB-DTPA. A more detailed analysis of each soil can be found in Appendix A.

The DTPA and AB-DTPA extracts have been described in Chapter 2. All DTPA and AB-DTPA extracts were filtered through a Whatman no. 42 or equivalent filter prior to analysis by ICP-AES. In addition to filtering, the AB-DTPA extracts were acidified prior to analysis. A 2-ml aliquot of the AB-DTPA extract was acidified with 0.25 ml of conc. HNO_3 . The samples were ready for simultaneous multielement determinations after shaking for 10 minutes to get rid of the carbonate-bicarbonate matrix to prevent clogging of the capillary tip in the ICP-AES nebulizer. The DTPA extracts were read directly without acidification.

Total elemental analysis was determined on 21 soils after complete sample dissolution following the method 3-5.3 as outlined by Soltanpour et al. (1982). Selected chemical properties of the soils used in this study are located in Table 3.2. A more detailed analysis of each soil can be found in Appendix B.

The soil digestion procedure consists of weighing 1.0 g of the 100-mesh (0.15 mm) soil into a 100-ml Teflon beaker followed by the addition of 10 ml of conc. HNO_3 and 10 ml of $HClO_4$. The beaker was covered with a Teflon watchcover and heated at 200° C for 1 hour. The cover was removed and heating continued until the volume was reduced to 2-3 ml. The samples were cooled, followed by the addition of 5 ml $HClO_4$ and 10 ml of HF, covered with a Teflon watch cover and

	рН		AB-DTPA		То	tal Digest	
		Pb	Cđ	Zn	Pb	Cđ	Zn
	1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 - 1999 -			ug,	/g		
Max.	7.50	698	21.4	498	3132	44.0	2185
Min.	6.75	34.9	0.8	33.3	151	3.4	197
Mean	7.15	243	4.9	180	992	12.0	748
		Manan man - 11 - 11 - 11 - 11 - 12 - 12 - 12 - 1				n man an 19 de <u>as san an am a</u> mhaidh anns daois	

Table 3.2 Selected chemical properties of the twenty-six soils used to compare AB-DTPA extracts and total soil digests.

heated overnight at 200°C. After removal from the hot plate and allowed to cool, the solutions were transferred quantitatively into a 50-ml volumetric flask and brought to volume. The solution was then ready for ICP-AES determinations.

The filtered extracts and total soil digests were analyzed for Pb, Cd, Zn and Ni using an ICP-AES. Operational parameters used for determinations of Pb, Cd, Zn and Ni are listed in Table 3.3.

Results and Discussion

The regression analysis of DTPA extracts on AB-DTPA extracts for Pb, Cd, Zn and Ni from 26 contaminated Colorado soils are shown in Figures 3.1 and 3.2. The correlation coefficients (r) were 0.96 (Pb), 0.99 (Cd), 0.99 (Zn) and 0.90 (Ni), indicating that the DTPA and AB-DTPA soil tests were highly correlated. Correlation coefficients (r) for Fe, Mn and Cu were 0.96, 0.75 and 0.97, respectively. All r values are significant at the 5% level of probability. On the average AB-DTPA extracted more Pd, Cd, Zn, Ni, Fe and Cu than DTPA. The DTPA extracted slightly more Mn than AB-These results tend to agree with those of Severson et DTPA. (1981). Severson et al. (1981) reported that the al. methods of Soltanpour (AB-DTPA) and Lindsay (DTPA) provide similar relative precision of duplicate analyses for all DTPA-extractable metals (Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn) except for Pb. For Pb, Soltanpour's method was more precise

Element	Spectral line, nm
Pb	220.3
Cđ	214.4
Zn	206.2 x 2
Ni	213.6 x 2
Mo	202.2

Table 3.3 Parameters used for simultaneous determinations of Pb, Cd, Zn and Ni by the ICP-AES method.*

* Jarell-Ash 750 Atomcomp. Sample flow rate: 0.7 cm³/min. Argon pressure: 5.624 kg/cm² (80 lb/inch²). Coolant (Argon) flow: 17 dm³/min. Capillary used: Tungsten carbide (0.D. = 0.99 mm, I.D. = 0.25). Height of observation above coil: 15 mm. Incident power: 1.25 kw. Reflected power: < 3 watts.</pre>



AB-DTPA Cd ug/g

Figure 3.1 Regression of AB-DTPA extracts on DTPA extracts for Pb and Cd.



AB-DTPA Ni ug/g

Figure 3.2 Regression of AB-DTPA extracts on DTPA extracts for Zn and Ni.

than Lindsay's method for topsoil and spoil materials collected from coal strip mines in the Western Energy Region.

The regression of AB-DTPA extracts on total soil digest for Pd, Cd, and Zn from 21 contaminated soils are shown in Figures 3.3 and 3.4. The correlation coefficients (r) were 0.92 (Pb), 0.93 (Cd) and 0.97 (Zn). All r values are significant at the 5% level of probability indicating that the AB-DTPA soil test is highly correlated with total soil digests for these contaminated garden soils. On the average AB-DTPA extracted 25% of the total Pb.

A Boston Task Force on Pb has determined that total soil Pb levels in excess of 500 ug/g are hazardous to human health (Spittler and Feder, 1979). The regression equation (Figure 3.3) demonstrates that an AB-DTPA Pb value greater than 100 ug/g would contain 500 ug/g total Pb. Currently the CSU-STL screens all routine AB-DTPA extracts for values greater than 100 ug/g. Customers are notified if this level is exceeded.

Conclusions

Twenty-six contaminated soils were extracted with DTPA and AB-DTPA. Total soil digests were carried out on 21 contaminated soils. All soil extracts and digests were analyzed for Pb, Cd, Zn and Ni using ICP-AES.

A high degree of correlation (r) was found between DTPA and AB-DTPA extracts for Pb (0.96), Cd (0.99), Zn (0.99) and



Figure 3.3 Regression of AB-DTPA extracts on total soil digests for Pb and Cd.



Figure 3.4 Regression of total soil digests on AB-DTPA extracts for Zn.

Ni (0.90). Total soil digests exhibited a high degree of correlation (r) with AB-DTPA extracts for Pb (0.92), Cd (0.93) and Zn (0.89).

In summary, the AB-DTPA soil test has an advantage over the DTPA soil test and the total soil digestion procedure. The AB-DTPA soil test utilizes a 15 minute extraction time while the DTPA and total soil digestion times are considerably longer. In addition, the AB-DTPA soil test does not utilize caustic acids required for total soil dissolution. If an ICP-AES is available the AB-DTPA soil test has the following advantages for evaluating contaminated soils:

- 1. The AB-DTPA extraction procedure is simple and rapid.
- 2. Simultaneous multielement extraction is possible for macro (P and K) and micronutrients (Fe, Mn, Cu and Zn) in addition to heavy metals (Pb, Cd and Ni) and trace elements (B, Se and As).

Evaluation of a Nitric Acid Digestion Procedure for Lead, Cadmium, Zinc, Nickel and Molybdenum in Plant Tissue by Plasma Emission Spectroscopy

Abstract

A Nitric acid digestion procedure for plant tissue analysis utilizing an ICP-AES was evaluated by Pb, Cd, Zn, Ni and Mo. Analysis by ICP-AES of National Bureau of Standards (NBS) reference materials 1571 (orchard leaves), 1573 (tomato leaves) and 1575 (pine needles) digested with nitric acid compared well with the NBS certified values. The elemental composition of crested wheatgrass, <u>Agropyron</u> cristatum, and spinach Spinacia oleracea, grown on contaminated soils and mine dumps were comparable using nitric-perchloric and nitric acid digestion procedures. A plant washing procedure was found to be essential in removing Pb, Cd, Zn, Fe, Al, and Ti contaminating soil from plants prior to analysis.

