

Project Progress Report

The Role of Inorganic Chemical Fertilizers and Soil Amendments on Trace Element Contents of Cropland Soils in California

**California Department of Food and Agriculture
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Introduction

Chemical fertilizers are fundamentally important to the crop production worldwide. Fertilizers used in agricultural production however frequently contain potentially hazardous trace elements that may accumulate in the receiving soils and may be inadvertently transferred through the human food chain, thus seriously impacting the consumers (Anderson, 1997; Singh, 1991). In the past 30 years, the accumulation of pollutant in cropland soils through the long-term fertilizer applications has been extensively investigated (Mulla and Page, 1977; Pezzarossa et al., 1990; Popova, 1991; Camelo et al., 1997). Among the potential hazardous elements most often found are As and Cd in phosphate fertilizers and As and Pb in micro-nutrient (Fe, Mn, and Zn) supplements.

Potential human health implications through exposures of food harvested from long-term fertilized crop production fields have been demonstrated (McLaughlin and Singh, 1999). The maximum Cd content of fertilizers has been proposed (or adopted) in at least 10 countries. The numerical limits ranged from 10 to 450 mg Cd per kg of product, depending on the intensity of the fertilizer ingredients in the products (McLaughlin, 1995). The State of Washington screened selected fertilizers and trace elements supplements that are used for crop production and concluded that, on an annual basis, amounts of trace elements added on through the non-waste-derived fertilizers posed a level of risk similar to the waste-derived fertilizers (Bowhay, 1997). Regulatory agencies in the U. S. have initiated reviews on the merits of setting numerical limits for the maximum amounts of potentially toxic metals in fertilizers (Anonymous, 1999; Cooney, 1997). California Department of Food and Agriculture drafted human health risk-based upper limits for As, Cd, and Pb in inorganic commercial fertilizers (Foster Wheeler Environmental, 1997).

The amounts of potentially toxic metals introduced into the soil through the application of fertilizers are small, relative to the total amounts in surface soils where fertilizers are customarily incorporated. Under the ordinary cultivation conditions, the Cd inputs to cropland from P fertilization may vary from 1 to 10 g per hectare per year (McLaughlin and Singh, 1999). The annual concentration increments cause by this amount of mass input are not readily detectable unless the practice has continued for a long period of time. In addition, the trace element mass input from fertilizers must also be balanced against other sources of inputs (such as atmospheric fallout and irrigation water) and outputs (such as crop uptake, surface erosion, deep leaching, etc.). It is essential that field based data on the trace element accumulations is generated to justify the need of regulatory actions. The purpose of the study is to development field-based data on As, Cd, and Pb contents of cropland soils in California and assess the potential for As, Cd, and Pb to accumulate in cropland soils through repeated fertilizer applications..

Methods

Three approaches are used to investigate whether As, Cd, and Pb have accumulated in cropland soils in California due to the application of inorganic chemical fertilizers.

1. Sampling of California Benchmark Soils To Establish Baseline Concentrations of As, Cd, and Pb in Soils.

In 1950, R. Arkley established 50 California Benchmark Soils that were representative of soils distributed in California. These soils were again sampled for elemental analyses Bradford et al. (1996). Because the benchmark soils are located at primarily undisturbed or marginally developed area, the elemental contents of these soils represent the baseline values for soils in California. These soils will be sampled in 2001. The As, Cd, Pb, Zn, and P contents of the soils will be determined.

A comparison of the baseline values over this time span will provide a snapshot on the changes on elemental compositions of California soils.

2. Sampling Vegetable Growing Soils Across The State To Examine The Impact of Fertilization on As, Cd, and Pb Contents.

In croplands, As, Cd, and Pb are introduced by the application of either P fertilizers and/or Fe/Mn/Zn supplements. Although the concentration of As, Cd, Pb in the amendments used may be elevated, the actual mass inputs usually is relatively speaking small, because the annual fertilization rate for crop production is small. Unless the cropland soils has received repeated applications of fertilizers over long periods of time, the change on the As, Cd, and Pb concentration of the receiving soils will not be readily detectable. The vegetable growing fields were chosen for the investigation because they are heavy fertilized and, in many parts of California, multiple cropping per year for vegetable production is common.

For most growers, detail historical records on farming operations do not exist. As a result, it is not possible to trace the fertilizer application history of a given field. There was also no record on the trace element concentrations of the fertilizers used in the past. As the P and Zn will accumulate in the soil with applications, we decided to use P and Zn as the reference points to evaluate whether As, Cd, and Pb accumulated in the soils through the applications of P fertilizers and micro-nutrient supplements. It was hypothesized that the accumulation has occurred if As, Cd, and Pb concentrations of soils increase with the increase of P and/of Zn concentrations in the soil, provided the soils are from the same geomorphological region. To make sure that the samples were representative of the region and covered a wide spectrum of cultivation practice, a large number of samples need to be collected.

The vegetable production area selected for the sampling were Imperial/Coachella Valleys, Oxnard/Ventura Coastal Plain, Santa Maria/San Luis Obispo Valleys, Salinas Valley, and Lower Central Valley. Each area is considered as a geomorphologically homogeneous region.

3. Sampling Vegetable Plants Corresponding to The Collected Soil Samples

In soil sampling, a very small volume of soils in a field is collected. As a result, the determined elemental contents of soil may be subject to spatial variations. In each sampling location, 5 replications were taken to account for the possible spatial variability in field sampling and in elemental distributions. The root system of plants extends and covers a considerably larger area of the soil than the amount of soil extracted by the sampling auger. Therefore, the elemental contents of the plant tissue are reasonable integrators of the elemental contents of soils over a much larger area and its values are less susceptible to spatial variability.

In addition to sampling the soil, we also collected plant tissue samples that corresponded to each soil sample collected. The As, Cd, and Pb contents of plant tissues will be assayed. It was hypothesized that As, Cd, and Pb concentrations of the plant tissue increase in proportion with the P and/or Zn concentrations of the soils and that increased concentrations of these elements are indications that they are accumulating in the fertilizer receiving soils.

4. Quality Control and Quality Assurance

To insure that the samples taken across the State and at different times were consistent and to insure that the chemical determinations are accurate and precise, a quality assurance and quality control (QA/QC) plan was developed and tested prior to the commencement of field sampling and chemical analysis. The QA/QC procedures were followed for all soil and plant tissue sampling and for chemical determination.

The details of the QA/QC plan may be found in the Appendices Section of this report.

5. Trace Element Mass Balance

To account for the role of fertilizer applications on the trace element build up in cropland soils, it is essential that a mass balance model be constructed. This model should account for all inputs and outputs of a trace element, its chemical reactions in the soil, its extractions by plants, and its loss through atmospheric, terrestrial, and aquatic routes.

We use arsenic as the starting point for the model construction because its chemistry in the soil is more complex than Cd and Pb. The chemical reaction

modeling will determine the soil solution concentrations of the element that, in turn, determines the extent of plant uptake. By linking the outputs from the chemical modeling with LEACHEM (a surface and subsurface solute transport model), the losses through surface runoff and leaching may be accounted for.

Work Completed

1. Benchmark Soils:

- All of the benchmark soil sampling locations have been identified from records of the archived soil samples and marked onto current topographic maps.
- Samples were collected from 38 of the 50 locations. These samples are being processed for chemical analyses.
- In two locations, the access to the site was denied by the property owners.
- A field trip has been scheduled in the week of June 3 – 8 to collect soil samples at 10 locations in northern California.

2. Soil and Plant Sampling of Vegetable Growing Fields.

- At present, we have collected samples in two for the 5 identified areas. The chemical analyses of soils in these two areas are essentially completed. The plant tissue samples have been digested and are awaiting the chemical analyses.
- Plans are being developed for sampling the remainder areas in the summer.

3. Trace Element Mass Balance Model

A simplified mass balance model to evaluate fate of arsenic in soil has been assembled. The working draft of the model description may be found in Appendix IV.

Results

1. California Benchmark Soils – 1967

- The Cd, Pb, Zn, and P contents of benchmark soils collected in 1967 were determined. The results indicated that the Cd and Pb contents of the soils collected from undisturbed and marginally developed area in California were not related to the P or Zn concentrations of the corresponding soils (Figures 1 – 4).

2. Area A

- We have completed determinations of As, Cd, Pb, Zn, and P of all soil samples collected in Area A. The plant tissue corresponding to these soil samples have been digested and the chemical analyses is in progress.
- The P contents of soils in this area varied from 200 to 900 mg kg⁻¹. The As, Cd, and Pb concentrations of the soils were 3 – 10, 0.3 – 1.6, and 14 – 22 mg kg⁻¹, respectively (Figures 5 – 7). It was difficult to establish any trend with respect to the P in soils, as the data scattering was considerable.
- Replications of each sampling location were factored in and the data means and the corresponding error ranges were re-plotted (Figures 8 – 10). It appeared that the As contents of soils in area A were not influenced by the P concentrations of the soils. However, the Cd and Pb concentrations of soils increased linearly with the soil P concentrations. The linear regression was significant at $p < 0.05$.
- The Zn contents of soils in Area A varied from 20 to 80 mg kg⁻¹. There was no clear trend between As, Cd, and Pb contents of the soils and the Zn contents of the soils (Figures 11 – 13).

3. Area B

- We have completed the determinations of Cd, Pb, Zn, and P in soil samples collected in Area B. We are determining the As concentrations of the soils as this report is being assembled. The plant tissues have been digested and are awaiting the chemical determinations.
- In Area B, the P concentrations of the soil varied from 500 to 2500 mg kg⁻¹. The wide P concentration range was indicative of the range of P fertilizers that had been applied in the past. The corresponding Cd concentrations of the soils varied from 0.3 (approximately background level) to 2.4 mg kg⁻¹ (Figure 14). The Cd in the soil increased linearly with the concentration of P in the soils, indicative of the contribution of P fertilization on the Cd accumulation in soils (Figure 15).
- However, the Pb concentrations of the soils was not significantly affected by the increase of P in the soil, indicating that P fertilization did not contribute to the Pb accumulation in the soils (Figure 16).
- There is no trend that the Cd or the Pb concentrations of the soils were influenced by the Zn concentrations of the soils (Figures 17 and 18).