Introduction

Nitric-perchloric acids have been widely used for the digestion of plant tissues (Blanchar et al., 1965; Behan and Kincaide, 1970; Zossoski and Borau, 1977). Wet digestion procedures utilizing perchloric acid have two disadvantages; first, HCl0, requires special hoods and very careful handling due to its explosive nature, and second, needlelike $KClO_A$ crystals often form during digestion due to high plant potassium concentrations. To overcome these problems a wet digestion procedure using nitric acid was developed by Havlin and Soltanpour (1980) for simultaneous analysis of P, K, Ca, Mg, Na, Zn, Fe, Mn and Cu using ICP-AES. Incomplete oxidation of any organic matter is overcome due to the high temperature (6000-10,000 K) of the plasma (Fassel and Knisley, 1974). This same nitric acid digestion procedure used in conjunction with an ICP-AES has been used to evaluate B (Gestring and Soltanpour, 1981). More recently Boon (1984) utilized the nitric acid and ICP-AES for correlating the plant concentrations of Pb, Cd, Ni and Mo when plants were grown on a wide range of contaminated soils using a modified Neubauer Test.

Plant tissue samples are almost always contaminated with soil, especially if samples are collected from grazing pastures (Fleming, 1965; Healy et al., 1974). The importance of washing plant tissue collected from areas of high levels of soil contamination has been discussed (Boon, 1984).

Steyn (1969) showed that washing plant tissue with 0.1 to 0.3% detergent solution was satisifactory in removing soil contamination. A variety of detergents and dilute acids have been evaluated for removing soil contamination prior to plant analysis (Askley et al., 1960; Baher et al., 1964; Labanauskas, 1968; Ashby, 1969). More recently, Zimdahl and Foster (1976) developed a plant washing technique for removing Pb contaminated soil from plant roots prior to analysis. Previous studies (Arvik and Zimdahl, 1974) showed that this procedure removes surface Pb but not absorbed lead.

Soil contamination of plant tissue can be identified by using any element which is present in relatively large concentrations in soils and relatively low concentrations in plants. Elevated levels of Fe and Ti are commonly used to identify soil contamination in plant tissue (Fleming, 1965; Cherney and Robinson, 1983). Any plant tissue analysis in excess of 10 ug Ti/g must be strongly suspected of being contaminated with soil. Cherney and Robinson (1983) suggested that the nitric acid digestion procedure of Havlin

and Soltanpour (1980) is ineffective in determining soil contamination by Ti analysis.

The objectives of this study were to compare the nitric acid plant digestion procedure with standard methods for analysis of Pb, Cd, Zn and Ni, using the ICP-AES technique. In addition, the contribution of soil contamination was evaluated.

Materials and Methods

Three plant samples from the National Bureau of Standards: orchard leaves (1571), tomato leaves (1573), and pine needles (1575) were digested with nitric acid according to the procedure outlined by Havlin and Soltanpour (1980). A summary of the nitric acid digestion procedure for use with ICP-AES is given below:

- weighed 0.5 to 1.0 g of plant tissue into 50 ml Taylor tube;
- 2) added 10 ml conc. nitric acid and allowed to stand over night;
- 3) heated samples at 125°C for 4 hours and allowed to cool;
- 4) diluted to 12.5 ml with conc. nitric acid, further diluted to 50 ml with distilled water, then mixed and allowed amorphous silica to settle;
- 5) aspirated directly into plasma for ICP-AES analysis.

Additional plant materials (crested wheatgrass, <u>Agropyron</u> <u>critatum</u>, and spinach, <u>Spinacea oleracea</u>) were digested by the nitric acid procedure and a nitric-perchloric acid digestion procedure. The nitric-perchloric procedure

described below was previously described by Havlin and Soltanpour (1980).

One gram of dried plant tissue ground to pass a 20 mesh screen was weighed directly into a 50 ml Taylor digest tube (graduated 25 mm x 200 mm, Corning No. 7952). Ten ml of the digestion acid (4:1 nitric-perchloric mixture) was added to each tube and allowed to predigest over night. The tubes were then placed in alumunum heating blocks which are 36 x 36 cm and capable of holding 45 tubes per block. The nitric-perchloric digests were heated at 200°C until the volume was reduced to 2 ml, the original volume of $HC10_A$ acid in the 4:1 mixture. At this point the solution was colorless and contained a fluffy-white precipitate of amor-Upon cooling $KClO_4$ crystals formed. phous silica. The volume was then brought to 12.5 ml with conc. hydrochloric acid and then to the 50 ml mark with distilled-deionized If $KClO_A$ crystals were still present the tubes were water. heated (60-80 °C) to bring the $KC10_A$ into solution. As soon as the amorphous silica settled the digests can be read on the ICP-AES directly using standards containing the same matrix (acid to water) as the samples.

The plant washing technique (Zimdahl and Foster, 1976) used to evaluate the contribution of soil contamination to plant tissue is outlined below:

- 1) the plant tissue was rinsed with copious tap water;
- washed in distilled water containing 0.5% laboratory detergent for 30 seconds;

- 3) rinsed in distilled water for 30 seconds;
- 4) washed in 3N nitric acid for 30 seconds;
- 5) rinsed in distilled water for 30 seconds and blotted dry.

Results and Discussion

The analytical results from the nitric acid digests of Standard Reference Materials 1571, 1573, and 1575 are listed in Tables 3.4 through 3.6, respectively. These data illustrate that the nitric acid digestion procedure gave values similar to the NBS certified values. One notable difference is with the Fe concentrations. Other researchers (Havlin and Soltanpour, 1980; Jones, 1977; Gestring, 1982) have also noted Fe values below NBS certified values for both wet digestion and dry combustion methods. A slightly higher B value was noted for NBS 1573 (Table 3.5). This slightly higher value for NBS 1573 has been previously reported (Gestring and Soltanpur, 1981).

Two different plant species (<u>Agropyron cristatum</u> and <u>Spinacia oleracea</u>) were analyzed by both the nitric and nitric-perchloric acid digestion procedures. The means and standard deviations for both plant samples and each element are listed in Tables 3.7 and 3.8. The data in Table 3.7 illustrate that the nitric acid digest method performs as well as the nitric-perchloric method. There was no significant difference ($\alpha = 0.05$ level) between methods for Mg, Pb, Cd and Mo. For Table 3.8 no significant difference between methods for P, Fe, Zn, Mn, Pb, Cd, Ni and Mo. Although the

Element	NBS	Nitric
P%	0.21 <u>+</u> 0.01	0.19 <u>+</u> 0.003
K&	1.47 <u>+</u> 0.03	1.46 <u>+</u> 0.05
Ca%	2.09 <u>+</u> 0.03	2.00 <u>+</u> 0.03
Мg ¥	0.62 ± 0.02	0.57 <u>+</u> 0.01
Nat	0.0082 ± 0.0006	0.007 ± 0.002
Fe ug/g	300 <u>+</u> 20	226 <u>+</u> 2.49
Zn ug/g	25 <u>+</u> 3	22.9 <u>+</u> 3.09
Cu ug/g	12 + 1	13.7 <u>+</u> 0.76
Mn ug/g	91 <u>+</u> 4	90 <u>+</u> 0.78
B ug/g	33 <u>+</u> 3	34.4 <u>+</u> 1.61
Pb ug/g	0.11 <u>+</u> 0.01	0.09 <u>+</u> 0.04
Ni ug/g	0.3 <u>+</u> 0.1	0.32 ± 0.19
Mo ug/g	0.3 <u>+</u> 0.1	0.32 <u>+</u> 0.19

Table	3.4	Elemental composition	of NBS Reference	Material
		1571 (Orchard Leaves)	determined in ni	tric acid
		digests.		

NBS	Nitric
0.34 <u>+</u> 0.02	0.33 <u>+</u> 0.01
4.46 + 0.03	4.19 <u>+</u> 0.07
3.00 <u>+</u> 0.03	2.67 + 0.03
(0.7)	0.61 <u>+</u> 0.03
NR	0.03 <u>+</u> 0.002
62 <u>+</u> 6	55.7 <u>+</u> 0.002
690 <u>+</u> 25	485.3 <u>+</u> 4.04
238 + 7	217 + 1.0
11 <u>+</u> 1	11 <u>+</u> 0.26
(30)	35.3 <u>+</u> 0.43
6.3 <u>+</u> 0.3	6.06 <u>+</u> 0.91
(3)	2.85 <u>+</u> 0.24
NR	2.25 <u>+</u> 0.13
NR	1.43 <u>+</u> 0.18
	NBS 0.34 ± 0.02 4.46 ± 0.03 3.00 ± 0.03 (0.7) NR 62 ± 6 690 ± 25 238 ± 7 11 ± 1 (30) 6.3 ± 0.3 (3) NR NR

Table	3.5	Elemental	compo	sition of	NBS	Standard	l Refere	nce
		Material	1573	(Tomato	leave	es) det	ermined	in
		nitric act	ld dige	ests				

() Non-certified values

NR Not reported

Element	NBS	Nitric
Kł	0.37 + 0.02	0.37 + 0.02
Ca%	0.41 ± 0.02	0.42 + 0.02
Mg%	NR	0.12 <u>+</u> 0.005
Na%	NR	0.003 <u>+</u> 0.001
Fe ug/g	200 <u>+</u> 10	171 <u>+</u> 12
Zn ug/g	NR	63.2 <u>+</u> 6.7
Cu ug/g	3.0 <u>+</u> 0.3	4.3 <u>+</u> 0.3
Mn ug/g	675 <u>+</u> 15	682 <u>+</u> 28
B ug/g	NR	27.9 + 2.8
Pb ug/g	10.8 <u>+</u> 0.5	9.9 <u>+</u> 0.6
Cd ug/g	<0.05	0.16 <u>+</u> 0.03
Ni ug/g	(3.5)	2.53 <u>+</u> 0.11
Mo ug/g	NR	0.42 ± 0.11

Table 3.6 Elemental composition of NBS Reference Material 1575 (Pine Needles) determined in nitric acid digests.

() Non-certified values

NR Not reported

Element	Nitric-perchloric	Nitric
P%	0.12 <u>+</u> 0.003	0.13 <u>+</u> 0.001
Kŧ	1.11 <u>+</u> 0.05	1.10 <u>+</u> 0.02
Cat	0.27 + 0.004	0.29 <u>+</u> 0.006
Mg %	0.08 <u>+</u> 0.003	0.08 <u>+</u> 0.001
Fe ug/g	119.40 <u>+</u> 3.85	89.88 <u>+</u> 8.44
Zn ug/g	117.80 <u>+</u> 3.63	124.80 <u>+</u> 1.64
Cu ug/g	3.16 <u>+</u> 0.06	3.80 <u>+</u> 0.25
Mn ug/g	18.52 <u>+</u> 0.58	19.72 <u>+</u> 0.41
Pb ug/g	13.02 <u>+</u> 0.35	13.22 + 0.41
Cd ug/g	0.84 <u>+</u> 0.06	0.87 <u>+</u> 0.10
Ni ug/g	0.19 <u>+</u> 0.11	0.47 + 0.26
Mo ug/g	1.62 <u>+</u> 0.68	1.45 <u>+</u> 0.16

Table 3.7 Elemental composition of crested wheatgrass, Agropyron cristatum, grown on existing mine dumps, determined in nitric-perchloric and nitric acid digests.

Element	Nitric-perchloric	Nitric
Pŧ	0.63 + 0.01	0.65 + 0.05
K %	4.33 + 0.13	6.95 <u>+</u> 0.41
Cat	1.53 <u>+</u> 0.04	1.63 <u>+</u> 0.09
Мдғ	0.74 + 0.02	0.78 + 0.03
Nat	0.14 + 0.006	0.16 <u>+</u> 0.01
Fe ug/g	307.40 <u>+</u> 8.08	307.20 <u>+</u> 19.5
Zn ug/g	329.60 + 10.6	335.00 <u>+</u> 10.9
Cu ug/g	9.93 <u>+</u> 0.33	10.78 <u>+</u> 0.59
Mn ug/g	27.40 <u>+</u> 0.56	28.10 <u>+</u> 0.85
Pb ug/g	30.72 <u>+</u> 9.51	30.54 + 4.23
Cd ug/g	7.56 <u>+</u> 0.31	7.54 <u>+</u> 0.31
Ni ug/g	2.54 <u>+</u> 0.27	2.28 <u>+</u> 0.48
Mo ug/g	2.32 + 0.46	1.87 <u>+</u> 0.17

Table 3.8 Elemental composition of Spinach, <u>Spinacia</u> oleracea, grown on contaminated soils, determined in nitric-perchloric and nitric acid digests.

other values are statistically different the results were considered acceptable for diagnostic purposes and environmental monitoring.

The importance of washing plant tissue collected from soils highly contaminated with Pb, Cd and Zn can be clearly seen (Table 3.9). Iron and Pb values decreased four-fold in the washed samples. Cadmium concentration was 1.6 fold lower in the washed sample while Zn was 1.3 times lower. The observed drops in metal concentration following washing is consistent with other reports (Gordon, 1972; Johnson and Eaton, 1980). These results demonstrate the necessity of washing plant materials prior to analysis if useful predictions of plant concentrations are to be achieved.

Conclusions

The nitric acid digestion procedure used in conjunction with an ICP-AES for simultaneous multielement analysis of the digest provides a rapid and precise method for plant tissue analysis. The procedure is appropriate for plant analysis for macro- and micronutrients. This same procedure is appropriate for B, Pd, Cd, Zn, Ni and Mo. A washing procedure prior to analysis is essential when plants are collected from areas of highly contaminated soils.

lement	Unwashed (ug/g)	Washed (ug/g)
Fe	1711	400
Al	830	162
Ti	25	6.8
Pb	118	28.4
Cđ	13.0	8.1
Zn	204	154

Table 3.9 Elemental composition of washed and unwashed spinach grown on contaminated soil digested using nitric acid.

CHAPTER 4

FIELD SAMPLING - ASPEN, COLORADO

Evaluation of Aspen Mine Dump Materials for Lead, Cadmium and Zinc Using AB-DTPA Soil Extracts, Total Soil Digests and Plasma Emission Spectroscopy

Abstract

Samples of mine dump materials were taken to complete dissolution with a mixture of HNO_3-HClO_4-HF acids. Digests were subsequently analyzed for Pb, Cd and Zn using an ICP-AES. Ranges for total Pb, Cd and Zn were 240-21,700 ug/g, 13.3-223 ug/g, and 144-20,000 ug/g, respectively. Most of the mine dump materials contain sufficient Pb to pose potential health hazards resulting from the ingestion of the mine dump materials. Metal concentrations increased with decreasing particle size. However, no apparent aerial contamination has been noted.

To completely eliminate the exposure of small children to the mine dump materials several reclamation recommendations were developed. The two recommendations for the mitigation and reclamation of mine dump materials include burial under an impervious material such as asphalt or coverage with a suitable plant growth material with subsequent revegetation for stabilization and erosion control. Five areas of contamination were identified. In general, these areas correspond to the Durrant, Smuggler and Cowenhoven mine dump, the mined area at the base of Shadow Mountain, and the smelter area along Castle Creek.

Introduction

Soil concentrations greater than 500 ug/g total Pb have been considered hazardous to human health if ingested (Spitler and Feder, 1979). Many obvious mine dumps exist in Aspen, Colorado and are a result of the historic silver mining in the area.

The mining history of Aspen, Colorado began in 1879. The Bennett party crossed a pass west of Leadville, Colorado on July 4, 1879 and established a mining camp named Independence in commemoration of the day. When they reached the spring at the foot of what was to become Aspen Mountain they encountered the Hopkins party. Both groups set out to prospect and established claims on Aspen and Smuggler Mountains. Since they were trespassing on Ute Land, they called their settlement Ute City. The name was changed the next year to Aspen due to the abundance of the trees in the valley (Bancroft, 1951).