- For majority of the soils, the Cd contents varied from 0.01 to 0.4 mg kg⁻¹. Only three out of 50 soils exhibited Cd concentrations >0.4 mg kg⁻¹.
- The Pb concentrations of the benchmark soils varied from 4 to 25 mg kg⁻¹. These concentration levels were well within the range of background Pb concentrations of soils reported in the scientific literature.

Future Work

1. Chemical Determinations and Data Analysis

We are wrapping up the chemical determinations of samples that were collected from Areas A and B. These data will be collectively analyzed using the conventional parametric statistical methods.

2. Continue The Soil Sampling of Soils and Plants

We still need to complete the soil sampling at three of the identified vegetable growing area. When the data from Area A and B are analyzed, there may be a need to collect additional samples to substantiate data. We plan to use the summer to complete the soil samplings.

3. Continue The Construction of Mass Balance Model

We will continue the development of the mass balance model by simulating the typical conditions of California soils and identify the sensitivities of model parameters.

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APPENDICES

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| Appendix I | Soil and Plant Sampling Protocols |
| Appendix II | Protocol for Quality Control/Quality Assurance for Chemical Analysis – Trace Elements |
| Appendix III | Protocol for Determination of Dioxin Concentrations in California Cropland Soils |
| Appendix IV | A Simplified Mass Balance Model To Evaluate Arsenic fate in Soil (working draft) – B. bar-Yosef |

Appendix I

Soil and Plant Sampling Protocols

1. Introduction

CDFA is initiating a study to evaluate the potential of trace elements accumulation through normal and regular fertilizer applications on California's cropland soils. The study consists of four parts and will emphasize the accumulation of arsenic, cadmium, and lead.

- A. Trace Elements in Benchmark Soils – Fifty benchmark soils in California were sampled in 1967. Most of the sampling sites were on cropland. As circumstances permit, soils at these sites will be sampled again in 2000. The concentrations of As, Cd, and Pb of soils collected in 1967 and 2000 will be determined and compared. The comparison will provide an indication on the accumulation of As, Cd, and Pb in soil under cultivation.
- B. Trace Element Build-up in Heavily Fertilized Soils – The As, Cd, and Pb may accumulate in cropland soils through primarily application of P fertilizers and Fe and Zn supplements. Soils that have received heavy application of P fertilizers and trace element supplements (such as the soils used for vegetable and forage crop production) will be targeted for field sampling. If As, Cd, and Pb are accumulating in the soils, we expect to observe an increasing trend when the data are plotted as Cd vs. P, As vs P, and Pb vs. Zn.
- C. Mass Balance of Trace Elements Inputs and Outputs – The extent of As, Cd, and Pb accumulation on cropland soils, if occurred, is expected to be slight and not readily detectable. A mass balance-based model is developed to estimate the extent of accumulation over long periods of time. For this purpose, fields sites will be selected to monitor the inputs and outputs of As, Cd, and Pb for two consecutive years. The data will than be used to determine the rate constants of the mass balance model.
- D. Trace Element Concentrations of Plant Tissues – While the trace element inputs through fertilizer and soil amendment applications may not be readily detectable from the analysis of the trace element contents of the soils, plants grown on the fertilized soils may absorb the trace elements introduced through the fertilizer applications. When the heavily fertilized soils are sampled, the above ground vegetation will be sampled at the same time. The As, Cd, and Pb concentrations of the plant tissues will be determined. If As, Cd, and Pb are accumulating in the soils, we expect to observe an increasing trend when the data are plotted as plant Cd vs. soil P, plant As vs soil P, and plant Pb vs. soil Zn.
- E. Background Level Dioxin in Soils – In addition to the above-outlined tasks, separate soil samples will be obtained at the same sampling locations and forwarded to California Department of Toxic Substances for Dioxin screening.

To accomplish the tasks in this research plan, appropriate sampling sites must be identified and a large number of soil and plant tissue samples must be obtained across the state. University of California maintains Cooperative Extension Offices at every county for dissemination of information for agricultural production. A University of California, Division of Agriculture and Natural Resources Work Group, with memberships of Cooperative Extension Specialists and Farm Advisors, will be organized to assist in the identification of sampling sites and collection of soil and plant tissue samples.

2. Objective – Developing Soil and Plant Tissue Sampling Protocol and Chemical Analyses QA/QC Plan

The As, Cd, and Pb accumulation of cropland soils is expected to be slight. Field sampling and the subsequent chemical analyses must therefore be able to detect small differences of the concentration changes in the soils. To produce credible results, consistent protocols for selecting sampling locations,

collecting soil and plant tissue samples, processing collected samples, and determining trace element concentrations are essential to produce credible results. The purpose of the protocols for sampling and QA/QC plans for chemical analyses are as follows:

- A. Develop a clear and concise site selection and soil sampling procedure for members of work group to follow.
- B. Collect soil and corresponding plant tissue samples that may be used to
 1. Evaluate As, Cd, and Pb accumulation in cropland soils in California
 2. Establish baseline concentrations of dioxins in California soils
 3. Account for spatial variability of fields

3. Procedures

A. Selection of Site

1. For Trace Elements (As, Cd, and Pb)
 - a. 1967 benchmark soil sampling sites will be re-sampled in 2000.
 - b. Sites received heavy and repeated P fertilizer application.
 - c. Sites that received frequent applications of trace metal supplements.
 - d. Selection of sites will emphasize major agricultural production areas in California (Imperial/Coachella Valley, San Joaquin Valley, and Salinas Valley).
2. For Dioxins – Samples will be obtained from the same locations as those for trace elements. Soils for dioxin analysis will be selected from this pool pending on the outcome of trace element determinations.

B. Site description

1. Provide detailed description of the location (i.e. marker; longitude/latitude, road/map directions, etc.)
2. Record time that sample is collected (i.e. end of the growing season), locations of the field where samples are taken (minimum 20m. from edges of the field), type of cropping, information on the owner and/or manager

C. Soil Sampling

1. Soil Collection – Use 2” bucket auger, if possible. Otherwise, use a trenching method. Clean the tools used for collection after each sample is taken. Collect 4 – 5 sub samples in a 3 m x 3 m area and composite.
2. Number of samples – Collect 3 – 5 samples at approximately 15 - 20 m apart (exact number and distance will be determined later).
3. Volume of sample – Approximately 500 g for trace elements and 100 g for dioxin analyses, field-screened to pass a sieve with 1mm openings, store in separate containers. For samples borne for dioxin analysis, avoid contact with paper products.
4. Storage containers
 - a. Samples for As, Cd, and Pb analyses will be contained in plastic bags inside paper carton
 - b. Samples for dioxin analysis will be stored at field moisture content in a glass bottle. California Department of Toxic Substances Control will provide the containers.
5. Field storage/shipping - Following their collection, samples will be stored in ice-packed thermo-insulated storage chest and transferred to cold room or refrigerator with temperature set at 1 – 4°C.

D. Plant Tissue Sampling

1. Locations - Plant tissue samples will be obtained, when possible, at the same locations and the same time of soil sampling
2. Type of samples
 - a. The youngest fully developed leaves at flowering will be sampled
 - b. Edible portions of the plant will be sampled when available
3. Storage container – samples will be placed in plastic bags
4. Field storage/shipping – Following their collection, samples will be stored in an ice-packed thermo-insulated storage chest and transferred to a cold room or refrigerator with temperature set at 1 – 4 °C.

E. Sample Processing

1. Store samples in a cold room 1 – 4°C until processing
2. Weigh to determine field weight
3. Soil samples will be air dried in a glasshouse to a constant weight
4. Mix, sub-sample, and grind for analysis
5. Plant tissue samples will be washed, placed in paper bags, oven dried at 65°C, ground to pass a screen with 0.1 mm openings, and sub-sampled for analysis

F. Sample digestion – For soils, follow EPA Method 3052 (microwave digestion with HNO₃ and HF). For plant tissue, use a HNO₃ + H₂O₂ microwave digestion method.

G. Analysis – Atomic absorption spectroscopy will be used. The QA/QC include determinations of recovery of certified standards, recovery of spiked analyte, precision of analysis by duplicated samples, and method of detection limits.

H. Organization of Task Force

1. A UC Division of Agriculture and Natural Resources Work Group will be formed to handle the site identification and soil and plant tissue sampling
2. Membership includes UC faculty, CE specialists, and Farm Advisors
3. Responsibilities
 - a. Review and finalize sampling protocols
 - b. Identify and approve all sampling sites
 - c. Collect, package, and ship samples to appropriate locations for analyses
 - d. Review and analyze the data
 - e. Review and approve the final report

I. Organization of Advisory Committee

1. Function – provide inputs in experimental procedures and review results/findings
2. Membership should include representatives from
 - a. Grower associations
 - b. Fertilizer industry
 - c. Related State Agencies
 - d. UC Division of Agriculture and Natural Resources
 - e. Environmental advocates

Appendix II

Quality Control/Quality Assurance for Chemical Analysis – Trace Elements

Soil samples will be air dried in a glass house until constant temperature, stored in plastic bags inside paper containers. For chemical analysis, aliquots of stored soils are ground to pass a screen with 0.075 mm openings using mortar and pestle.

Plant tissue samples are soaked in detergent solution for 5 minutes, rinsed with deionized water, dried in an oven at 65°C, ground with a rotary mill to pass a screen with 0.1 mm openings. The following procedures will be followed to solubilize soil and plant material for chemical analyses.

1. Soil

EPA Method 3052 will be followed in soil digestion. Aliquots of 0.25 – 0.5 g of soil are weighed into the Teflon-lined microwave digestion vessel and are digested with 9 ml of concentrated HNO₃ and 3 ml of HF. The samples will then be irradiated in the microwave at 100% power for 15 minutes. The temperature should be maintained at 175°C for a minimum of 9.5 minutes. After the samples have cooled, they will be diluted to a known volume and, if necessary, filtered.