Silver was mined both as native silver and in sulfide compounds such as argentite (Ag_2S) . Other sulfide ores associated with the mineral deposits included galena (PbS), sphalerite (ZnS), and pyrite (FeS₂). Non-sulfide minerals

included smithsonite $(ZnCO_3)$, cerussite $(PbCO_3)$, siderite $(FeCO_3)$, and barite $(BaSO_4)$ (Volin and Hild, 1950).

By 1892 the annual silver production was running at \$10,000,000. The year round population of Aspen had grown to over 11,000. The town had three banks, ten churches, three large schools, a \$20,000 hospital, a \$90,000 opera house, a court house rivaling all but two other counties, a modern electric hotel and six newspapers (Bancroft, 1951). Mine dumps (Figure 4.1) were common sights by 1892 as was the Aspen Union Smelter which was built on the banks of Castle Creek (Figure 4.2). Mine dumps, smelters, concentrators and mining claims as they existed in 1896 are shown on a Willit's Map (Exhibit 1).

In July, 1893 the Sherman Act was passed by Congress which demonetized silver. Eighteen hundred miners were laid off, banks failed, and a depression settled in on Several mining operations continued including the Aspen. Smuggler mine which produced the world's record silver nugget in 1894 (Figure 4.3). The nugget was trimmed to 1,840 pounds to allow removal from the shaft. The nugget assayed 93% pure silver. The final production figures for (1879-1918) the Aspen area mines total more than \$105,000,000 (Bancroft, 1951). The objectives of this study were to evaluate Aspen mine dump materials for Pb, Cd and Zn using AB-DTPA soil extracts and total soil digests.



Figure 4.1 Smuggler mine dumps, Aspen, Colorado



Figure 4.2. Aspen Union Smelter, Aspen, Colorado



Figure 4.3 World's record silver nugget, Smuggler mine, Aspen, Colorado

Materials and Methods

Visible mine dumps or areas suspected of being historical mine dumps were sampled, extracted with AB-DTPA or digested and analyzed for Pb, Cd, and Zn using an ICP-AES. Areas that appeared to be contaminated with mine dump materials were compared to an 1896 Willit's Map of Aspen (Exhibit 1). Several other areas of suspected contamination were identified from the Willit's Map.

Sampling of mine dump material consisted of taking composite samples from each site. Five to ten subsamples were obtained from the top 15 cm from each site to form the composite sample. Samples were air dried, ground with a high-density aluminum oxide auger and passed through a 2-mm stainless steel sieve. All analytical results are based on the fraction passing through the 2-mm sieve. Further sieving was conducted on the sample containing the highest Pb, Cd, and Zn concentrations to obtain coarse (2-0.5 mm), intermediate (0.5-0.047 mm) and fine (<0.047 mm) fractions. Three of the mine dump material samples were collected by Tom Dunlop of the Aspen/Pitkin Environmental Health Depart-Two of the samples (1 and 2) were grab samples while ment. the third (3) was a composite consisting of 27 subsamples. Figure 4.4 shows the approximate sample loca-All three samples were analyzed by the Colorado tions. State Department of Health and the results appear in Appendix C as samples 1-3.



Figure 4.4 Approximate locations of the Aspen/Pitkin Environmental Health Department samples.

Soil pH was determined on saturation paste using a glass-calomel combination electrode (U.S. Salinity Laboratory Staff, 1954). The method of Soltanpour and Schwab (1977) as modified by Soltanpour and Workman (1979) was used to determine AB-DTPA extractable levels of Fe, Mn, Cu, Pb, Cd and Zn. This procedure is described in detail in the soil testing section (Chapter 2). Total digests were carried out on a number of mine dump materials using HNO_3 - $HClO_4$ -HF acids. This procedure (Soltanpour et al., 1982) has been outlined in Chapter 3.

All mine dump material extracts and digests were analyzed using an ICP-AES which was calibrated using standards of the same solution matrix as the samples.

Results and Discussion

Selected chemical properties of the mine dump materials are listed in Table 4.1. Total Pb, Cd and Zn concentrations ranged from 240-21,700 ug/g, 13.3-233 ug/g, and 144-20,000 ug/g, respectively. Chemical analysis for each individual sample are given in Appendix C.

The pH values for the mine dump materials ranged from 6.95-7.95. Although a combination of both sulfide and carbonate materials were present in or near the ore bodies (Volin and Hild, 1950) it is apparent that the overall pH is on the neutral to alkaline side. A neutralization of any acidity produced by the oxidation of sulfide minerals must have occurred to result in the near neutral pH. Due to the
			<u></u>	
		Tota	L conc. (ug,	/g)
	рH	Pb	Cđ	Zn
Mean	7.46	6375	53.4	3077
Range	6.95-7.95	135-21,700	13.3-223	144-20,000
n	13	21	16	16

Table 4.1 Selected chemical properties of Aspen Mine Dump Materials

low solubility of Pb, Cd and Zn at higher pH values, it becomes doubtful if any significant groundwater contamination could result from the Aspen mine dump materials.

Most of the Pb values for the mine dump materials are high enough to pose potential health hazards for the ingestion of this material. Mine dump materials containing greater than 500 ug/g total Pb or greater than 100 ug/g AB-DTPA extractable Pb should not be allowed to come into contact with children.

Analysis of various particle size fractions of the Smuggler Mine dump materials is presented in Table 4.2. These analyses demonstrate the increase in metal concentrations with decreasing particle size which is consistent with previous reports (Spitler and Feder, 1979; Johnson and Eaton, 1980). The Cd:Zn ratio is approximately 1:100 which is near the ratios reported by Schroeder et al. (1967).

The increased metal concentration of the small particle size material raises concern over the possibility of aerial contamination eminating from the site. A high-volume air sampler was placed on the site by Tom Dunlop (Director -Aspen/Pitken Environmental Health Department). Subsequent air monitoring demonstrated that aerial contamination was not significant. In fact, Pb levels were approximately 10 times lower than the Federal Standard of 1.5 ug/m³. Air data are on file at the Aspen/Pitkin Enviromental Health Department in Aspen, Colorado.

Trace element	Coarse (2-0.5 mm)	Intermediate (0.5-0.047 mm)	Fine <0.047 mm)
		ug/g	
Cđ	158	186	250
Cu	140	207	273
Pb	7,607	15,033	20,400
Zn	15,850	22,100	27,200

Table 4.2 Total element concentrations for different physical sizes of metaliferous spoil.

Several recommendations for reclamation of the mine dumps were made to the Aspen City Council and to the Pitkin County Board of Commissioners. Reclamation recommendations centered around covering the mine dump materials with a suitable cover and revegetating for stabilization and erosion control. Subsequent mitigation methods were developed to bury the mine dump materials under the Aspen airport runway extensions. A final plan was developed to bury the mine dump materials from the Smuggler Mine under roads and parking lots at the Centennial Residential complex. Five inches of the mine wastes were to be covered with ten inches of road base limestone material with a final cover of two inches of asphalt. This method of mitigation long term and permanent. Heavy metals would be was eliminated as a source of contamination in the air, surface water, soils, plants and groundwater.

The areas of highest metal concentration are identified on Exhibit 1. These areas appear to correspond with the Durrant, Smuggler and Cowenhoven mine dumps, the smelter operations on Castle Creek and the mined area at the base of Shadow Mountain.

Conclusions

Aspen mine dump materials contain high levels of total Pb, Cd and Zn. Ranges for total Pb, Cd and Zn ranged from 240-21700 ug/g, 13.3-223 ug/g and 144-20,000 ug/g, respectively. The concentrations of Pb, Cd and Zn increased with

decreasing particle size. However, no aerial contamination was noted. Most of the mine dump materials contain sufficient Pb to pose potential health hazards from ingestion.

Five areas of contamination were identified. These correspond to the Durrant, Smuggler and Cowenhoven mine dumps, the mined area along Shadow Mountain, and the Smelter area along Castle Creek.

Evaluation of Lead, Cadmium, and Zinc Contaminated Garden Soils Using the AB-DTPA Soil Test abd Plasma Emission Spectroscopy

Abstract

Sixty-five garden soils from Aspen, Colorado were extracted with AB-DTPA and analyzed for Pb, Cd and Zn using ICP-AES. Extractable concentrations of Pb ranged from 9.2 -808 ug/g. Extractable concentrations of Cd and Zn ranged from 0.2 - 14.2 ug/g and 8.4 - 484 ug/g, respectively. The chemical analyses for the soils is presented.

Many of these soils contain sufficient quantities of Pb and Cd to pose potential health risks from the ingestion of contaminated soil. Soil Pb concentrations greater than 100 ug/g AB-DTPA extractable should be considered hazardous to human health if ingested.

Introduction

Heavy metal contamination of garden soils has been well documented. The three primary sources of metal contamination of garden soils include deteriorating paints from older

homes, automobile emissions, and mining and smelting of metaliferous ores (copper, lead, zinc). Contamination of garden soils is environmentally important since many of these metals will produce adverse effects on health if entering the food chain.

Garden soils in Great Britain have been reported to contain Pb, Cd and Zn values ranging from 920-5897 ug/g, 1.6-40 ug/g, and 189-9064 ug/g, respectively (Davies and Roberts, 1975). Davies and Ginnever (1979) reported slightly lower values for Pb and Zn but higher values for Cd from other contaminated garden soils in Great Britain. Cadmium concentrations ranged 2.0-97 ug/g while Pb and Zn ranged 54-2612 ug/g and 28-7810 ug/g, respectively. Davies (1978) reported EDTA extractable levels for Pb ranging from 10-680 ug/g. Cadmium and Zn levels ranged 0.3-3.1 ug/g and 3.8-744 ug/g.

Contaminated garden soils from Wollongong, New South Wales, Australia contained mean Cu, Zn, Pb and Cd contents of 847 ug/g, 229 ug/g, 13.3 ug/g and 1.99 ug/g, respectively. From the soil chemical analysis it becomes obvious that the main ore being smelted is copper. Roberts et al. (1974) reported that garden soils in Toronto, Ontario contained Pb ranging 355-8750 ug/g. Garden soils not in the smelter area had Pb values ranging 57-240 ug/g.

Contaminated garden soils have been reported from a number of cities within the United States. Mielke et al. (1983) found substantial Pb, Zn and Cd contamination in

Baltimore, MD. Elevated Pb, Cd and/or Zn levels have been reported for Boston (Spittler and Feder, 1979; Preer and Rosen, 1977), for Washington, D.C. (Preer et al., 1980; Hornick et al., 1980), for New York (Kneip, 1981) and for Cambridge, MA (Nicklow et al., 1983).

The general concensus is that emphasis should be placed on eliminating the exposure of young children to soils containing more than 500-1000 ug/g total Pb (Spitler and Feder, 1979).

Materials and Methods

Soil samples were collected from Aspen gardens. Stainless steel tools and plastic lined containers were used to minimize any contamination during soil sampling. Soils were sampled to a depth of 15 cm. Each soil sample was composited from at least three separate subsamples obtained at one meter intervals from each other. These subsamples were thoroughly mixed and placed in plastic lined containers for transport to the laboratory.

Soil samples were air-dried upon arrival at the CSU-STL. At the CSU-STL, a high density aluminum oxide auger made by the Coors Porcelain Co., Golden, Colorado, was used for grinding soil samples. This grinder minimizes the degree of soil contamination with trace elements. The ground soils were then passed through a 2-mm stainless steel sieve. Soil samples were stored in plastic lined containers.

Soil pH was determined on saturation pastes using a combination electrode (U.S. Salinity glass-calomel Laboratory Staff, 1954). Organic matter was determined using a modified Walkley-Black procedure involving K₂Cr₂O₇ and H_2SO_A as outlined by Graham (1959). Electrical conductivity (EC) was determined on a saturation extract (U.S.Salinity Laboratory Staff, 1954). Water extractable NO_3 was determined by shaking 5 g of soil with 20 ml of distilled water, using Ca(OH)₂ to prevent dispersion. After filtering, the extracts were analyzed for NO_3 by the chromotropic acid method as described by Sims and Jackson (1971). The method of Soltanpour and Schwab (1977) as modified by Soltanpour and Workman (1979) was used to determine AB-DTPA extractable levels of P, K, Zn, Fe, Cu, and Mn. This procedure is described in Chapter 2.

Results and Discussion

The results of garden field sampling in Aspen, Colorado are summarized in Table 4.3. Chemical analysis for each individual soil can be found in Appendixes A and D.

The AB-DTPA extractable Pb, Cd and Zn ranged from 9.2-808 ug/g, 0.2-14.2 ug/g and 8.4-484 ug/g, respectively. Fifty-eight percent of the garden soils contain greater than 100 ug/g AB-DTPA extractable Pb. These soils could be hazardous and exposure of these soils to children should be eliminated.

	РЪ	Cđ	Zn
		ug/g	
Mean	172	2.5	120
St. dev.	155	3.0	118
Range	9.2 - 808	0.2 - 14.2	8.4 - 484
n	65	65	63

Table 4.3 Summary of AB-DTPA extractable Pb, Cd and Zn in Aspen garden soils

Most of the garden soils are of high fertility and would not require additions of fertilizers for optimum growth. The sufficiency nutrient level required for N, P, K, Fe, Mn, Cu and Zn are given in Table 4.4. With the exception of nitrate-nitrogen and occasionally phosphorus the garden soils appear to be inherently fertile. This is due, in part, to the long term cultivation of these gardens, the high concentration of mineral matter contributed to the garden soils from the historic mining industry in Aspen, and the apparently high organic matter content.

Conclusions

Sixty-five garden soils from Aspen, Colorado were extracted with AB-DTPA and analyzed for Pb, Cd, and Zn. Extractable concentrations of Pb ranged from 9.2-808 ug/g. Extractable concentrations of Cd and Zn ranged from 0.2-14.2 ug/g and 8.4-484 ug/g, respectively. Most of the soils appear to be inherently fertile requiring little or no fertilizer additions for optimum growth of vegetable crops.

Over fifty-eight percent of the soils contain AB-DTPA extractable Pb concentrations greater than 100 ug/g and could pose potential health problems to children if the soil was ingested.

Element	Sufficiency level ¹ ug/g	Mean Value Aspen Garden Soil ug/g
NO3*	42	47
P	14	45
к	180	402
Fe	10	69
Mn	0.5	12
Cu	0.2	13
Zn	1.5	120

Table 4.4	Sufficiency	(AB-DTPA ext	ractable)	nutrient	levels
	and mean value	ues for Aspe	n garden s	soil	

*for organic matter greater than 2.0

¹Dr. J. Ellis, personal communication.

Nitric Acid Digestion and Plasma Emission Spectroscopy for Evaluating Lead, Cadmium and Zinc Concentrations in Vegetables Grown in Aspen Gardens

Abstract

Eighty plant tissue samples were sampled from Aspen, Colorado gardens. Plant tissue was digested using a nitric acid procedure followed by metal analysis with an ICP-AES. In general, leafy portions of plants took up the highest concentrations of Pb, Cd and Zn. Root crops were intermediate and took up less metals than leaves but more than Concentrations of Pb, Cd and Zn in the leafy fruits. portions ranged: <5.0 - 45 ug/g, 0.6-17.6 ug/g and 6-444 ug/g, respectively. Concentration ranges in roots were <5.0 - 12 ug Pb/g, <0.5 - 3.1 ug Cd/g and 16.3 - 150 ug Zn/g. Vegetable fruits were <5.0 for Pb, ranged <0.5 - 2.7 ug Cd/g and 46 -17 ug Zn/g. An exception to the Pb uptake into leafy portions of the plant was noted for members of the genus and species, Brassica oleracea. Even when grown on highly contaminated soils the plant Pb concentration was always below detection limits (5 ug/g). However, this same trend was not noted for Cd and Zn.