2. Plant Tissue

Aliquots of 0.2g of the plant tissue will be weighed into the Teflon microwave digestion vessel and digested with 2 ml of concentrated HNO₃ and 2 ml of concentrated H₂O₂. The samples will then be irradiated in the microwave for 15 minutes at 100% power. After the samples have cooled, they will be diluted to a known volume and, if necessary, filtered.

Concentrations of arsenic, cadmium, and lead in the digested soil and plant tissue solutions are determined by atomic absorption spectroscopy. A Perkin Elmer Atomic Absorption Spectrophotometer will be used. Afterwards, the metal concentrations in solution ($\mu\text{g ml}^{-1}$) will be converted to metal concentrations in soil or plant tissue expressed in $\mu\text{g g}^{-1}$ dry weight.

3. Quality Assurance

During the course of chemical analyses, the following quality assurance (QA) and quality control (QC) parameters will be determined. Data that do not meet the QA/QC requirements will be rejected and analysis repeated until the QA/QC requirements are met.

A. Accuracy

NIST standards for soil or plant material will be analyzed with each set of analyses being performed. The percent recovery will be calculated as follows:

$$R = 100 * (C_m / C_{sm}) \quad [\text{Eq. 1}]$$

where, R = percent recovery

C_m = measured concentration of standard reference material

C_{sm} = actual concentration of standard reference material

The percent recovery for each element should be >90% for the analysis to be acceptable.

B. Recovery

To provide bias information regarding sample preparation and analysis for all of the total analyses of plant tissue and soil, one sample per set will be spiked with analytical grade standard at a level approximately equal to 50% of the analyte concentration just prior to sample digestion. Percent recovery of each element for each procedure will be calculated and recorded. For each sample spike i , the percent recovery P_i will be calculated by,

$$P_i = 100 * (A_i - B_i) / T_i \quad [\text{Eq. 2}]$$

where A_i = the analytical result from the spiked sample
 B_i = the analytical result from a separate analysis of the unknown sample
 T_i = the known value of the spike

Average percent bias (Bias) is calculated from average percent recovery [$P = \Sigma(P_i)/n$, for $i = 1$ to n] for the sample spike by:

$$\text{Bias} = P - 100 \quad [\text{Eq. 3}]$$

The spike percent recovery should be >90% for the analysis to be acceptable.

C. Precision

Analyses will be done in duplicate to provide short-term precision estimates, and means and relative percent difference (RPD) will be recorded. The duplicate RPD should be <5% for the analysis to be acceptable.

$$\text{RPD} = [(C_1 - C_2) / ((C_1 + C_2) / 2)] * 100 \quad [\text{Eq. 4}]$$

where, RPD = relative percent difference
 C_1 = the larger of the two observed values
 C_2 = the smaller of the two observed values

D. Method Detection Limit (MDL)

A method detection limit will be established and periodically reevaluated for each sample matrix type and for each measurement method. The smallest detectable quantity is related to the standard deviation of sample analyses at or near zero analyte concentrations. The MDL will be determined by the analyses of seven or more replicates of spiked matrix sample. The standard deviation of the responses (S_m), in concentration units, is used to calculate the MDL as follows:

$$\text{MDL} = S_m (t_{.99}) \quad [\text{Eq. 5}]$$

where, $t_{.99}$ = "Student's t value" appropriate for a one-tailed test at the 99% confidence level and a standard deviation estimate with $n-1$ degrees of freedom.

Appendix III
Dioxin Concentrations in California Cropland Soils
Proposed Additions to Protocol
Draft, April 7, 2000

Introduction

CDFA is planning a study to evaluate the potential for the build-up of trace metals and dioxin-like substances in agricultural lands through the use of soil amendments and/or fertilizers. Dioxin-like substances have been identified in certain soil amendments, but little information is available on whether normal application of dioxin-containing soil amendments and/or fertilizers can lead to the accumulation of dioxins in soils. In addition to the soil amendment component of the study, CDFA is planning to study the dioxin content of cropland soils at two points in time by analysing both archived and new soil samples from locations identified in the Benchmark Soils Study.

Objectives

The major objectives of the dioxin component of the project are:

1. Analyse soil samples from locations identified in the original Benchmark Soils Study for dioxin-like substances. This would provide information on the distribution of dioxin-like substances in agricultural lands throughout California.
2. Analyse soil samples from cultivated agricultural fields to assess the impact of soil amendments and/or fertilizers on the concentrations of dioxin-like substances.
3. Analyse samples of soil amendments and/or fertilizer for dioxin-like substances. Ideally, samples already analysed by CDFA for other constituents should be analysed to integrate the characterization.
4. Analyse archived Benchmark Soils for dioxin-like substances. This would provide information on the historic distribution of dioxin-like substances in agricultural land. A comparison to the distributions obtained through Objective #1 may provide information on temporal changes.

Approach

A. Selection of Sites

Soil samples will be collected from locations to be decided in conjunction with the Trace Metals component of this project. Special precautions need to be taken to minimize any contamination of samples that could invalidate the results. These precautions include:

Obtain soil samples from locations away from:

- Wooden structures (to minimize any dioxins from pentachlorophenol-treated wood)
- Burn sites
- Roads (a minimum of 50 m away from roads used by diesel powered vehicles)
- Sheds, water pumps or other structures where pesticides may have been loaded/mixed.
- Transformers (to minimize PCB leaks)
- Any other obvious sources of dioxins (incinerators, waste burn piles)

B. Site description

Same as with Trace Metals component.

C. Soil Sampling

Sampling depth

- Benchmark Soil sites: Collect soil from the top 1 cm of soil using a metal spoon. This may be a different procedure than the one used for metals. The soil can be placed directly into the glass jar without sieving or drying. About 50 g of soil is required.
- Cultivated sites: Collect soil from the same location and depth as for the Trace Metal component. Pass through 1 mm sieve. A metal spoon can be used to sub-sample from the sieved sample collected for the Trace Metal component. Place in glass jar without drying. About 50 g of soil is required.
- Archived Benchmark soils: The paper containers used for storing the archived soils may be a source of contamination. Collect a sample from the center of the container avoiding the container walls. About 50 g of soil is required.

Containers and sampling devices

Pre-cleaned glass containers with Teflon-lined screw caps will be provided to the sample collectors by HML/DTSC. The metal spoons need to be water rinsed and air dried between samples to avoid cross-contamination. Alternatively, new spoons should be used with each sample.

Storage and shipping

Soil samples collected for dioxin analysis should be shipped to HML/DTSC where they will be stored in a cold room @ 1-4 °C until processing. Whereas a large number of samples will be collected, only a limited number of them will be analysed. Proper sample identification and record keeping is essential.

D Sample selection for dioxin analysis

Given the high cost of dioxin analysis, an effort will be made to minimize the number of analyses while maximizing the information obtained. Most samples for Objective #1 will be analysed as composites, i.e., all samples from the same location will be mixed together (in the laboratory) and a sub-sample analysed. Samples for Objective #2 will be analysed after the metals analyses are completed. This will allow the selection of appropriate samples for dioxin analysis, based on e.g., high or low content of metals, P, TOC, etc. Samples for Objective #4 will be analysed only if results from samples for Objective #1 indicate high enough concentrations to warrant the analysis of archived samples. Samples for Objective #3 will be composited by brand. In every case where compositing will be performed, a random sub-set will be analysed individually to estimate variability.

E Sample Analysis

Soil samples will be oven dried and analysed by isotope dilution using High Resolution Mass Spectrometry according to HML Method 880, with all required QA/QC parameters. In brief, samples are analysed in batches of six and one method blank is included with every batch. Ten percent of the samples are analysed in duplicate to assess precision. Certified reference material (soil) will be analysed prior to the beginning of this project and at two points in time during the project. The target analytes consist of the seventeen 2,3,7,8-substituted dioxins and furans and the twelve dioxin-like PCBs shown on the attached Table 1. One ¹³C-labeled internal standard will be used for each analyte in every sample. Detection limits are expected to be between 0.1-1 pg/g (ppt). The results will be reported on a dry weight basis.

F Quality Assurance

A Quality Assurance Project Plan (QAPjP) will be written for this project. The QAPjP will be reviewed and approved by HML's QA Officer.

Data Analysis

After the chemical analysis and data validation are completed, the results will be summarized and tabulated. The WHO-Toxic Equivalents (TEQ) will be calculated for each sample as an expression of overall dioxin activity. Each of the stated Objectives will be evaluated in collaboration with UCR and CDFA.

- For Objective #1, distributions of TEQs and prevalent congeners will be examined. The representativeness of this distribution will be evaluated and compared to other US and world data. If data are representative, these distributions may be used for risk assessments and policy decisions.
- For Objective #2, dioxin and TEQ levels will be examined in a correlation table with other relevant variables (P, metals, TOC, etc.). Correlated variables may be used in a multiple linear regression model to determine the contributors to dioxin concentrations.
- For Objective #3, various brands of amendments with measurable dioxin content may be identified, and more focussed follow up studies may be required to assess the extent of the contamination and source of the dioxins. Additionally, based on CDFA's chemical analyses of these samples, markers for dioxins may be identified through correlation analysis, facilitating follow up studies by screening for the presence of the markers at significant cost savings.
- For Objective #4, paired comparison of current to archived soils may reveal (increasing?) trends.

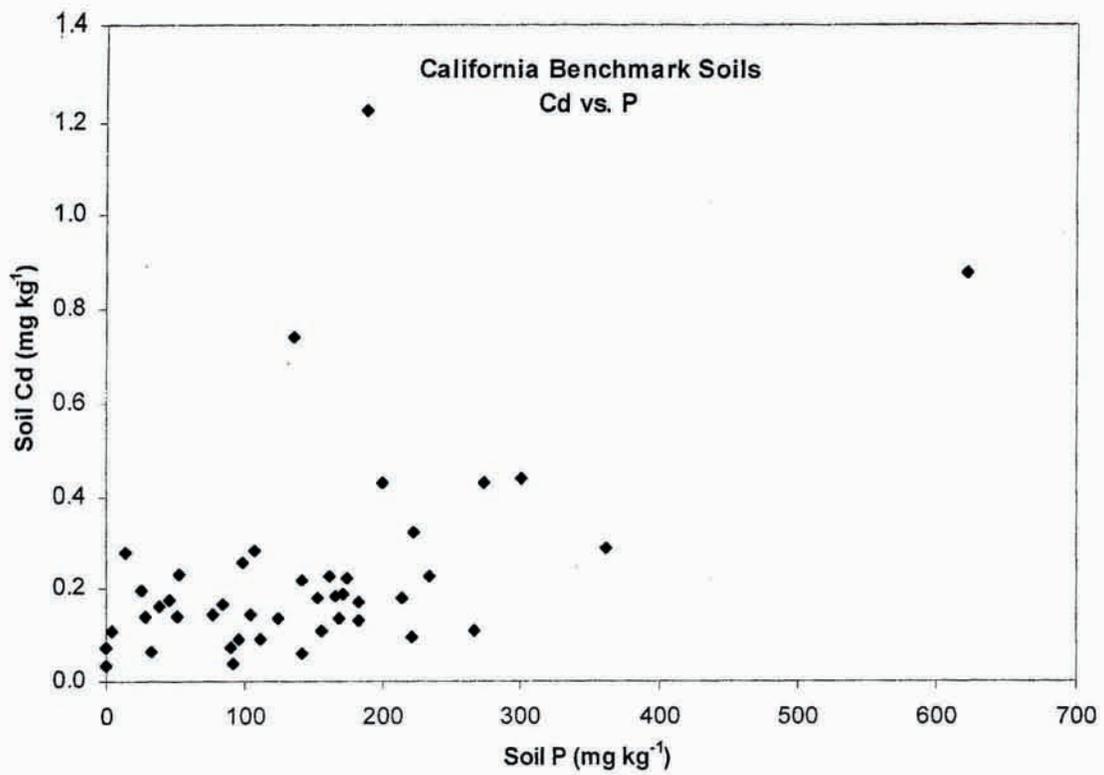


Figure 1. The Cd concentrations of California Benchmark Soils in relation to their P concentrations – 1967 samples.

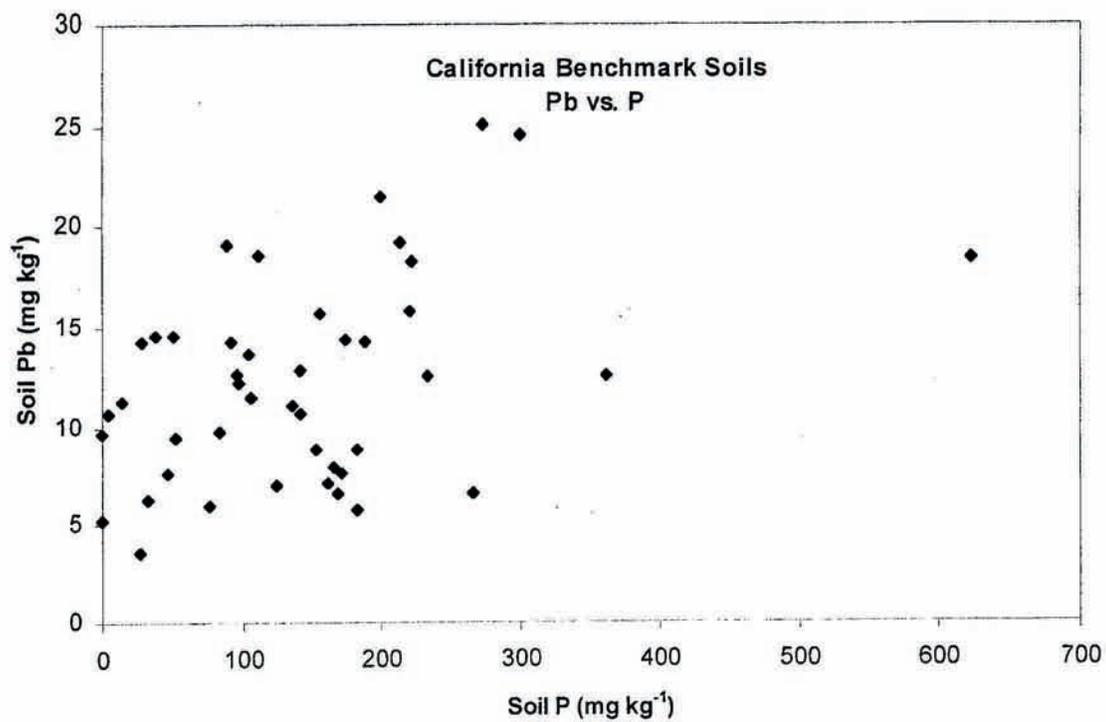


Figure 2. The Pb concentrations of California Benchmark Soils in relation to their P concentrations – 1967 samples.

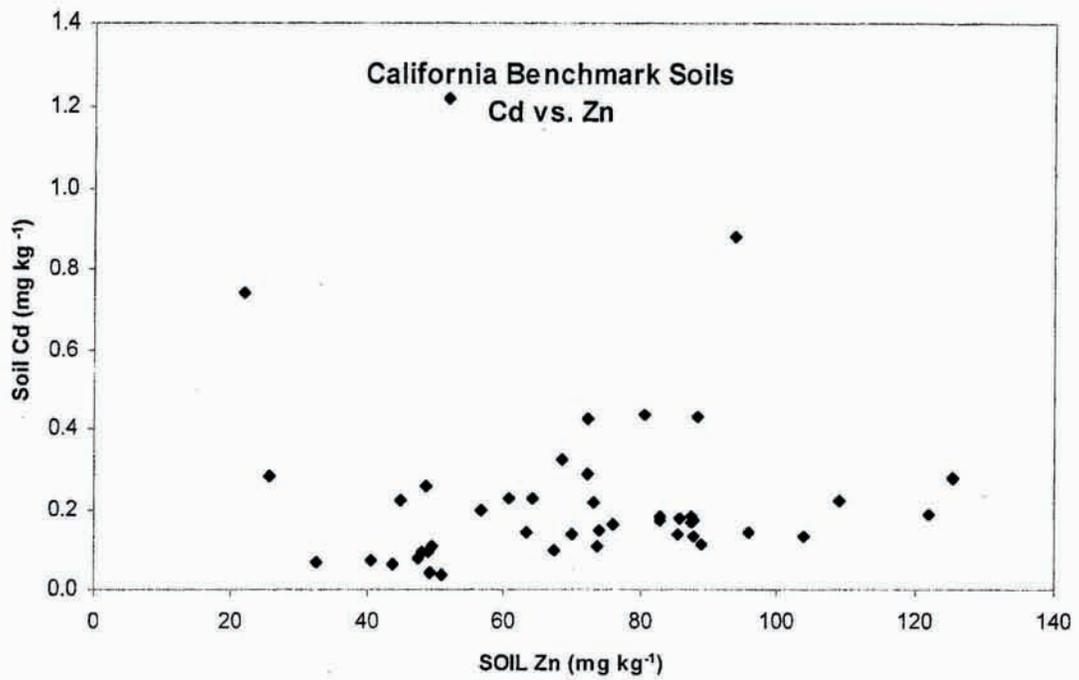


Figure 3. The Cd concentrations of California Benchmark Soils in relation to their P concentrations – 1967 samples.

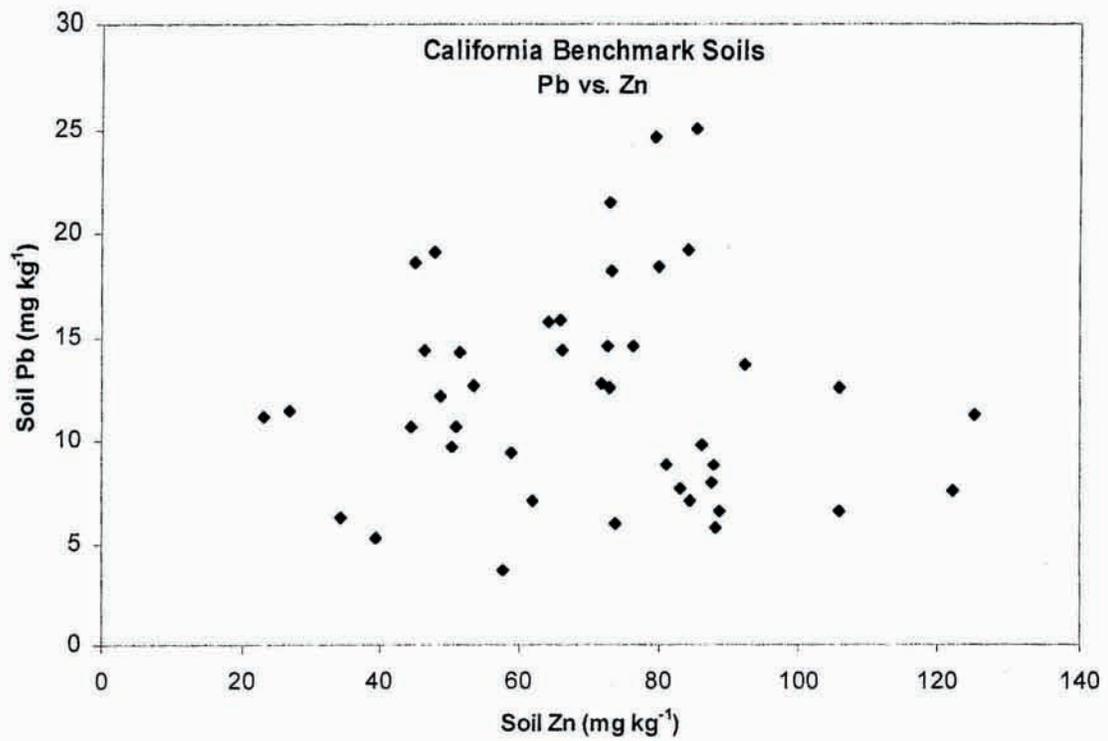


Figure 4. The Pb concentrations of California Benchmark Soils in relations to their P concentrations – 1967 samples.