Introduction

Heavy metal uptake into vegetable crops has been well documented. The general sources for the contamination has been attributed to automobile emissions, deteriorating house paint, mining and smelting operations. Plant concentrations of Pb, Cd and Zn are important due to their possible adverse health effects when entering the food chain in high concentrations.

Leafy vegetables have been reported to exhibit higher levels of heavy metals than other plant parts (Motto et al., 1970; Ter Haar, 1970; Preer and Rosen, 1977; Spitler and Feder, 1979). Normal leaf Pb concentrations range up to 20 ug Pb/g. An average range for Cd is 0.5-2 ug/g.

Lead and Cd content of leafy vegetables grown in Boston contaminated gardens ranged 7-42 ug Pb/g and 0.8-9.1 ug Cd/g, respectively. Beet greens contained the highest concentration of Pb followed by chard and lettuce (Preer and Rosen, 1977).

Hemphill et al. (1973) reported a high value of 1324 ug Pb/g in leaf lettuce grown near a lead smelter in Missouri. Vegetables grown around a smelter area in Canada contained leaf lettuce Pb levels of 0.7-40 ug/g. Radish roots contained 0.6-28 ug Pb/g and tomato fruit contained 0.25-0.40 ug Pb/g. Lettuce grown on contaminated soils in Australia contained mean Pb, Cd and Zn concentrations of 23, 4.5 and 316 ug/g, respectively. Other leaf vegetables contained significantly lower metal concentrations (Beavington, 1975). Spitler and Feder (1979) analyzed garden vegetables grown on Boston contaminated soils and found that fruits took up less Pb than roots and roots less than tops. This same general trend has been noted by others (Roberts et al., 1974; Lagerwerff and Brower, 1974; Hutchinson et al., 1974;

Preer et al., 1980). The recent work by Nicklow et al. (1983) appear to dispute these previous findings.

Materials and Methods

Plant tissue samples were collected from Aspen gardens. Plants were washed in the field with copious quantities of tap water. The plants were further washed according to the procedure of Zimdahl and Foster (1976) as outlined in Chapter 3.

Plant tissue was dried in a forced air oven at 70 C. Plant material was ground in a stainless steel Wiley Mill to pass a 20-mesh screen. One gram of dried, ground plant material was weighed directly into a 50 ml Taylor digestion tube. The nitric acid procedure of Havlin and Soltanpour (1980) as described in Chapter 3 was used for plant digestion. All plant tissue digests were analyzed for Pb, Cd and Zn using an ICP-AES.

Results and Discussion

Eighty plant tissue samples were analyzed for Pb, Cd and Zn. A summary of the results is given in Table 4.5. Leafy portions of plants generally took up the highest concentrations of Pb, Cd and Zn followed by roots and vegetable fruits (Tables 4.6 - 4.8). These findings are consistent with those reported by other workers (Roberts et al., 1974; Lagerwerff and Brower, 1974; Hutchinson et al., 1974; Preer and Rosen, 1977; Spitler and Feder, 1979; Preer et al, 1980). Graphic examples of this trend can be found

Table 4.5 Summary of Pb, Cd and Zn concentrations in plant tissue from Aspen gardens.

Plant	tissue	Pb	Cđ	Zn
			ug/g	
Leaf		ND - 60	0.6 - 17.6	36 - 444
Root		ND - 12	0.5 - 3.6	16.3 - 150
Fruit		ND	ND - 2.7	46 - 107
ND	non-de	etectable (Pb <	5 ug/g; Cd < 0.5	ug/g)

Plant tissue	N	Pb (ug/g)	Cđ (ug/g)	Zn (ug/g)
Lettuce	14	ND - 45	0.8 - 11.9	48.6 - 170
Spinach	16	ND - 41.4	0.9 - 10.3	141 - 472
Beet tops	7	ND - 24.9	0.7 - 7.6	36 - 444
Onion tops	4	ND - 6.8	0.9 - 3.2	-
Cabbage	3	ND - 6.6	0.7 - 7.2	54 - 114
Broccoli leaves	3	ND - 6.8	0.6 - 4.3	16 - 154
Chive	1	10	1.3	-
Tomato leaves	1	16	2.4	46.3
Strawberry leaves	1	12	1.2	-
Raspberry leaves	1	60	2.2	-
Potato leaves	1	10.6	17.6	59.1
Horseradish leaves	1	ND	3.1	44.1

Table 4.6 Pb, Cd and Zn concentrations in leaves of crops grown in Aspen contaminated garden

N number of samples

ND non-detectable (Pb < 5 ug/g)

Plant tissues	N	Pb (ug/g)	Cd (ug/g)	Zn (ug/g)
Beet	7	ND - 8.5	0.5 - 2.2	28 - 150
Onion	4	ND	1.0 - 2.1	-
Carrot	2	ND - 12	1.0 - 3.6	19 - 60
Potato	1	ND	0.6	16.3
Horseradish	1	ND	3.1	44.1

Table 4.7 Pb, Cd and Zn concentrations in roots of crops grown in Aspen contaminated gardens

N number of samples

ND non-detectable (Pb < 5 ug/g)

Plant tiss	ue N	Pb (ug/g)	Cđ (ug/g)	Zn (ug/g)
Peas	5	ND	ND - 2.7	46 - 60
Broccoli	4	ND	0.6 - 2.0	70 - 107
Garlic	1	ND	1.0	-
Zucchini	1	ND	ND	65.4
Bush bean	1	ND	ND	-
N	number of	samples		

Table 4.8 Pb, Cd and Zn concentrations in fruits of crops grown in Aspen contaminated gardens

ւբ

non-detectable (Pb < 5 ug/g; Cd < 0.5 ug/g)</pre> ND

in Figures 4.5 through 4.7. The dashed line in Figures 4.5 through 4.7 corresponds to the lower limits of detection (11d). These three gardens represent a low (72.0), medium (213) and high (461) range of AB-DTPA extractable Pb.

The plant data presented in Figure 4.7 identifies an exception to the high Pb concentrations in the leafy portion of the plant. Cabbage and broccoli leaves contained Pb concentrations below the detection limit (5 ug/g), while lettuce contained up to 33 ug Pb/g. Both broccoli and cabbage belong to the genus and species, Brassica oleracea. These findings are consistent with Nicklow et al. (1983) who demonstrated that collard and kale, which belong to the same genus and species, contained the lowest Pb content when grown on Massachusetts contaminated soils. They recommend that other members of Brassica oleracea be studied to determine if they also take up low Pb concentrations. The findings in Aspen substantiate the need for further research into Pb uptake in the Brassiceae.

Based on the results of Spitler and Feder (1979), recommendations to the Boston Gardening Community for the 1978 season for gardens with high lead levels (greater than 1000 ug/g total lead), were to confine gardening in such soils to fruiting crops which showed minimal Pb uptake even in highly concentrated soil. Where soil Pb was in the medium range (500-1000), gardeners were advised to avoid leafy greens or develop container plots of clean soil for such crops. Harvesting plant tops was also discouraged in



Figure 4.5 Lead uptake into vegetables grown on a low level contaminated soil.



Figure 4.6 Lead uptake into vegetables grown on a medium level contaminated soil.



Figure 4.7 Lead and cadmium uptake into vegetables grown on a high level contaminated soil.

these gardens. These same recommendations appear to be applicable to the Aspen community and have been presented (Boon, 1982).