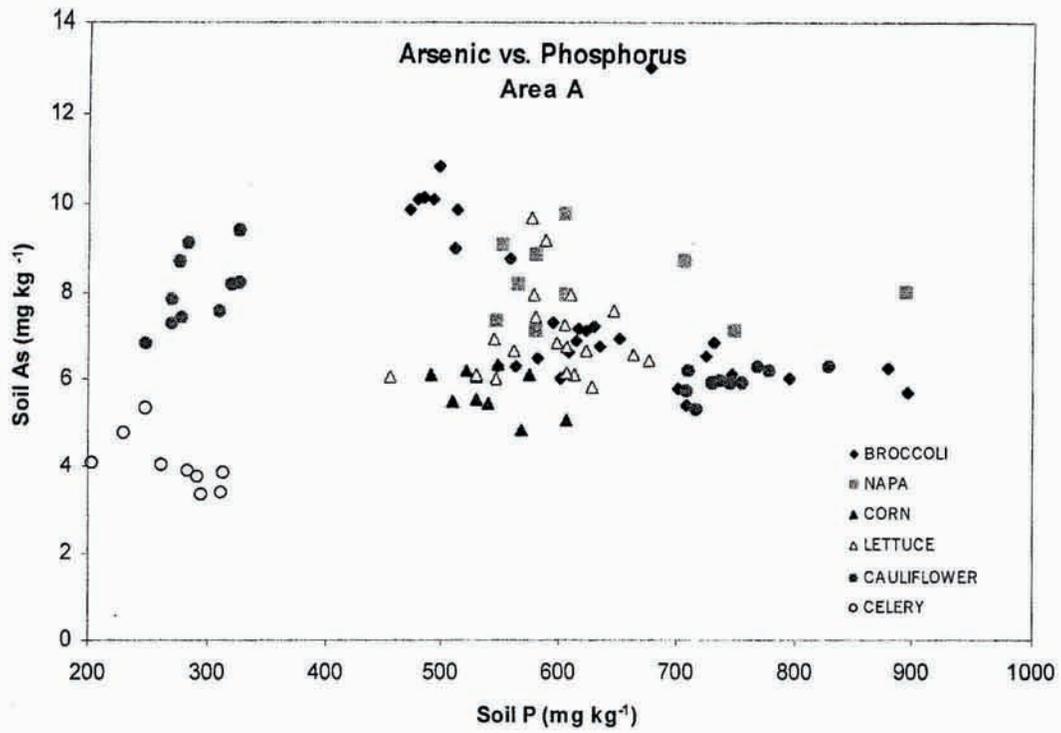


Figure 5. The As concentrations of soils in Area A in relation to their P concentrations.

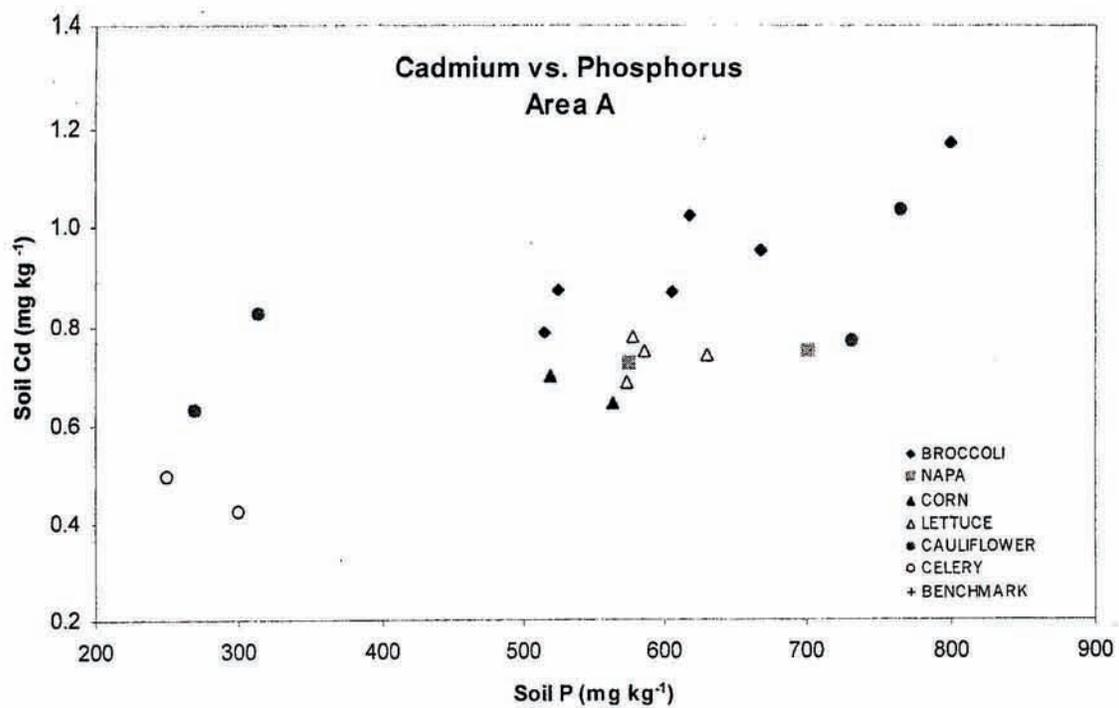


Figure 6. The Cd concentrations of soils in Area A in relations to their P concentrations.

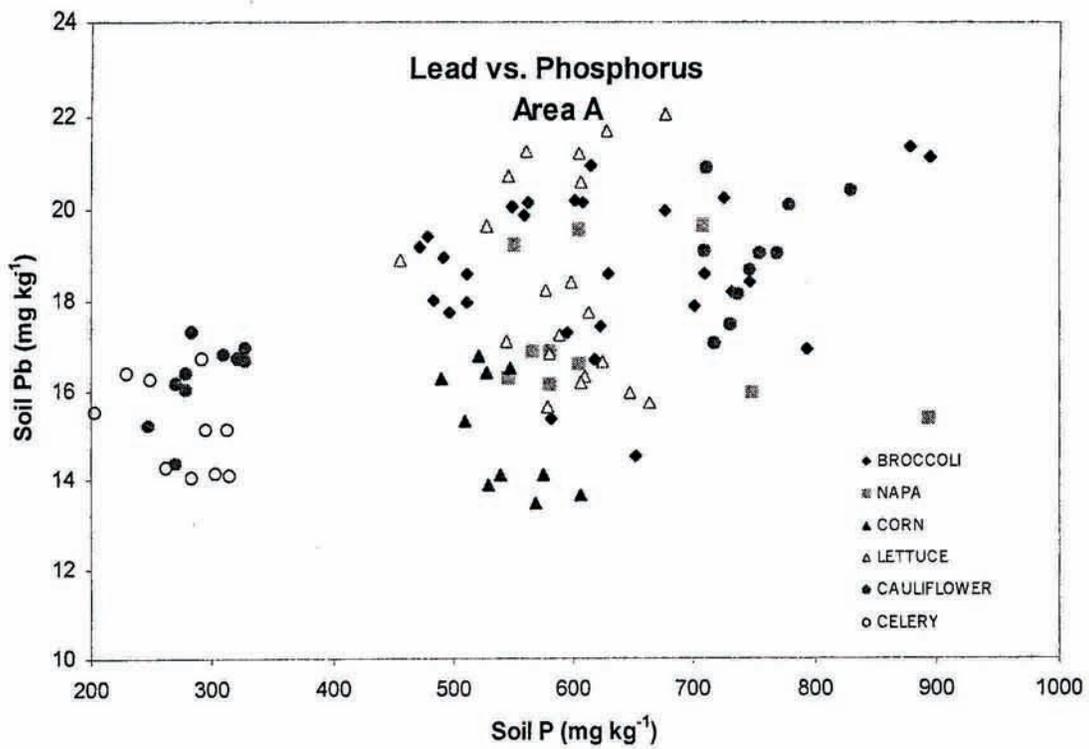


Figure 7. The Pb concentrations of soils in Area A in relation to their P concentrations.

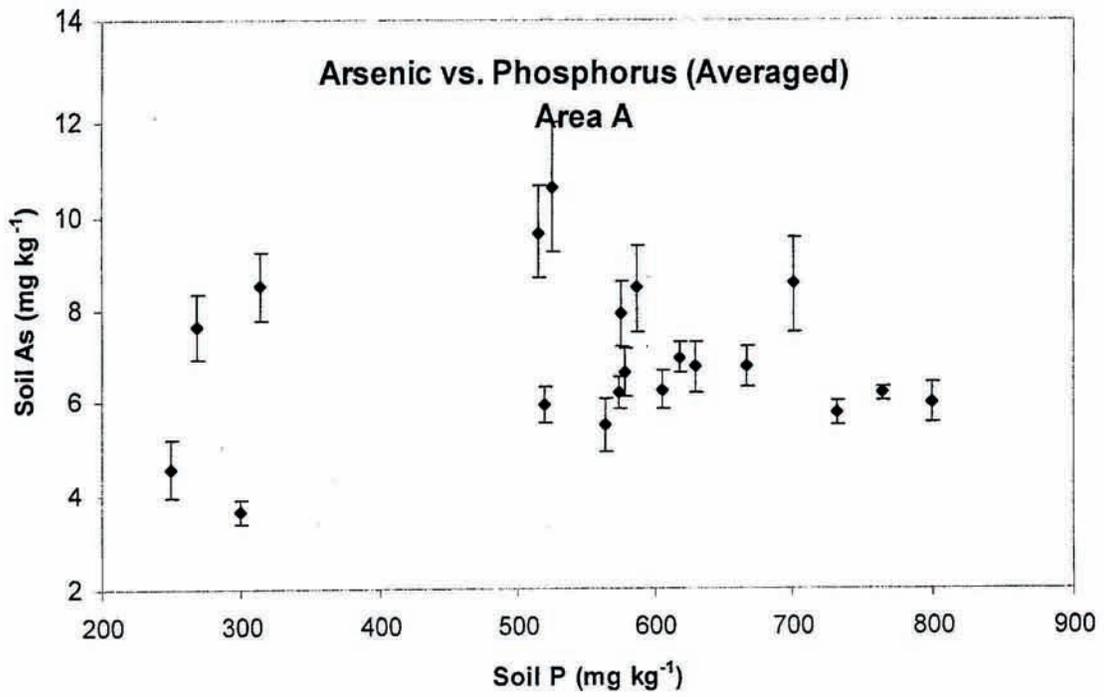


Figure 8. Variability (mean and standard deviation) of As concentrations of soil samples collected in Area A.