Regression analysis of Pb and Cd concentrations in lettuce and spinach on AB-DTPA extractable soil Pb and Cd were compared to determine if the AB-DTPA soil test is capable of predicting Pb uptake into these garden plants. Figure 4.8 displays the regression data. The AB-DTPA is an accurate predictor of Pb and Cd concentrations in lettuce and spinach for these Aspen contaminated garden soils. Regression coefficients (r) were 0.95 and 0.86, for Pb and Cd respectively.

Conclusions

Garden vegetables from Aspen, Colorado were analyzed for Pb, Cd and Zn. In general, leafy portions of the plant took up the highest metal concentration followed by roots. Fruiting portions of the plants did not accumulate Pb but did accumulate Cd and Zn but at lower concentrations than leaves. Members of the genus and species <u>Brassica oleracea</u> did not take up Pb even when grown on highly contaminated soils.

The AB-DTPA soil Pb level is highly correlated with the Pb concentration in lettuce and spinach (r = 0.95). A similar high degree of correlation (r = 0.86) was also noted for AB-DTPA Cd and plant Cd.





Figure 4.8 Regression of AB-DTPA extracts on plant concentrations of Pb and Cd.

CHAPTER 5

CONCLUSIONS

The ammonium bicarbonate-DTPA (AB-DTPA) soil test was evaluated for its effectiveness in predicting contaminated soils and mine dump materials. The first study correlated the AB-DTPA soil test with the DTPA soil test for Pb, Cd, Zn The AB-DTPA soil test was highly correlated (r) and Ni. with the DTPA soil test for Pb (0.96), Cd (0.99), Zn (0.99) and Ni (0.90). In addition, the AB-DTPA soil test was highy correlated (r) with total soil digestion for the elements Pb (0.92), Cd (0.93) and Zn (0.89). The regression equation for AB-DTPA Pb on total Pb predicts that an AB-DTPA soil Pb level in excess of 100 ug/g will contain greater than 500 ug/g total Pb. Values exceeding these levels have been reported to pose potential health hazards from the ingestion of contaminated soil by children. Efforts should be directed to eliminating the exposure of children to soils containing greater than 100 ug Pb/g when extracted by AB-DTPA.

Analysis of National Bureau of Standard (NBS) plant material demonstrated that the nitric acid digestion procedure can be used for the evaluation of Pb, Cd, Zn, Ni and Mo in addition to elements P, K, Ca, Mg, Na, Fe, Cu, Mn, and B in plants.

The results of field sampling in Aspen, Colorado indicate that many of the gardens tested (58%) contained Pb levels that may pose potential health hazards to children from the ingestion of contaminated soil. Total soil digests of mine dump materials demonstrated that most of these materials would also pose potential health hazards from ingestion by children. Recommendations for the reclamation of these contaminated areas were presented to both the Aspen City Council and the Pitkin County Commissioners. Reclamation activities had begun but were temporarily curtailed by the Environmental Protection Agency. Local and State agencies will continue to reclaim the contaminated areas of Aspen.

The results of field sampling of Aspen vegetables demonstrated that leafy vegetables take up more Pb, Cd and Zn than root crops. Root crops were intermediate and took up less metals than leaves but more than fruits. Lead was never detected in vegetable fruits. In addition, it appears that members of the genus and species, <u>Brassica oleracea</u>, did not take up lead even when grown on highly contaminated soils. Further studies on the mechanisms of lead exclusion in the Brassica's is warranted. However, caution must be exercised and it is recommended that soil and plant analysis be conducted if individuals are concerned with contamination.

The AB-DTPA soil test was a good predictor of Pb and Cd concentrations in lettuce and spinach. Correlation coefficients (r) were (0.95) and (0.96) for Pb and Cd, respectively.

In conclusion, the AB-DTPA soil extracts have been shown to be highly correlated with DTPA soil extracts for Pb, Cd, Zn and Ni contaminated soils. The nitric acid plant digestion procedure was shown to be appropriate for analyzing plants grown on contaminated soils when used in conjunction with ICP-AES. These methods offer distinct advantages over other methods for evaluating and monitoring soils and plants for elements of environmental concern. These methods should reduce the time and cost for environmental screening programs concerned with contaminated soil and plants.

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APPENDICES

APPENDIX A

Selected Chemical Parameters or Soils Used in the Regression of AB-DTPA or DTPA extracts

								ав-Г	DTPA (ppm)				DTPA							
Sample #	рН	EC	₿ OM	N0 ₃ -В	I P	к	Zn	Fe	Mn	Cu	Nİ	Pb	Cđ	Zn	Fe	Mn	Cu	Nİ	РЪ	Cđ
1	7.2	0.2	4.7	6	26	332	16.7	51.4	7.0	7.0	0.4	7.9	0.3	11.3	41.1	14.2	4.7	0.3	5.3	0.2
2	7.8	0.4	2.2	35	20	331	9.8	38.3	2.9	2.7	0.2	21.2	0.3	6.6	26.5	5.9	1.2	0.2	15.7	0.2
3	7.1	1.9	6.9	55	+60	614	72.5	61.8	18.5	7.2	0.5	26.5	0.8	41.8	46.3	14.3	2.7	0.3	12.1	0.5
4	7.0	0.3	6.0	23	37	259	73.3	76.0	3.7	3.2	0.78	61.7	1.4	46.5	60.7	6.0	1.1	0.5	37.0	1.0
5	7.5	0.2	6.3	13	+60	441	75.2	49.8	9.3	5.0	0.8	66.8	0.8	57.7	48.1	17.0	2.2	0.7	40.6	0.7
6	7.5	0.3	6.7	31	+60	380	23.9	38.3	11.4	3.9	0.4	18.8	0.4	16.9	36.6	14.1	1.5	0.3	10.9	0.3
7	7.2	0.7	6.2	+99	37	393	26.8	49.6	20.4	5.0	0.5	21.4	0.5	16.0	38.2	20.4	1.7	0.3	10.8	0.3
8	7.1	0.9	6.9	+99	+60	476	48.6	45.2	14.6	5.8	1.3	36.2	0.7	29.7	53.2	21.3	2.2	1.0	18.5	0.5
9	6.6	0.6	6.7	88	+60	539	5.4	29.9	14.1	2.8	1.4	4.1	0.3	3.3	22.2	16.3	0.9	0.8	2.3	0.2
10	6.9	0.2	5.1	18	+60	210	56.2	61.5	15.4	5.5	0.8	113	1.1	33.2	32.2	13.9	2.2	0.6	49.4	0.7
11	7.4	0.2	5.1	9	+60	485	32.7	88.6	6.0	6.3	0.7	29.1	0.6	22.2	57.4	9.2	2.5	1.0	17.8	0.5
12	7.7	0.4	6.8	75	3	376	19.2	242	14.4	30.8	1.3	127	1.3	11.2	184.0	27.7	16.2	0.6	69.5	1.0
13	7.1	0.2	5.4	17	+60	253	66.4	93.9	10.1	10.4	0.7	79.0	1.8	45.0	75.0	12.2	5.0	0.3	49.5	1.4
14	7.4	2.7	6.7	12	9.	0 130	90.5	30.8	10.5	4.7	0.3	212	1.9	66.2	32.3	13.6	2.0	0.6	142	1.6
15	7.5	0.3	5.1	36	5.	0 142	197	132	8.6	15.8	0.8	453	2.6	134	82.1	9.2	7.7	0.4	396	2.4
16	7.4	0.4	6.5	39	+60	275	36.8	61.4	12.8	5.4	0.6	21.4	0.6	23.2	43.1	12.2	1.9	1.2	11.8	0.4
17	7.5	0.7	6.9	72	+60	1069	79.0	43.0	19.5	8.8	1.5	157	1.7	44.9	38.7	22.7	3.8	0.7	76.4	1.2
18	7.40	2.0	4.5	65.3	+60	539	384	38.1	3.5	4.0	0.6	484	14.2	349	24.5	8.8	3.4	0.4	417	16.0
19	7.10	1.9	3.3	75.1	+60	310	40	70.5	3.1	2.2	0.3	41.5	0.9	25.1	42.6	11.0	1.0	1.0	21.7	0.8
20	7.10	1.4	5.5	80.8	+60	340	377	83.1	4.4	24.8	0.8	523	8.2	314	63.5	10.4	16.5	1.0	315	7.7
21	6.95	1.4	-	-	+60	540	277	79.2	11.0	19.0	1.0	478	4.5	186	72.9	12.2	10.4	1.0	279	3.6
22	6.80		-	-	47.	9 418	53.6	66.8	19.7	5.2	0.6	90.9	1.1	39.6	52.6	47.5	2.7	0.7	56.4	1.0
23	7.35	-	-	-	+60	603	87.3	64.6	24.5	8.2	1.2	217	2.0	51.6	38.1	31.3	3.9	1.1	105	1.6
24	6.75	2.1	-	-	34.	5 1 9 3	127	59.7	5.9	3.5	0.5	167	2.6	99.5	42.3	8.7	1.9	0.5	187	2.3
25	7.40	1.9	-	-	41.	2 288	122	67.1	8.7	5.2	1.3	181	2.3	79.2	41.5	12.0	2.4	1.1	28 9	2.1
26	6.90	1.1	-	-	35.	9 199	152	46.0	7.7	3.1	0.4	182	2.5	101	30.2	7.7	1.4	0.3	138	2.0