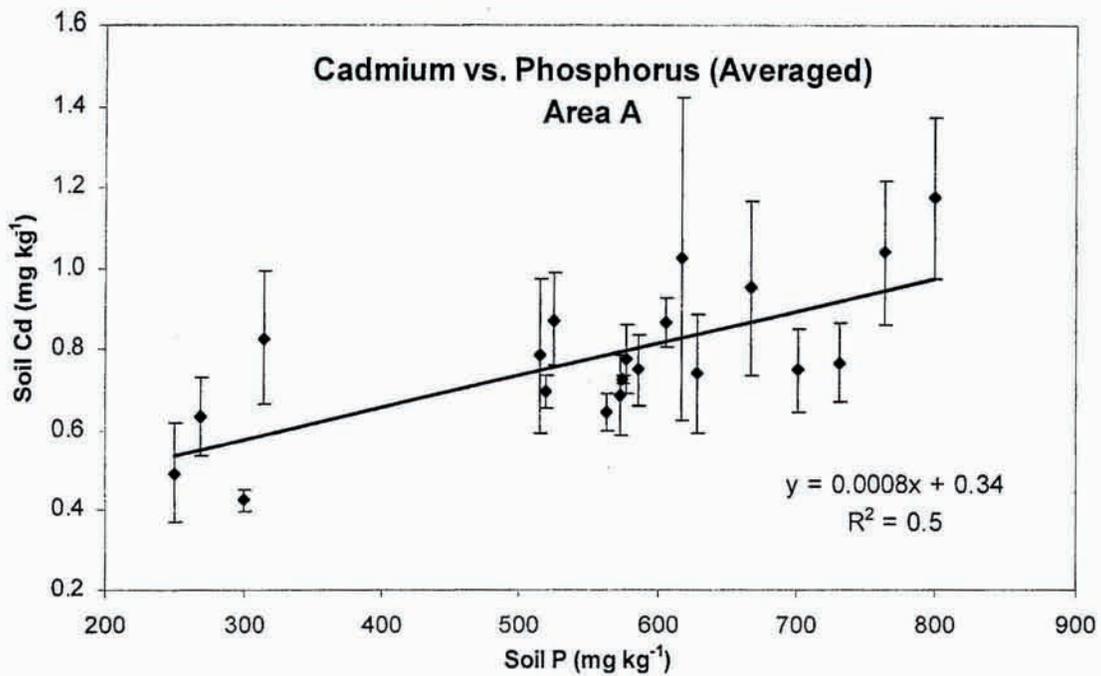


Figure 9. Variability (mean and standard deviation) of Cd concentrations of soil samples collected in Area A.

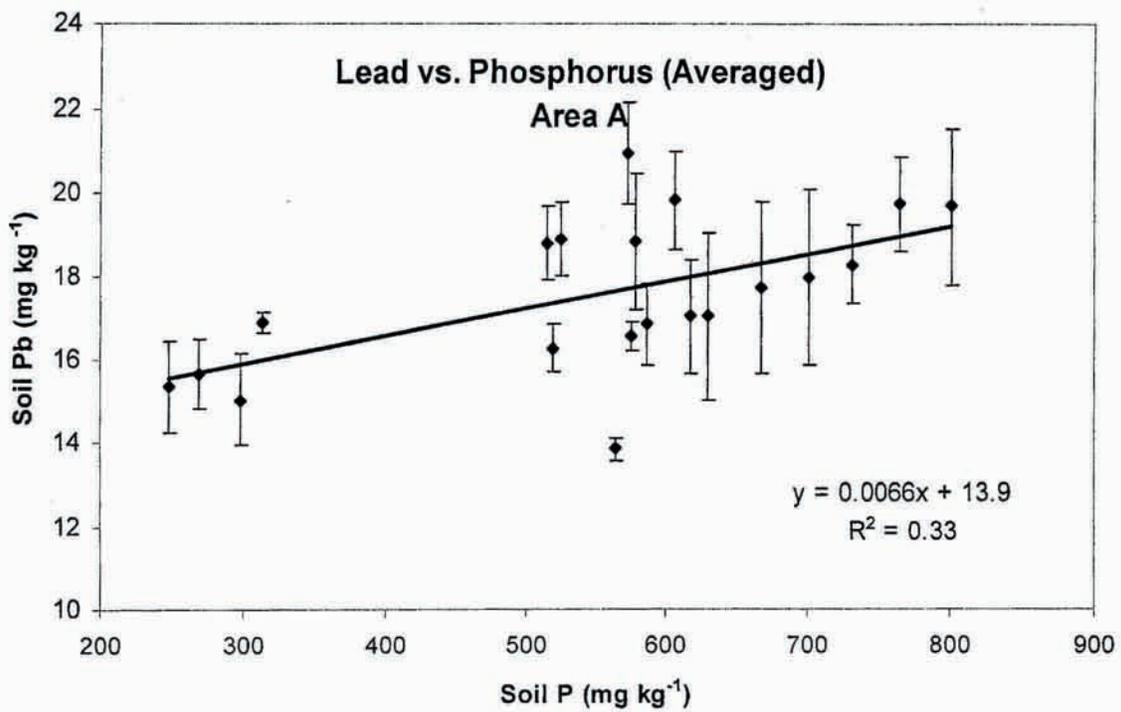


Figure 10. Variability (mean and standard deviation) of Pb concentrations of soil samples collected in Area A.

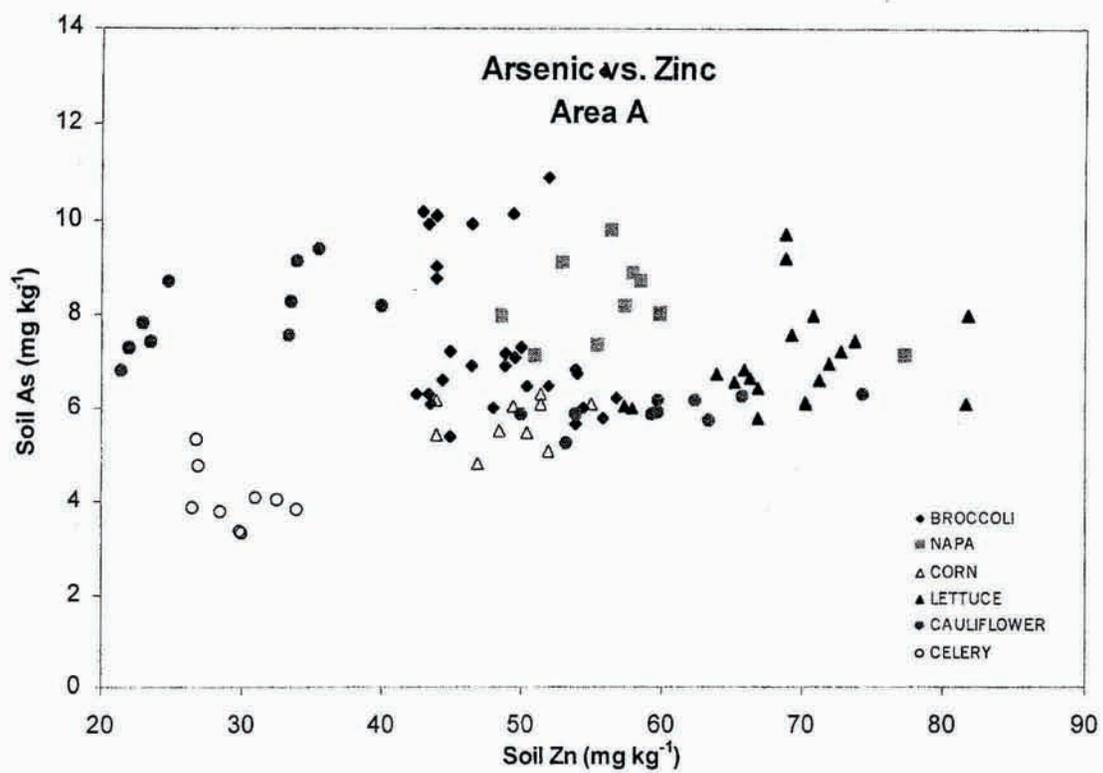


Figure 11. The As concentrations of soils in Area A in relation to their Zn concentrations.

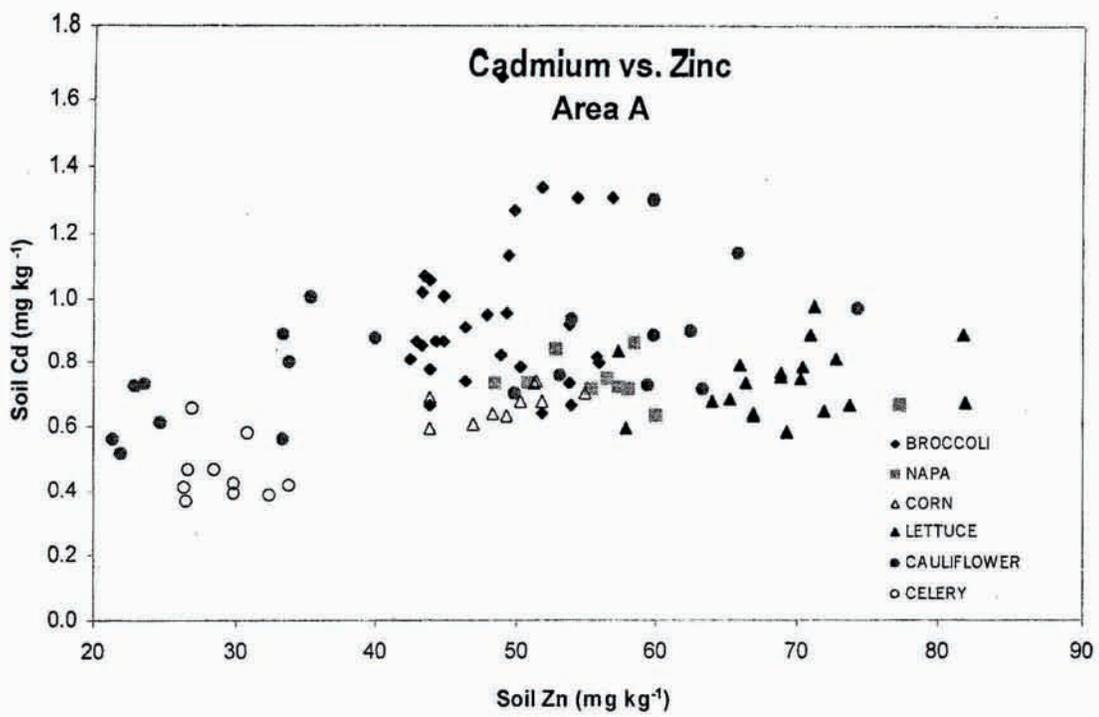


Figure 12. The Cd concentrations of soils in Area A in relation to their Zn concentrations.

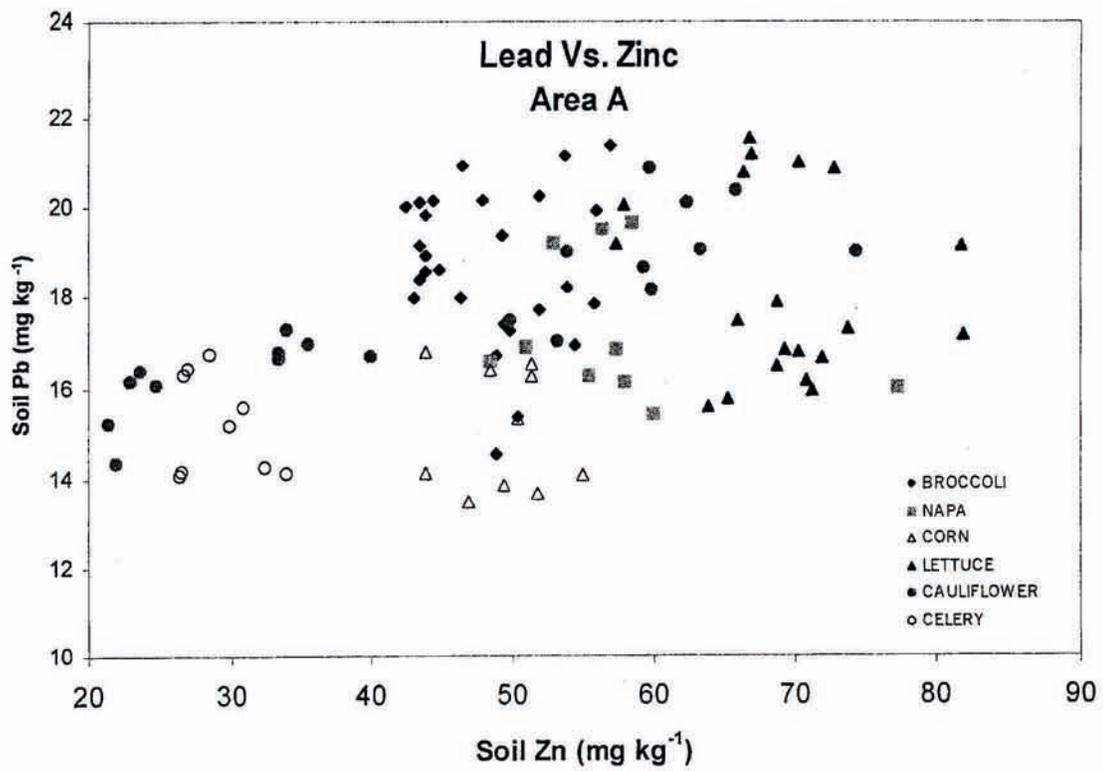


Figure 13. The Pb concentrations of soils in Area A in relation to their Zinc concentrations

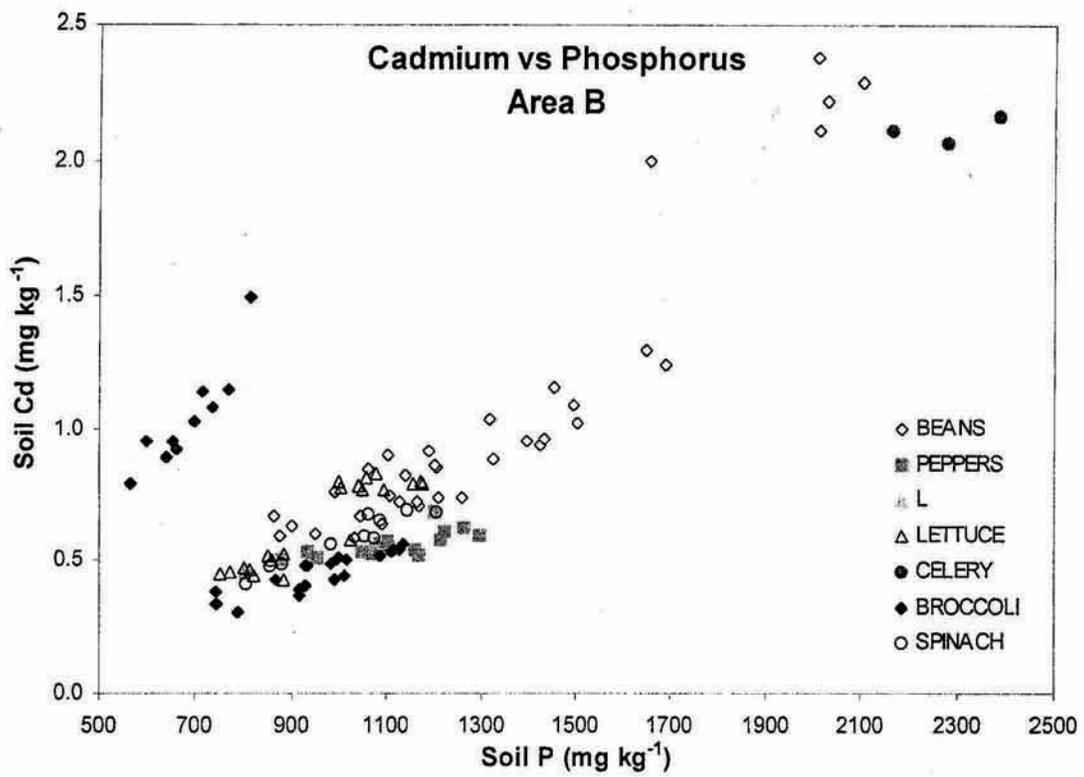


Figure 14. The Cd concentrations of soils in Area B in relation to their P concentrations.

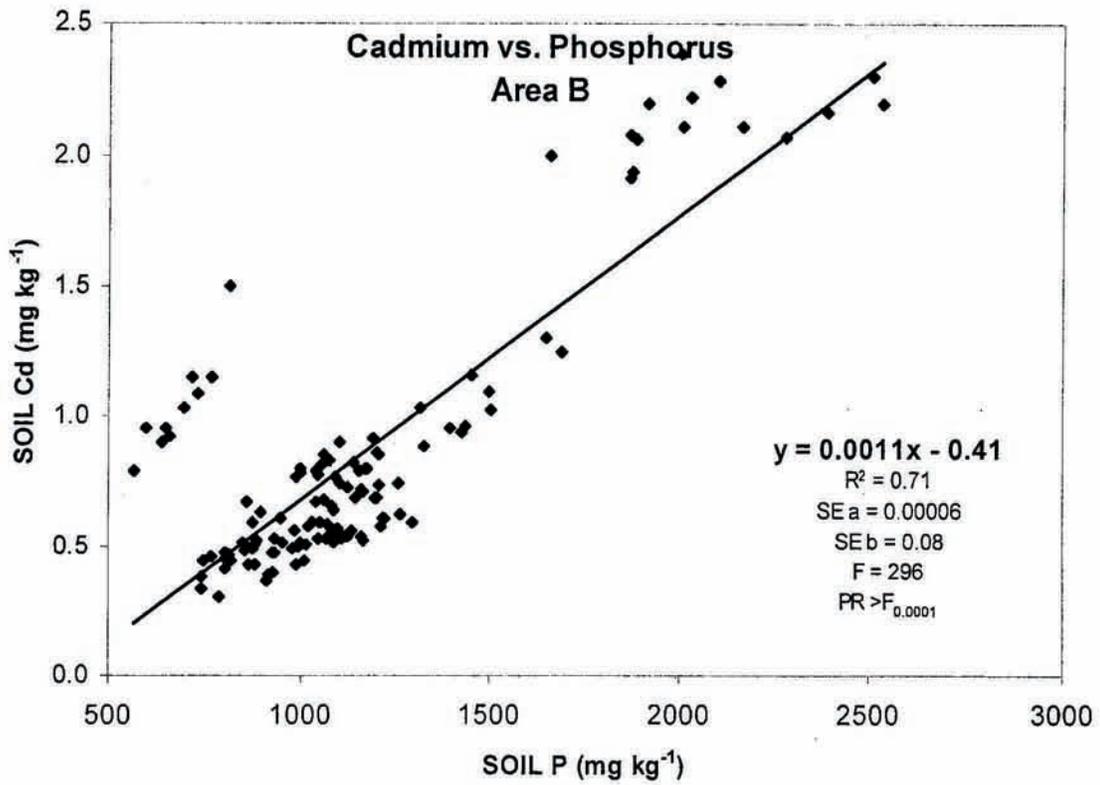


Figure 15. The linear regression between Cd of soils in Area B and their P concentrations.