APPENDIX B

SELECTED CHEMICAL PROPERTIES FOR SOILS USED IN THE REGRESSION OF AB-DTPA EXTRACTS ON TOTAL SOIL DIGESTS

		AB-DTPA	<i></i>		HF					
рH	Pb	Cđ	Zn	Pb	Cđ	Zn				
7.25	92.7	0.8	42.5	1080	7.1	383				
7.30	194	1.7	110	793	8.8	628				
6.9	182	2.5	152	703	7.7	601				
7.4	181	2.3	122	1010	10.2	754				
6.75	167	2.6	127	507	5.6	377				
7.15	133	2.6	170	557	8.9	635				
7.10	162	3.1	125	664	10.2	576				
6.95	478	4.5	277	1570	12.6	845				
6.95	54.6	1.6	60.4	322	6.9	367				
6.80	90.9	1.1	53.6	931	5.7	296				
7.35	217	2.0	87.3	815	10.6	857				
7.50	543	13.0	318	1709	20.4	1510				
7.25	351	14.0	498	1176	19.4	1175				
7.50	347	8.7	246	1050	13.6	860				
7.40	698	21.4	476	3132	44.0	2185				
7.35	42.8	1.0	43.6	232	4.1	245				
7.20	45.5	0.86	41.7	183	3.4	199				
7.0	34.9	0.95	33.3	151	3.4	197				
7.10	549	8.10	369	1892	19.3	1225				
7.05	497	8.39	385	2132	24.0	1555				

APPENDIX C

SELECTED CHEMICAL PROPERTIES ASPEN MINE TAILINGS

		HF ug/g							
Sample #	рH	РЪ	Cđ	Zn	Cu				
1	7.35	3520	13.3	_	-				
2	7.15	9950	38.3	-	-				
3	7.35	21,700	223	-	-				
4	7.20	3490	32.5	1480	102				
5	7.35	9950	64.5	5400	194				
6	7.35	17,350	200	20,000	194				
7	7.60	2625	29.0	1175	186				
8	7.95	11,550	29.5	1655	127				
9	7.70	665	19.0	145	158				
10	7.55	970	25.5	800	156				
11	6.95	240	19.0	144	76				
12	7.85	5650	55.0	1745	1270				
13	-	5100	26.5	1620	99.0				
14	_	4625	27.2	1600	100				
15	-	11,500	33.0	2370	110				
16	-	135	-	-	-				
17	-	11,455	-	-	-				
18		2106	-	-	-				
19	-	2288	-	-	-				
20	-	2353	-	-	-				
21	7.70	6996	19.3	1863	100				
Mean	7.46	6375	53.4	3077	221				

APPENDIX D

	AB-DTPAAB-DTPA											
Sample #	рH	EC	\$ 0M	N03-N	P	к	Zn	Fe	Mn	Cu	Pb	Cđ
27	7.1	0.3	6.5	8	52	380	110	62.5	9.7	6.7	100	2.5
28	7.5	0.4	5.9	84	7	218	23.2	44.0	7.5	9.2	97.9	0.8
29	7.6	3.3	4.6	19	+60	441	50.1	72.8	10.9	7.7	59.3	0.8
30	7.7	0.5	6.1	41	+60	656	75.8	48.6	14.1	9.4	152	1.7
31	7.3	3.6	4.0	+99	+60	677	48.6	94.8	15.9	3.9	72	1.1
32	7.5	0.9	5.3	25	+0	197	131	129	22.5	7.6	213	2.1
33	7.5	1.0	6.5	48	+60	322	149	79.3	21.0	7.1	192	-
34	7.4	2.5	4.3	+99	59	563	470	9.7	6.4	2.7	632	17.7
35	8.0	1.0	2.7	20	36	453	8.4	87.3	11.3	3.1	9.2	0.2
36	7.3	2.7	4.2	+99	59	919	78	40.7	10.6	8.7	192	2.2
37	7.1	1.9	4.3	13	+60	392	379	42.9	27.2	6.2	429	6.4
38	7.5	1.1	-	7	17	120	378	31.1	4.8	13.3	351	8.9
39	7.3	-	-	-	13.8	184	42.5	48.3	2.6	4.4	92.7	0.8
40	7.3	2.0	-	-	-	-	-	-	-	-	194	1.7
41	6.9	1.1	-	-	35.9	199	152	46.0	7.7	3.1	182	2.5
42	7.4	1.9	-	-	41.2	288	122	67.1	8.7	5.2	181	2.3
43	6.8	2.1	-	-	34.5	193	127	59.7	5.9	3.5	167	2.6
44	7.2	-	-	-	26.8	223	170	46.2	4.9	3.9	133	2.6
45	7.1	-	-	-	-	-	-	-	-	-	162	3.1
46	7.0	1.4	-	-	+60	540	277	79.2	11.0	19.0	478	4.5
47	7.0	-	-	-	-	-	-	-	-	-	54.6	1.6
48	-	-	-	-	+60	157	484	60.4	26.7	12.8	145	2.0
49	-	-	-	-	+60	1771	95	42.1	36.7	11.2	68.4	1.8
50	-	-	-	-	+60	729	100	130	25.9	17.1	283	1.5
51	-	-	-	-	14.9	34.7	44	39.6	11.5	233	215	1.5
52	-	-	-	-	5.3	41.9	11.1	271	6.3	17.3	24.9	0.3
53	-	-	-	-	35.9	350	23.1	63.3	14.4	3.2	28.7	0.6
54	-	-	-	-	7.2	182	23.8	51.8	7.6	5.9	50.2	0.8
55	-	-	-	-	+60	370	236	102	7.2	21.7	292	3.6
56	-	-	-	-	58	398	82.1	69.3	12.0	20.1	181	2.0
57	-	-	-	-	+60	271	268	77.8	7.8	22.4	461	4.8
58	-	-	-	-	45.0	744	59.7	74.5	12.5	1.67	5.4	0.2
59	-	-	-	-	41.6	746	4.4	26.5	12.8	3.5	1.4	0.4
60	-	-	-	-	44.1	289	132	28.5	10.7	9.2	324	5.1
61	-	-	-	-	4.9	241	3.4	40.3	4.6	3.6	4.2	0.1
62	-	-	-	-	29.0	331	60.4	76.8	8.6	47	201	1.5
63	-	-	-	-	+60	435	59.9	69.2	9.9	8.6	77.5	1.1
64	-	-	-	-	+60	370	236	102	7.2	21.7	292	3.6
65	-	-	-	-	+60	729	99.8	130	25.9	17.1	283	1.5

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