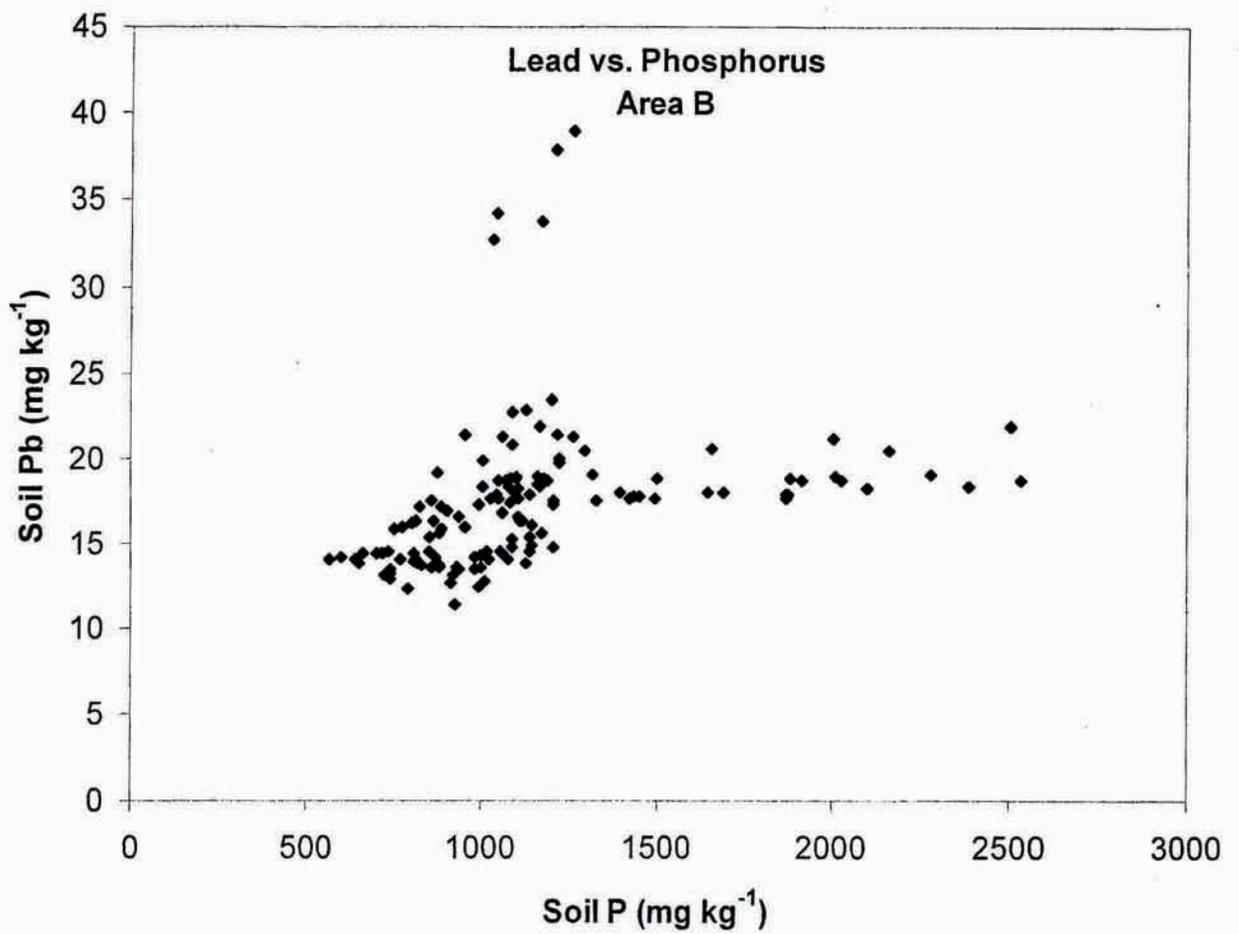


Figure 16. The Pb concentrations of soils in Area B in relation to their P concentrations.

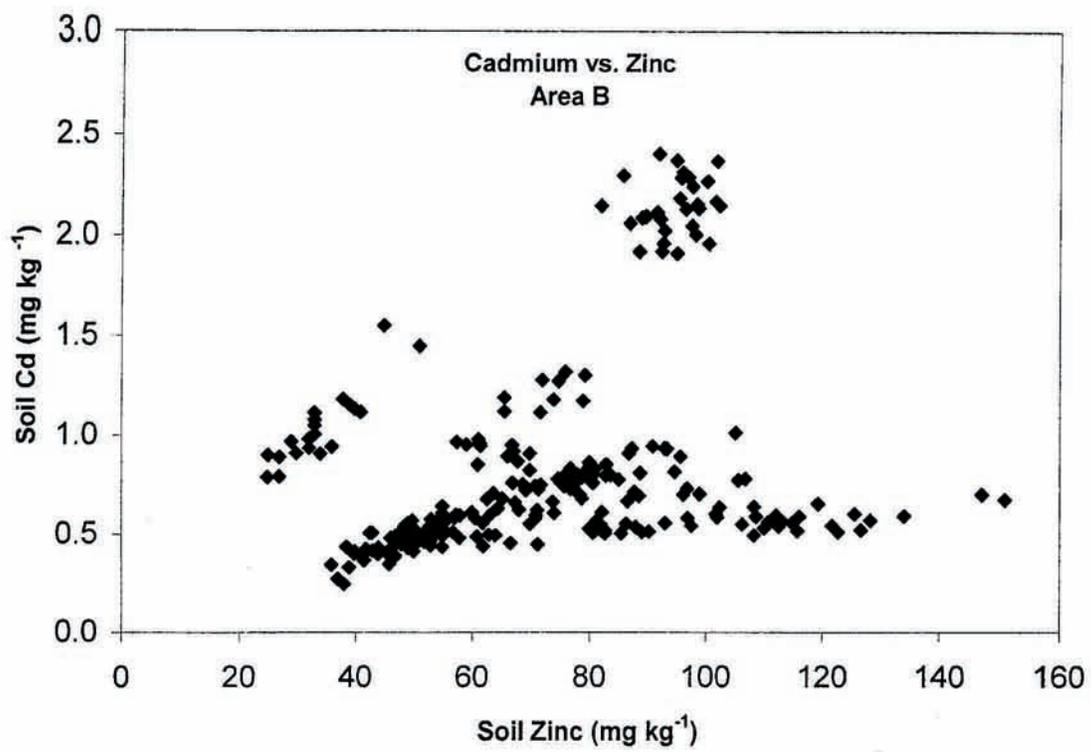


Figure 17. The Cd concentrations of soils in Area B in relation to their Zn concentrations.

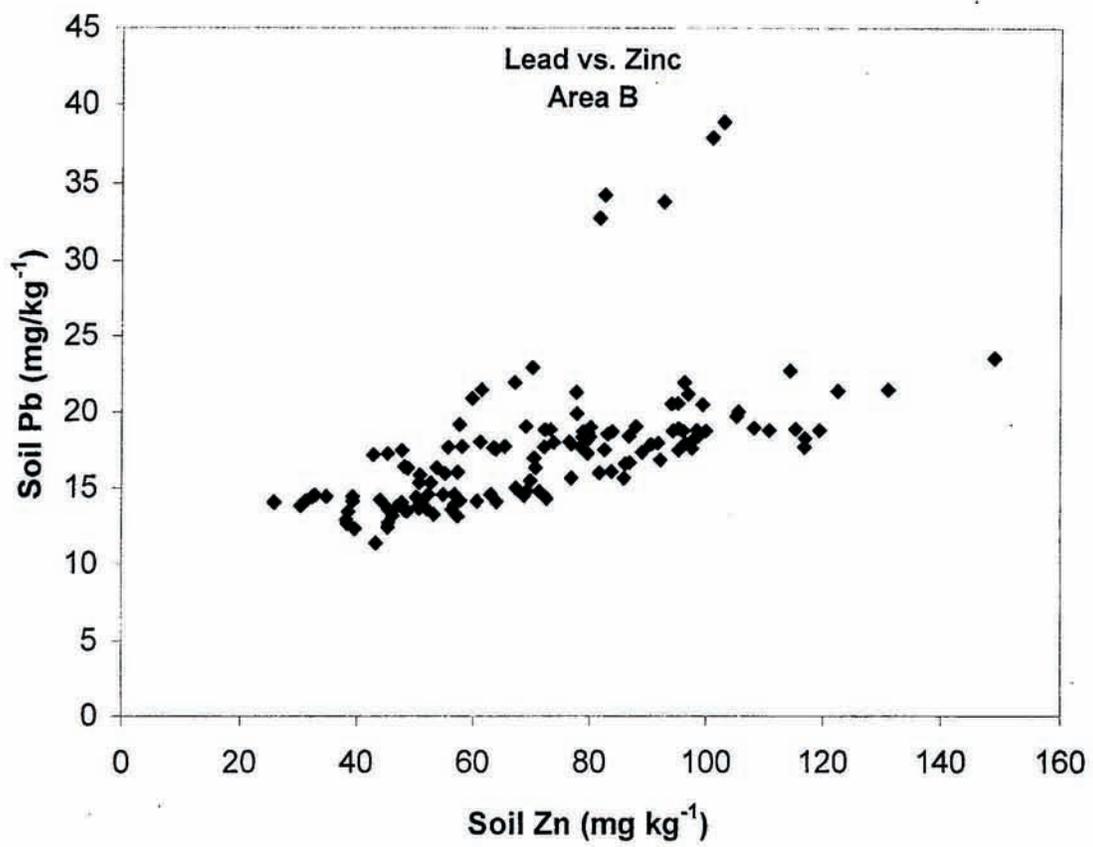


Figure 18. The Pb concentrations of soils in Area B in relation to their Zn concentrations.